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This chapter has been published in the Treatise of Geochemistry (<https://doi.org/10.1016/B978-0-323-99762-1.00024-3>). Please refer to that version - if you cannot get a copy, please email me at [penny\\_wieser@berkeley.edu](mailto:penny_wieser@berkeley.edu).

**Determining the Pressure – Temperature – Composition (P-T-X) conditions of magma storage**

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9  
10 **Key Points**

- 11 • Many mineral-melt barometers have standard errors of  $\pm 2\text{--}3$  kbar ( $\pm 7\text{--}11$  km), which limits their ability  
12 to provide detailed constraints on magma storage in relatively thin-crust settings (MORB and OIB).
- 13 • Different models/equations can yield very different PT conditions; model choice must be considered as  
14 one of the largest sources of systematic error in a given study.
- 15 • The paucity of independent test datasets for many methods makes it difficult to truly assess their  
16 performance; statistics calculated using the calibration dataset where only 1 variable is treated as an  
17 unknown are overly optimistic of performance in natural systems.
- 18 • It has become increasingly clear that melt inclusion studies which did not account for the vapour bubble  
19 may have underestimated storage depths by more than a factor of 2, requiring re-evaluation of melt  
20 inclusion volatile contents and storage depths globally.

21 **Key words**

- 22 1. Mineral Thermobarometry
- 23 2. Thermodynamics
- 24 3. Melt Inclusions
- 25 4. Fluid inclusions
- 26 5. Raman Spectroscopy
- 27 6. Hygrometry
- 28 7. Chemometry
- 29 8. Experimental Petrology
- 30 9. FAIR Research Framework
- 31 10. MELTS modelling
- 32 11. Pyroxene
- 33 12. Amphibole
- 34 13. Plagioclase

35 **Abstract (100 words)**

36 Determining the pressures and temperatures at which melts are stored in the crust and upper mantle, and the  
37 major element composition, redox state and volatile contents of these melts, is vital to constrain the structure  
38 and dynamics of magmatic plumbing systems. In turn, constraining these parameters helps understand the  
39 geochemical and structural evolution of the Earth's lithosphere, and periods of unrest at active volcanoes. We  
40 review common thermobarometers, hygrometers and chemometers based on mineral and/or liquid  
41 compositions, before discussing recent advances in melt and fluid inclusion barometry, Raman-based elastic  
42 thermobarometry, and thermodynamic modelling methods. Where possible, we investigate the accuracy and  
43 precision of each technique, and the implications for the application of each method to different research  
44 questions.

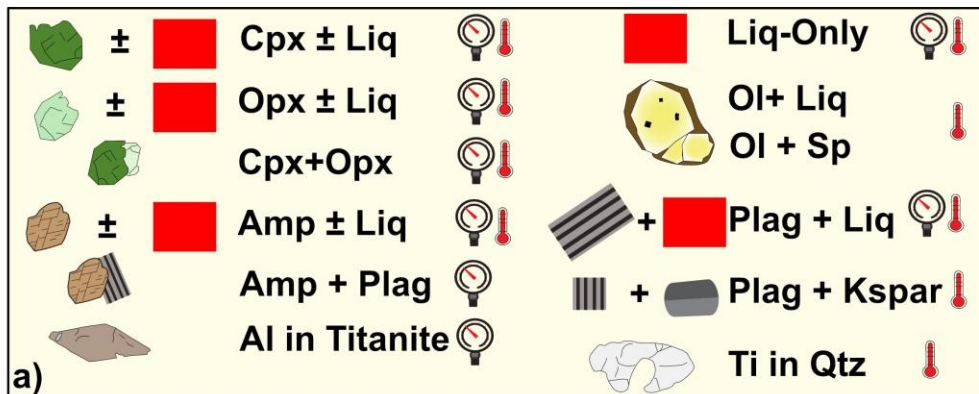
45 **1. Introduction.**

46 Determining the pressures, and therefore depths, at which magmas are stored and evolve in the crust  
47 and upper mantle is vital to understand the chemical and structural evolution of volcanic plumbing systems,  
48 with implications for our understanding of the formation of mineral deposits, and the evolution of the Earth's  
49 lithosphere (Lee and Anderson, 2015). Precisely constraining magma storage depths at a specific volcano using  
50 past eruptive deposits can also provide vital context to help inform the interpretation of monitoring signals  
51 during periods of volcanic unrest (e.g., distinguishing magmatic and hydrothermal signals, Pritchard et al., 2019).

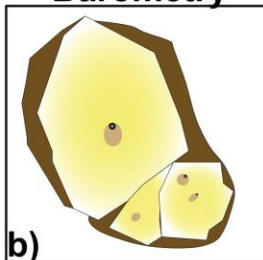
52           Constraining the temperatures of different magmatic processes can reveal the thermal evolution of  
53 magmatic systems and are vital inputs for many other common workflows in igneous petrology, such as  
54 calculations of timescales from elemental diffusion in erupted crystals (termed “diffusion chronometry” or  
55 “geospeedometry”). In fact, because diffusion rates are strongly sensitive to temperature (following an  
56 Arrhenius relationship), uncertainty in temperature is one of the largest sources of error when obtaining  
57 timescales using these chronometers (Chakraborty and Dohmen, 2022; Costa et al., 2020). For example, Mutch  
58 et al. (2019a) show that timescales calculated from Cr diffusion in spinel change from ~4000 years at 1190°C to  
59 ~1000 yrs at 1230°C. Thus, uncertainty in temperatures affects interpretations of timescales of crustal residence  
60 (Mutch et al., 2019a), re-awakening from quiescence to eruption (Shamloo and Till, 2019), and calculations of  
61 magma ascent rates (Mutch et al., 2019b). Of course, accurately constraining magma storage depths is also vital  
62 for magma ascent rate calculations, where the speed is calculated by dividing the depth to the inferred magma  
63 body by the time calculated from diffusion chronometry (Barth et al., 2019; Klügel, 1998).

64           Here, we describe a multitude of approaches to determine the pressures (P) and temperatures (T) at  
65 which magmas were stored in the lithosphere, as well as the chemistry of these stored melts (Fig. 1). We pay  
66 particular attention to differences between models (Section 1.1) and the precision and accuracy of calculations  
67 (Section 1.2). For barometers, we first evaluate variations in crustal thickness in a wide variety of tectonic  
68 settings to provide context when interpreting the precision of different barometry methods (Section 1.3). Then,  
69 we review the methods used to convert measured mineral compositions with or without an equilibrium melt  
70 into magma storage pressures and temperatures (mineral barometry and thermometry), and to calculate the  
71 chemistry and H<sub>2</sub>O contents of the melts from which a specific mineral composition grew (chemometry and  
72 hygrometry respectively, Section 2).

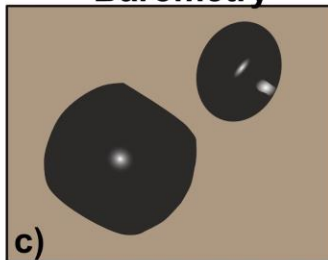
## Mineral Thermobarometry



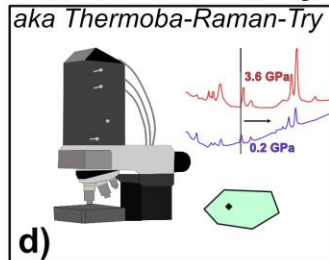
### Melt Inclusion Barometry



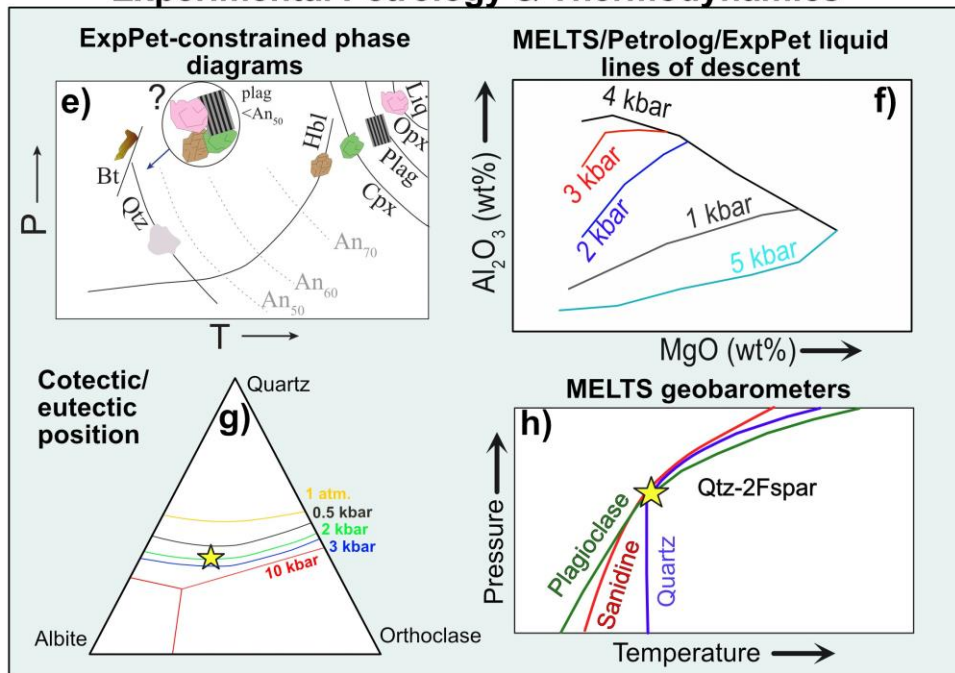
### Fluid Inclusion Barometry



### Elastic thermobarometry



## Experimental Petrology & Thermodynamics



73

74 *Figure 1: Summary of some of the methods used to determine pressures and temperatures of magma storage.*  
 75 *Part e) adapted from Rutherford (2003), f) from Cashman and Edmonds (2019), g) and h) adapted from Gualda*  
 76 *et al. (2012) and Gualda and Ghiorso (2014), respectively.*

77 We also evaluate the methods and uncertainties involved in melt inclusion barometry, with a specific  
 78 focus on the influence of CO<sub>2</sub> stored within melt inclusion vapour bubbles on calculated pressures (Section 3).  
 79 The general proliferation of Raman spectroscopy in the Earth Sciences (Dubessy et al., 2012) has not only been  
 80 important for performing direct measurements of melt inclusion vapour bubbles; it has also pushed forwards  
 81 two other barometric methods. First, Raman spectroscopic measurements of fluid inclusions can provide a  
 82 substantially faster method of calculating storage depths than traditional microthermometric techniques

83 (Section 4). Second, Raman measurements of mineral inclusions in-situ can also be used to calculate pressures  
84 and temperatures (thermobarometry, Section 6). Experimental petrology not only underpins the formulation  
85 and calibration of mineral-melt thermobarometers and volatile solubility models, it can also be used to provide  
86 direct constraints on magma storage in a specific volcanic system (Section 7). Finally, we discuss approaches  
87 using thermodynamic constraints on phase stability in igneous systems (Section 8), methods not covered in  
88 detail in this review (Section 9) and summarize the general proliferation of community data repositories and  
89 open-source tools to help inform model calibration, and aid calculations of magma storage conditions (Section  
90 10).

### 91 1.1 Assessing and comparing models

92 When calculating pressure, temperature, and/or melt chemistry from the composition of erupted  
93 melts, crystals and their inclusions, the result can be highly sensitive to the choice of  
94 model/equation/parameterization, relating the measured quantity (e.g., Cpx, Amp, melt inclusion composition)  
95 to the intensive variable (e.g., P, T). Below, we discuss the origin of all these different models, and best practices  
96 for model intercomparison.

97 Mineral thermobarometry (Section 2) utilizes chemical reactions involving the crystallization or re-  
98 equilibration of minerals which are accompanied by a change in volume (sensitive to P) and/or a change in  
99 entropy (sensitive to T, e.g., Putirka, 2008). Chemometry (and hygrometry) relies on the fact that the  
100 composition of crystallizing/re-equilibrating phases is sensitive to the composition of the melt phase. Some  
101 thermobarometry and chemometry expressions are firmly rooted in thermodynamics, with compositional terms  
102 and the functional form of the equation determined from a specific reaction. Typically, these expressions have  
103 coefficients attached to thermodynamic terms which are calibrated empirically using the measured  
104 compositions of minerals in experiments conducted at well-constrained P-T-fO<sub>2</sub>-H<sub>2</sub>O conditions (e.g., the  
105 Plagioclase-Liquid hygrometer of Waters and Lange, 2015).

106 More commonly, available equations have a general form based on thermodynamics, with the addition  
107 of empirically derived terms to improve the fit to the calibration dataset (e.g., Neave and Putirka, 2017). For  
108 example, many of the Cpx-Liq barometers of Putirka (2008) have a functional form based on Jadeite exchange  
109 between the liquid and Cpx, which is associated with a change in volume, so is P sensitive (Putirka et al., 1996):

$$110 P = a + \frac{bT}{10^4} + \frac{cT}{10^4} \ln(\text{Jd}^{\text{Cpx-Liq}}) + \dots [\text{Equation 1}]$$

111 Empirical terms help to improve the fit between the calculated parameter and the known experimental  
112 conditions. The inclusion of these terms may be informed at least in part by thermodynamic reasoning (e.g.,  
113 Masotta et al., 2013; Neave and Putirka, 2017; Putirka, 2008). For example, Putirka (1996) EqP1 has a term for  
114 the cation fractions of Na and Al:

$$115 \text{EqP1} = \text{Equation 1 terms} \dots + 367 (X_{\text{Na}}^{\text{Liq}} * X_{\text{Al}}^{\text{Liq}}) [\text{Equation 2}]$$

116 The fact that the best fit involved the multiplication of Na and Al cation fractions implies that these two  
117 components have identical activity coefficients (Putirka et al., 1996). However, the thermodynamic  
118 interpretation is often obscured by decisions to reduce the complexity of equations, such as wanting to avoid  
119 introducing multiple temperature-dependent terms (see Equation 12 of Putirka et al., 1996). In general, as  
120 calibration datasets have grown larger, more empirical terms have been added that have a less clear  
121 thermodynamic basis. For example, Putirka (2008, Eq31) has many additional terms relative to EqP1, including  
122 terms for the Ca, Na, K, Si, Mg and Fe<sub>t</sub> liquid cation fractions, H<sub>2</sub>O in the liquid, and for EnFs, DiHd, and Al cation  
123 fractions in the Cpx:

$$124 \text{Eq31} = \text{Equation 1 terms} \dots + 106 X_{\text{Ca}}^{\text{Liq}} - 166 (X_{\text{Na}}^{\text{Liq}} + X_{\text{K}}^{\text{Liq}})^2 - 50.2 X_{\text{Si}}^{\text{Liq}} * (X_{\text{Mg}}^{\text{Liq}} + X_{\text{Fe}}^{\text{Liq}}) - 3.2 \log(\text{DiHd}) - \\ 125 2.2 \log(\text{EnFs}) + 0.86 \log(X_{\text{Al,6 cat}}^{\text{Cpx}}) + 0.4 * \text{H}_2\text{O} [\text{Equation 3}]$$

126 New models not only arise through the addition of such empirical terms, but also through the recalibration of  
127 the coefficients of older equations. For example, Masotta et al. (2013) recalibrate the coefficients of the Putirka  
128 (2008) equations for a new calibration dataset of alkaline magmas. Other thermobarometers are purely  
129 empirical, including terms and mathematic expressions like logs, exponentials, and different powers which  
130 improve the fit to the calibration dataset without a firm tie to the thermodynamics of a specific chemical  
131 reaction. For example, the liquid-only thermometer of Helz and Thornber (1987) was calibrated based on the  
132 linear relationship between MgO and T in melting experiments on samples from the Kilauea Iki lava lake. The  
133 amphibole-only barometer of Ridolfi and Renzulli (2012) uses multivariate least squares regression to determine

134 the relationship between P and amphibole composition across a number of different P ranges, with highly  
135 variable functional forms (Eq1a, Eq1b and Eq1e take the exponential of amphibole cation fractions, Eq1c and  
136 Eq1d do not). The results from these equations are selected or combined using an algorithm to give a single P.  
137 This algorithm was then tweaked by Ridolfi (2021), generating yet another model.

138 Most recently, machine learning approaches using regression trees have been used to parameterize the  
139 relationship between mineral and melt composition and experimental conditions (e.g., Higgins et al., 2022;  
140 Jorgenson et al., 2022; Petrelli et al., 2020). These approaches have no underlying thermodynamic basis. They  
141 are trained using measured oxide contents, rather than thermodynamically informed mineral components such  
142 as Jadeite, Diopside etc. The lack of thermodynamic basis may affect their ability to extrapolate beyond the  
143 compositions and P-T conditions for which they are calibrated. One advantage is that these models can be easily  
144 updated as new experimental data becomes available if the code for model training is released.

145 The diversity of empirical, thermodynamic, and machine-learning models for mineral-based  
146 thermobarometry/hygrometry/chemometry has resulted in a somewhat overwhelming choice of models to  
147 calculate magma storage conditions. Concerningly, these different models can return vastly different results.  
148 Wieser et al. (2023a) show that different Cpx-Liq and Cpx-only thermobarometers applied to the same Cpx-Liq  
149 pair passing equilibrium tests yield pressures spanning >10 kbar and temperatures spanning >100°C. Clearly,  
150 model choice is one of the largest sources of uncertainty when performing such calculations.

151 Melt inclusion barometry uses volatile solubility models to calculate the pressure at which a specified  
152 melt composition (major+volatile elements) is volatile saturated, for a specified temperature. The formulation  
153 of these solubility models ranges from being purely empirical (Liu et al., 2005; Shishkina et al., 2014) to purely  
154 thermodynamic (Ghiorso and Gualda, 2015; Papale et al., 2006). Some models lie between these end members,  
155 having a general form indicated by thermodynamics and some empirical coefficients accounting for silicate melt  
156 composition (semi-empirical, e.g., Dixon, 1997; Iacono-Marziano et al., 2012). Even for fully thermodynamical  
157 models, the sign and magnitude of many coefficients attached to thermodynamic terms have been criticized as  
158 being physically implausible (see Ghiorso and Gualda, 2015 and Wieser et al. 2022a for discussion of the Papale  
159 et al. 2006 model). In addition to their different functional forms, the calibration datasets of solubility models  
160 are also highly variable with respect to the range of melt compositions, fluid compositions, and P and T. For  
161 example, the model of Shishkina et al. (2014) was calibrated on variably alkaline, relatively mafic melts, and  
162 expresses volatile solubility empirically using the cation fractions of Ca, K, Na, Mg, Fe, Si and Al for CO<sub>2</sub>, and K  
163 and Na for H<sub>2</sub>O. In contrast, the solubility model of Dixon (1997) was calibrated on a more restricted range of  
164 relatively mafic tholeiitic to alkaline melt compositions. This model has a thermodynamic form, with an empirical  
165 correction for the effect of melt composition that is only dependent on the concentration of SiO<sub>2</sub> in the melt.  
166 The model MagmaSat (Ghiorso and Gualda, 2015) was calibrated on a very wide range of melt compositions  
167 (tholeiite and alkaline, from basalts to rhyolites), and is a fully thermodynamic model sensitive to all the  
168 commonly measured major oxide species. Unsurprisingly, given these differences in model formulation and  
169 calibration datasets, calculated saturation pressures can vary greatly between models, with systematic offsets  
170 of at least a factor of two not being uncommon (Wieser et al., 2022a).

