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A new calibration of the OPAM thermobarometer for anhydrous and hydrous mafic systems

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**ABSTRACT**

Melt-based thermobarometers are essential tools to recover pre-eruptive magma storage conditions through their application to bulk rock and liquid chemistry. In active volcanic systems, thermobarometric results can be combined with independent geophysical data during or after an eruption to validate conceptual models. In this contribution, we revisit the thermobarometer for melts equilibrated with the mineral assemblage of olivine + plagioclase + augitic clinopyroxene (OPAM). We first demonstrate that the most widely applied OPAM thermobarometer suffers from both random and systematic uncertainty even for anhydrous melts, and that the uncertainty increases proportionally with melt H$_2$O. To address this issue, we use a modern compilation of anhydrous and hydrous OPAM-saturated experiments to regress a new melt-based OPAM thermometer and barometer. Our new equations recover a validation dataset with a standard error estimate (SEE) of $\pm 1.1$ kbar and $\pm 35$ °C for pressure and temperature respectively, as well as a low systematic uncertainty that does not depend on melt H$_2$O. Additionally, we present a novel statistical approach to determine the probability that a given melt is OPAM-saturated, which can be used alongside petrographic observations. Our thermobarometer and saturation test are presented as a straightforward R script which reads from an input csv file to be populated with natural data. We benchmark the new calibrations on the products of the 2015 eruption of Wolf Volcano (Isabela Island, Galápagos) and the 2014-2015 Holuhraun eruption (Iceland), both of which have independent geophysical estimates of magma storage that agree well with our thermobarometric results.

**KEYWORDS**

Multiple saturation; OPAM; thermobarometry; basalt; Galápagos; Iceland

**INTRODUCTION**
Thermobarometry, the retrieval of pressure \((P)\) and temperature \((T)\) information from magmas, provides a quantitative window into the physicochemical structure of magmatic systems (Blundy and Cashman, 2008; Grove et al., 1992; Neave and Putirka, 2017; Putirka, 2008). Thermobarometric equations relate \(T\) (°C) and \(P\) (kbar) to the measured composition \((X)\) of a melt and/or mineral(s) using equilibrium crystallisation experiments (Putirka, 2008). Equations may have a general form grounded firmly in thermodynamics with additional empirical terms to improve the goodness of fit (e.g., Masotta et al., 2013; Neave and Putirka, 2017; Putirka, 2016), or be purely empirical and consist only of compositional variables with or without \(P\) and \(T\) terms as independent variables (e.g., Jorgenson et al., 2022; Ridolfi and Renzulli, 2012). Irrespective of the calibration strategy, thermobarometers have significant scope as petrological volcano monitoring tools. For example, \(P\) data can independently validate geophysical estimates of pre-eruptive magma storage depth during or after eruptions (Hartley et al., 2018; Stock et al., 2018; Ubide et al., 2023) or catalogue past changes in magma \(P\) and \(T\) for eruptions of volcanoes that lack a protracted historical monitoring record (Bouvet de Maisonneuve et al., 2021; Higgins et al., 2021a; Jorgenson et al., 2024; Weber et al., 2020).

Therefore, access to accurate, precise, and readily applicable thermobarometers is an essential component of volcanic hazard management and eruption forecasting.

Melt-based thermobarometers (e.g., Blundy, 2022; Grove et al., 1992; Helz and Thornber, 1987; Wilke et al., 2017; Yang et al., 1996) are a particularly useful implementation of the method as \(P-T\) estimates can be derived from the chemistry of a single phase which is often easily recovered from matrix glass, melt inclusions, or whole-rock data. However, to be reliably applied, the input melt composition must represent a true equilibrium liquid, free from the effects of magma mixing or crystal accumulation which are rife in magmatic systems (Cashman and Blundy, 2013; Kent et al., 2010; Passmore et al., 2012). Melt-based thermobarometry equations regress melt composition against \(P\) or \(T\) by assuming that the melt
is buffered by a discrete, low-variance phase assemblage; the mineral proportions change in response to $P$, $T$, and bulk composition, imparting a predictable chemical control on the coexisting melt. Such “multiple saturation thermobarometers” are broadly applicable in both high-melt-fraction and low-melt-fraction magmatic systems, recording $P$-$T$ conditions at the point where melts decouple (via eruption or melt migration) at a speed that is too rapid for further chemical equilibration with the buffering crystal assemblage (Solano et al., 2014; Jackson et al., 2018; Lissenberg et al., 2019; Blundy, 2022).

The OPAM thermobarometer is a melt-based multiple-saturation thermobarometer relying on equilibrium between the mineral assemblage olivine $+$ plagioclase $+$ augitic clinopyroxene (the olivine gabbro cotectic; Herzberg, 2004). Early work showed that the location of the OPAM cotectic was strongly $P$ dependent, and could be parameterised as a function of melt major element composition ($\text{Ca+Mg+Al+Si+Fe+Na}$; Shi, 1993, 1992). Later, the effect of minor elements ($\text{K, Ti, Cr}$) were deemed significant to capture the melt composition effect within the form of the cotectic equation (Grove et al., 1992; Voigt et al., 2017; Yang et al., 1996). The Yang et al (1996) equations remain the most widely applied calibration of the OPAM cotectic (e.g., Baxter et al., 2023; Bell et al., 2021; Hartley et al., 2018; Stock et al., 2018); this model comprises three empirical equations which regress the molar proportion of three melt-compositional cations ($\text{Al, Ca, Mg}$) as separate functions of $\text{Na, K, Fe, Ti, Si, and } P$ (kbar). Originally, these $P$-dependent equations were developed as a method to model basaltic fractional crystallisation and were not strictly proffered as a barometer (Yang et al., 1996). The calibration experiments were predominantly performed at 1 atmosphere (1 atm; $n=164$) and extrapolated across a range of crustal magma storage conditions (>1 atm to 10 kbar) using only a small number of high-$P$ experiments ($n=26$). The hydrous, high-$P$ experiments used to calibrate the Yang et al (1996) equations span up to ~2 wt.% $\text{H}_2\text{O}$ (Baker and Eggler, 1987), theoretically limiting their applicability to low-$\text{H}_2\text{O}$ ocean
island and mid-ocean ridge settings. However, the explicit effect of H₂O was not tested, even though OPAM-saturated (OPAM₅₅₅) melts are stable across a wide range of melt H₂O content (0-7.7 wt% H₂O; Fig. 1a), with increasing H₂O suppressing the T and MgO (wt%) of OPAM saturation (Fig. 1b). In general, constraining the effect of H₂O on thermobarometric models is vital given that the addition of even moderate concentrations (much less than 2 wt%) to anhydrous compositions can have a drastic effect on phase equilibria in basaltic systems (Almeev et al., 2012, 2007; Husen et al., 2016). Yang et al., (1996) also presented a separate thermometric equation that regressed T (°C) as a function of the same melt composition variables (Na, K, Fe, Ti, Si) plus P as an independent variable. The quoted uncertainty of the Yang et al (1996) thermometer is ±20 °C, based on the observation that 170 of the 190 calibrant experiments are recovered with a T residual of ±20 °C or less. However, this assessment of uncertainty was self-validated by Yang et al (1996), calculated with the calibration experimental dataset rather than an independent set of experiments.

Hartley et al., (2018) first implemented the three Yang et al (1996) P-dependent compositional equations as a cohesive barometer, returning the P that minimised the χ² misfit between measured Al, Ca, and Mg content and those predicted by the three equations. The Yang et al (1996) equations were solved at 0.01 kbar intervals between -5 and 15 kbar until the misfit χ² was minimised, indicating the unique P of convergence. The misfit χ² is defined by the general equation:

\[
\chi^2 = \sum_{i=1}^{3} \left( \frac{X_i - Y_i}{\sigma_i} \right)^2
\]

where Xᵢ are the measured cation fractions of Al, Ca, and Mg, Yᵢ are the cation fractions predicted from the three Yang et al (1996) equations, and σᵢ is a term for analytical uncertainty.
that allows some leeway in the convergence. As well as providing the $P$ that minimised the misfit $\chi^2$, Equation 1 also returns a measure of the convergence quality or probability of fit ($P_F$). Hartley et al (2018) repurposed this quantitative information as a probability that the melt was $\text{OPAM}_{\text{SAT}}$, using it to screen natural melts that would not yield a reliable $P$ of three-phase saturation. A low $P_F$ indicates that the three Yang et al (1996) equations do not intersect closely in multidimensional space outside of analytical uncertainty and so there is no unique $P$ solution for the input melt. Hartley et al (2018) suggested setting a cut off for $P_F$ at <0.8, which was determined by observing the $P_F$ above which the $P$ of an experimental dataset was reproduced with low random and systematic uncertainty by the Yang et al (1996) equations, applied through Equation 1. Their test dataset contained 157 $\text{OPAM}_{\text{SAT}}$ experiments including some of those used to calibrate the Yang et al (1996) equations as well as several more recent studies. Hartley et al (2018) found that the systematic (+1 kbar) and random (±2.5 kbar) uncertainties when using the whole dataset dropped after removing around 40% of the $\text{OPAM}_{\text{SAT}}$ experiments, which all had $P_F<$0.8, yielding new lower systematic (+0.34 kbar) and random (±1.32 kbar) uncertainties for the $P_F$-filtered dataset. However, by using experiments from the Yang et al (1996) equations in their test dataset, the model performance was, again, partially self-validated by Hartley et al (2018). Further, the removal of around 40% $\text{OPAM}_{\text{SAT}}$ experiments raises questions about the reliability of their quoted ±1.32 kbar barometer uncertainty if no methodological or analytical reason for their omission can be found.

suite of newer studies (n=250). Using a filter of $P_F \geq 0.8$, they found that only 92 experiments remained (37%) which had been reproduced with a mean absolute error of ±1.13 kbar. The Baxter et al., (2023) test of the Hartley et al (2018) method contains the same issues of self-validation and unexplained filtering of OPAM SAT experiments which remain to be justified.

The Yang et al (1996) cotectic equations have also featured in other implementations of the melt-based OPAM thermobarometer. Michael and Cornell (1998) rearranged the Ca Yang et al (1996) equation for $P$ and used it as a stand-alone barometer; rearranging multiple linear regressions in this way is mathematically incorrect (Hartley et al., 2018). Voigt et al (2017) presented an updated parameterization of the three $P$-dependent Yang et al (1996) equations by considering Cr, Fe$^{2+}$ and Fe$^{3+}$ as additional variables, although there is no reproducible method with which to apply and test their equations (e.g., Baxter et al., 2023). Kelley and Barton (2008) calculated the liquid compositions at 0.1 kbar increments with the three Yang et al (1996) cotectic equations, converted them to normative mineral compositions, regressed $P$ against the calculated and original compositions, and finally computed the mean $P$. This unduly complex method performs significantly worse than the original Yang et al (1996) barometer applied via the approach of Hartley et al (2018) when tested using OPAM SAT experiments (Baxter et al., 2023).

In this contribution, we re-visit the OPAM thermobarometer using the wealth of new experimental data available since the implementation of Yang et al (1996). An experimental dataset of OPAM SAT experiments with no obvious quality issues are compiled. These experiments span 0-7.7 wt% H$_2$O and 0.5-10 kbar, encompassing the full crustal spectrum of OPAM SAT melts. By first omitting studies which were used to calibrate the Yang et al (1996) equations, we test the robustness of the filtering method of Hartley et al (2018) and the quoted Yang et al (1996) $P$ uncertainty (±1.13 kbar) of Baxter et al., (2023) using a truly independent test dataset. Based on these findings, we highlight the large true uncertainty associated with
the Yang et al (1996) thermometer and barometer, exacerbated by increasing melt H$_2$O. In light of this, we present a new empirical thermometer and barometer for OPAM$_{SAT}$ melts at anhydrous-hydrous conditions and crustal pressures (0.5-10 kbar) as a function of melt composition. We also introduce a new statistical method for determining the probability that a melt is OPAM saturated which allows for application of our geothermobarometer to natural melts where petrological constraints on multiple saturation are unavailable. Our equations are applied to basaltic erupted products from the 2015 eruption of Wolf Volcano (Isabela Island, Galápagos archipelago) and the 2014-2015 Holuhraun eruption (Iceland) which both have extensive petrographic, geochemical, and geophysical records (Halldórsson et al., 2018; Hartley et al., 2018; Stock et al., 2020, 2018).

METHODS

Database Assembly and Filtering

OPAM$_{SAT}$ experiments were collected from the Library of Experimental Phase Relations (LEPR; Hirschmann et al., 2008), corrected for typos and copy errors, and supplemented with experiments published after circa 2008. Experiments conducted at 1 atm were excluded to avoid issues of rapid disequilibrium crystal growth in 1 atm experiments (Mollo et al., 2010; Ziberna et al., 2017) and to prevent an overweighted regression at pressures (depths) irrelevant to pre-eruptive magma storage (Neave and Putirka, 2017). Any studies not reporting the abundances of mineral run products were not considered further. The upper $P$ was limited to 10 kbar where OPAM$_{SAT}$ data become sparse, resulting in extrapolation over large $P$ intervals. Ten kbar (~32 km in oceanic crust; Putirka, 1997) encapsulates the thickness of most oceanic crust and is the $P$ limit of the thermobarometer calibration of Yang et al (1996). No filter was used for melt H$_2$O as the pre-existing H$_2$O content of a magma is rarely known
which would limit the confident application of our updated equations. Experiments crystallising major silicate phases outside of OPAM (biotite, amphibole, orthopyroxene, garnet) were removed. However, we retained experiments which crystallised Fe-oxide phases, despite Putirka (2008) finding that strictly OPAM$_{\text{SAT}}$ experiments (i.e., without Fe-oxides) led to an improved fit, as removing these experiments may also limit the model applicability in natural systems. Removing experiments crystallising major silicate phases outside of OPAM is important as the critical assumption of an OPAM thermobarometer is that the melt is buffered by a common assemblage of olivine + plagioclase + augitic clinopyroxene whose compositions and proportions change as a function of $P$ and $T$. A total alkali filter was not initially applied, although we discuss the role of alkalis later; while Hartley et al (2018) state that the OPAM thermobarometer should be avoided for transitional or alkali basalts due to poor performance, this is at odds with the Yang et al (1996) equations which are calibrated using some alkalic melt compositions. Indeed, our compiled OPAM$_{\text{SAT}}$ experiments span to alkalic melt compositions (Fig. 1c).

The liquid cation fractions of experimental melts were calculated using the method outlined in Table 1 of Putirka (2008), and are denoted by X followed by the oxide subscript (e.g., $X_{\text{AlO}_{1.5}}$). Additional experiments were removed which did not report $X_{\text{KO}_{0.5}}$ (i.e., where it is not clear whether potassium is legitimately absent or not reported; 29 experiments) and/or which exhibited iron loss or gain greater than 20% (7 experiments). Outliers, defined as an abnormal value at odds with the regular distribution of the dataset, were subsequently appraised in the remaining data by inspecting x-y plots of liquid cation fractions. The potential for outliers is high due to the difficulty of performing and analysing experimental run products. However, the dataset appeared largely coherent, and few outliers were identified. The exception was scatter at high and low $X_{\text{CaO}}$, which was removed using a filter of $0.04 < X_{\text{CaO}} < 0.14$ (n=12), and a single experiment (Y0206-1) from Neave et al (2019) which showed anomalously
heterogeneous glass compositions. Our final OPAM\textsubscript{SAT} compilation (n = 249) is reported in Supplementary Table 1a, including the mean and range of key variables (Supplementary Table 1b). A full reference list for all experiments can be found in Supplementary Table 1c. To our knowledge, this dataset consists of good-quality OPAM\textsubscript{SAT} experiments for calibrating or testing OPAM thermobarometers. However, to address our earlier comment on the limitation of the Baxter et al., (2023) and Hartley et al (2018) studies, we subset our OPAM\textsubscript{SAT} compilation (n=249) to remove all calibrant experimental studies named in Table 4 of Yang et al (1996) when testing the performance of the Yang et al (1996) barometer and thermometer (n=199; marked in Supplementary Table 1a).