171 In stark contrast to uncertainties associated with model choice when performing mineral  
172 thermobarometry or melt inclusion barometry, fluid inclusion barometry (Section 4) relies on the CO<sub>2</sub> equation  
173 of state to convert the measured density of a CO<sub>2</sub>-rich fluid into a P for a specified entrapment temperature.  
174 Other than an ideal gas law (which does a poor job at high P), different published CO<sub>2</sub> equation of states predict  
175 very similar P for a given CO<sub>2</sub> density and T (~ 1–5% difference, Böttcher et al., 2012; Lamadrid et al., 2017; Span  
176 and Wagner, 1996; Sterner and Pitzer, 1994; Wieser and DeVitre, 2023). For example, at 1150°C for  $\rho_{CO_2} = 0.8$   
177 g/cm<sup>3</sup>, the relatively simple empirical expression of Sterner and Pitzer (1994) gives 5.008 kbar, while the more  
178 complex thermodynamic model of Span and Wanger (1996) gives 4.956 kbar (~3% difference). However, the  
179 conversion between measured CO<sub>2</sub> density to depth is substantially less simple when trapped fluids contain  
180 other species, such as H<sub>2</sub>O or SO<sub>2</sub> (Hansteen and Klugel, 2008; Hurai, 2010). It is difficult to estimate the initial  
181 molar ratios of each species, and EOS for these mixed fluids are poorly constrained, if parameterized at all. Fluid  
182 inclusion barometry is also not immune to systematic error; re-equilibrium of the host crystal during magma  
183 ascent can increase the inclusion volume, reduce the CO<sub>2</sub> density and thus the calculated pressure/depth  
184 (Hansteen and Klugel, 2008; Wanamaker and Evans, 1989).

185 Thermodynamic approaches to determining the conditions of magma storage and evolution are also  
186 sensitive to the choice of model (Section 8). Thermodynamic models are typically constructed from two key  
187 components: (i) a dataset of standard state properties (e.g., enthalpy of formation, heat capacity, etc.) for all

188 minerals of interest, and (ii) solution models for phases with variable compositions, which describe how  
189 composition influences the thermodynamic properties of the phase. Within igneous petrology and volcanology  
190 the MELTS ‘family’ of thermodynamic models is the most widely used (Ghiorso et al., 2002; Ghiorso and Sack,  
191 1995; Gualda et al., 2012). The original MELTS model was developed by Ghiorso and Sack (1995), building on the  
192 thermodynamic database of Berman (1988) to include thermodynamic models of relevant igneous solid  
193 solutions (e.g., Ghiorso, 1990; Ghiorso and Sack, 1991; Sack and Ghiorso, 1994, 1991, 1989). Since the release  
194 of this original MELTS model, various updates have been published. pMELTS includes a revised liquid  
195 thermodynamic model optimised for mantle-like bulk compositions (Ghiorso et al., 2002). Rhyolite-MELTS  
196 v.1.0.2 incorporates changes to the thermodynamic properties of quartz and the orthoclase endmember of the  
197 alkali feldspars to enable the eutectic behaviour of high-silica rhyolitic magmas to be recreated (i.e.  
198 crystallization over a narrow T range, Gualda et al., 2012). Rhyolite-MELTS v1.2.0 incorporates the mixed H<sub>2</sub>O-  
199 CO<sub>2</sub> fluid model MagmaSat and is recommended for use away from the granitic ternary minimum. Rhyolite-  
200 MELTSv1.1.0 incorporates the updated CO<sub>2</sub> solubility model, but retains the old H<sub>2</sub>O solubility model of rhyolite-  
201 MELTSv1.0.2 for calculations at the ternary minimum (Ghiorso and Gualda, 2015).

202 An alternative group of thermodynamic models developed by Tim Holland, Roger Powell and co-  
203 workers (Holland and Powell, 2004, 1998, 1990) have traditionally been utilized in metamorphic studies  
204 (Tamblyn et al., 2020), but have recently been updated for applications to mantle melting and igneous systems.  
205 For example, Jennings and Holland (2015) expand the model system, optimizing its performance for calculations  
206 of peridotite melting behaviour and the phase relationships of basaltic liquids at crustal to mantle conditions.  
207 Most recently, Holland et al. (2018) presented an updated thermodynamic database that is calibrated on a range  
208 of compositions, from peridotites through to granites. The Holland dataset is mostly accessed through a variety  
209 of software tools. THERMOCALC calculates the location of known phase boundaries and mineral reactions  
210 (Powell et al., 1998), while Perple\_X (Connolly, 2009, 2005) and Theriak-Domino (de Capitani and Petrakakis,  
211 2010) use a Gibbs Free Energy minimization approach to calculate the phase assemblage and compositions  
212 specified P-T conditions.

213 Comparisons between the MELTS and Holland-Powell families of models are relatively uncommon;  
214 Jennings and Holland (2015) compare the results of mantle melting calculations, and Hernández-Urbe et al.  
215 (2022) compare the equilibrium crystallization behaviour of an mid oceanic ridge basalt (MORB) magma.  
216 Importantly, Hernández-Urbe et al. (2022) do not compare fractional crystallization pathways, noting that these  
217 would be “relatively laborious” with current software tools. The recent release of MAGEMin, a Gibbs Free Energy  
218 minimisation package utilizing the Holland et al. (2018) thermodynamic models written in the programming  
219 language C (Riel et al., 2022) allows MELTS-like workflows to be performed including fractional crystallization.  
220 MAGEMin has a Julia interface and can be run in Python3 using pyMELTScalc (Gleeson et al. 2023), greatly aiding  
221 model intercomparison between the Holland and MELTS databases (see Section 8). There are also several more  
222 empirical models which have been used as alternatives to MELTS to model fractional crystallization in magmas,  
223 and therefore could place constraints on P and T (see Section 8). These include COMAGMAT (Ariskin et al., 1993)  
224 and Petrolog3 (Danyushevsky and Plechov, 2011). In Section 8, we show that the choice of thermodynamic  
225 model to use (and even the version of MELTS used) has a large influence on calculations of magma storage  
226 conditions (see also Hernández-Urbe et al., 2022).

227

## 228 **1.2. Statistics to compare models**

229 When trying to decide which model/equation to use to calculate magma storage conditions, and when  
230 assessing whether the chosen method has sufficient resolution to address the science question of interest, it is  
231 important to consider both accuracy and precision. Accuracy describes how close the measurement/calculation  
232 is to the true value, while precision describes how close repeated measurements/calculations are to one  
233 another. For example, if you measure a small, very homogenous region of a Cpx crystal five times using an  
234 electron probe microanalyser (EPMA), and calculate Cpx-only pressures from these measurements, you may  
235 obtain 5, 5.5, 6, 4.9, and 6.2 kbar. The precision could be quantified using 1 standard deviation of these  
236 measurements (e.g., ±0.47 kbar). However, the Cpx may have formed at 8 kbar, in which case these calculations  
237 are relatively precise, but inaccurate (mean offset of 2.5 kbar). It is also worth distinguishing between random  
238 and systematic errors. Random error describes scatter about the true value (affecting precision, not accuracy),  
239 while systematic error describes a constant offset from the true value (affecting accuracy not precision).

240 Most publications calibrating new mineral-melt thermobarometers or chemometers describe the fit  
241 between calculated and experimental values for a given parameter using the root mean square error (RMSE)

242 and the  $R^2$  value (see Table 1, RMSE= standard error estimate, SEE, for linear regressions). When equations are  
 243 applied to natural systems, these RMSE errors are often quoted as the error on the calculation. This is  
 244 problematic for several reasons. The RMSE and  $R^2$  alone do not properly distinguish between random and  
 245 systematic error, so fails to capture different model performances. Many different metrics (Table 1) can be  
 246 useful to assess model performance.

247

Metric	Good at	Bad at
$R^2$ value: Correlation coefficient of the linear regression between the measured (x) and predicted (y) value.	Assessing precision and random uncertainty. Low precision (lots of random uncertainty) = low $R^2$ value.	Assessing accuracy and systematic uncertainty.
Gradient and Intercept of the linear regression	Assessing systematic uncertainty, which will generate a gradient different from 1, and an intercept different from zero.	Assessing precision/random uncertainty (as averages all measurements).
Root mean square error (RMSE) aka. SEE $RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - y_i)^2}$	Describes how concentrated the data is around the linear regression.	Struggles to distinguish between low precision and accurate vs. high precision with a systematic offset. Sensitive to outliers.
Mean Absolute Error (MAE) $MAE = \frac{1}{N} \sum_{i=1}^N  x_i - y_i $	Similar to the RMSE but no squared term. Gives less weight to larger errors than the RMSE	Struggles to distinguish between low precision and accurate vs. high precision with a systematic offset
Mean Bias Error (MBE) $MBE = \frac{1}{N} \sum_{i=1}^N (x_i - y_i)$	Identifies average model bias, as no absolute or squared term.	Doesn't identify random error, as + and - errors cancel out.

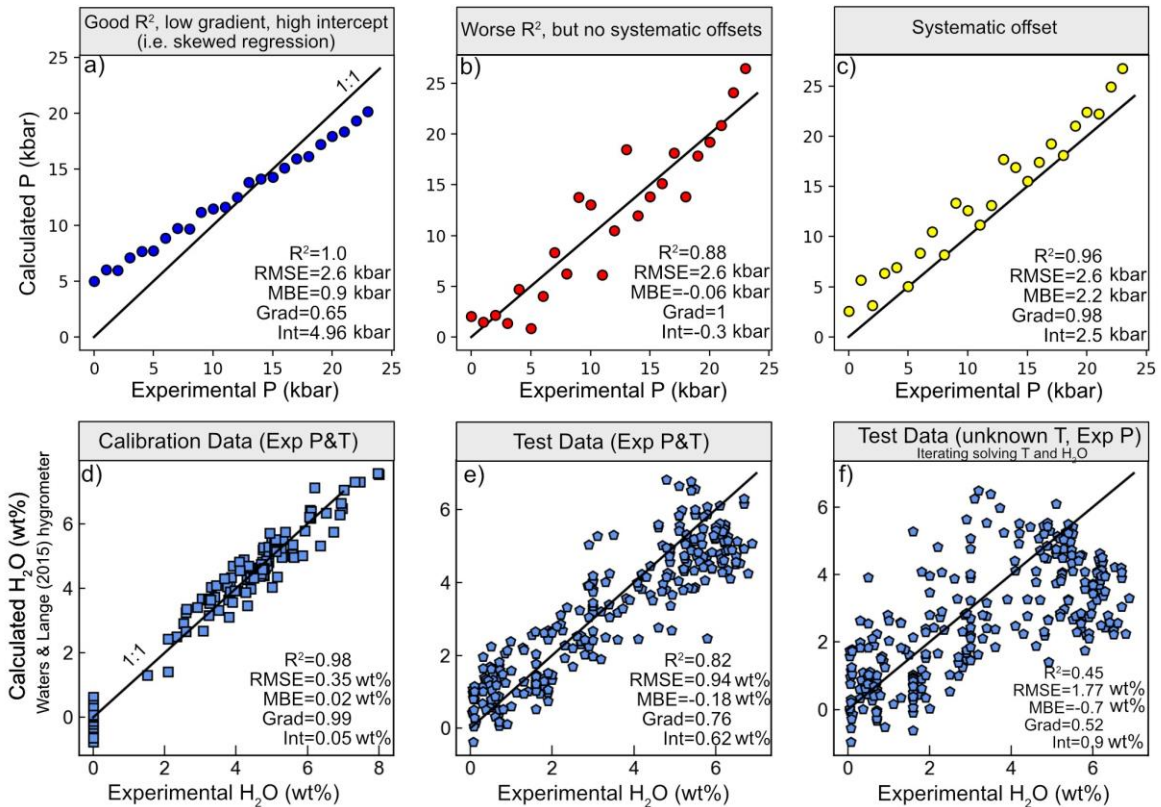
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249 *Table 1: Metrics used to assess models, where x is the measured parameter (e.g., P, T) and y is the model-*  
 250 *predicted parameter. RMSE and SEE are identical for a linear regression, for higher order regressions, they differ*  
 251 *as only the SEE accounts for the degrees of freedom.*

252

253 In Fig. 2, we demonstrate the issues associated with using *only* the root mean square error (RMSE)  
 254 and  $R^2$  to assess model performance. Instead, we suggest that the RMSE,  $R^2$ , gradient, intercept and MBE should  
 255 all be presented on figures to allow assessment of both random and systematic uncertainty (e.g. Putirka et al.  
 256 2003). To demonstrate this, we compare the relative performance of three hypothetical barometers, plotting  
 257 the experimental P on the x axis, and the calculated P on the y axis (Fig. 2). All barometers have the same RMSE  
 258 error. However, it is visually apparent that their performance varies greatly. While Fig. 2a has a very high  $R^2$   
 259 value, its low gradient and high intercept reveals that it substantially overpredicts P at  $P < 12$  kbar, and  
 260 underpredicts P at  $P > 12$  kbar. While Fig. 2b has a lower  $R^2$  value, it has no substantial systematic offsets, meaning  
 261 it is a far more accurate barometer across a wide range of pressures than that shown in Fig. 2a (indicated by the  
 262 gradient close to one, an intercept close to zero, and the low MBE). The barometer in Fig. 2c also has a gradient  
 263 close to 1, but the higher intercept and MBE indicate that it systematically overpredicts at all pressures. Clearly,  
 264 if you wish to distinguish the absolute depth of magma storage, perhaps to compare to geophysical inversions  
 265 of magma storage depths, or signals of unrest, the barometer in Fig. 2b is the best, despite its lower  $R^2$ . However,  
 266 if you only wish to distinguish differences in storage pressures between different crystal populations (without  
 267 caring about the actual depth), the barometer in Fig. 2a is the best, as it is the most precise. Use of all 5 metrics  
 268 in tandem is essential for identifying systematic and random uncertainty.





269  
 270 *Figure 2: Schematic figure showing the limitations of using just  $R^2$  and RMSE to assess thermobarometers. a-c)*  
 271 *Three hypothetic barometers with the same RMSE, but vastly different performance. d-f) Comparing*  
 272 *experimental and calculated  $H_2O$  using the Waters and Lange (2015) hygrometer for: d) the calibration dataset*  
 273 *using experimental  $T$  and  $P$ , e) the ArcPL dataset using experimental  $T$  and  $P$ , and f) the ArcPL dataset iteratively*  
 274 *solving  $H_2O$  and  $T$  (using Eq24a of P2008, see Section 2.8 for more detail).*

275  
 276 It is also challenging to directly compare the quoted RMSE and  $R^2$  values from different models,  
 277 because these statistics are not calculated in an equivalent manner. Many of the statistics reported in the  
 278 abstracts of papers proposing new models describe the fit to the calibration dataset (e.g., the commonly quoted  
 279  $\pm 1.7$  kbar value for the Cpx-Liq barometer of Putirka et al. 2003; the  $\pm 0.35$  wt%  $H_2O$  value for the Waters and  
 280 Lange, 2015, Plag-Liq hygrometer). In other papers, the number reported in the abstract is the fit to a test dataset  
 281 (e.g., Jorgenson et al., 2022; Petrelli et al., 2020), which inevitably makes the equation look “worse” than one  
 282 assessed using calibration data. Indeed, it is apparent in the main text of many thermobarometry papers that  
 283 the RMSE is much larger when applied to test data not used in the calibration dataset, or when applied to a  
 284 global dataset containing a mix of new and calibration data (e.g., RMSE=4.2 kbar for the Cpx-Liq Putirka et al.  
 285 2003 barometer vs. the commonly quoted RMSE=1.7 kbar, Fig. 3a). The size of the test dataset can also vary  
 286 greatly, influencing the statistics. For example, the test dataset of Petrelli et al. (2021) only contains 59  
 287 experiments conducted at  $<15$  kbar, which come from only 4 studies. Some reported statistics are calculated  
 288 using only experiments for a select subregion of compositional space (e.g., Neave and Putirka, 2017 for Cpx-Liq  
 289 equilibria in tholeiites), while others report the fit for a global dataset with a much larger compositional range,  
 290 again leading to larger apparent errors (e.g., Putirka 2008). For many equations, a paucity of experimental data  
 291 resulted in all data being used for calibration, leaving no test dataset (e.g., Waters and Lange, 2015 for Plag-Liq  
 292 hygrometry, Ghiroso and Gualda, 2015 for volatile solubility). Additionally, some proportion of the error in any  
 293 quoted statistic (e.g. RMSE) will represent uncertainty in the experimental data used for testing (both analytical  
 294 and experimental sources of scatter), making it difficult to differentiate failures of the calibration equation vs.  
 295 the data used to assess it. This is a particular problem for models where higher quality data was saved for  
 296 calibration, with less strict filters applied to test data (Putirka et al. 2003, 2008, K. Putirka, written comms).

297  
 298 Ideally when calibrating any new equation/model (for thermobarometry, chemometry, volatile solubility  
 299 modelling etc.), data should be subdivided into a test dataset and a calibration dataset. It is then standard

300 practice for many machine learning workflows to further subdivide the calibration dataset into train and  
301 validation datasets (this split may be made repeatedly during model training, e.g., Petrelli et al. 2020). The train-  
302 validation split allows investigation of the effect of adding/removing terms, changing the regression algorithm,  
303 and tweaking the regression tuning parameters. Only once the model is fully tweaked should it be applied to the  
304 test dataset to assess its performance on unseen data. While it is then tempting to continue to change  
305 parameters to improve the fit to the test dataset, this strategy is generally criticized in the world of machine  
306 learning, as it means the testing dataset has “leaked” into the training of the model, so no longer provides an  
307 independent assessment of the model validity. The complete isolation of a testing dataset prior to model tuning  
308 and choice of parameters is important for machine learning and other regression workflows, because otherwise  
309 it is difficult to assess model performance on samples which are distinct in P-T-X space from those used in model  
310 calibration (Lones, 2021). To address this, in some biomedical studies, a test dataset is kept completely separate,  
311 and held under “lock and key” by a honest broker to avoid such leakage (Dobbin and Simon, 2011; Shedden,  
312 2008). In igneous petrology, the difficult balance to strike is between having a large test dataset to robustly  
313 assess model performance, versus having too small a calibration dataset to adequately capture variation in melt  
314 or mineral composition.

315

316 It is also worth noting that the RMSE value is an average for the fit across the entire P or T range, while the actual  
317 error when applied to natural samples will vary as a function of P and T. RMSE and  $R^2$  values are also not always  
318 calculated across the same P and T range (e.g., 0–40 kbar for Putirka, 2008, 0–20 kbar for Petrelli et al. 2020).  
319 These pressure ranges are also often far larger than the pressure ranges of interest in volcanic systems, and  
320 models tend to perform worse at lower pressures (Putirka, 2008).

321

322 Finally, mineral-melt thermobarometers and chemometers are often assessed using experimental data, where  
323 T, P (and often  $H_2O$  and  $fO_2$ ) are constrained. In natural systems, it is common that several intensive parameters  
324 are poorly constrained. For example, a T and  $H_2O$ -sensitive barometer is normally assessed using the test  
325 dataset, inputting the experimental temperature and the measured  $H_2O$  content in the experimental charge.  
326 Similarly, thermometers with P-sensitive terms are normally assessed using the experimental P, and  
327 hygrometers are assessed using experimental T and P. In natural systems, the most common scenario is that  
328 *both* P and T are unknown, so must be iteratively solved using a thermometer and a barometer. Thus, to estimate  
329 a realistic error when applied to natural systems, statistics should be calculated by iteratively solving the same  
330 variables that would be unknown in natural samples. Of course, this adds additional uncertainty; when applying  
331 a T-sensitive barometer, any deviation from the true T will affect the calculated P. Additional uncertainties  
332 related to parameters which cannot be iteratively solved (e.g., uncertainty in  $H_2O$  in Cpx-Liq thermobarometers)  
333 should be propagated with Monte-Carlo techniques using a realistic uncertainty for  $H_2O$  in a specific system of  
334 interest (e.g. Wieser et al. 2022b).