**Asserting OPAM saturation**

Determining OPAM saturation is critical for reliable application of the thermobarometric equations which rely on this equilibrium assemblage. We stress that the most valid method for determining multiple saturation is to use petrographic indicators such as texturally equilibrated OPAM mineral phases (i.e., euhedral, not resorbed). For bulk rock analyses of magmas considered as putative melts, “petrological cannibalism” (Cashman and Blundy, 2013) may make quantitative textural analysis (e.g., crystal size distributions) and/or chemical mapping essential to elucidate exogenous OPAM crystal populations (Higgins et al., 2021b; Neave et al., 2017, 2014; Sheldrake and Higgins, 2021). For example, a hallmark of less-evolved basaltic magmas is high-An\# phenocrysts, or phenocryst cores, at disequilibrium with their matrix glass (Neave and Namur, 2022). Significant crystal accumulation may be identified by strong correlations between modal mineral abundances and mineral-compatible trace elements, although it can also be necessary to identify and correct for an accumulated mush liquid in addition (Passmore et al., 2012). Magmas which have accumulated crystals should have their bulk chemistry corrected by mass balance, akin to a post-entrapment
crystallisation correction for melt inclusions, before using any melt-based thermobarometer. Finally, we note that the petrographic absence of a phase in hand sample does not preclude its presence in the crystallising assemblage. This is often termed “cryptic fractionation” and manifests itself in mid-ocean ridge basalts as the “pyroxene paradox” whereby the chemical mass balance between minerals, glass, and whole rock requires clinopyroxene that is conspicuously lacking as a phenocryst (Dungan and Rhodes, 1978; Grove et al., 1992; Herzberg, 2004; Kelley and Barton, 2008; Lissenberg et al., 2019). Based on the range of processes which may prevent a magma from representing an OPAM_{SAT} melt, it is preferable to use clean, unaltered, microlite-free glass compositions in petrographically characterised magmas as the input for OPAM thermobarometry.

An alternative, or a complement, to petrographic analysis is a melt-based binary classifier to distinguish OPAM_{SAT} melts from OPAM undersaturated (OPAM_{UNSAT}) melts. A classifier is particularly useful for processing large regional or global datasets where original samples cannot be obtained, or whole rock data where multiple saturation cannot be petrographically determined. Previous methods include graphical (Maclennan et al., 2001; Yang et al., 1996), empirical (Kelley and Barton, 2008), and statistical or probabilistic (Baxter et al., 2023; Hartley et al., 2018) approaches. The latter remains the most widely applied but suffers from false negatives whereby OPAM_{SAT} experimental melts with no explainable defect are classified as OPAM_{UNSAT} melts (Baxter et al., 2023; Hartley et al., 2018). A saturation classifier must work to limit, as much as feasibly possible, the presence of false positives (false report of OPAM_{SAT} melts) or false negatives. The aim of an OPAM saturation binary classifier, or any binary classifier for that matter, is to identify or engineer differences between the two categories of data so they can be mathematically discriminated from one another. We have developed a simplified statistical approach, presented as an R script (R Core Team, 2023),
which returns a probability of OPAM saturation ($P_{\text{SAT}}$) using our up-to-date experimental dataset.

We first consider a set of critical oxides which must be reported and non-zero (i.e., chemically measured in either an experimental or natural melt) to use our saturation test. The critical oxides are chosen by inspecting our OPAM$_{\text{SAT}}$ compilation and are expressed in wt% in their raw form: SiO$_2$, Al$_2$O$_3$, MgO, FeO, CaO, Na$_2$O, K$_2$O, TiO$_2$. For the entire saturation test process, all experimental and natural melts are normalised to 100 wt% anhydrous considering just these eight critical oxides. The eight critical oxides also perform an essential, non-negotiable, first-pass test for identifying OPAM$_{\text{SAT}}$ melts, by using them to define a series of OPAM convex hulls. A convex hull is a polygon that connects the outer ring of points in an X-Y plot, in this case a Harker plot of two critical oxides (e.g., SiO$_2$[x] versus Al$_2$O$_3$[y]; Fig. 2a). The OPAM convex hull is expanded to account for an average relative analytical uncertainty of $\pm$5%. We define the OPAM convex hull for the 28 pairwise combination of the 8 critical oxides and use it as an initial test to verify if a natural or experimental melt of unknown saturation state could be OPAM$_{\text{SAT}}$. In other words, if a melt subjected to the saturation test does not fall inside all 28 OPAM convex hulls, the melt does not represent a reasonable approximation of an OPAM$_{\text{SAT}}$ melt in multi-dimensional space based on our current experimental knowledge. The OPAM convex hull test provides a rapid method to preliminarily screen melts that are being applied beyond the range of current OPAM$_{\text{SAT}}$ experiments.

Our OPAM$_{\text{SAT}}$ experimental dataset is combined with OPAM$_{\text{UNSAT}}$ melts from the large experimental compilation of Weber and Blundy (2023). The OPAM$_{\text{UNSAT}}$ melts are those experiments that contain up to two of the three major OPAM mineral phases (olivine $\pm$ plagioclase $\pm$ augitic clinopyroxene) plus or minus Fe-oxides, and are performed under pressurised conditions at $\leq$10 kbar. Further, we filter these OPAM$_{\text{UNSAT}}$ melts to ensure they
too are within the 28 OPAM convex hulls as described above. The result is an OPAM\textsubscript{UNSAT} dataset that is coincidentally identical in size to our OPAM\textsubscript{SAT} dataset (n=249), together forming our “saturation dataset” (n = 498; Fig. 2; Supplementary Table 2a; full references in Supplementary Table 2b). These 498 experiments are used to define the probability that a melt of unknown saturation state (e.g., a natural melt composition) is OPAM\textsubscript{SAT} given that it first satisfies the OPAM convex hull test.

The experimental data of the saturation dataset are combined with the natural (unknown) dataset to produce a single, coherent “input dataset” for comparison. Next, all melts within the input dataset have their oxide melt chemistry transformed. Raw compositional data carry only relative information and are subject to nonnegative and constant-sum (100 wt\%) constraints (Boschetty et al., 2022). Instead, ratios between compositional data better measure variability which can be achieved using log-ratio transformations that map data into an unconstrained Euclidian space (Chayes, 1971). We use the isometric log ratio (ilr) which yields seven isometric log ratios (one less than the number of critical oxides) that preserve the geometric properties of the raw data and have a non-singular covariance matrix (Boschetty et al., 2022; Egozcue et al., 2003; Equation 2). The ilr is calculated using the “ilr” function in the “compositions” package (Boogaart et al., 2023) of R (R Core Team, 2023) as follows:

\[
\text{ilr}(x) = \sqrt{\frac{-i}{i+1}} \ln \left[ \frac{g(x_1, \ldots, x_i)}{x_{i+1}} \right], \quad i = 1, 2, \ldots, D - 1 \quad (2)
\]

where, x is a raw melt compositional analysis, i is a specific part, D is the total number of parts (8, the number of critical oxides), and g(x\textsubscript{i}) is the geometric mean of the parts of x given by:
Next, using the newly ilr-transformed data, a Euclidian distance matrix is calculated for the input dataset:

\[ d_E = \sqrt{\sum_{i=1}^{n} (x_i - y_i)^2} \]  

where \( d_E \) is the Euclidean distance matrix, \( i \) is the number of parts (7, the number of isometric log ratios from Equation 2), and \( x \) and \( y \) are the two compositional analyses being considered. The entire Euclidian distance matrix is normalised between 0 (closest) and 1 (furthest) according to:

\[ d_{E(norm)} = \frac{d_E^i - \min(d_E)}{\max(d_E) - \min(d_E)} \]  

where \( d_E^i \) is a single entry in the Euclidian distance matrix (\( d_E \)).

To predict whether an unknown (natural) entry in the input dataset is OPAM\textsubscript{SAT} or OPAM\textsubscript{UNSAT} we use the \( n \) closest experimental points according to the scaled distance matrix \( (d_{E(norm)}) \). The sensitivity to \( n \) is assessed in the results section. The \( n \) closest scaled distances are used in a weighted equation which returns the probability of OPAM saturation \( (P_{SAT}) \):

\[ P_{SAT} = \sum_{i=1}^{n} [(1 - d_{E(norm)}^i) \cdot V_{SAT} / n] \]  

where \( V_{SAT} \) is the numerical saturation value of each of the \( n \) points \( (V_{SAT} = 0 \) for an OPAM\textsubscript{UNSAT} melt; \( V_{SAT} = 1 \) for an OPAM\textsubscript{SAT} melt). If Equation 6 returns \( \geq 0.5 \) then the
unknown value is considered more likely to be OPAM_{SAT} and if it returns <0.5 then it is considered more likely to be OPAM_{UNSAT}. The above mathematics reduces to a quantitative question, which is posed for each compositional datapoint of unknown saturation state in the input dataset in turn: “of the n closest experimental points of known saturation state to our datapoint of unknown saturation state, how many of those n experiments are OPAM_{UNSAT} and how many are OPAM_{SAT} in scaled multidimensional chemical space”? Equations 2 and 3 transform the experimental and unknown data, Equations 4 and 5 define distance using the newly transformed data, and Equation 6 weights the n experiments by their distances to the unknown melt. This approach has two advantages: (i) unevenly distributed experiments in P-T-X space are accounted for by Equation 6, giving a smaller weight to chemically distal experiments; (ii) Equation 6 has a probabilistic meaning such that an unknown melt sitting in a part of multidimensional chemical space which is occupied by many OPAM_{SAT} melts will return a high saturation probability, whereas a diffuse mixture of OPAM_{SAT} and OPAM_{UNSAT} experiments will return a lower saturation probability.

**Initial variable selection, regression methodology, and model validation**

To derive an improved OPAM thermobarometer we regress new T and P equations using our OPAM_{SAT} experimental compilation (n = 249; Supplementary Table 1a). Regression identifies the “best fit” equation that describes a dataset by minimising a cost function, in this case (and most typically) the sum of the squared residuals. We follow the reverse approach to multilinear regression which initially includes all possible variables in the fitting process, fits a function, identifies the variable of lowest significance, and removes it from the fit. This process is performed iteratively using the “lm” function in the “stats” package of R (R Core Team, 2023) until all variables and coefficients in the fit are significant. The t-value and p-value are the common measures of significance, where the p-value is the probability that any
observed relationship is due to chance and the t-value is the ratio between a fit coefficient and its standard error. Fit coefficients with higher t-values (e.g., >3) and low p-values (<0.01) indicate a good fit to the data. We use a stopping rule such that all variables must have t-values >3 to be considered a converged fit. A small number of additional outliers (\( P = 6; \ T = 3 \)) were identified during the fitting process, based on residuals 1.5 times higher than the interquartile range of all residuals, and these were omitted from the regression (e.g., Blundy, 2022).

The starting variables to initialise the iterative regression process should logically describe the OPAM cotectic position as a function of \( \text{P-T-X} \). The OPAM cotectic is \( P \)-sensitive, largely due to expansion of the clinopyroxene stability field at higher \( P \) (Bender et al., 1978; Grove et al., 1992; Lissenberg et al., 2019), with increasing melt \( \text{H}_2\text{O} \) content also suppressing plagioclase saturation to lower \( T \) at fixed \( P \) (Sisson and Grove, 1993; Yoder, 1965). \( \text{CaO-MgO-Al}_2\text{O}_3-\text{SiO}_2 \) (CMAS; Libourel et al., 1989; Presnall et al., 1978; Shi, 1992; Yang et al., 1996) in addition to \( \text{FeO} \) (Shi, 1993), \( \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{and TiO}_2 \) (Yang et al., 1996) are the major elements which have previously been used to characterise the OPAM cotectic (i.e., the eight critical oxides used for our OPAM saturation test). Increasing \( \text{Cr}_2\text{O}_3 \) promotes clinopyroxene saturation, which prompted the reformulation of the three Yang et al (1996) cotectic equations by Voigt et al (2017). However, we omit \( \text{Cr}_2\text{O}_3 \) from our fit routine due to a lack of consistent reporting in both experimental and natural data which would prevent its wide application and robust testing. Oxides are normalised to 100 wt\% (anhydrous) and converted to liquid cation fractions (e.g., \( X_{\text{Al}0.5} \)) for fitting (see Table 1 of Putirka, 2008 for an example conversion). Composite variables implicated by other studies of basaltic melt equilibria such as \( X_{\text{Si}0.2} \times X_{\text{Ti}0.2} \), \( (X_{\text{Si}0.2})^2 \) (Yang et al., 1996), \( \text{Ca#} \ (X_{\text{Ca}0}/[X_{\text{Ca}0} + X_{\text{Na}0.5}]) \), \( \text{Al#} \ (X_{\text{Al}0.5}/[X_{\text{Al}0.5} + X_{\text{Si}0.2}]) \) (Neave and Namur, 2022), and \( X_{\text{Ca}0}/X_{\text{Al}0.5} \) (Voigt et al., 2017) were also included. The latter positively correlates with clinopyroxene saturation \( T \) as well as the Mg\# of the liquidus
clinopyroxene (Voigt et al., 2017), whereas alkalis modulate olivine stability (Grove et al., 1992; Meen, 1990).

Around 10 points or more are required per fit variable (Harrell, 2015) meaning our 13 initial variables require around 130 experiments. Therefore, we are required to split our experimental dataset into two roughly equal parts: a “training dataset” (n = 126) to regress the model and a “validation dataset” (n = 123) to recover independent performance statistics. We partition entire experimental studies into each dataset, rather than splitting all data randomly, to assess the role of systematic error between experimental studies (see Discussion). We achieve this using a splitting algorithm which repeatedly partitions studies randomly into the training and validation dataset until the number of entries in each dataset are 125±5. There is sufficient chemical overlap between the two datasets (Supplementary Fig. 1). Once the thermometer and barometer are regressed using the training dataset, the validation dataset is used to recover the following metrics of average model performance: the standard error estimate of the fit (SEE; Equation 7); the slope, intercept, and R² of a plot of predicted (X) versus experimental P or T (Y; Piñeiro et al., 2008); and the mean absolute error (MAE; Equation 8).

\[
SEE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (predicted_i - experimental_i)^2} \quad (Equation \ 7)
\]

\[
MAE = \frac{1}{N} \sum_{i=1}^{N} |predicted_i - experimental_i| \quad (Equation \ 8)
\]

Our thermobarometer and saturation test are presented as a straightforward R script which reads from an input csv file to be populated with melt data. The R script, input csv file template, and simple instructions for use (i.e., downloading R, opening and running the script)
are provided in the Supplementary Material and on the code repository GitHub
(https://github.com/OJHiggins/HS2024_OPAM). The R script output retains the original data
structure of the input csv file and manages unlimited additional descriptor columns (field
location, sample names, etc).

RESULTS

Independent test of the Yang et al (1996) OPAM thermobarometer

To independently test the performance of the Yang et al (1996) thermobarometer we
use our OPAM$_{SAT}$ compilation minus the experimental studies named in Table 4 of Yang et al
(1996; n=199). The barometer calculations were made using the Yang et al (1996)
implementation of Baxter et al (2023) which applies the method of Hartley et al (2018) and so
also returns their probability of OPAM$_{SAT}$ ($P_f$). The Yang et al (1996) thermometer is not
applied in Baxter et al (2023) so we instead use the liquid cation output from Baxter et al (2023)
and calculate $T$ ourselves using the Yang et al (1996) thermometer equation. The limit of H$_2$O
for the Yang et al (1996) thermobarometer is not officially stated but is probably capped at ~2
wt% H$_2$O based on the upper concentration in their calibration experiments. To inspect the
uncertainty of the Yang et al (1996) thermobarometer as a function of melt H$_2$O, we calculate
the SEE (Equation 7) and MAE (Equation 8) for experiments with an H$_2$O $\leq$ H$_2$O$_{\text{max}}$. We vary
H$_2$O$_{\text{max}}$ between 0 and 7.2 wt% H$_2$O to yield an uncertainty metric of the Yang et al (1996)
equations at every melt H$_2$O content in the test dataset. Whilst melt H$_2$O exceeding ~2 wt%
would likely result in a significant drop in the Yang et al., (1996) thermobarometer
performance given the significant melt-compositional control of melt H$_2$O (Fig. 1), we would
expect their thermobarometer to reproduce experimental values close to the quoted
uncertainties at anhydrous and low-H$_2$O conditions.
Of the 199 input OPAM$_{SAT}$ experiments in our Yang et al., (1996) test dataset, only 7 pass the Hartley et al (2018) saturation filter of $P_F \geq 0.8$ which is 4% of all experiments or 13% of anhydrous (0 wt% H$_2$O) experiments. As outlined above, our OPAM$_{SAT}$ compilation contains no obvious experimental outliers and so should be a robust test of the number of false negatives produced by an OPAM saturation classifier. Our observation is consistent with that of Baxter et al (2023) where only 92 of their 250 OPAM experiments have a $P_F \geq 0.8$ (37%) and only 23 of these were conducted at >1 atm (9%). Hartley et al (2018) deliberately tuned their $P_F$ to limit false positives which, in a binary classifier, will be counterbalanced by a higher number of false negatives; whilst we acknowledge the important step forward by Hartley et al (2018) in the pre-screening of OPAM$_{SAT}$ melts before applying the Yang et al., (1996) thermobarometer, the false negative rate is very high and likely underrepresented by Baxter et al (2023).