335

336 Using the T-sensitive Plag-Liq hygrometer of Waters and Lange (2015) as an example, we  
337 demonstrate how the apparent performance of an equation can vary based on the number of constrained  
338 intensive parameters, and the dataset used to test it. First, we show  $H_2O$  contents for the model calibration  
339 dataset using experimental temperatures (Fig. 2d). This comparison yields the RMSE quoted in the abstract of  
340 the Waters and Lange (2015) paper that is commonly quoted in the literature as the error on the method ( $\pm 0.35$   
341 wt%). Next, we evaluate this hygrometer using a newly compiled test dataset of variably hydrous experiments  
342 at 0–17 kbar spanning from basalts to dacites (ArcPL, Wieser et al., 2023a-b). We only include experiments where  
343  $H_2O$  was measured using quantitative methods (Fourier Transform infrared spectroscopy - FTIR, secondary ion  
344 mass spectrometry - SIMS, Raman, calibrated volatiles-by-difference, solubility laws, see Section 2.8), and  
345 discard experiments which were present in the Waters and Lange (2015) calibration dataset. Using experimental  
346 T to calculate  $H_2O$  for this new test dataset yields statistics that are noticeably worse than those calculated from  
347 the calibration dataset (e.g.,  $\pm 0.94$  wt% vs.  $\pm 0.35$  wt%, Fig. 2e). In a scenario where T is not known (i.e., when  
348 this method is applied to natural systems), the statistics decline further: iterating the hygrometer with the Plag-  
349 Liq thermometer of Putirka (2008, Eq24a) results in a RMSE of  $\pm 1.77$  wt% (Fig. 2f, see Section 2.8 for detailed  
350 discussion). Thus, simply quoting the uncertainty from the original publication may underestimate the error by  
351 a factor of  $\sim 5$  when applied to natural systems. We observe similarly large declines in model performance  
352 moving from calibration to test data to iterative solving for many mineral-melt equilibria (see Section 2, and  
353 Wieser et al. 2023a).

354

355 Thus, at present, it is not possible to select the best thermobarometer for a given application simply  
356 based on quoted statistics alone. Instead, to pick the most suitable model, it is worthwhile to check the natural

357 compositions of interest vs. the calibration range of the model of interest (calibration datasets for many models  
358 are available in Thermobar, Wieser et al. 2022b). After identifying models calibrated on suitable compositions,  
359 we encourage authors to compile a test dataset of experimental compositions most similar to their system.  
360 Ideally these experiments would not have used during calibration of the model. If the planned workflow in the  
361 natural system will involve iterative calculations, these same iterative workflows should be applied to the test  
362 dataset. These tests will provide a more realistic estimate of the uncertainty associated with the calculation than  
363 simply quoting RMSE values. If there is very little data to help pick, it may be best to perform calculations using  
364 several different equations calibrated on relevant compositional and P-T ranges. An average for all these models  
365 could be calculated, with the difference between models giving insight into the error in the calculation. At the  
366 moment, only a very small proportion of studies compare the results from multiple equations (e.g., Erdmann et  
367 al., 2016; Geiger et al., 2018; Sas et al., 2017; Sheehan and Barclay, 2016 for Cpx-Liq equilibrium, Rasmussen et  
368 al., 2022; Wieser et al., 2021 for volatile solubility).

369

### 370 **1.3. What accuracy and precision are required?**

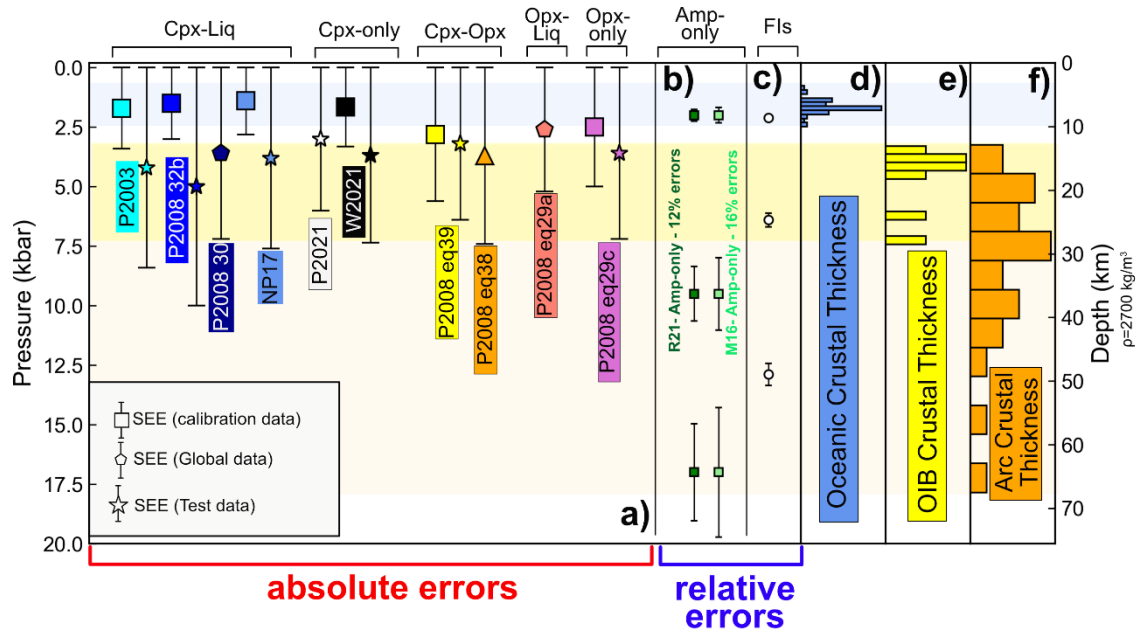
371 In the 2008 RiMG short course, K. Putirka described his Cpx barometer as: '*a chisel, not a pen knife*' (K.  
372 Putirka, written comms). Once realistic estimates are made of the precision and accuracy of different  
373 thermobarometers using relevant test datasets, it is worth thinking about what scientific questions can be  
374 addressed with confidence within the associated uncertainties of each methods. Petrological barometers  
375 calculate pressure, which can be converted into depth by making assumptions about crustal and upper mantle  
376 densities. Converting pressures to depths allows comparisons to geophysical inversions of magma storage  
377 locations within the crust (e.g., Rasmussen et al., 2022), and to field observations in exposed crustal and upper  
378 mantle sections. Thus, it is useful to think of errors in the context of crustal and lithospheric thicknesses  
379 worldwide.

380 Oceanic crust formed away from the influence of mantle plumes ranges in thickness from ~5–8.5 km,  
381 with an average thickness of  $\sim 7 \pm 0.8$  km (White et al., 1992). Assuming an average density of 2900–3000 kg/m<sup>3</sup>  
382 (Afonso et al., 2007), this corresponds to an average Moho pressure of ~2 kbar. To be able to conclusively pull  
383 apart different crustal storage geometries (e.g., upper vs. lower crust) and distinguish between storage regions  
384 at different levels in the crust, a RMSE error of  $\pm 0.25$ –0.5 kbar would be needed. No mineral-based barometers  
385 applicable to MORB lavas achieve anything like this precision (Fig. 3a vs. d). In fact, even if magma is stored  
386 below the Moho (e.g., in slow spreading ridges, Bennett et al., 2019; Drignon et al., 2019), available mineral-  
387 melt models can't confidently differentiate upper mantle vs. crustal storage.

388 Crust in ocean island basalts (OIBs) is thicker than in MORB settings because the newer volcanic pile  
389 rests on top of older oceanic crust (total crustal thickness of 14–24 km in Hawai'i, Leahy et al., 2010; 14–15 km  
390 in La Palma, Ranero et al., 1995), and/or because the plume increases melting extents at the mid-oceanic ridge  
391 (e.g., ~11–39 km in Iceland). The elevated crustal thickness in OIBs, corresponding to pressures of 3–4 kbar or  
392 greater, means that mineral-based barometers with uncertainties of 2–3 kbar can begin to distinguish storage  
393 at the Moho vs. the shallow (e.g., Gleeson et al., 2021). Mineral-based barometers are also aided by the fact  
394 that OIB lithosphere can be extremely thick relative to MORB as a result of conductive cooling as the oceanic  
395 crust moves away from the ridge (e.g., 45–60 km thick in the Galápagos, Gibson and Geist, 2010; 50–110 km  
396 thick in the Hawaiian Islands, Li et al., 2004), and many OIB magmas are stored at sub Moho depths (e.g., Barker  
397 et al., 2021; DeVitre et al., 2023; Gleeson et al., 2021). Again, this makes uncertainties of 2-3 kbar less  
398 problematic. It is only in volcanic arcs, and particularly continental arcs with thicker crust (Profeta et al., 2016)  
399 that mineral-melt barometers can reliably distinguish between storage in the upper, middle and lower crust.

400 While mineral-melt thermobarometers often show a reasonably constant error regardless of the  
401 pressure, solubility models show a clear increase in error at higher volatile contents, so are best described using  
402 percentage errors (e.g., H<sub>2</sub>O =  $\pm 10\%$  and CO<sub>2</sub> =  $\pm 20\%$  for Shishkina et al., 2014, H<sub>2</sub>O =  $\pm 10\%$  and CO<sub>2</sub> =  $\pm 17\%$  for  
403 Iacono-Marziano et al., 2012). Systematic offsets between solubility models also tend to increase reasonably  
404 proportionally with increasing P (Wieser et al., 2022a). Even the large errors resulting from volume estimates  
405 during vapour bubble reconstructions when performing melt inclusion barometry (more detail in section 3) are  
406 percentage, not absolute errors. Many uncertainties associated with fluid inclusion barometry scale with  
407 pressure (Fig. 3, see Section 4). In general, methods with percentage errors that scale with the value of the  
408 quantity, rather than absolute errors, are better suited to distinguishing subtle variations in magma storage in  
409 relatively thin-crust tectonic settings (Fig 3b-c). Interesting, Ridolfi (2021) and Mutch et al. (2016) express the  
410 errors on their amphibole barometers as percent errors (e.g. 12- 16%, see Fig. 3b), although, these errors only

411 describe the fit to the calibration data, and their magnitude is highly debated (see Erdman et al. 2016, and  
 412 section 2.6).



413

414 *Figure 3: Comparison of quoted errors on barometers to estimates of crustal thickness (assuming  $\rho=2700 \text{ kg/m}^3$ ).*  
 415 *a) We anchor each method with an absolute uncertainty such that the upper part of the  $1\sigma$  error bar sits at 0*  
 416 *kbar. This visualization shows the range of pressures/depths which cannot be statistically distinguished from*  
 417 *storage at the surface. The symbol shape represents whether the quoted SEE/RMSE was for the calibration*  
 418 *dataset, a test dataset, or global data. b-c). Relative (%) uncertainties are shown for different pressures. for e),*  
 419 *we calculate FI errors assuming an uncertainty in  $\text{CO}_2$  density of  $\pm 0.01 \text{ g/cm}^3$  and  $\pm 50 \text{ K}$  for entrapment T).*  
 420 *Oceanic crustal thickness compilation from Chen (1992), OIB thicknesses compiled for this study (see supporting*  
 421 *information), Continental arcs from Profeta et al. (2016). Errors for melt inclusions are highly sensitive to bubble*  
 422 *volumes, so a generic example cannot be given (see Fig. 24b). Abbreviations: **P2003**: Putirka et al. (2003), **P2008**:*  
 423 *Putirka (2008), **NP17**: Neave and Putirka (2017), **W2021**: Wang et al. (2021), **R21**: Ridolfi (2021), **M16**: Mutch et*  
 424 *al. (2016).*

#### 425 1.4. Influence of analytical error on precision and accuracy

426 Measurement of any quantity in igneous systems is subject to analytical error. Mineral and melt  
 427 compositions are typically measured using an electron microprobe (EPMA), which is associated with random  
 428 and systematic uncertainties (see Wieser et al. 2023b for a more detailed discussion). Pressure estimates from  
 429 melt inclusions rely on volatile measurements by FTIR or SIMS, EPMA measurements of the host and melt phase,  
 430 Raman spectroscopy measurements of the vapour bubble, and estimates of the relative volume of the vapour  
 431 bubble (see Section 3 for a detailed discussion). Pressure estimates from fluid inclusions rely on measurements  
 432 of the fluid using Raman Spectroscopy/Microthermometry, and an independent estimate of T using mineral or  
 433 mineral-melt thermometry (e.g. using EPMA analyses). Thermodynamic methods of inverting liquid  
 434 compositions or liquid lines of descent rely on EPMA or energy-dispersive spectroscopy (EDS) measurements of  
 435 glasses, or whole-rock X-ray fluorescence (XRF) measurements.

436 As many of the methods discussed in this review rely on EPMA analysis, we briefly discuss the  
 437 uncertainties relating to this method. The fundamentally random process of x-ray generation, and subsequent  
 438 detection by spectrometers is a significant source of uncertainty, termed ‘counting statistics’. The magnitude of  
 439 this uncertainty depends on the concentration in the sample and the beam current and voltage (affecting x-ray  
 440 production), and the analysis time and spectrometer efficiency (affecting x-ray detection). Most simply, unless  
 441 long count times and higher beam currents are used, low concentration elements (<1 wt%) tend to be associated  
 442 with relatively large percentage errors. When analytical errors on all measured oxides are propagated through  
 443 thermobarometry equations using Monte-Carlo methods, they can generate a large range in calculated P and T.

444 For example, Wieser et al. (2023b) show that measurement of  $\text{Na}_2\text{O}$  in crustal Cpx using popular  
 445 analytical conditions (e.g., 10 s, 10 nA) yields a  $1\sigma$  error of  $\sim 10\text{--}40\%$ . Most importantly, the magnitude of this  
 446 error is often underestimated by factors of 2–4X because secondary standards with higher  $\text{Na}_2\text{O}$  concentrations

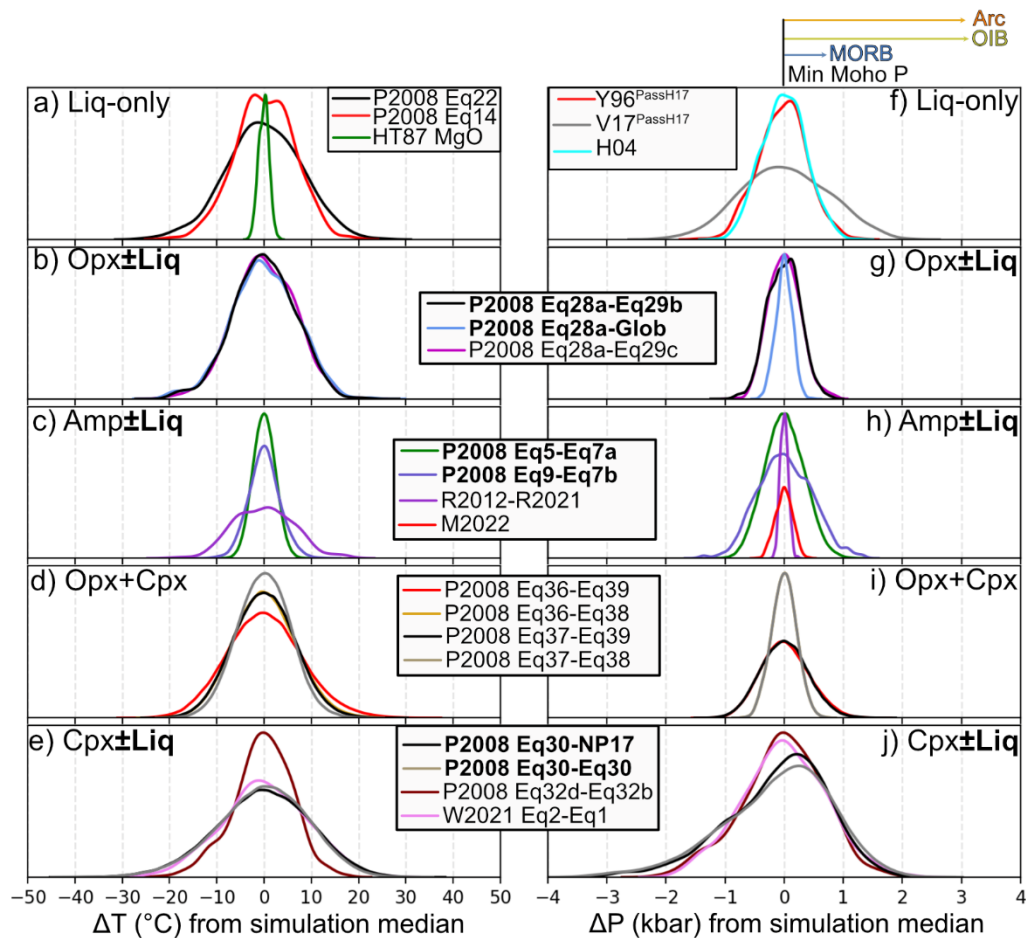
447 than the sample are routinely used to assess precision. Secondary standards should only be used to assess  
448 accuracy, not precision, as precision of an EPMA analysis is very closely related to the concentration of the  
449 element of interest, so varies greatly depending on the individual mineral composition. The large imprecision of  
450 many Na<sub>2</sub>O in Cpx measurements is problematic because this oxide is often used to calculate the abundance of  
451 the P-sensitive Jadeite component. Propagating typical analytical errors through popular expressions for Cpx-Liq  
452 thermobarometry can generate highly correlated PT arrays spanning 3–5 kbar, which could be incorrectly  
453 interpreted as transcrustal storage (Wieser et al., 2023b-c). Analytical errors also affect the experimental data  
454 used to calibrate thermobarometers. As many experimental studies perform <5 measurements on each phase,  
455 random analytical error does not get sufficiently averaged out, so the reported phase composition may not be  
456 the true phase composition (affecting model calibration, and calculated statistics on test data, see Wieser et al.  
457 2023b, see also Section 2.3).

458 To visually demonstrate the effect of analytical precision on different mineral-melt thermobarometers,  
459 we perform Monte-Carlo simulations using Thermobar (Wieser et al., 2022b, Fig. 4). We use analytical errors  
460 estimated by the EPMA based on counting statistics for experimental phase compositions reported by  
461 Krawczynski et al. (2012). For each phase, we produce 500 synthetic compositions with each element normally  
462 distributed about a measured value in the experiment, with the standard deviation equal to that estimated by  
463 the EPMA. We also include ±5% relative error for H<sub>2</sub>O in the liquid, which is a very conservative estimate of the  
464 error associated with FTIR and SIMS measurements. For two-phase equilibrium (e.g., Cpx-Liq), we consider all  
465 possible matches between the 500 synthetic compositions for each phase (250,000 pairs total). We then perform  
466 thermobarometry calculations on all synthetic compositions, showing the spread of calculated P and T relative  
467 to the median of the distribution (Fig. 4).

468 In general, the influence of analytical error on calculated T is relatively minor ( $1\sigma < 20^\circ\text{C}$ ). The broadest  
469 distribution of calculated temperatures comes from equations that are very sensitive to melt H<sub>2</sub>O content, such  
470 as Liq-only T from P2008 Eq14 and Eq22 (Fig. 4a), Opx-Liq T from P2008 Eq28a (Fig. 4b), and Cpx-Liq T from  
471 P2008 Eq30 (Fig. 4e). For calculated P, the spread of simulations is highly variable, with barometry methods  
472 sensitive to a component with a relatively low concentration showing a very wide spread of pressure (e.g., Na in  
473 Cpx, Fig. 4j). In contrast, barometers sensitive to high concentration elements show very narrow distributions  
474 (e.g., Al in Amphibole, Ridolfi, 2021, Medard and Pennec, 2022, Fig. 4h).

475 We also test the OPAM liquid barometer, where pressures are calculated from the composition of melts  
476 co-saturated in olivine, plagioclase, and augite (see Section 2.2). As the experiments of Krawczynski et al. (2012)  
477 are too H<sub>2</sub>O-rich for OPAM, we use estimates of analytical precision for measurements of submarine basaltic  
478 glasses from the Galápagos Spreading Centre (Gleeson and Gibson, 2021). Notably, the analytical errors have a  
479 very similar magnitude to those from Krawczynski et al. (2012). This method is very sensitive to analytical  
480 uncertainty, returning a similar range of calculated pressures to Cpx-based mineral-based barometers. The  
481 model of Voigt et al. (2017) is particularly sensitive, because of the inclusion of a term for the Cr content of the  
482 liquid, which has a low concentration, so is associated with poor analytical precision.