The Yang et al., (1996) predicted $T$ and experimental $T$ show poor correspondence, with an increasing overestimation of $T$ with increasing melt H$_2$O (Fig. 3a). The few OPAM$_{SAT}$ experiments with $P_F \geq 0.8$ (large symbols in Fig. 3a) generally lie close to the 1:1 line. Despite a strong relationship between the quality of Yang et al., (1996) $T$ prediction and melt H$_2$O, several anhydrous experiments still show considerable and systematic $T$ overestimation. The relationship between uncertainty and melt H$_2$O can be more clearly observed in Fig. 3b, where both the SEE and MAE increase quasi-linearly between 0 wt% H$_2$O ($n = 53$) and $\leq 7.2$ wt% H$_2$O ($n = 199$). At anhydrous conditions, the SEE is $\pm 35$ °C and the MAE is $\pm 29$ °C which is more than the $\pm 20$ °C quoted by Yang et al., (1996) but comparable to many widely applied melt-based and mineral-based thermometers (e.g., Putirka, 2008). However, the Yang et al., (1996) calibration is theoretically applicable to melts with up to $\sim$2wt% H$_2$O based on the calibration dataset and is often applied in low-H$_2$O, but not anhydrous, natural systems (e.g., Iceland, the Galápagos; Hartley et al., 2018; Stock et al., 2018). As an example, the H$_2$O of
matrix melts and nominally anhydrous minerals in basalts from the Galápagos span 0.06-0.77 wt% and 0.09-2.54 wt% respectively (Gleeson et al., 2021; Fig. 3b). At the upper limit of these natural melt H2O contents, the SEE is ±69 °C and the MAE is ±55 °C in addition to the systematic uncertainty highlighted in Figure 3a.

The Yang et al., (1996) predicted P and experimental P show the same relationship as for T (Fig. 3c), with a systematic overestimation of predicted P with increasing melt H2O. Again, the few experiments with Pf ≥0.8 (large symbols in Fig. 3c) generally lie close to the 1:1 line. Contrary to the suggestion of Baxter et al (2023), we observe no strong relationship between Pf, offset between predicted and experimental P, and melt alkali content (Na2O+K2O [wt%]; square symbols in Fig. 3c). We question the utility of their melt alkali filter given that changing the maximum permissible Na2O+K2O of an input melt from 6.16 wt% to 5 wt% resulted in a reduction of only ±0.03 kbar in the MAE according to Table 1 of Baxter et al (2023). The Yang et al., (1996) MAE of ±1.13 kbar quoted by Baxter et al (2023) is a substantial underestimate; for anhydrous melts using our independent dataset the SEE is ±3.29 kbar and the MAE is ±2.54 kbar, more than double their quoted value. These results underscore the significant effect that filtering large quantities of OPAMSAT experiments can have on the quoted uncertainty. For H2O contents in the range of melts from the Galápagos, the SEE and MAE rise to ±4.96 and ±3.83 kbar respectively (Gleeson et al., 2021; Fig. 3d). In short, the Yang et al (1996) barometer suffers from significant systematic (Fig. 3c) and random (Fig. 3d) uncertainty when tested by an independent OPAMSAT dataset, even at anhydrous conditions.

**OPAM**SAT prediction

To assess the performance of our binary classifier for OPAM**SAT** melts as a function of n, we treat each experiment from the saturation dataset (n = 498) in turn as an unknown and predict the saturation state (OPAM**UNSAT** or OPAM**SAT**). We score our approach using the
number of true positives (TP), false positives (FP), true negatives (TN), and false negatives (FN). The combination of these metrics defines the accuracy (A) and precision (P) of the algorithm, as well as the true positive rate (TPR), false positive rate (FPR), true negative rate (TNR), and false negative rate (FNR) (Equation 9a–f; Fig. 4):

\[
TPR = \frac{TP}{TP + FN} \quad (Equation \ 9a)
\]

\[
FPR = \frac{FP}{FP + TN} \quad (Equation \ 9b)
\]

\[
TNR = 1 - FPR \quad (Equation \ 9c)
\]

\[
FNR = 1 - TPR \quad (Equation \ 9d)
\]

\[
A = \frac{TP + TN}{TP + TN + FP + FN} \quad (Equation \ 9e)
\]

\[
P = \frac{TP}{TP + FP} \quad (Equation \ 9f)
\]

The predictive performance of our OPAM binary classifier varies as a function of n, where n is the number of points considered to define the local state of OPAM saturation in multidimensional space, and can be divided into three broad behaviours (grey shading in Fig. 4; i-iii):

(i) Predictive performance is good (accuracy=0.81-0.74; precision=0.91-0.78) but erratic or “spiky” (2 ≤n <10). The FPR increases with n but remains broadly low (0.06-0.20).

(ii) Classifier performance begins to drop off as n increases, with accuracy (0.75-0.63) and precision (0.81–0.70) decreasing over a wide range of n (11≤n<40). The FNR increases and the TPR decreases in tandem but the FPR and TNR both remain stable.

(iii) All performance metrics largely plateau at n ≥40, except for an increasing FNR (0.5-0.68) and decreasing TPR (0.47-0.32).
Using the calculated performance metrics, our preferred n value is 11, coinciding with the end of the spiky behaviour whilst maximising predictive performance (ii; Fig. 4; Supplementary Table 3). At n=11, our approach has an accuracy of 0.75, a precision of 0.78, a TPR of 0.7, and a FPR of 0.2. Therefore, when assessing the saturation state of a natural melt of unknown saturation state, the saturation states of the 11 closest experimental melts are considered. Our approach is not a “model” sensu stricto, but rather a probability map of local compositional space detailing the likelihood that a given melt is OPAMSAT. Theoretically, our method can continuously evolve as experiments are added, particularly at the margins of the OPAM convex hulls. However, whilst the performance metrics of our model offer improvements over the original saturation test of Hartley et al (2018), our model does not unequivocally identify OPAMSAT melts (Fig. 4). It is highly likely that the diffuse overlap in chemical space between OPAMSAT and OPAMUNSAT melt compositions (e.g., Fig. 2) makes a perfect mathematical solution impossible. As such, our saturation test should be used in combination with petrographic and geochemical indicators where possible and should always be usurped by these methods. The key advantage of our approach is that it acknowledges the local diffuseness of the multidimensional space occupied by OPAMSAT and OPAMUNSAT melts when calculating P_{SAT}.

New OPAM thermobarometer performance

The successful fits for $P$ (Equation 10a) and $T$ (Equation 10b) of OPAMSAT melts as a function of the melt composition are as follows:

$$P(kbar) = 90.74 - (257.77 \times X_{SiO_2}) + (33.99 \times X_{AlO_{1.5}}) + (106.83 \times X_{MgO})$$

$$- (194.34 \times X_{CaO}) - (50.55 \times X_{NaO_{0.5}}) + (189.62 \times (X_{SiO_2})^2) (Equation 10a)$$
\[ T(°C) = -9201 + (10331 \times X_{SiO_2}) + (7128 \times X_{FeO}) + (10004 \times X_{MgO}) + (7691 \times X_{NaO_{0.5}}) + (9658 \times X_{KO_{0.5}}) + (9574 \times Al\#) + (19921 \times [X_{SiO_2} \times X_{TiO_2}]) + (1303 \times [X_{CaO}/X_{AlO_{1.5}}]) \] (Equation 10b)

where \( X \) followed by the oxide subscript denotes liquid cation fractions calculated using the method outlined in Table 1 of Putirka (2008) on an anhydrous basis, all Fe is considered as FeO, and Al\# \( \left( X_{AlO_{1.5}}/\left[X_{AlO_{1.5}} + X_{SiO_2}\right] \right) \) is on a molar basis. Coefficient standard errors, p-values, and t-values are listed in Supplementary Table 4, with scatter assumed to include normally distributed error (e.g., analytical and experimental uncertainty).

Performance metrics for our new OPAM thermometer and barometer are calculated using the same validation dataset (n = 123). The new thermometer has a SEE of ±35 °C and an MAE of ±30 °C, with low systematic offset relative to the 1:1 line (grey line in Fig. 5a) shown by slope (1.00) and intercept (7 °C) values close to 1 and 0, respectively (Fig. 5a). For the closest comparison to the quoted uncertainty of ±20 °C for the Yang et al (1996) thermometer, the MAE of our own training dataset is ±21 °C although our MAE is applicable for a much wider range of melt H$_2$O. The new barometer has a SEE of ±1.13 kbar and an MAE of ±0.9 kbar (Fig. 5b). As with our thermometer, the systematic offset relative to the 1:1 line of our new barometer is modest (slope = 0.98, intercept = 0.17 kbar). It is difficult to compare uncertainty with the Yang et al (1996) barometer as we have asserted that truly independent test statistics were not produced by Hartley et al (2018) or Baxter et al (2023; Fig. 3). However, the quoted uncertainty of Baxter et al (2023) on their partially self-validated and heavily filtered test dataset is an MAE of ±1.13 kbar. Our performance statistics are calculated using an independent validation dataset and are applicable to a range of melt H$_2$O contents spanning 0 to 7.7 wt%. Furthermore, the MAE of our new \( P \) calibration is similar to the quoted MAE value of the gabbronorite (CHOMPI) melt-based barometer of Blundy (2022; MAE=±1.3 kbar) and
the SEE of the clinopyroxene-liquid barometer of Neave and Putirka (2017; SEE=±1.4 kbar).

Therefore, our calibration can complement other independent models and, indeed, produces comparable results (see Discussion).

Given the strong control of melt H$_2$O on the uncertainty of the Yang et al., (1996) thermobarometer performance (Fig. 3), we also assess any systematic uncertainty in $P$ and $T$ residuals (experimental $P$ or $T$ minus predicted $P$ or $T$) for our new OPAM thermobarometric equations (Equation 10a, Equation 10b) as a function of melt H$_2$O. As the melt H$_2$O concentration is universally higher in volcanic arcs (Wallace, 2005) compared to mid-ocean ridge basalts (MORB) and ocean island basalts (OIB; Michael, 1995; Sobolev and Chaussidon, 1996), we also categorise experimental studies as either arc or MORB/OIB where these labels are unambiguous (Fig. 5c, Fig. 5d). When using these categories there is a tendency for the $T$ of OIB and MORB experiments to be underestimated, with an average residual of $+24$ °C compared to a mean of $+7$ °C for arc experiments (Fig. 5c). For $P$, there is no clear relationship between the calculated residuals and geodynamic setting, with relatively sharp distributions centred on zero (Fig. 5d). Overall, compared to the very large effect observed for the Yang et al., (1996) equations (Fig. 3), melt H$_2$O only weakly dictates systematic uncertainty in $T$ (Fig. 5c) and has little effect on systematic uncertainty in $P$ (Fig. 5d) for our new OPAM thermobarometer.

**DISCUSSION**

**Perspectives on thermobarometer performance and usability**

The calibration and testing of our improved OPAM barometer (Equation 10a) and thermometer (Equation 10b) as a function of OPAM$_{SAT}$ melt composition has highlighted three considerations for future thermobarometers.
In a correlation matrix between SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, MgO, CaO, Na$_2$O, K$_2$O, T, and P using our newly compiled OPAM$_{SAT}$ dataset (n=249; Supplementary Fig. 2), P is the third most correlated variable with T and T is the most correlated variable with P (correlation coefficient = 0.51). The original Yang et al., (1996) thermometer regresses T as a function of OPAM$_{SAT}$ melt composition and P, in contrast to Equation 10b which is a P-independent thermometer. Whilst the addition of a P term undoubtedly leads to an improved fit for many thermometers (e.g., Neave and Putirka, 2017; Putirka, 2016, 2008), the incorporation of a P term makes it difficult to deconvolve whether any relationship between P and T is methodological or thermodynamic. In other words, can P and T be considered two truly independent variables? The strong correlation between P and T is a thermodynamic consequence for high-melt-fraction, hydrous experiments close to the liquidus due to the strong dependency of volatile solubility and P on liquidus T (Bohlen et al., 1982). However, in lower-melt-fraction experiments further from the liquidus, some of the correlation between P and T will also be partly due to the methodological tendency to perform high-T experiments at lower P and vice versa. This tendency relates to the need for experimentalists to have large melt pools to analyse in their experimental charges, requiring a methodological consideration of liquidus T which is a function of P. By applying P-dependent thermometers and T-dependent barometers in natural systems, this experimental bias may consequently be introduced into geological interpretations of natural systems, leading to spurious correlations between the two variables. Therefore, we advise that P and T remain purely independent when calibrating thermobarometers, or that both dependent and independent equations are provided where alternative constraints on P or T are available (e.g., Putirka, 2016).

Our binary classifier to determine the probability that a melt is OPAM$_{SAT}$ highlights the need for new standards in how binary classifiers are benchmarked and tested between studies. In the case of testing thermobarometric equations (e.g., Equation 10a, Equation 10b),
the SEE (Equation 2) and MAE (Equation 3) are standardised metrics which can robustly compare different thermobarometer performance between studies (e.g., Fig. 3, Fig. 5). In contrast, testing classifiers requires a clear description of prior assumptions, akin to the prior assumption term described in the equation of Bayes Theorem. For example, the performance metrics for our new binary classifier outlined in Figure 4, such as the accuracy and precision, are valid for the prior assumptions that: (i) the experimental melt is in equilibrium with between one and three of olivine + plagioclase + clinopyroxene, with or without Fe-oxides; (ii) the melt of unknown saturation state, be it a newly performed experimental melt or a natural melt composition, passes the OPAM convex hull test. The latter assumption is determined mathematically by our model and marked in the output csv files generated by our R script, yet the former requires at least some petrographic or geochemical knowledge from the user prior to model application. Consistently stating these prior assumptions is vital if the performance of future new and improved OPAM classifiers are to be fairly and consistently compared with existing models.

The residuals for experimental $P$ or $T$ minus predicted $P$ or $T$ of our new models are generally centred at or close to zero and there is little systematic uncertainty identified by the fit between predicted and measured values (Fig. 5). Despite this, there is clear clustering of individual studies on either side of the 1:1 line between predicted and experimental $P$ or $T$ (Fig. 5), demonstrating that inter-study effects partly control the thermobarometer uncertainty according to the validation dataset statistics. This intra-study clustering effect is often apparent in machine learning thermobarometers where multiple train-validation dataset splits show the effect that partitioning of studies between these two datasets can have on model performance (Higgins et al., 2021a; Jorgenson et al., 2022; Petrelli et al., 2020). Understanding, constraining, and correcting for these inter-study or inter-laboratory effects is central to
developing future barometers which can reliably predict global datasets with uncertainties comparable to those quoted for the original regression.

Application to two geophysically monitored volcanic eruptions

The $P$-$T$-$X$ of magma during storage and ascent plays a leading role in modulating eruptive dynamics (Higgins and Caricchi, 2023; Popa et al., 2021). Therefore, quantitative tools to describe pre-eruptive magmatic $P$-$T$-$X$, such as the new thermobarometric equations presented here, can be useful to: (i) petrologically monitor active volcanoes during protracted eruptions, particularly to compare evolving geochemical and geophysical signals (Hartley et al., 2018; Longpré et al., 2014; Magee et al., 2018, 2020; Saunders et al., 2012; Stock et al., 2018); (ii) understand medium-term and long-term evolution in magma storage conditions by studying multiple temporally constrained volcanic deposits (Bouvet de Maisonneuve et al., 2021; Forni et al., 2018; Giordano and Caricchi, 2022; Higgins et al., 2021a; Smithies et al., 2023; Weber et al., 2020). To assess the utility of our new thermobarometer for studying volcanic systems, we apply our calibration to the OPAM$_{SAT}$ melts of two case study eruptions (the 2015 eruption of Wolf Volcano, Galápagos; the 2014-2015 Holuhraun eruption, Iceland). Both eruptions have been geophysically, geochemically, and petrographically studied in detail, providing a means of independent validation and comparison with our updated thermobarometric predictions. For the two case study eruptions we present $P$ and $T$ predictions with our new thermobarometer for both unfiltered (all samples which pass the OPAM convex hull test; $n = 76$ of 76 for Wolf and $n = 102$ of 114 for Holuhraun) and filtered ($P_{SAT}$≥0.5; $n = 70$ of 76 for Wolf and $n = 45$ of 102 for Holuhraun) data. In doing so we keep track of any compositional bias, if present, introduced to our $P$ and $T$ predictions by the probabilistic filtering. The full dataset of melt compositions for both volcanic systems are presented in Supplementary Table 5.
The 2015 eruption of Wolf Volcano, Galápagos

The Galápagos Archipelago is one of the most volcanically active regions on Earth, with eruptions occurring at a repose period of ~2 years (Bernard et al., 2019). The archipelago is the surface manifestation of the Galápagos plume which impinges on the base of ~10 Ma-old, ~11 km-thick oceanic crust (Feighner and Richards, 1994). Wolf Volcano, on the north of Isabela Island, is an active volcano in the western Galápagos (Geist et al., 2005). The 2015 eruption produced ~0.01 km$^3$ of monotonous basaltic lava and tephra from circumferential and radial vents (Bernard et al., 2019; Stock et al., 2020, 2018). We apply our new OPAM thermobarometer to the 2015 whole rock and matrix glass measurements from Wolf Volcano (Stock et al., 2020, 2018). All petrological $P$ (kbar) estimates are converted to depth (km) relative to the surface using a polynomial fit to the Hawaiian ocean crust $P$-depth relationship of Putirka (1997; Equation 11; $R^2 = 0.96$) as per Stock et al. (2018):

$$\text{Depth (km)} = -0.02086^2 \cdot P(\text{kbar}) + 3.36352 \cdot P(\text{kbar}) + 0.46170 \quad (\text{Equation 11})$$