483 Overall, the effect of propagated analytical error on P and T depends greatly on the selected equation  
484 (e.g., Fig. 4f and i), as well as the analytical conditions used. Thus, studies should propagate EPMA-estimates of  
485 counting statistic errors from each analysis not secondary standards using their chosen equation. Analytical  
486 errors should be propagated for all thermobarometric techniques, including melt inclusion and fluid inclusion  
487 barometry (see Section 5 for an example). If propagated analytical errors are of similar magnitude to the  
488 resolution required to investigate the geological process of interest, time must be spent optimizing analysis (See  
489 section 2.3). Counting statistics are of course, only one source of analytical uncertainty. There are also notable  
490 offsets between different EPMA laboratories (e.g., Wieser et al. 2023b), and even between different operators  
491 on the same EPMA (see Kohn and Spear, 1991). These systematic uncertainties will increase the spread in  
492 calculated P and T for a given liquid, or crystal vs. that shown on Fig. 4.



493  
 494 *Figure 4: Monte Carlo simulations of the influence of analytical precision on thermometry (a-e) and barometry*  
 495 *(f-j) calculations. All panels except f show analytical uncertainties from EPMA counting statistics from*  
 496 *Krawczynski et al. (2012) with H<sub>2</sub>O of ±5%. As OPAM (panel f) is not applied to arc magmas, we propagate EPMA*  
 497 *errors from natural Galápagos glasses from Gleeson and Gibson (2021). The bars at the top show approximate*  
 498 *minimum and maximum Moho pressures from each tectonic setting (see Fig. 3).*

499

## 500 2. Mineral Thermobarometry and Chemometry

501 The seminal review of Putirka (2008, hereafter P2008) summarizes several decades of  
 502 thermobarometric work, and proposes a large number of new empirical expressions linking the compositions of  
 503 Cpx±Liq, Opx±Liq, Cpx+Opx, Plag±Liq, and Plag+Kspar to P and T. These new equations have similar forms to  
 504 those published in older papers, but have recalibrated coefficients, and additional terms to improve  
 505 performance when applied to the large compilation of experiments published in 2008 (LEPR; Library of  
 506 Experimental Phase Relationships, Hirschmann et al., 2008). In the same issue, Anderson et al. (2008)  
 507 summarized available P-T constraints on granitic rocks. To avoid repetition, we largely focus on new methods  
 508 developed since 2008, as well as assessing the performance of these 2008 models using new experiments  
 509 published in the last 15 years. Specifically, we assess models using a new test dataset of experiments conducted  
 510 on arc magma compositions (ArcPL – Arc post LEPR, Wieser et al. 2023a-b) at variably hydrous (H<sub>2</sub>O= 0–16.6  
 511 wt%, median=4.7 wt%) crustal conditions (0–17 kbar). Importantly, the experiments in this new dataset were  
 512 not used during the calibration of most models, and any overlaps were removed when testing a specific model.  
 513 Our focus on arcs is partially a result of the experimental data available not used in model calibration, but also  
 514 reflects the fact there has been very little focus on this tectonic setting, despite the fact it is one of the few places  
 515 where the crust is thick enough that mineral-based barometers may be able to resolve different crustal storage  
 516 regions within uncertainty (Fig. 3). For methods not applicable to arc magmas (e.g. OPAM, section 2.2), we  
 517 compile other available experiments. For many methods, there are not sufficient ‘test’ experiments available for  
 518 MORB, OIB and alkali lavas to build on the comparisons presented by Masotta et al. (2013), Masotta and Mollo  
 519 (2019), Neave et al. (2019) and Neave and Putirka (2017), so we refer readers to these papers.

520

## 521 **2.1. Liquid-only thermometry**

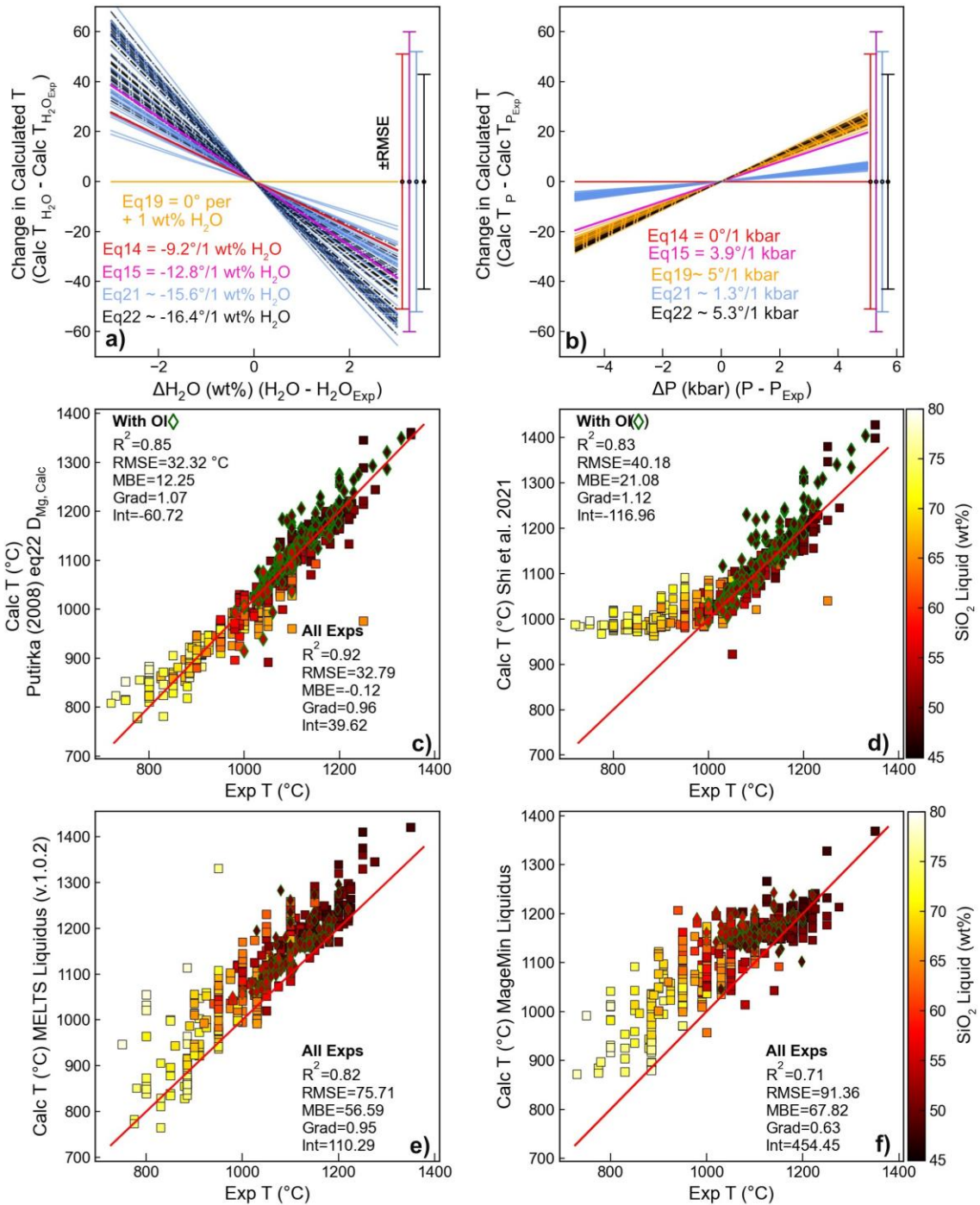
522 A huge variety of liquid-only thermometers exist, with varying complexity and calibration ranges. For  
523 example, the thermometer of Helz and Thornber (1987) uses just the MgO content of the liquid, calibrated on  
524 compositions from the Kīlauea Iki lava lake. In contrast, P2008 eq14 has terms for the MgO, FeO<sub>t</sub>, Na<sub>2</sub>O, K<sub>2</sub>O,  
525 H<sub>2</sub>O and Mg# in the liquid, and was calibrated/tested on 1536 olivine-saturated liquids. There are also a number  
526 of olivine-liquid thermometers with a term for the partitioning of Mg between olivine and liquid ( $D_{Mg}^{Ol-Liq}$ ). In  
527 their supporting spreadsheet, Putirka (2008) replace this term with the theoretical value of  $D_{Mg}$  predicted by  
528 Beattie (1993) to produce a liquid-only thermometer. Here, we discuss the best-performing thermometers for  
529 our new test dataset.

530 As P and H<sub>2</sub>O may be poorly constrained in many systems, we first assess the sensitivity of various  
531 thermometers to these parameters. We randomly select 40 experiments - for each liquid composition, we make  
532 100 duplicates with the experimental H<sub>2</sub>O content perturbed by ±3 wt% (Fig. 5a), and separately perturb the  
533 experimental P by ±5 kbar (Fig. 5b). We take the calculated T at these perturbed values and subtract the  
534 calculated T at the measured P and H<sub>2</sub>O ( $\Delta T$ ,  $\Delta P$ ). Thermometers with a H<sub>2</sub>O term show variable, but relatively  
535 high sensitivity to H<sub>2</sub>O, with the average calculated T dropping by ~9 to 16°C per wt% H<sub>2</sub>O added (Fig. 5a). For  
536 comparison, we show the quoted RMSE of each thermometer. Uncertainty in H<sub>2</sub>O of 3 wt% introduces a  
537 systematic error comparable in size to the stated RMSE (Fig. 5a). Thermometers are substantially less sensitive  
538 to P; uncertainty in P of 5 kbar results in <30°C of variation. Even a full 10 kbar of uncertainty in P doesn't exceed  
539 the quoted RMSE (Fig. 5b).

540 Given the sensitivity of calculated temperatures to H<sub>2</sub>O, we only use experiments where H<sub>2</sub>O was  
541 determined using quantitative methods (calibrated volatile-by-difference, FTIR, SIMS, Raman spectroscopy). We  
542 perform calculations using experimental P and measured H<sub>2</sub>O, because there are no suitable liquid barometers  
543 or hygrometers to iteratively solve all unknowns. For the ArcPL dataset, the best liquid-only thermometer is an  
544 adapted version of the Ol-Liq thermometer of P2008 Eq22, where the olivine  $D_{Mg}$  term is replaced with the  
545 calculated  $D_{Mg}$  value from Beattie (1993), converting it into a Liq-only thermometer (Fig. 5c). Surprisingly, this  
546 adapted Ol-Liq thermometer does a very good job of predicting T in experiments without olivine, including melts  
547 with high SiO<sub>2</sub> contents (square symbols). We also use the new liquid-only thermometer calibrated on  
548 experiments containing olivine from Shi et al. (2021). This thermometer performs very well for experiments  
549 containing olivine, with slightly better statistics than Eq22 $D_{Mg}$  (Fig. 5d). Unsurprisingly, given it was calibrated  
550 with Ol-bearing liquids in mind, it drastically overpredicts T at MgO <~ 2–3 wt% for experiments without olivine  
551 (Supporting Fig. 1) – although this still presents an interesting contrast with Eq22 $D_{Mg}$ .

552 We also calculate the liquidus T using rhyolite-MELTS v1.2.0, v.1.0.2 and pMELTS (Gualda et al. 2012;  
553 Gualda and Ghiorso, 2015, Ghiorso et al., 2002, Fig. 5e, Supporting Fig. 2). All three versions of MELTS give similar  
554 statistics; pMELTS has the higher R<sup>2</sup> and lowest MBE and RMSE (R<sup>2</sup>=0.89, MBE=44°C, RMSE=58°C), but shows  
555 significantly worse performance than v1.0.2 for the lowest T liquids. It is notable that the MBE for all 3 versions  
556 is relatively high (44–56°C vs. -0.12°C for eq22 $D_{Mg}$ ), which demonstrates that MELTS consistently overestimates  
557 liquidus temperatures (Fig. 5e). The other disadvantage of MELTS calculations vs. empirical approaches is the  
558 additional computational expense; 2000 liquidus calculations take 47 minutes using pyMELTScalc through  
559 alphaMELTS for Python compared with 0.015 seconds using eq22 $D_{Mg}$  through Thermobar on a desktop  
560 computer with 128 Gb RAM and a 10-core 10<sup>th</sup> generation Intel i-9 processor. Liquidus temperatures can also  
561 be calculated using the Holland et al. (2018) thermodynamic model, implemented through the Julia-based Gibbs  
562 Free Energy minimization software MAGEMin (Reil et al. 2022). The fit between the experimental and calculated  
563 T is considerably worse than that achieved by rhyolite-MELTS v1.2.0, with temperatures often overestimated by  
564 100–200°C, particularly for experiments performed at <1100°C (Fig. 5f). These calculations take similar times to  
565 MELTS calculations. In summary, if melt H<sub>2</sub>O contents are well constrained, empirical liquid-only thermometers  
566 such as eq22 $D_{Mg}$  of Putirka (2008) perform surprisingly well across a surprisingly wide range of melt  
567 compositions.

568



569

570 *Figure 5: Assessing Liquid-only thermometers. a-b) Sensitivity of calculated T to H<sub>2</sub>O (a) and pressure (b). For 40*  
 571 *randomly selected experiments (each represented by a line), we perturbate the experimental H<sub>2</sub>O content by ±3*  
 572 *wt% (a), and pressure by ±5 kbar (b). These plots show that increasing H<sub>2</sub>O causes a drop in calculated T, and an*  
 573 *increase in P causes a smaller increase in T. c-f) Experimental T vs. calculated T for experiments where H<sub>2</sub>O was*  
 574 *measured by quantitative methods (FTIR, SIMS, Raman, calibrated volatiles by difference). Experiments*  
 575 *containing olivine are shown as green-outlined diamonds, and experiments without olivine as black-outlined*  
 576 *squares. All symbols are colored by the SiO<sub>2</sub> content of the melt. MELTS (part e) and MAgEMin (part f) liquidus T*  
 577 *calculated using Fe<sup>3+</sup>/Fe<sub>T</sub>=0.15 (calculated T are not very sensitive to Fe<sup>3+</sup> but having Fe<sup>3+</sup>>0 is necessary for the*  
 578 *algorithm to converge).*

579



## 580 2.2. Liquid-only barometry

581 Barometric methods based on the composition of silicate melts rely on the fact that the thermodynamic  
582 variance of the system (i.e., the degrees of freedom) is lower in multi-phase saturated systems, so the melt  
583 composition contains information about the conditions of magma storage. This is typically discussed with  
584 regards to magma evolution along mineral cotectics, or at invariant points such as eutectics, where the degrees  
585 of freedom is close to zero (i.e., high-silica rhyolites, Ludden, 1978; Vogt, 1931). The positions of these cotectics  
586 and eutectics are sensitive to pressure because of differences in the volume of common igneous minerals. Thus,  
587 if the influence of P and melt composition on the location of cotectics/eutectics can be determined by  
588 thermodynamic or empirical parameterisations, measured compositions of lavas saturated in the required  
589 phases can be used to calculate P (e.g., Grove et al., 1992; Gualda et al., 2012; Wilke et al., 2017; Yang et al.,  
590 1996, Fig. 1g).

591 Thermodynamic approaches to liquid-only barometry have become increasing common in the last  
592 decade, with the rhyolite-MELTS thermodynamic models used to assess the storage pressure of evolved,  
593 rhyolitic magmas from several locations worldwide (Gualda and Ghiorso, 2014; Harmon et al., 2018; Pamukcu  
594 et al., 2015). The application of thermodynamic methods to liquid-only barometry is addressed in detail in  
595 Section 8. Here, we instead focus on empirical methods calibrated using experimental data.

### 596 2.2.1. OPAM Barometry

597 Experimental work on the location of the olivine-plagioclase-augite-melt (OPAM) cotectic has been  
598 ongoing for at least 3 decades. Early work constrained the position of the OPAM cotectic at 0.001 kbar in the  
599 simplified CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS)+FeO (Shi, 1992) and CMAS+FeO+Na<sub>2</sub>O systems (Shi, 1993). Further  
600 experiments on natural MORB compositions demonstrated that minor components in the liquid phase (e.g., Ti,  
601 Na, and K) and the expansion of the clinopyroxene stability field at higher pressures strongly influences the  
602 cotectic position (Grove et al., 1992; Yang et al., 1996). Using these observations, Grove et al. (1992) provided a  
603 set of empirical equations to locate the position of the olivine+plagioclase+melt and OPAM cotectics as a  
604 function of melt chemistry and pressure. Yang et al. (1996, hereafter Y96) built on this work with an updated  
605 parameterisation for the location of the OPAM cotectic, expressing the Mg, Ca, and Al molar fractions ( $X_{Mg}$ ,  $X_{Ca}$ ,  
606 and  $X_{Al}$ ) of an OPAM-saturated melt as a function of P and the remaining molar fractions (e.g.,  $X_{Si}$ ,  $X_{Ti}$ ). For  
607 example, their expression for the molar fraction of Ca has the following form:

$$608 X_{Ca} = 1.133 - 0.00339 * P(kbar) - 0.569 * X_{Na} - 0.776 * X_K - 0.672 * X_{Ti} - 0.214 * X_{Fe} - 3.355 * X_{Si} +$$
$$609 2.830 * X_{Si}^2 \text{ [Equation 4]}$$

610 These equations were updated by Voigt et al. (2017, hereafter V17), who used new experimental data to show  
611 that Cr<sub>2</sub>O<sub>3</sub> has a strong influence on clinopyroxene phase stability. Their equations have the same functional  
612 form, with an addition of a term for the molar fraction of Cr, separate terms for ferrous and ferric Fe molar  
613 fractions, and updated coefficients for the other parameters:

$$614 X_{Ca} = 1.07 - 0.02707 * P(GPa) - 0.634 * X_{Na} - 0.618 * X_K - 0.515 * X_{Ti} - 0.188 * X_{Fe^{2+}} - 0.597 *$$
$$615 X_{Fe^{3+}} - 3.044 * X_{Si} + 2.477 * X_{Si}^2 - 9.367 * X_{Cr} \text{ [Equation 5]}$$

616 Herzberg (2004) (hereafter H04), develop an alternative approach, relating P to liquid components projected  
617 onto an Anorthite, Diopside, Enstatite ternary diagram from Olivine:

$$618 P(GPa) = -9.1168 + 0.2446 * (0.4645 * En + An)$$
$$619 -0.001368 * (0.4645 * En + An)^2 \text{ [Equation 6]}$$

620 Despite the greater simplicity of pressure calculations using the H04 OPAM parameterisation, the Y96  
621 and V17 molar fraction equations have formed the basis of most OPAM barometry over the last decade (V17:  
622 Bell et al., 2021; Stock et al., 2018, Y96: (Baxter et al., 2023; Caracciolo et al., 2022, 2020; Halldórsson et al.,  
623 2022). The methods used to extract pressure information from these expressions vary. Early studies used the  
624 equations of Y96 to calculate the position of the OPAM cotectic at multiple pressures and plotted these positions  
625 on an olivine-clinopyroxene-quartz pseudoternary diagram (projected from plagioclase). Visual comparison of  
626 the position of the calculated OPAM cotectic to natural melt compositions projected onto the same  
627 pseudoternary diagram were used to estimate the pressure of magma storage (Geist et al., 1998; Maclennan et  
628 al., 2001). Kelley and Barton (2008) use a complex approach calculating theoretical and measured normative  
629 mineral components at different pressures, regressing these components against pressure to determine the  
630 best fit for each measured sample. More recent studies have determined the pressure of the minimum misfit

631 between calculated  $X_{Mg}$ ,  $X_{Ca}$ , and  $X_{Al}$  using the equations of Y96 or V17, and measured  $X_{Mg}$ ,  $X_{Ca}$ , and  $X_{Al}$  in their  
632 samples without requiring the conversion to normative mineral components (Hartley et al. 2018).

633 Regardless of the calculation method used to obtain P, OPAM barometry requires input melt  
634 compositions to be saturated in all 3 solid phases (olivine, clinopyroxene, and plagioclase). Solving for pressure  
635 using the equations of Y96 or V17 for samples that are not saturated in all 3-phases could lead to erroneous  
636 results and may explain the wide range in calculated P estimated for some systems (e.g., 1.4– 7.7 kbar at Laki in  
637 Iceland; Kelley and Barton, 2008). Therefore, it is important to determine which samples are co-saturated before  
638 interpreting OPAM calculations. One way to ensure 3-phase saturation in the target melts is via textural  
639 observations, such as petrographic observations of euhedral crystals with no disequilibrium textures.  
640 Alternatively, in systems with abundant whole-rock or matrix glass data spanning a range of MgO contents,  
641 comparing liquid lines of descent with mass balance approaches or fractional crystallization models (e.g.,  
642 MELTS, Petrolog3, Danyushevsky and Plechov, 2011; Gualda et al., 2012) can be used to confirm 3-phase  
643 saturation.

644 An approach that can be applied to individual liquid compositions without textural or LLD context to  
645 calculate P and check for cosaturation was developed by Hartley et al. (2018). They determined the probability  
646 of three-phase saturation using a Chi-squared distribution to calculate the misfit between the predicted ( $X_i^{Pred}$ )  
647 and measured ( $X_i^{Meas}$ ) molar fractions for Mg, Ca and Al:

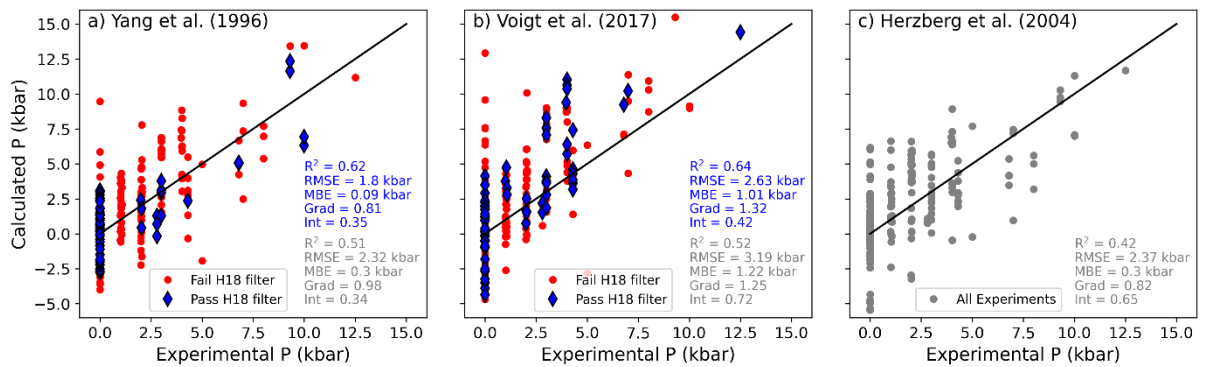
$$648 \chi^2 = \sum_{i=1}^3 \left[ \frac{X_i^{Meas} - X_i^{Pred}}{\frac{\sigma_{X_i}}{100} X_i^{Meas}} \right]^2 \text{ [Equation 7]}$$

649 Here,  $\sigma_{X_i}$  is an estimate of the relative analytical uncertainty for each cation under consideration  
650 (expressed as a percentage). As  $X_i^{Pred}$  is a function of the system pressure, users can determine the best-fit  
651 model pressure by locating the position of the minimum possible  $\chi^2$  value ( $\chi^2_{Min}$ ). To assess whether the melt  
652 is truly three-phase saturated, Hartley et al. (2018) compare  $\chi^2_{Min}$  to the cumulative distribution function of  
653 the Chi-squared distribution with 2 degrees of freedom. A probability is selected as a cut off value (e.g.,  $p=0.05$ ,  
654  $p=0.2$ ); Hartley et al. use a probability of fit,  $P_f$ , which can be thought of as 1 minus the p value. If  $\chi^2_{Min}$  is less  
655 than the critical value of the chi squared cumulative distribution function for this chosen cut off (i.e., p-value  
656 and  $n=2$  degrees of freedom), the liquid is assumed to be three-phase saturated. By considering the results of  
657 OPAM calculations on experimental melt compositions (including the Yang et al. 1996 calibration data), Hartley  
658 et al. (2018) determine that a ‘probability of fit’ filter of  $p \sim 0.2$  ( $P_f = 0.8$ ) results in a good fit between the  
659 experimental and calculated pressures, while minimising the number of ‘false negatives’ (i.e., melt compositions  
660 which are OPAM saturated, but would fail this test). The minimisation method and co-saturation check of Hartley  
661 et al. (2018) (hereafter H18) has been utilised by several studies investigating the storage conditions of MORBs  
662 and OIBs (Bell et al., 2021; Stock et al., 2018, Baxter et al., 2023; Caracciolo et al., 2022, 2020; Halldórsson et al.,  
663 2022).

664 Baxter et al. (2023) evaluated the performance of the Y96 equations using 315 OPAM saturated  
665 experimental melt compositions, ranging from 1 atm to 12.5 kbar pressure. They filter these experiments using  
666 the H18 filter and exclude those with  $MgO < 4$  wt%, leaving 95 experiments. Comparing calculated and  
667 experimental pressures for these filtered experiments yields a RMSE of  $\pm 1.51$  kbar, which is similar to the  
668 ‘random error’ of  $\pm 1.32$  kbar estimated by Hartley et al. (2018, definition uncertain). However, both studies  
669 evaluated the performance of the Y96 equations using a dataset which included some experiments used in the  
670 Y96 calibration. For example, 57% of the 95 experiments assessed by Baxter et al. (2023) are part of the Y96  
671 calibration dataset. If we rerun their comparison using only experimental data that was not used in the Y96  
672 calibration the RMSE increases from  $\pm 1.51$  kbar to  $\pm 1.89$  kbar. A particular issue is that only 7/41 of the remaining  
673 experiments were conducted at  $> 0.001$  kbar, making it very hard to assess the performance of the Y96  
674 barometer without new test data at higher pressures.

675 To test the performance of all three OPAM barometers listed here (Y96, V17, and H04), and the success  
676 of the H18 filter, we compile an experimental dataset of OPAM saturated experiments not used to calibrate  
677 either Y96 or V17.  $N=188$  overlap with the dataset of Baxter et al. (2023), with  $N=38$  experiments not in that  
678 compilation. Fig. 6 demonstrates that there are strong correlations between the calculated and experimental  
679 pressures for all OPAM methods when the H18 saturation check is not applied ( $R^2$  of 0.51, 0.52, and 0.42 for  
680 Y96, V17, and H04 respectively, all symbols, grey statistics on Fig. 6). Despite having the highest  $R^2$  value of the  
681 three methods tested here, calculated pressures determined using the V17 expressions display the largest  
682 uncertainties (RMSE=3.19 kbar) and a systematic offset to high pressures (MBE = 1.22 kbar, Fig. 6b). The Y96

683 expression has a smaller systematic offset (gradient=0.98, MBE=0.3 kbar), as well as a lower RMSE (2.32 kbar,  
 684 Fig. 6a). The parameterisation of H04 also returns a relatively low RMSE (2.37 kbar) and similar MBE to the Y96  
 685 method (0.3 kbar), but has a lower gradient of the correlation (0.82; Fig. 6c).



686

687 *Figure 6: Experimental vs. calculated P using the OPAM expressions of Yang et al. (1996), Voigt et al. (2017) and*  
 688 *Herzberg (2004) for OPAM-saturated experiments on MORB-like compositions. The calculated pressure was*  
 689 *determined using the Chi-squared method of Hartley et al. (2018, H18) for the Yang et al. (1996) and Voigt et al.*  
 690 *(2017) equations (a,b). Samples passing the co-saturation filter of Hartley et al. (2018) are shown as blue*  
 691 *diamonds, while those that fail are shown as red circles. The filter is not applicable to the method of Herzberg et*  
 692 *al. (2004, part c). Statistics using all experiments are shown in grey text, statistics for experiments passing the*  
 693 *H18 filter are shown in blue text.*

694 The larger uncertainty and systematic offset in pressures estimated using V17 likely originates from the  
 695 sensitivity of these expressions to the  $\text{Cr}_2\text{O}_3$  content of the melt phase. Only 53 of the 225 experiments used in  
 696 this analysis (~24%) report melt  $\text{Cr}_2\text{O}_3$  contents, despite most experiments using natural basalt compositions  
 697 that likely contain at least trace amounts of  $\text{Cr}_2\text{O}_3$ . Adding  $\text{Cr}_2\text{O}_3$  into the melt phase changes the stability of  
 698 pyroxene (see Fig. 3, Onuma and Tohara, 1983), and thus the pressure estimated by OPAM barometry (Voigt et  
 699 al., 2017). Consequently, the systematic offset to higher pressures obtained by applying the V17 expressions to  
 700 our compiled experimental database might result from the absence of reported  $\text{Cr}_2\text{O}_3$  in most experiments, and  
 701 uncertainty as to whether Cr was even present in starting materials (Wieser et al. 2023b). Additionally, it is  
 702 unclear how precise the analyses of  $\text{Cr}_2\text{O}_3$  in these experiments are; typical analytical conditions can result in  
 703 large errors for this low concentration oxide (propagating into a much wider spread of pressures than using Y96  
 704 or H04, Fig. 4f). Despite its poor performance on our test dataset, we cannot rule out the possibility that V17  
 705 may be the best parameterization in natural Cr containing systems, even if it behaves poorly on Cr-free  
 706 experiments. Further experimental work on Cr-bearing experiments where the Cr content of the melt was  
 707 characterized with high precision at a range of pressures are required to assess the performance of the V17  
 708 expressions as an OPAM barometer in natural systems.

709 Interestingly, although all  $N=225$  experiments were OPAM saturated, only 27% ( $N=61$ ) pass the H18  
 710 cosaturation filter when the equations of Y96 are used (blue diamonds, Fig. 6a). While the statistics for calculated  
 711 vs. experimental pressures are greatly improved using only experiments which pass the filter, it is concerning  
 712 how many false negatives this filter produces, particularly as only 18 of the experiments which passed the filter  
 713 were performed at pressures above 0.001 kbar. To further assess the performance of the H18 saturation filter,  
 714 we isolated experiments on MORB-like compositions that are saturated in only one or two ( $N = 172$ ) of the three  
 715 key mineral phases in OPAM barometry. Using the Y96 expression, 19% of these non-OPAM saturated  
 716 experiments pass the H18 co-saturation filter (false positives). These results demonstrate that the H18 co-  
 717 saturation filter should not be used in isolation to identify which samples are suitable for OPAM barometry.  
 718 Therefore, petrological observations of three-phase saturation remain critical for determining pressures via  
 719 OPAM barometry.

720 To date, OPAM barometry has mostly been used to evaluate the storage pressure of MORBs, or  
 721 tholeiitic to transitional OIBs (these compositions broadly overlap with the calibration dataset of Yang et al.  
 722 1996). Unfortunately, the uncertainty associated with OPAM barometry assessed using our independent test  
 723 dataset (RMSE = 1.8 – 2.32 kbar, Fig. 6) indicates that this method does not have the resolution to distinguish  
 724 between upper vs lower crustal storage at most mid-ocean ridges. However, at hotspot influenced ridges (e.g.,  
 725 Iceland) and regions of plume derived volcanism (e.g., ocean islands), the thickened crust (Fig. 3e) means that  
 726 OPAM can provide insights into the characteristics of magma storage in these locations if independent checks

727 for 3–phase saturation are performed prior to pressure calculation (via petrographic observations or liquid line  
728 of descent analysis). For example, melt inclusion and matrix glass data from Barðarbunga, Iceland, indicates that  
729 there is a slight difference in the entrapment pressure of melt inclusions and the final equilibration pressure of  
730 the matrix glasses (Hartley et al. 2018; Caraccioli et al. 2022).

### 731 **2.2.2. Other liquid-based barometers**

732 The effect of H<sub>2</sub>O on phase boundaries in the OPAM system has not been investigated in detail, meaning  
733 this method cannot be applied to arc magmas with confidence. To provide a liquid-based thermobarometer with  
734 application to more hydrous systems like volcanic arcs, Blundy (2022) create parametrizations for the stability  
735 of clinopyroxene-hornblende-orthopyroxene-magnetite-plagioclase-ilmenite (CHOMPI) as a function of P, T, and  
736 the ratio of H<sub>2</sub>O and CO<sub>2</sub> in the fluid, including a cosaturation check to establish whether CHOMPI phases were  
737 present based on just a liquid composition. However, Wieser et al. (2023d) show this cosaturation test classifies  
738 ~44% of ArcPL experiments lacking the CHOMPI assemblage as CHOMPI-saturated (false positives), and  
739 unsurprisingly these experiments show a poor correspondence between calculated and experimental pressure  
740 (as the system is not low variance). The logic behind the CHOMPI approach has been generalized to liquids  
741 saturated in a wider variety of phases by Weber and Blundy (2023), who apply a regression tree machine learning  
742 algorithm to a training dataset of liquids ranging from basalt to rhyolite. As this model is still being tweaked and  
743 is currently a preprint (Weber, written comms), we do not comment on it further.

### 744 **2.3. Clinopyroxene±Liquid**

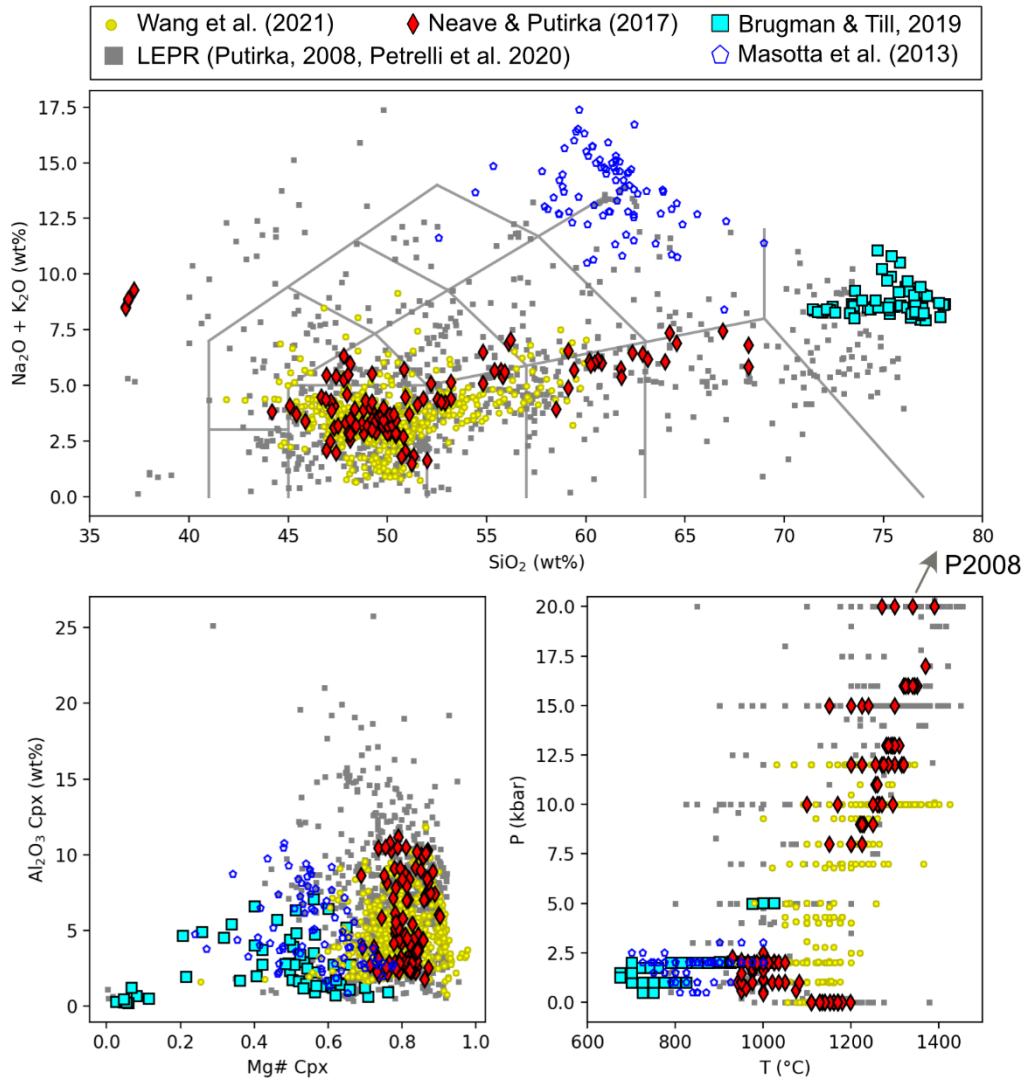
745 The majority of Cpx-Liq thermobarometers rely on the exchange of diopside hedenbergite (DiHd,  
746 CaFeSi<sub>2</sub>O<sub>6</sub>) and Jadeite (Jd, NaAlSi<sub>2</sub>O<sub>6</sub>) between Cpx and liquid. Here, we briefly summarize the most recent  
747 parameterizations of Cpx equilibrium, and workflows that have been developed for calculating P and T in natural  
748 systems. A detailed discussion of pre-2008 models can be found in Putirka (2008, and refs within), and a  
749 description of the best Cpx-Liq models for our test dataset and sensitivity to P and T as well as the best  
750 equilibrium tests to use can be found in Wieser et al. (2023a-b).

751 Putirka (2008) propose a number of equations based on Cpx-Liq equilibria (Eq30, Eq31, Eq32c for P,  
752 Eq33 for T), expanding and recalibrating the models of Nimis (1995) and Putirka et al. (1996, 2003) to account  
753 for an increase in experimental data, particularly hydrous experiments. More recently, several new equations  
754 have been calibrated which focus on a more limited subset of compositional space than these global regressions  
755 (Fig. 7). Neave and Putirka (2017) calibrate a Cpx-Liq barometer for application to tholeiitic basalts from ocean  
756 island settings (specifically Iceland) using 6 experimental studies (N=113 experiments) with mafic-intermediate  
757 compositions, and pressures ranging from atmospheric to 20 kbar (Neave and Putirka, 2017, Fig. 7, red  
758 diamonds). Masotta et al. (2013) conduct experiments and compile available literature data on trachytic to  
759 phonolitic compositions (Fig. 7, blue pentagons), to calibrate a Cpx-Liq barometer applicable to more alkaline  
760 compositions, which are poorly represented in the calibration dataset of P2008. Their expressions have a very  
761 similar/identical form to those of Putirka (2008), with recalibrated coefficients. Brugman and Till (2019) note  
762 that in high-silica melts, there is very little Al<sub>2</sub>O<sub>3</sub> in Cpx (<2 wt%), and the calculated Jd component is very low or  
763 even zero. Along with the fact that high Si compositions are very poorly represented in P2008, they showed that  
764 this results in existing Cpx-Liq thermometers overestimated temperatures in evolved melts by up to 170°C. Thus,  
765 Brugman and Till (2019) compiled recent studies from the literature on rhyolitic compositions (e.g., Almeev et  
766 al., 2012; Bolte et al., 2015; Gardner et al., 2014) supplemented with their own experiments on the Scaup Lake  
767 Rhyolite (Fig. 7, cyan squares), to calibrate a new thermometer for highly evolved melts which is independent  
768 of Jadeite, P, and H<sub>2</sub>O content.

769 Another key shift in the use of Cpx-based barometry since 2008 has accompanied the rapid rise in  
770 programming literacy amongst petrologists, allowing the development of new workflows based on existing  
771 thermobarometry equations. For example, while experimental studies have clearly paired Cpx and liquid  
772 compositions, it is significantly more challenging in natural systems to identify such pairs. Typically, a given  
773 volcanic eruption will erupt a narrow range of liquid compositions along with a much more chemically diverse  
774 crystal cargo, incorporating Cpx crystals grown from a wide variety of melt compositions. Additionally, many  
775 whole rock compositions are a mix of crystals and melts, so are not representative of true liquids (Reubi and  
776 Blundy, 2009; Ubide et al., 2022). A variety of algorithms have been developed to try to identify matched pairs,  
777 by combining erupted Cpx compositions with liquids erupted over a longer time period at a given edifice, or even  
778 compilations of whole-rock data from an entire volcanic region.

779 For example, Maclennan et al. (2001) assessed magma storage pressures of basalts from the Icelandic  
780 Northern Volcanic Zone by filtering possible Cpx-Liq matches using the K<sub>D</sub> equilibrium test of Putirka (1999).