All whole rock and matrix glass data bar six measurements return a strong indicator for OPAM saturation ($P_{SAT}$) using our new saturation test (0.81±0.16; mean±1σ), agreeing with petrographic and thermodynamic modelling results which attest to three-phase saturation (Stock et al., 2020). Due to the strong indication for OPAM saturation in all samples, unfiltered and filtered ($P_{SAT} \geq 0.5$) melts record an identical $T$ of 1151±15 °C (mean±1σ) using Equation 10b (Fig. 6a). The restricted whole rock compositions result in a tighter range of $T$ (1172±2 °C) compared to matrix glass (1144±11 °C). The overall OPAM$_{SAT}$ $T$ range is in strong agreement with clinopyroxene thermometry for glomerocrystic (1164±11 °C), phenocrystic (1151±9 °C), and tephra-hosted (1164±15 °C) clinopyroxene from Stock et al. (2018; Fig. 6a).
New OPAM P estimates for unfiltered Wolf samples (n = 76), calculated with Equation 10a and converted to depth (km) using Equation 11, are 8.6±2.2 km for matrix glass and 9.6±0.8 km for whole rock. The OPAM\textsubscript{SAT} depths compare well with estimates derived using the Yang et al., (1996) barometer and P\textsubscript{F} ≥0.8 filter of Hartley et al., (2018; 9.7±2.8 km; A and B vs L in Fig. 6b). Filtering our new OPAM\textsubscript{SAT} depths (P\textsubscript{SAT}≥0.5; n=70) yields near identical values for matrix glass (8.6±2.3 km; C in Fig. 6b) and identical values for whole rock (9.6±0.8 km; D in Fig. 6b) compared to the unfiltered results. The three different textural sub-classes of clinopyroxene identified by Stock et al. (2018) record appreciably wider and systematically deeper storage depths (glomerocrystic = 9.7±2.5 km, phenocrystic = 11±2.8 km, tephra-hosted = 10±3.1 km; mean±1σ; I, J, and K in Fig. 6b), where P is calculated using clinopyroxene-melt barometry (Neave and Putirka, 2017). Inversion of interferometric synthetic aperture radar (InSAR) measurements indicates a shallow source at ~1 km depth (E in Fig. 6b) and deep sources at ~6.1 to 8.8 km (F, G, and H in Fig. 6b). Encouragingly, our new OPAM barometer produces depth results which are consistent with the depth of the deep magma source identified by InSAR inversion (F, G and H in Fig. 6a). Therefore, we corroborate the findings of Stock et al (2018) that magmas feeding the 2015 Wolf eruption were sourced predominantly from the lower crust and not the shallow-crustal InSAR source at ~1 km (E in Fig. 6b). In detail, the mean values of all petrographic indicators of magma storage depth (pressure) are systematically higher than those from the InSAR inversions. As alluded to by Stock et al (2018), we interpret this offset as InSAR signals returning deformation specifically at the top of a vertically protracted magma storage region whereas petrological estimates are recording crystallisation and/or equilibration deeper within that same storage region. We note that the mean depths recovered using our new OPAM barometer are most consistent with the InSAR results (Fig. 6b).
The island of Iceland is the surface expression of a plume-ridge interaction between the Mid-Atlantic Ridge and a mantle plume, resulting in anomalously thickened oceanic crust (15-44 km; Darbyshire et al., 2000; Jenkins et al., 2018) due to an increased mantle potential temperature that enhances melt supply. A variable mantle melt flux has been posited as a control on magma storage pressures on Iceland (Baxter et al., 2023), producing highly variable depths for the erupted melts from various volcanic zones. The 2014-2015 Holuhraun eruption was a basaltic fissure event that originated from within the Bárðarbunga volcanic system in central Iceland, producing >1.4 km$^3$ of lava and tephra (Pedersen et al., 2017). The eruption represents a remarkable case study for testing models of magma storage conditions due to extensive pre- and syn-eruptive geochemical, seismic, and ground deformation datasets (Ágústsdóttir et al., 2016; Gauthier et al., 2016; Gudmundsson et al., 2016; Halldórsson et al., 2018; Hartley et al., 2018; Sigmundsson et al., 2015). Further, it allows us to directly verify our new OPAM thermobarometer against the results of Hartley et al. (2018), who developed their implementation of the Yang et al., (1996) barometer to assess the evolution of magma storage depths during the 6-month Holuhraun eruption. We apply our new OPAM thermobarometer to melt inclusion and matrix glass measurements from the Holuhraun eruption and, for direct comparison with Hartley et al. (2018), our $P$ (kbar) estimates are converted to depth (km) relative to the surface using a fixed crustal density of 2.86x10$^6$ kg/m$^3$.

Unlike samples from Wolf Volcano (Fig. 6a), Holuhraun melts show a lower and more diverse range of $P_{\text{SAT}}$ using our new saturation test (0.46±0.19; mean±1σ; Fig. 7a). Considering all compositions unfiltered for $P_{\text{SAT}}$ ($n = 102$), $T$ ranges from 1135 to 1254 °C (1193±31 °C) except for a single outlier at 1098 °C (Fig. 7a). Three $P$ values, not plotted but included in the $P$ statistics, return negative $P$ estimates. When our new OPAM $P$ results are converted to depth, unfiltered matrix glass (7.1±1.7 km; A in Fig. 7b) and melt inclusions (8.8±4.4 km; B in Fig.
729 overlap. Using a filter of $P_{\text{SAT}} \geq 0.5$ ($n = 45$), only 2 of 9 matrix glass values remain (5.2 km and 8.7 km; C in Fig. 7b), whereas melt inclusions cover a similar range to the unfiltered data (9.3±4.7 km; D in Fig. 7b). The wide spread of the melt inclusion depths is consistent with clinopyroxene-liquid barometry (Neave and Putirka, 2017) applied to clinopyroxene crystals that were screened for textural equilibrium (Halldórsson et al., 2018; 8.2±5 km; G in Fig. 7b).

The unfiltered depth results of the Yang et al (1996) equations implemented by Hartley et al (2018) are similar to our unfiltered OPAM depths for both matrix glass (6.6±2.4 km; H in Fig. 7b) and melt inclusions (10.2±4.2 km; I in Fig. 7b). However, the Hartley et al (2018) OPAM depths filtered for $P_f \geq 0.8$ are notably deeper and less dispersed for melt inclusions (11.9±3.5 km; K in Fig. 7b) compared to their unfiltered values, whereas matrix glass (6.8±2.4 km; J in Fig. 7b) are near identical to their unfiltered values. This observation shows that the saturation filter of Hartley et al (2018) has a much stronger effect on skewing $P$ to higher values for certain melt compositions than our new saturation test (Fig. 7b). Given the very-high false negative rate of the saturation test of Hartley et al (2018) there may be a compositional bias which is artificially deepening values as a result of applying their probabilistic filter. As with observations from Wolf Volcano, our OPAM barometry results are consistent with independent geophysical estimates of magma storage via the range of pre-eruptive seismicity (3-9 km; Sigmundsson et al., 2015) and the most common earthquake hypocentral depth (6±1 km; Ágústsdóttir et al., 2016), particularly for matrix glass. Therefore, we concur with Hartley et al (2018) that the 2014-2015 Holuhraun eruption represents a case study in which petrological and geophysical data can be reconciled.

**CONCLUSIONS**

We have calibrated a new barometer (Equation 10a) and thermometer (Equation 10b) for melts equilibrated with the mineral assemblage of olivine + plagioclase + augitic
clinopyroxene ± Fe-oxides, using an expanded dataset of anhydrous and hydrous experiments (Fig. 1, Fig. 2). The necessity to calibrate an updated OPAM thermobarometer arises from the most widely used calibration (Yang et al., 1996) being unable to reliably reproduce an independent dataset of experimental pressures and temperatures (Fig. 3). Previous attempts to calculate the true predictive performance of the Yang et al (1996) barometer by Hartley et al (2018) and Baxter et al., (2023) were hindered by: (i) testing datasets which were not independent of the Yang et al (1996) calibration dataset; and (ii) a statistical filtering process for OPAM saturation which removed large swathes of experiments that were demonstrably suitable for OPAM barometry. Therefore, the mean absolute error (MAE) of ±1.13 kbar quoted by Baxter et al., (2023) for the Yang et al (1996) barometer is a substantial underestimate. Rather, our independent test dataset yielded a MAE of ±2.54 kbar and a SEE of ±3.29 for the Yang et al (1996) barometer which increases significantly with melt H₂O (Fig. 3d). The Yang et al., (1996) thermometer performs passably at anhydrous conditions (SEE = ±35 °C; MAE = ±29 °C) but the uncertainty increases dramatically with increasing melt H₂O even at concentrations well within the range of their original calibration dataset (Fig. 3b).