781 Winpenny and MacLennan (2011) devised a more complex test for Cpx-Liq equilibrium, using equation 35 of  
 782 Wood and Blundy (1997) for  $K_D$ , and trace element equilibrium tests. Specifically, they use trace elements  
 783 measured in Cpx, and then use the partition coefficients from Wood and Blundy (1997) to calculate the expected  
 784 trace element contents of equilibrium liquid compositions. By comparing these predicted liquid compositions to  
 785 available trace element data for compiled liquids (for Ce or La, Nd or Sm, and Yb, Dy and Y depending on data  
 786 availability), they assess all possible matches between Cpx erupted at Borgarfraun, and ~1000 whole-rock and  
 787 glass analyses from Icelandic Basalts for equilibrium. However, this method requires trace element data in both  
 788 Cpx and liquids/whole-rock, which isn't widely available in the literature for different volcanic systems (and is  
 789 rarely collected as part of thermobarometric studies). Furthermore, the trace element partition coefficients used  
 790 in these calculations are highly sensitive to the temperature of the system, complicating calculations (Sun and  
 791 Liang, 2012; Wood and Blundy, 1997).



792

793 *Figure 7: Calibration range of Cpx-Liq and Cpx-only thermobarometers. Since the compilation of the LEPR*  
 794 *database in 2008 (Hirschmann et al., 2008) used to calibrate Putirka (2008) and Petrelli et al. (2020, grey*  
 795 *squares), many new thermobarometers have focused on specific regions of compositional space: Brugman and*  
 796 *Till (2019, cyan squares), Masotta et al. (2013, blue pentagons), Neave and Putirka (2017, red diamonds). TAS*  
 797 *lines drawn using Stevenson (2015).*

798

799 Neave and Putirka (2017) and Neave et al. (2019) develop an R code (also used by Gleeson et al., 2021  
 800 and Stock et al., 2018) to identify equilibrium Cpx-Liq pairs using components which can be calculated from  
 801 elements measured routinely by electron microprobe (Diopside-Hedenbergite, DiHd; Enstatite-Ferrosilite, EnFs;  
 802 Calcium Tschermak, CaTs). Specifically, they assess the difference in the measured components in the Cpx and

803 the equilibrium components calculated from the liquid composition using Eq35 of P2008 for  $K_D$ , equations from  
804 Mollo et al. (2013) for DiHd and EnFs, and from Putirka (1999) for CaTs. As the selected  $K_D$  equilibrium equation  
805 is sensitive to T, and the DiHd, EnFs and CaTs equations sensitive to P and T, equilibrium tests must be calculated  
806 concurrently with P and T estimates. A computationally optimized algorithm loosely based on the Neave R  
807 algorithm which was never publicly released was incorporated in the Open-Source Python3 tool Thermobar  
808 (Wieser et al. in 2022b). This tool allows comparison of 100s of Cpx and Liq within seconds, with highly  
809 customizable equilibrium filters. Even with fast matching codes, identifying Cpx-Liq pairs is associated with  
810 substantial uncertainty regarding choice of equilibrium tests, and the chosen cut-off parameter (see Wieser et  
811 al. 2023a for arc magmas). In many systems, very few to no matches are found with erupted liquids, requiring  
812 generation of synthetic liquids to match to measured Cpx (e.g., Scruggs and Putirka, 2018). Another approach is  
813 to pair Cpx rims with matrix glass or groundmass separates (Klügel et al., 2020), although because this method  
814 focuses on rims, it may only reveal the depth of the uppermost storage chambers (neglecting deeper pressure  
815 information preserved in core compositions).

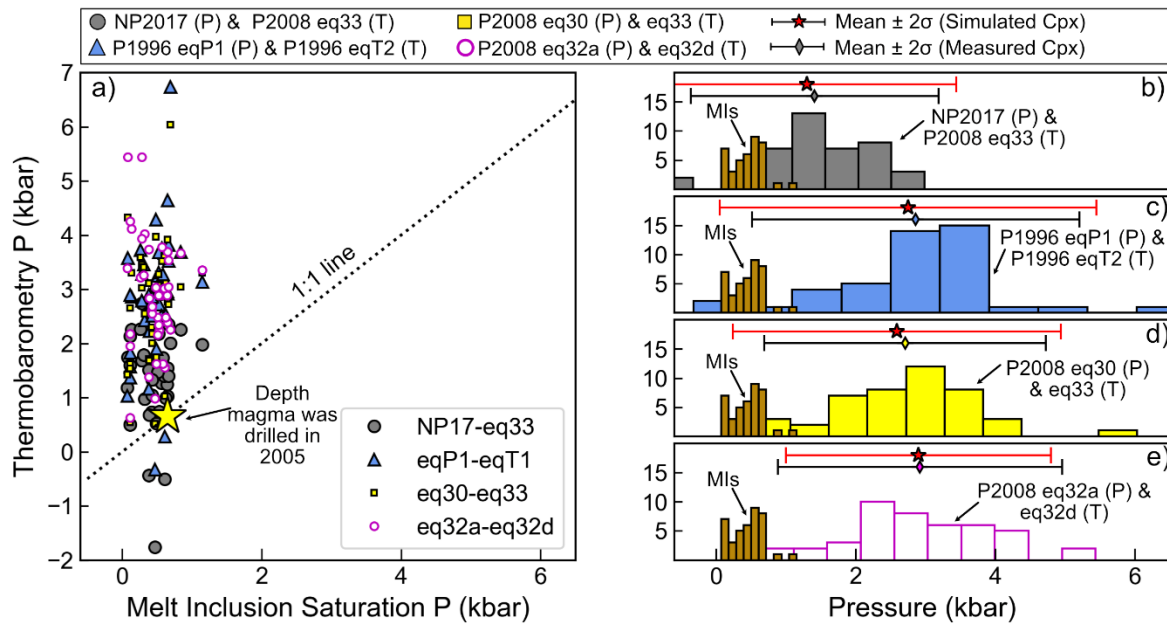
816 Issues associated with identifying equilibrium liquids can be circumvented using Cpx-only barometers.  
817 Putirka (2008) present two Cpx-only barometers (eq32a-b) and a Cpx-only thermometer (eq32d). Wang et al.  
818 (2021) show that these (and other existing) Cpx-only thermobarometers perform poorly in mafic and  
819 intermediate melt compositions. To address this, Wang et al. (2021) select 559 experiments conducted at 0–12  
820 kbar with liquid SiO<sub>2</sub> contents between 42–60 wt% to calibrate a new barometer which is independent of T and  
821 H<sub>2</sub>O (Fig. 7, yellow circles). They use the PyTorch python library (Paszke et al., 2019) to implement a gradient  
822 descent algorithm to select Cpx cation components to include in a non-linear term for a Cpx-only barometer,  
823 rather than selecting components based on thermodynamic reasoning. They also present a thermometer, which  
824 is independent of P but requires knowledge of the H<sub>2</sub>O content of the liquid.

825 Most recently, supervised machine learning methods have been applied to Cpx-based equilibrium to  
826 develop thermobarometry expressions (e.g., random forests, Higgins et al., 2022, extra trees, Jorgenson et al.,  
827 2022; Petrelli et al., 2020). Unlike more traditional empirical thermobarometers which are underlain by  
828 thermodynamic principles, measured oxide data are fed into these algorithms, rather than calculated  
829 components such as Jadeite. Wieser et al. (2023a) show that the Cpx-only barometers of Wang et al. (2021) and  
830 Jorgenson et al. (2022) show similar performance to popular Cpx-Liq barometers for the ArcPL dataset, justifying  
831 the use of Cpx-only barometers as an alternative to trying to identify equilibrium liquids. That said, just because  
832 Cpx-Liq and Cpx-only barometry show similar performance, it is worth nothing that neither approach performs  
833 particularly well, with neither method yielding  $R^2 > 0.74$ , or RMSE  $< 2.1$  kbar. Additionally, all expressions have  
834 low gradients, overpredicting at lower pressures, and underpredicting at higher pressures.

835 The relatively poor performance of Cpx-based barometry on independent test datasets (e.g., high  
836 RMSE, low gradients, inability to distinguish magma storage within ~10–15 km) is at least partially the result of  
837 low analytical precision when measuring Na<sub>2</sub>O in experiments used to calibrate and test barometers (see Wieser  
838 et al. 2023b, and Section 1.4). Of course, analytical precision also affects measurements of natural samples and  
839 can result in an anomalously large spread of calculated P and T, which can be incorrectly attributed to  
840 transcrustal storage because of spurious trends in P-T space. For example, Wieser et al. (2023c) show that a the  
841 entire P-T range of the lunar Cpx analysed by Luo et al. (2023) can be explained by the propagation of analytical  
842 uncertainty. To further demonstrate the importance of error propagation, we calculate pressures using Cpx and  
843 melt inclusion compositions from the first two weeks of the 2018 eruption of Kīlauea Volcano (Wieser et al.,  
844 2022c). Cpx-hosted melt inclusions yield relatively shallow saturation pressures, which overlap very well with  
845 the pressure at which a highly evolved magma was drilled in this region in 2005 (Teplow et al., 2009, yellow star,  
846 Fig. 8a). We use the PEC-corrected melt inclusion compositions and analyses of the Cpx composition close to the  
847 melt inclusion to calculate Cpx-Liq and Cpx-only pressures. These barometers return a much greater spread of  
848 pressures than melt inclusion saturation pressures, with a notable offset to significantly higher values (Fig. 8). In  
849 fact, these calculated depths are similar to the 3–4 kbar estimated by Putirka (2008) for Cpx erupted during the  
850 Pu’u O’o eruption of Kīlauea. However, there are no other geological or geophysical indications that Cpx-  
851 saturated magmas are stored this deep.

852 To interpret the large spread of calculated pressures, we simulate 5000 Cpx compositions, with the  
853 variability of each oxide following a normal distribution centred on the mean measured Cpx composition, with  
854 a standard deviation equal to the average counting statistic precision estimated from the EPMA output. We  
855 calculate pressures using these 5000 synthetic Cpx paired with the average liquid composition, and show  $\pm 2\sigma$  of  
856 these simulations as a red error bar (Fig 8b-e). The simulated spread in calculated pressures resulting from  
857 analysis of an entirely homogenous Cpx using typical EPMA operating conditions almost exactly matches the

858 observed spread in calculated pressures ( $2\sigma$  error bars for each overlain on each histogram). This illustrates how,  
 859 without sufficient averaging of individual analyses, it would be easy to incorrectly invoke storage at a range of  
 860 pressures spread throughout the crust. While iteration of Putirka (2008, eq30) for T and Neave and Putirka  
 861 (2017) for P produces calculated pressures that align within error of the melt inclusion saturation pressures, the  
 862 other Cpx-based barometers estimate far too high pressures compared to melt inclusions and drilling depths.  
 863 This demonstrates both the lack of precision and accuracy of Cpx-based methods. Even without analytical  
 864 uncertainty, the RMSE on these barometers mean there is no way to reliably distinguish storage at  $\sim 0.5$  kbar  
 865 from storage at 4 kbar; limiting the applicability of these methods in systems where magma is stored in the  
 866 upper part of a relatively thin crust.



867  
 868 *Figure 8: Comparison of melt inclusion saturation pressures (Wieser et al. 2022c), and Cpx-Liq and Cpx-only*  
 869 *barometry for samples erupted during the first two weeks of the 2018 Kīlauea eruption. a) Melt inclusion*  
 870 *saturation pressures calculated in MagmaSat (Ghiorso and Gualda, 2015) using VESlcal (Iacovino et al., 2021)*  
 871 *cluster tightly at shallow pressures. These pressures are very similar to the pressure at which an evolved magma*  
 872 *body was drilled in 2005 in the same area (yellow star, Teplow et al. 2009). Cpx-Liq and Cpx-only pressures*  
 873 *calculating using PEC-corrected melt inclusion-host pairs show substantial scatter, extending to substantially*  
 874 *deeper pressures. b-e) Histograms showing calculated pressures for each iterative mineral barometry calculation.*  
 875 *Error bars with black lines show  $\pm 2\sigma$  for these calculations. Red error bars show  $\pm 2\sigma$  for Monte-Carlo simulations*  
 876 *for the mean composition of each Cpx and Liq, with 5000 Cpx compositions simulated using estimates of*  
 877 *analytical precision for these Cpx measurements.*

878  
 879 The relatively poor performance of many Cpx-based barometers can also be attributed to the fact that  
 880 many expressions are parameterized in terms of Cpx components (e.g. Jd, DiHd) calculated from EPMA oxide  
 881 data (e.g., Neave and Putirka, 2017, Putirka, 2008). An alternative technique calculates site occupancy and cell  
 882 volumes using a combination of single-crystal X-ray diffraction and measured oxide data (Dal-Negro et al., 1989).  
 883 This technique was used extensively in the 80s-90s, and was recently applied by Tommasini et al. (2022) to  
 884 natural Cpx crystals from Popocatepetl Volcano. They show that XRD-informed site assignments and the  
 885 resulting calculated mineral components differ greatly from the routines used by Neave and Putirka (2017) and  
 886 Putirka (2008) using EPMA data alone. This discrepancy between components calculated using EPMA data and  
 887 the true crystal structure may reflect an additional source of uncertainty plaguing Cpx-based barometers. Single  
 888 crystal XRD may also be vital to help us determine where Na is going (pairing with Al, Fe<sup>3+</sup> or Cr<sup>3+</sup>), which will  
 889 further enhance our understanding of how Cpx composition relates to pressure. However, while single-crystal  
 890 X-ray diffraction has been applied to natural crystals, the small size of experimental Cpx means that it is very  
 891 difficult to obtain these parameters for experiments in order to calibrate expressions using these parameters  
 892 (Dal-Negro et al., 1989, Tommasini et al. 2022). Additionally, a workflow involving XRD would be far more time

893 consuming from a sample preparation perspective than existing EPMA-based techniques, which may severely  
894 restrict its uptake by the community, even if it results in improved barometer performance.

895 A number of papers have also shown the importance of considering the petrogenetic history of a Cpx  
896 population when interpreting thermobarometry calculations. For example, Hammer et al. (2016) assessed the  
897 influence of disequilibrium crystal growth on Cpx barometry using X-ray mapping and quantitative spot analyses  
898 of clinopyroxene crystals from a post-shield ankaramite erupted from Haleakalā volcano, Hawai'i. Their work  
899 demonstrates the complexity of interpreting Cpx compositions in regions where disequilibrium growth  
900 processes occur. Specifically, texturally and compositionally distinct domains within individual crystals thought  
901 to have formed by high degrees of undercooling during crystallisation have distinct distributions of Cpx Jd  
902 contents, so return very different P estimates. They find offsets within individual crystals up to ~3.5 kbar. In  
903 contrast, Ubide et al. (2019a, 2019b) calculate P-T-H<sub>2</sub>O for different domains in sector zoned Cpx from Stromboli,  
904 and show remarkably constant results regardless of the textural context (although without individual calculated  
905 PTs, it is not possible to directly compare the statistical differences between these different studies). Clearly,  
906 further work is required to understand how the formation of different chemical domains in magmatic systems  
907 affect the distribution of P- and T-sensitive Cpx components, and thus the results from thermobarometric  
908 calculations.

909 The relatively recent appreciation that most magmas are stored in predominantly crystal-rich “mushy”  
910 environments also adds additional complexity to the interpretation of clinopyroxene-based barometric  
911 estimates, because clinopyroxene chemistry can be influenced by chemical processing in these crystal-rich  
912 regions. For example, residual melt compositions can be modified by reactive porous flow, driven by  
913 disequilibrium between a percolating melt phase and the surrounding crystal framework (Boulanger et al., 2020;  
914 Gleeson et al., 2021; Lissenberg and MacLeod, 2016; Sanfilippo et al., 2020). Critically, the melts formed from  
915 this process are rarely observed at the surface, which makes it difficult to quantify their chemistry to pair with  
916 erupted Cpx compositions. Cpx-Liq and Cpx-only barometry is also affected by the fact that reactive porous flow  
917 might drive interstitial melt compositions (and thus the Cpx compositions) outside the compositional range used  
918 to calibrate existing expressions (Fig. 7). Gleeson et al. (2021) demonstrate the importance of accounting for  
919 mush processes in their study of Cpx from wehrlite xenoliths found on Isla Floreana in the southern Galápagos.  
920 These crystals have Na<sub>2</sub>O contents up to ~1.3 wt% and returned apparent crystallisation pressures up to ~18  
921 kbar using the clinopyroxene-only thermobarometers of Putirka (2008; eq. 32b-32d). In contrast, Cpx-Opx  
922 barometry (using the same crystals), melt inclusion and clinopyroxene-liquid thermobarometry from  
923 neighbouring scoria cones on the same island indicate that magma storage was dominantly located at around  
924 ~7 kbar (Gleeson et al., 2022, 2021). Based on rare earth element signatures in these pyroxenes (elevated LREE  
925 contents relative to MREE and HREE contents) the authors concluded that the anomalously high pressure  
926 estimates of the wehrlitic clinopyroxene crystals result from chemical modification of Na<sub>2</sub>O (and REE) by reactive  
927 porous flow in olivine ±clinopyroxene mush zones. Comparison with other thermobarometric techniques (E.g.,  
928 Opx-Cpx, melt inclusions, Gao et al., 2022, Gleeson et al. 2021), as well as identifying trace element patterns  
929 indicative of reactive flow, provide one method to interpret the spuriously high pressure estimates returned  
930 from these cumulate Cpx.

931 In summary, to push Cpx-based thermobarometry forward, we need to improve the experimental  
932 datasets available to calibrate and test barometers (Wieser et al. 2023a-b), develop new methods to relate  
933 chemical components to parameters we can easily measure in natural samples and experimental charges  
934 (Tommasini et al. 2022), and increase our understanding of natural processes causing variation in Cpx  
935 compositions (Gleeson et al., 2021; Hammer et al. 2017, Neave et al., 2019; Ubide et al., 2019b, 2019a),

#### 936 **2.4. Orthopyroxene±Liq**

937 Beattie (1993) presented the first Opx-Liq thermometer based on the use of non-regular solution  
938 models to calculate saturation temperatures. Putirka (2008) then calibrated two different equations (Eq28a,  
939 28b) using the LEPR dataset, both of which are sensitive to P and H<sub>2</sub>O. Eq28a uses the composition of the Opx  
940 and Liq, while Eq28b only uses the composition of the liquid to calculate the temperature of Opx saturation.  
941 Wood (1974) published the first Opx barometer, which used the Al content of Opx in equilibrium with Garnet.  
942 Putirka (2008) calibrated a more widely applicable Opx-only barometer (Eq29c) and two Opx-Liq barometers  
943 (Eq29a, Eq29b) using the LEPR database. The main pressure-sensitive component in Eq29a is a Jadeite-like  
944 component in the Opx, while Eq29b uses the (Fe, Mg) Al<sub>2</sub>SiO<sub>6</sub> Opx component. Both equations also contain terms  
945 for other liquid cation fractions, and Opx cation fractions on the basis of 6 oxygens. Eq29c (Opx-only) uses the  
946 cation fractions of Al, Ca, Cr and Al in the Opx, as well as terms for T. It is worth noting that several of the Putirka  
947 (2008) Opx thermobarometers are prone to numerical issues resulting from the presence of logarithmic terms.