In contrast with the Yang et al (1996) P and T equations, our new OPAM barometer and thermometer accurately reproduce an independent validation dataset of P and T, with a SEE of ±1.1 kbar and ±35 °C, respectively, and low systematic offset between measured and predicted values (Fig. 5a, Fig. 5b). Importantly we also see no significant systematic P offset as a function of H₂O (Fig. 5d) up to 7.7 wt% in OPAM SAT melts (Fig. 1), and only minor T offset which is within the average thermometer uncertainty (Fig. 5c). We also provide a binary classifier to predict the probability that a melt of unknown saturation state is OPAM saturated based on a weighted distance matrix in multidimensional chemical space. Our new method improves on existing approaches, particularly with respect to false negatives (falsely predicting that a melt is not OPAM SAT), yielding an accuracy of 0.75 and a precision of 0.78 (Fig. 4). The
new binary classifier of OPAM saturation should be used in conjunction with detailed petrographic and geochemical analysis where possible, owing to the overlap of OPAM_{SAT} and OPAM_{UNSAT} melts in multidimensional chemical space which precludes the development of a perfectly efficient binary chemical classifier (Fig. 2). Our thermobarometer and saturation test are presented as a simple R script (R Core Team, 2023) which takes user input via a csv file of melt compositional data.

To test our implementation, we used two recent volcanic eruptions which have been petrographically, geochemically, and geophysically well studied (the 2015 eruption of Wolf Volcano, Isabela Island, Galápagos; the 2014-2015 Holuhraun eruption, Iceland). In both cases, our updated OPAM barometer is consistent with existing, independent petrological and geophysical magma depth estimates but provides constraints with the lowest uncertainties to date (Fig. 6, Fig. 7). Hence, given the relative ease and rapidity of whole-rock and glass analysis afforded by modern sample preparation and analytical equipment, our new thermobarometer can complement syn-eruptive geophysical measurements to aid hazard management during on-going volcanic crises (Re et al., 2021). Additionally, our calibration may have sufficient P and T resolution (SEE of ±1.1 kbar and ±35 °C, respectively) to identify discrete changes in magma storage conditions when studying the time-integrated stratigraphic record of past eruptions.

**FIGURE CAPTIONS**

Fig.1: (a) Temperature (°C) versus pressure (kbar); (b) melt MgO (wt%) versus melt CaO/Al_{2}O_{3}; and (c) melt SiO_{2} (wt%) versus melt Na_{2}O+K_{2}O (wt%) for OPAM_{SAT} equilibrium experiments, colour contoured for melt H_{2}O (wt%). Grey symbols are hydrous experiments for which a H_{2}O content is not reported. Diamonds are experiments from studies used to calibrate the Yang et al (1996) coticet equations. The black curvilinear boundary in (c) is the alkaline-
subalkaline transition boundary (Irvine and Baragar, 1971). Melt compositions are normalised to 100 wt% anhydrous with all Fe as FeO.

Fig. 2: (a) Melt SiO$_2$ (wt%) versus melt Al$_2$O$_3$ (wt%); and (b) melt SiO$_2$ (wt%) versus melt MgO (wt%) for OPAM$_{SAT}$ and OPAM$_{UNSAT}$. OPAM$_{SAT}$ experiments were compiled for this study and are presented in Supplementary Table 1a. OPAM$_{UNSAT}$ experiments (olivine ± plagioclase ± augitic clinopyroxene ±Fe-oxides) are from the compilation of Weber and Blundy (2023; Supplementary Table 2a). The OPAM convex hull is a polygon connecting the outermost OPAM-saturated points in X-Y space with ±5% relative added to account for analytical uncertainty (black field in both figures). Melts from the 2015 eruption of Wolf Volcano (Galápagos; Stock et al., 2018, 2020) and the 2014-2015 Holuhraun eruption (Iceland; Hartley et al., 2018) are also plotted (see Discussion; Supplementary Table 5). All experimental and natural melt compositions are plotted normalised to the 8 critical oxides used for the OPAM saturation test.

Fig. 3: Performance of the Yang et al (1996) thermometer and barometer for an independent test of 199 OPAM$_{SAT}$ experiments from studies not used in the original Yang et al (1996) calibration. (a) The predicted temperature (°C) versus experimental temperature (°C). (b) The SEE and MAE for temperature (°C) as a function of melt H$_2$O (wt%). The line for n shows the number of experiments with the corresponding melt H$_2$O content on the x axis or less used to calculate the SEE or MAE. (c) The predicted pressure (kbar) versus experimental pressure (kbar). (d) The SEE and MAE for pressure (kbar) as a function of melt H$_2$O (wt%). In (a) and (c) points are colour coded for melt H$_2$O (wt%) and large symbols indicate experiments which pass the statistical filter of Hartley et al (2018) with a $P_F \geq 0.8$ (see text for details). Solid line is 1:1 and dashed lines are the bounds of the quoted uncertainty for the Yang et al (1996)
thermometer (±20 °C) and barometer (±1.13 kbar) respectively. In (b) and (d) the ranges of
H₂O (wt%) measured for Galápagos melts and calculated from nominally anhydrous minerals
are shown (Gleeson et al., 2021).

Fig. 4: Performance (Equation 9a-9f) of our statistical test for OPAMₜₐₜ melts as a function of
n (the number of adjacent experiments considered in multidimensional space when testing if a
natural melt is OPAMₜₐₜ). Grey boxes (i, ii, iii) highlight changes in test performance as a
function of n and are discussed in text. The chosen n used for our statistical test is 11 (thick
dashed line) at the start of region (ii).

Fig. 5: The performance of our new OPAM thermobarometer using the compiled training and
validation data (Supplementary Table 1a). (a) Experimental temperature (°C) versus predicted
temperature (°C). (b) Experimental pressure (kbar) versus predicted pressure (kbar). (c)
Experimental temperature (°C) minus predicted temperature (°C) and (d) experimental pressure
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and experimental melt H₂O (wt%; points). In (a) and (b) summary statistics for training (grey
points) and validation (coloured points) datasets are provided in the plot area. Grey solid line
is the 1:1 line, black dashed lines are the bounds of the quoted validation SEE, and the black
solid line is a linear fit between predicted (x) and experimental (y) values. In (c) and (d)
geodynamic settings for experimental studies are either arc or ocean island basalt (OIB) plus
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Fig. 7: (a) Pressure (kbar) versus temperature (˚C) using our new OPAM thermobarometer for all matrix glass and melt inclusion data from the 2014-2015 Holuhraun eruption (Iceland; Hartley et al., 2018). Data points are colour contoured for $P_{\text{SAT}}$ using our binary classifier for OPAM$_{\text{SAT}}$ melts. (b) $P$ converted to depth using a fixed density of $2.86 \times 10^6$ kg/m$^3$ for petrological and geophysical methods discussed in text, with letters corresponding as follows: A = mean±1σ of all matrix glass values using Equation 10a; B = mean±1σ of all melt inclusion values using Equation 10a; C = mean±1σ of matrix glass values with $P_{\text{SAT}} \geq 0.5$ using Equation 10a; D = mean±1σ of melt inclusion values with $P_{\text{SAT}} \geq 0.5$ using Equation 10a; E = pre-eruptive seismicity (Sigmundsson et al., 2015); F = most common earthquake hypocentral depth (Ágústsdóttir et al., 2016); G = clinopyroxene-liquid barometry (Neave and Putirka, 2017) for clinopyroxene crystals screened for textural equilibrium (Halldórsson et al., 2018); H, I = OPAM barometry of glass and melt inclusions respectively using the Yang et al (1996)
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DATA AVAILABILITY
The data tables used in this article and additional supplementary figures described in text are available in its online supplementary material. The OPAM thermobarometer code and saturation test are available on GitHub as a combined R script (https://github.com/OJHiggins/HS2024_OPAM).

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