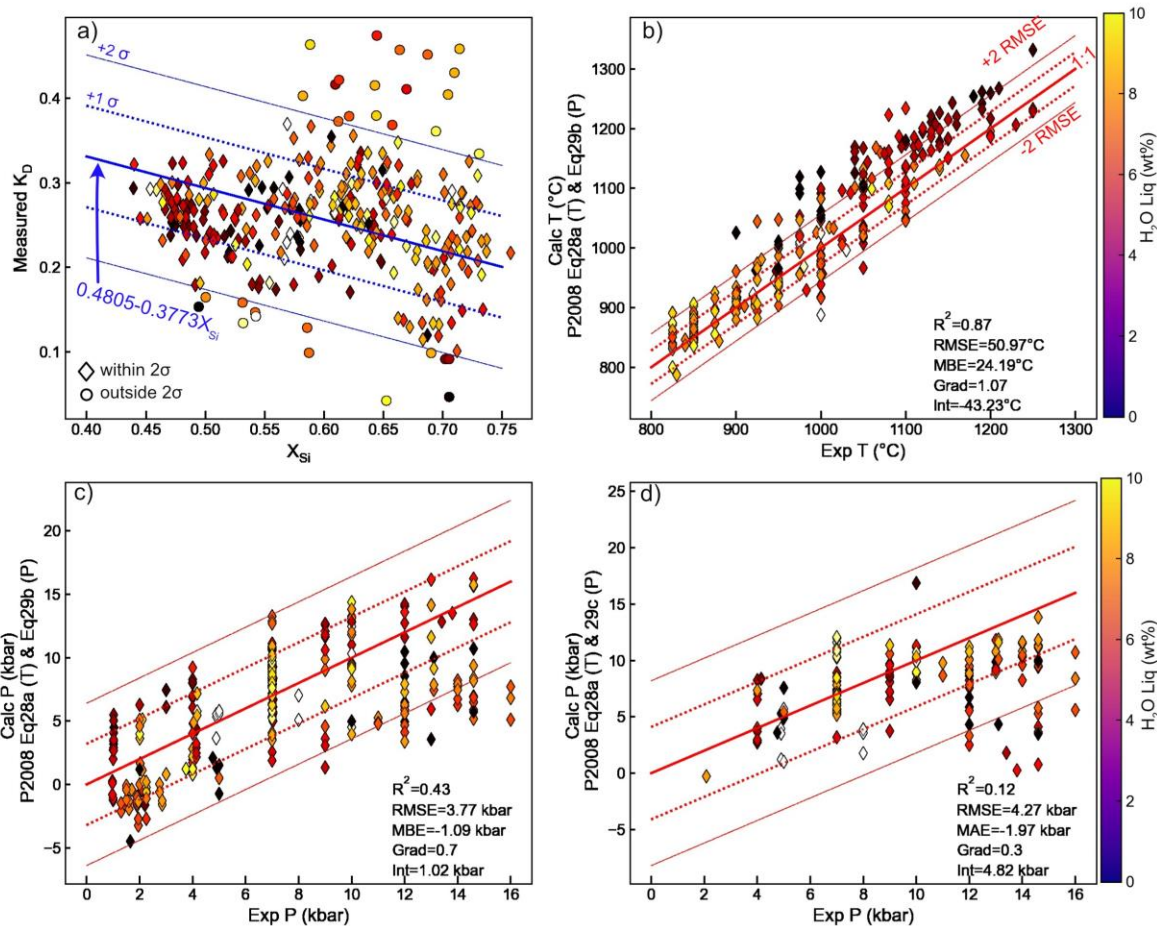
948 For example, Eq29c (Opx-only) has a term for the logarithm of the cation fraction of Cr in Opx. If Cr was not  
949 measured or reported in Opx, this term cannot be evaluated (the case for 63% of the experiments in our test  
950 dataset). Similarly, Eq28b has a term calculated from the log of the  $(\text{Fe, Mg})_2\text{Al}_2\text{SiO}_6$  component in the Opx  
951 divided by terms involving the cation fractions of Si, Al, Fe, Mn, and Mg in the liquid. In ~9% of experiments  
952 (mostly at <3 kbar, but a few at 5 and 8 kbar), the  $(\text{Fe, Mg})_2\text{Al}_2\text{SiO}_6$  component in the Opx is 0, the log of which  
953 yields infinity. A value of zero for the  $(\text{Fe, Mg})_2\text{Al}_2\text{SiO}_6$  component can also occur in Opx where the calculated  
954  $\text{Al}_{\text{VI}}$  component is zero, which is particularly common in low pressure Opx ( $\text{Al}_{\text{VI}}=0$  in 7% of the Opx considered  
955 here, all at <2.5 kbar). To address the numerical issue associated with the  $(\text{Fe, Mg})_2\text{Al}_2\text{SiO}_6$  component, in later  
956 versions of the spreadsheets from Putirka (2008), two additional Opx-Liq barometers were included (“Global”  
957 and “Felsic”). These equations simply use the ratio of the measured  $\text{Al}_2\text{O}_3$  content in Opx and Liq. The global  
958 model was calibrated on 795 Opx-Liq pairs, and the felsic model on 40 pairs.

959 In natural systems, it is even more difficult to assess the equilibrium relationships between erupted Opx  
960 and Liquid compositions than for Cpx-Liq, because only  $K_{D, \text{Fe-Mg}}^{\text{Opx-Liq}}$  has been widely explored as an equilibrium  
961 test. Putirka (2008) find that  $K_D$  in experimental charges roughly correlates with the cation fraction of Si in the  
962 liquid ( $X_{\text{Si}}$ ) ( $1\sigma=0.06$ ). In the ArcPL dataset, there is no significant correlation between  $K_D$  and  $X_{\text{Si}}$  ( $R^2=0.01$ , Fig.  
963 9a), although ~67% lie within the given error bound of the predicted value. In natural systems it is very plausible  
964 that liquids and orthopyroxenes that are not chemically related could yield  $K_D$  values passing these relatively  
965 broad equilibrium tests (particularly if  $2\sigma$  is used as the cut off). One way to avoid this problem is to use an Opx-  
966 only barometer (e.g., Eq29c of P2008), However, this equation contains a temperature-sensitive term, and given  
967 no Opx-only thermometer exists to our knowledge, a liquid composition may still need to be used to estimate  
968 (or iteratively calculate) the temperature.

969 Using experimental P and  $\text{H}_2\text{O}$  (that was measured by quantitative methods), Eq28a (Opx and Liq  
970 comps) and Eq28b (only Liq comps) are remarkably good thermometers. Eq28a has a slightly higher  $R^2$  (0.90 vs  
971 0.85), and lower RMSE (39 vs. 48°C, Supporting Fig. 3). Using experimental T and  $\text{H}_2\text{O}$  measured by quantitative  
972 methods, Eq29b is the best Opx-Liq barometer ( $R^2=0.58$ , RMSE=3.01 kbar, Supporting Fig. 4), and has a decent  
973 gradient and intercept relative to other mineral-melt barometers we evaluate in this review (grad=0.67, int=1.2).  
974 Eq29a performs slightly worse in terms of  $R^2$  and RMSE but has a slightly better gradient and intercept ( $R^2=0.50$ ,  
975 RMSE=3.65 Gradient=0.74, Int=0.3 kbar). The global barometer is noticeably worse ( $R^2=0.47$ , RMSE=3.47 kbar,  
976 grad=0.59, int=1.4). The Opx-only barometer (Eq29c) is difficult to compare because of the presence of many  
977 experiments without reported Cr measurements in Opx that return numerical errors; for available data,  $R^2=0.04$ ,  
978 RMSE=4.63 (Supporting Fig. 4d).

979 As discussed, it is probable in natural systems that neither T nor P is known, and melt  $\text{H}_2\text{O}$  is relatively  
980 uncertain. We investigate the sensitivity of calculated P to T, and calculated T to P (Fig. 10) by perturbing the  
981 experimental T by  $\pm 100^\circ\text{C}$  and P by  $\pm 5$  kbar. The Putirka (2008) Global and Felsic barometers have no T term, so  
982 show no changes in P with T. Eq29a (dark blue lines, Fig. 10a) shows a relatively small increase in calculated P  
983 with increasing T, while Eq29b shows a larger increase (light blue lines, Fig. 10a). Eq29c, the Opx-only barometer,  
984 shows variable sensitivity to T, with P increasing in some samples, and decreasing in others as T is increased  
985 (grey lines, Fig. 10a). The strong change in calculated P as a function of T for Eq29c, a drop of up to 10 kbar for  
986  $+100^\circ\text{C}$  for some samples, is problematic, as there is no way to determine temperature simply from Opx  
987 compositions at present. The three Opx-Liq thermometers also show variable changes with P (some increasing,  
988 some decreasing, Fig. 10b). However, the uncertainty in calculated T for changes in P of 10 kbar (equivalent to  
989 the crustal thickness in most arcs) is comparable to the stated RMSE on these thermometers.

990 Overall, the relatively large change in calculated P (and to a lesser extent T) with relatively small changes in the  
991 other parameter means that we can expect Opx-based thermobarometers to show far worse statistics when  
992 solved iteratively than when tested with only a single unknown.



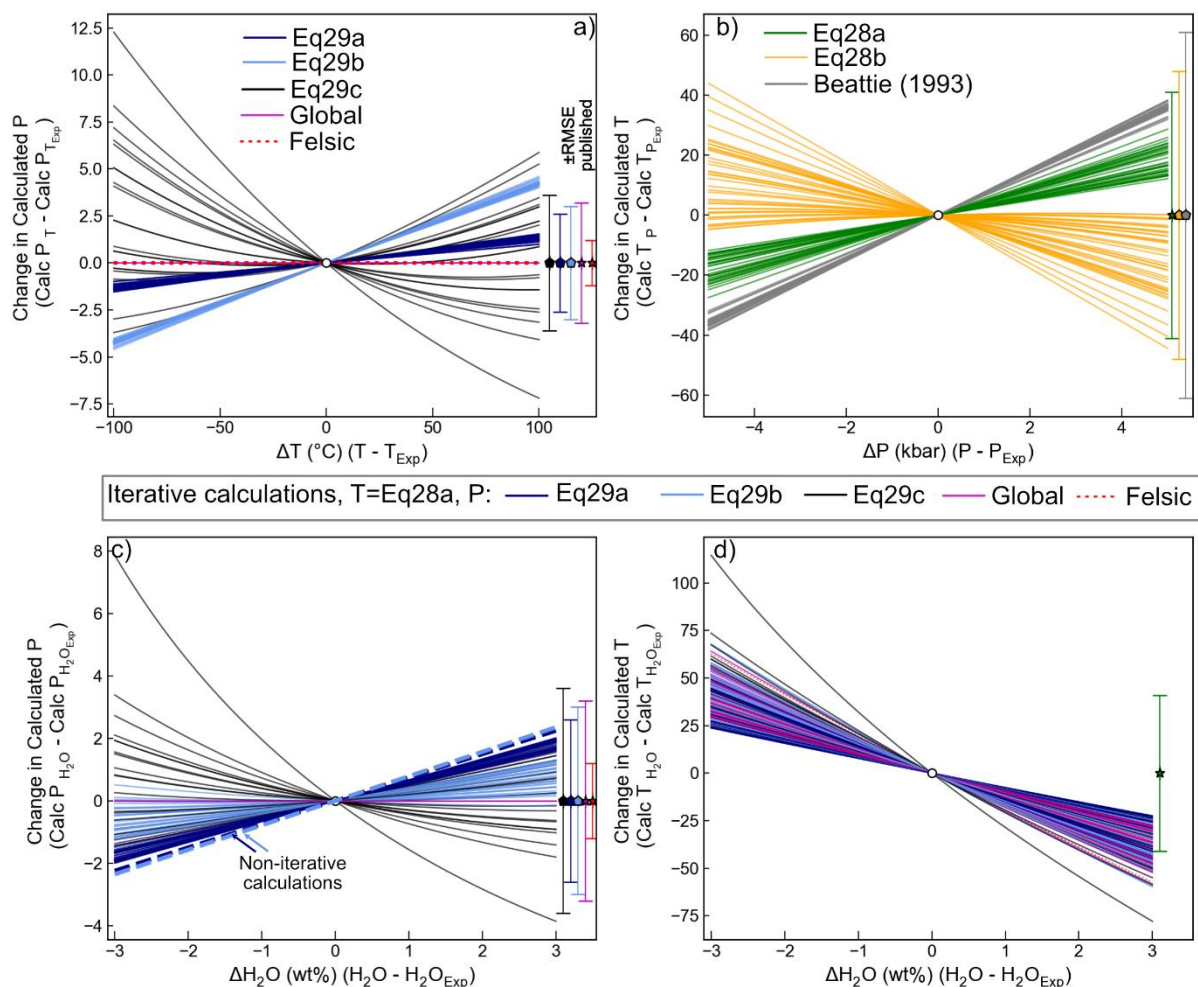
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994 *Figure 9: Opx-Liq and Opx-only thermobarometry. a) Comparison of measured  $K_D$  with that predicted from the*  
 995  *$X_{Si}$  content of the liquid using Putirka (2008). b-c) Comparison of calculated and experimental T and P by iterating*  
 996 *Eq28a(T) and Eq29b(P). d) Iteration of Eq28a (for T, Opx-Liq) with Eq29c (Opx-only, P) of Putirka (2008). Dotted*  
 997 *lines around the 1:1 line show  $\pm$  the quoted  $1\sigma$ , with dashed lines showing  $\pm 2\sigma$ . All symbols colored by  $H_2O$*   
 998 *content, with  $H_2O > 10$  wt% white, to emphasize the scale at lower  $H_2O$  contents.*

999 We also investigate the change in P when using iterative calculations when we perturb the experimental  
 1000  $H_2O$  content by  $\pm 3$  wt%. When T from Eq28a is iterated with all barometers, calculated T decreases with  
 1001 increasing  $H_2O$  (Fig. 10d). Iteration of Eq28a (T)-Eq29a (P) (dark blue line) and Eq28a (T)-Eq29b (P) (light blue  
 1002 line) show a small increase in calculated P with increasing  $H_2O$  content (Fig 10c). Both these barometers have  
 1003 terms multiplying  $H_2O$  by a constant, resulting in a consistent change in P for varying  $H_2O$  contents in non-  
 1004 iterative calculations (+0.748 kbar/1 wt%  $H_2O$  for Eq29a, and +0.784 for Eq29b, dashed blue lines, Fig. 10c).  
 1005 However, because increased  $H_2O$  contents cause T to drop using Eq28a (Fig. 10b), which causes a decrease in  
 1006 the calculated P (Fig. 10a), the influence of  $H_2O$  on calculated P in iterative calculations is slightly less than that  
 1007 obtained in calculations using the experimental T. This complex feedback between equations during iterative  
 1008 calculations results in a greater variability in the influence of  $H_2O$  on calculated P for different samples. Eq29c  
 1009 has no  $H_2O$  term but shows the strongest sensitivity to T (Fig. 10a), resulting in a large drop in P with increasing  
 1010  $H_2O$  when iterated with Eq28a (Fig. 10c). The high sensitivity of Eq29c to  $H_2O$  is concerning because an Opx-only  
 1011 barometer is most likely to be applied in systems where liquid compositions (and thus,  $H_2O$  contents) are poorly  
 1012 constrained. As the Global and Felsic barometers have no T or  $H_2O$  term, they show no sensitivity to  $H_2O$ .

1013

1014



1015

1016 *Figure 10: Assessing the sensitivity of Opx thermobarometry to variation in P, T and H<sub>2</sub>O for N=40 randomly*  
 1017 *selected experiments. a) Change in calculated P for perturbing the experimental T by ± 100 °C. b) Change in*  
 1018 *calculated T by perturbing P by ±5 kbar. c-d) Change in calculated P and T for iterative calculations perturbing*  
 1019 *experimental H<sub>2</sub>O content by ±3 wt%. For all plots, the calculated P or T at experimental conditions is subtracted*  
 1020 *from the calculation at experimental conditions (plotting at 0, 0). Calculations performed in Thermobar (Wieser*  
 1021 *et al., 2022b).*

1022 Ideally, given the effects of H<sub>2</sub>O on calculated P and T (Fig. 10c-d), we would only assess experiments  
 1023 where H<sub>2</sub>O is known by quantitative methods (as for Liq-only). However, only 147/324 experiments from 10/23  
 1024 studies have reported Opx-Liq compositions where H<sub>2</sub>O was measured quantitatively. Thus, all experiments are  
 1025 shown in Fig. 9, with the same calculations using only experiments with quantitative H<sub>2</sub>O measurements shown  
 1026 in Supporting Fig. 5 (the statistics for which are actually less favourable).

1027 Iterating the best thermometer (Eq28a) and barometer (Eq29b) yields a very good match to  
 1028 experimental T in ArcPL using experimental H<sub>2</sub>O contents (Fig. 9b). The thermometer performs worse for  
 1029 experiments with low H<sub>2</sub>O contents (darker symbols, < 2–3 wt%). Based on a similar observation for the LEPR  
 1030 dataset, Putirka (2008) suggest that Opx may re-equilibrate faster in hydrous liquids. Calculated P from iteration  
 1031 of Eq28a-Eq29b is reasonably accurate (Fig. 9c, grad=0.7, MBE=-1.09 kbar, int=-1 kbar), but very imprecise  
 1032 (RMSE=3.77 kbar), so this barometer will be of limited utility in relatively thin-crustal settings such as OIBs and  
 1033 MORBs (Fig. 3). Unlike for thermometers, there is no clear relationship between barometer performance and  
 1034 H<sub>2</sub>O content. Although we cannot perform very many calculations for Eq29c because of the absence of Cr data,  
 1035 calculated Opx-only pressures (Eq29c) iterated with Eq28a shows a reasonable correspondence to the 1:1 line  
 1036 (Fig. 9d) at <12 kbar, although substantially more experiments with reported Cr contents are required to robustly  
 1037 assess this barometer.

1038 Overall, Opx-Liq thermobarometry has been relatively neglected given its performance; no new  
 1039 calibrations have been proposed since 2008. In particular, the relative absence of systematic uncertainty when  
 1040 Opx-based barometers are tested on ArcPL contrast strongly with other mineral barometers discussed here. We  
 1041 suggest that future experimental and theoretical work to further develop Opx-based thermobarometry is  
 1042 warranted, with a particular focus on the development of more robust equilibrium tests. Ensuring starting  
 1043 materials contain Cr contents comparable to natural systems, and ensuring all elements are measured at high  
 1044 precision within experimental Opx (particularly Cr) may lead to improved thermobarometry calibrations. This  
 1045 may provide a particularly promising barometer in arc magmas, where Opx is relatively common, and magmas  
 1046 are relatively H<sub>2</sub>O-rich.

## 1047 2.5. Two Pyroxene (Cpx-Opx) Thermobarometry

1048 Two pyroxene (Cpx-Opx) thermobarometry is widely used in the literature, likely reflecting the fact that  
 1049 these phases crystallize together across a wide range of P, T, and H<sub>2</sub>O contents in a variety of tectonic settings.  
 1050 For example, Cpx-Opx thermobarometry has been applied to OIB basalts from the Galápagos by Gleeson et al.  
 1051 (2021), to mafic arc basalts from SW Japan by Zellmer et al. (2014), and to arc dacites from the Aucanquilcha  
 1052 Volcanic Cluster by Walker et al. (2013). Additionally, it is common that Cpx and Opx form crystal clusters, and  
 1053 calculations from these touching pairs are easier to justify than trying to select equilibrium liquids for each crystal  
 1054 (c.f. Opx-Liq and Cpx-Liq thermobarometry). Opx-Cpx thermobarometry can also be applied in systems where it  
 1055 is difficult to analyse the composition of the liquid (e.g., highly crystalline lavas or xenoliths, Gao et al., 2022;  
 1056 Gleeson et al., 2021).

1057 As discussed above for Opx-Liq equilibrium, one of the main limitations of Cpx-Opx thermobarometry  
 1058 is the paucity of equilibrium tests to help filter out pairs which are not in equilibrium (in experiments and natural  
 1059 samples). The only established equilibrium test compares the exchange of Fe-Mg in Cpx and Opx ( $K_{D,Fe-Mg}^{Cpx-Opx}$ ).  
 1060 Putirka (2008) suggest that  $K_D=1.09\pm 0.14$  in high temperature systems, while  $K_D=0.7\pm 0.2$  in subsolidus systems.  
 1061 However, it is difficult to know where to draw the line between these different filters; what value would be  
 1062 correct to use in a supra-solidus dacitic-rhyolitic melt that is a similar temperature to a subsolidus mafic  
 1063 cumulate?  $K_D$  values for our compiled experiments lie mostly within the high T bracket ( $\pm 1\sigma$  shown in pink),  
 1064 although a number extend to higher values (Fig. 11a). There is no strong relationship between T and measured  
 1065  $K_D$ . Another way to assess the equilibrium value would assume that the Cpx and Opx are each in equilibrium  
 1066 with the liquid, so the Opx-Cpx  $K_D$  value can be obtained from the Cpx-Liq and Opx-Liq  $K_D$  values from Putirka  
 1067 (2008):

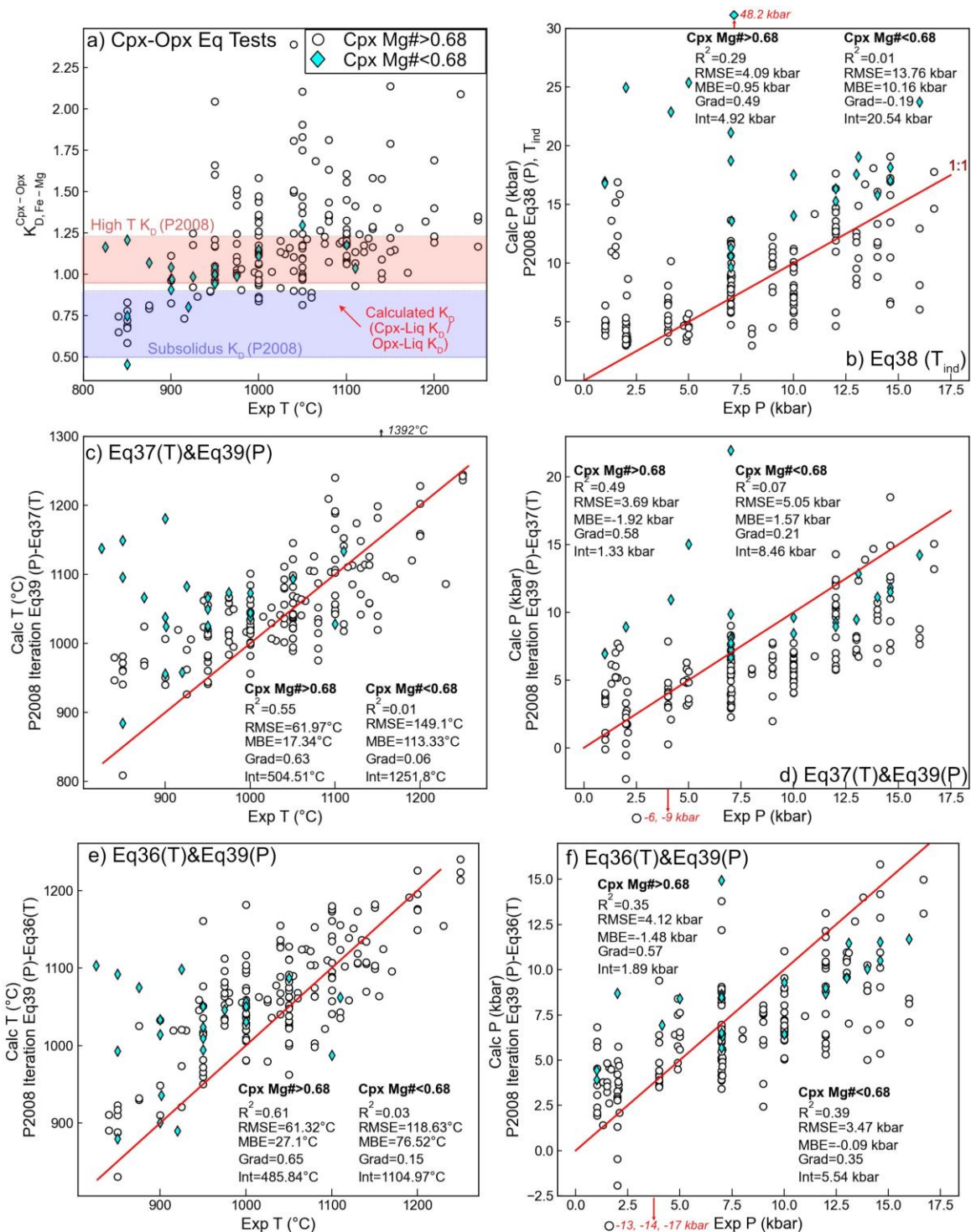
$$1068 K_{D,Fe-Mg}^{Cpx-Opx} = \frac{K_{D,Fe-Mg}^{Cpx-Liq}}{K_{D,Fe-Mg}^{Opx-Liq}} = \frac{e^{-0.107 - \frac{1719}{T(K)}}}{0.4805 - 0.3733 * X_{Si,Liq}} \text{ [Equation 8]}$$

1069 This approach could be advantageous, because there are far more Cpx-Liq and Opx-Liq experiments  
 1070 than Cpx-Opx experiments, so the individual Px-Liq equilibrium values are better constrained. Values calculated  
 1071 using this expression lay between the subsolidus and high T value (red dots, Fig. 11a), with very little variation  
 1072 with temperature. This is because higher T drives up the Cpx-Liq  $K_D$ , but higher T liquids tend to have lower Si  
 1073 contents, which drives up Opx-Liq  $K_D$ . Unfortunately, Equation 8 appears to underestimate the  $K_D$  value for many  
 1074 of the experimental samples given here, which is perhaps unsurprising as we find the Cpx-Liq  $K_D$  expression  
 1075 underestimates many of the Cpx-Liq  $K_D$  values (by up to ~0.5), while the Opx-Liq expression tends to  
 1076 overestimate many of the Opx-Liq  $K_D$  values. Dividing these two relatively uncertain quantities compounds  
 1077 errors. The fact so many of our experimental Cpx-Opx pairs sit outside any estimate of equilibrium could suggest  
 1078 that several are not in equilibrium, so should not be used to assess thermobarometers. However, we find no  
 1079 discrepancy between  $K_D$  and the offset between calculated and predicted P and T. This suggests instead, that  
 1080 more experimental and theoretical work is needed to robustly assess  $K_D$ . Thus, we proceed to assess  
 1081 thermobarometers using all Cpx and Opx pairs in the ArcPL compilation.

1082 The T-independent barometer of P2008 (Eq38) performs very poorly for high Mg# Cpx ( $R^2=0.29$ ,  
 1083 RMSE=4.09) and even worse for low Mg# Cpx (<0.68, cyan diamonds, Fig. 11b,  $R^2=0.01$ , RMSE=13.72). Iteration  
 1084 of P2008 Eq37–39 and Eq36–Eq39 show very similar statistics to one another for calculated P and T, with Eq36–  
 1085 Eq39 showing slightly better behaviour. Neither thermometer is very promising (Fig. 11c, e) producing more of  
 1086 a data cloud than a meaningful correlation. At lower temperatures, two pyroxene thermometers tend to  
 1087 overestimate temperatures (also noted by Ziberna et al., 2021). Iterated barometers are similarly disappointing;  
 1088 even for Cpx with Mg#>0.68, the RMSE is 3.69 kbar (Eq3 7–Eq39, Fig. 11d) and 4.12 kbar (Eq3 6–Eq39, Fig. 11c).

1089  
1090  
1091  
1092

Overall, we suggest that substantially more experiments where Opx and Cpx are stabilized at a variety of pressures and melt compositions are required to improve Cpx-Opx thermobarometers, particularly in more evolved systems with lower Cpx Mg#. Additional experiments would also help to better constrain controls over the equilibrium value at a variety of temperatures and melt compositions.



1093

1094 *Figure 11: Assessing two-pyroxene thermobarometers. a) Measured  $K_{D,Fe-Mg}^{Cpx-Opx}$  values for the ArcPL dataset*  
 1095 *against experimental T. The range of equilibrium values from Putirka (2008) for “HighT” and “Subsolidus”*  
 1096 *systems are shown as colored bars.  $K_D$  values calculated from the Cpx-Liq (T-dependent) and Opx-Liq (Si-*  
 1097 *dependent)  $K_D$  values (Equation 8) are shown as small red dots. b-f) Comparison of predicted and experimental P*  
 1098 *and T for different combinations of equations from P2008. 1:1 line shown in red. In all plots, Cpx-Opx pairs with*

1099 *Cpx Mg#<0.68 are colored cyan, and Mg#>0.68 colored white. To maintain scale, a few experiments returning*  
1100 *extreme values are excluded from plots. Their y coordinate is labelled with a red arrow.*

## 1101 **2.6. Amphibole thermobarometry and Chemometry**

1102 Amphibole (Amp)-only and Amp-Liq thermobarometry have been used extensively to calculate P and T  
1103 in volcanic and plutonic igneous systems (e.g., Higgins et al., 2022; Scruggs and Putirka, 2018). Amphibole  
1104 chemometers are also becoming widely used to probe the compositions of melts present at depth within  
1105 plumbing systems which are not always well represented at the surface (e.g., Humphreys et al., 2019; Zhang et  
1106 al., 2017).

### 1107 **2.6.1 Amphibole thermobarometry**

1108 Amphibole barometry stems from the seminal work of Hammestrom and Zen (1986), who showed that  
1109 the  $Al^{VI}$  and  $Al^{Tot}$  contents of hornblendes from calc-alkaline plutons emplaced at different depths correlate with  
1110 estimates of pressure, and that the same compositional-pressure relationships were seen in experimental  
1111 products. Hollister et al. (1987) analysed rim compositions from plutons where the pressure of emplacement  
1112 could be estimated from phase assemblages in the surrounding country rock. They confirmed the Al-pressure  
1113 relationship of Hammestrom and Zen (1986) and proposed an updated calibration. Additional calibrations have  
1114 also been developed for Amp-Plag, Amp-Garnet, and Amp-Plag-Qtz (see Molina et al., 2021 and refs. within).

1115 More recently, Mutch et al. (2016) present an Amp-only barometer parameterized in terms of  $Al^{Tot}$   
1116 calibrated using a dataset comprising: i) their new experiments on 3 different bulk compositions, ii) the  
1117 experiments of Johnson and Rutherford (1989), Schmidt (1992), Thomas and Ernst', 1990), iii) published analyses  
1118 from plutons with independent depth constraints (Ague, 1997; Hammestrom and Zen, 1986), and iv) their new  
1119 analyses on amphiboles from the Yerrington Batholith in Nevada. Mutch et al. (2016) exclude experiments where  
1120 garnet or phengite was stabilized, as this alters the  $Al^T$ -pressure relationship. Importantly, their compiled dataset  
1121 shows a curvature in  $Al^T$  vs. pressure space relationship at 0.5–3 kbar not seen by previous workers. They  
1122 parameterize this empirically relating pressure to a second order polynomial of  $Al^T$ .

1123 While  $Al^T$  in amphibole is controlled by both T and P, so can only be used as a barometer on an isotherm  
1124 or near a solidus (Médard and Le Pennec, 2022), correlations between P and  $Al^{VI}$  have been noted by Krawczynski  
1125 et al. (2012), Helz (1982), Larocque and Canil (2010) and Schmidt (1992) in a wide variety of systems. Médard  
1126 and Le Pennec (2022) present a T-independent barometer using a simple linear regression of P and  $Al^{VI}$ ,  
1127 calibrated on 47 published experimental compositions with Si-rich silicate melts in equilibrium with Biotite,  
1128 Plagioclase, and Magnetite. They state that this barometer has a RMSE of 0.86 kbar (or 0.72 kbar for <4 kbar).  
1129 They also test their expression on 22 biotite-bearing experiments not used in calibration, which lie within the  
1130 stated RMSE window. However, all their tests are at <4 kbar, which makes it difficult to evaluate the precision  
1131 of the barometer at higher pressures.

1132 Importantly, all the Al-based amphibole-only barometers discussed so far are only applicable in the  
1133 presence of certain phases. For example, Hammestrom and Zen (1986) warned about the applicability of their  
1134 regressions in rocks without quartz, where  $Al^T$  can be significantly higher at a given P. Mutch et al. (2016)  
1135 emphasize that their barometer should only be applied to amphibole rims in equilibrium with melts saturated  
1136 in plagioclase ( $An_{15-80}$ ), biotite, quartz, alkali feldspar, Fe-Ti oxides, and apatite (e.g., near solidus, low variance  
1137 volcanic systems). In higher T melts with fewer co-crystalizing phases and higher thermodynamic variance, the  
1138 equilibria controlling amphibole composition are still poorly understood (Putirka, 2016). Médard and Le Pennec  
1139 (2022) test their barometer using 7 Bt-free experiments, resulting in a RMSE of 1.4 kbar, which is a large % error  
1140 given these experiments were conducted at ~ 1–2 kbar. Thus, they suggest that this barometer should not be  
1141 used in biotite-free rocks. While limited in their applicability to silicic systems saturated in a large number of  
1142 phases, the amphibole-only barometers discussed thus far are extremely useful for determining pluton  
1143 emplacement depths and crustal exhumation rates in orogenic belts, or when investigating the formation and  
1144 evolution of Porphyry copper deposits (Anderson, 1996; Hollister et al., 1987; Mutch et al., 2016).

1145

1146 In contrast to these studies focused on low variance silicic systems, Ridolfi et al. (2010) compile calcic  
1147 amphibole analyses from experiments conducted on a wide range of melt compositions and phase assemblages  
1148 to generate an empirical amphibole-only thermometer (Eq1), oxybarometer (Eq2) and hygrometer (Eq3). Ridolfi  
1149 et al. (2010) justify the application of Amp-based methods in less evolved systems with fewer phases (and  
1150 therefore higher variance) by pointing out that most volcanic amphiboles exist close to their stability limits  
1151 (shown by abundant breakdown textures). They suggest that close to the amphibole stability curve, the variance  
1152 of the system is lower so amphibole composition is more closely related to P, T and  $fO_2$ . Ridolfi et al. (2010) also

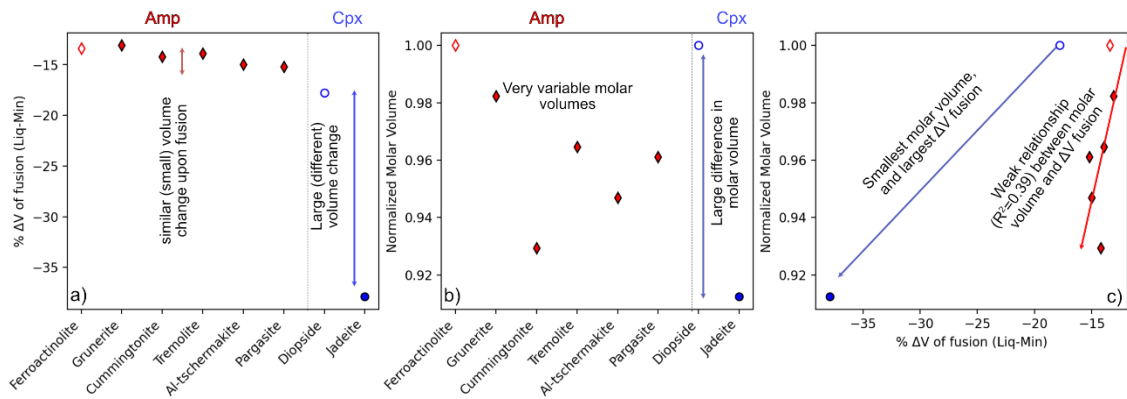
1153 present an Al<sup>T</sup> barometer calibrated on 9 amphiboles (Eq4) but find that attempts to perform a similar calibration  
1154 on their larger experimental dataset performs poorly, particularly for magnesiohastingsite amphiboles which  
1155 are common in nature, but sparse in available experiments.

1156         Ridolfi and Renzulli (2012) compile additional experiments and apply more stringent filters to produce  
1157 an amphibole-only barometer (e.g., removing amphiboles with  $1\sigma$  for  $\text{SiO}_2 > 0.9$  wt%, Piston cylinder experiments  
1158 conducted at  $< 6$  kbar etc.). Of the 61 experimental amphiboles remaining, 19 (31%) are magnesiohastingsite,  
1159 which is close to the proportion of magnesiohastingsites (42%) in their natural compilation. This is in stark  
1160 contrast to the dataset of Ridolfi et al. (2010), which contained no magnesiohastingsites (or pargasites or  
1161 kaersutites). Ridolfi and Renzulli (2012) create several different regressions to calculate P using amphibole cation  
1162 fractions calculated on the basis of 13 oxygens. For example, Eq. 1a was calibrated on N=61 experiments, and  
1163 expresses P in terms of the exponential of compositional terms (Si, Ti, Al, Fe, Mg, Ca, Na, K). However, using  
1164 comparisons to seismic depths from Ridolfi et al. (2010) for a variety of natural systems, they show that this  
1165 equation overestimates at low P, and underestimates at high P. They calibrate 4 additional expressions using a  
1166 smaller subset of analyses (N=20–41) in different pressure ranges (Eq1b and 1e use exponentials, 1c and 1d use  
1167 multilinear regressions). They present an algorithm where the user calculates P for each equation, and these  
1168 different values are averaged/combined in a variety of different ways to construct a final P.

1169         To test the expressions of Ridolfi and Renzulli (2012), Erdmann et al. (2014) compile a series of  
1170 experiments not used in their calibration dataset. While T, melt  $\text{SiO}_2$  content and  $f\text{O}_2$  are reasonably well  
1171 predicted in their new dataset, they demonstrate a very poor correspondence between calculated and  
1172 experimental P, and calculated and experimental  $\text{H}_2\text{O}$  contents. Erdmann et al. (2014) suggest the P discrepancy  
1173 results from the fact that the Si-Al content of an amphibole is more strongly related to the liquid composition  
1174 and T than P. In particular, they note that the calibration dataset of Ridolfi and Renzulli (2012) is skewed, with  
1175 amphiboles from felsic and intermediate melts clustered at lower P, and mafic to intermediate melts at higher  
1176 Molina et al. (2021a) also publish a short note stating that they test Ridolfi and Renzulli (2012) using a dataset  
1177 of experiments compiled by Molina et al. (2021b), and obtain “*unsustainable pressure estimates*”.

1178         Putirka (2016) further examine Amp-only and Amp-Liq equilibrium, presenting two P-independent  
1179 Amp-only thermometers (Eq5 and SiHbl), two P-dependent Amp-only thermometers (Eq6 and Eq8), two P-  
1180 independent Amp-Liq thermometer (Eq4b and Eq9), and a P-independent Liq-only amphibole saturation  
1181 thermometer (Eq4a). He also presents three T-independent Amp-Liq barometers (Eq7a, b, c). Using an extensive  
1182 test dataset, Putirka (2016) show that Amp-only and Amp-Liq equilibrium do a reasonably good job of predicting  
1183 pressure when averaged, but conclude that P estimates from individual amphibole grains are ‘*nearly useless for*  
1184 *understanding crustal processes*’. They hypothesize that the main limitation of Amp-based barometry is the fact  
1185 that none of the common amphibole components have particularly large changes in volume when they  
1186 precipitate from the liquid ( $\Delta V$  fusion), or large molar volume contrasts between different components in the  
1187 amphibole itself. For example, even though Jadeite in pyroxene is not a particularly sensitive barometer at  
1188 crustal conditions, relative to Diopside it has a significantly more negative  $\Delta V$  fusion (Fig. 12a), and a smaller  
1189 molar volume (8% smaller, Fig. 12b, Putirka, 2016). As Jadeite has both a smaller molar volume and a more  
1190 negative  $\Delta V$  fusion (Fig. 12c), the amount of Jadeite vs. Diopside in Cpx are sensitive to P. In contrast, there is a  
1191 pretty weak relationship between the  $\Delta V$  fusion and the molar volume for different amphibole components (Fig.  
1192 12b-c, Putirka, 2016). While the exchange of different amphibole components is not particularly P-sensitive,  
1193 Putirka (2016) do show that the partition coefficient of Al between amphibole and liquid is correlated to P,  
1194 explaining why amphibole barometers are normally parameterized in terms of Al and other oxides, rather than  
1195 explicitly calculated mineral components (e.g. Jadeite in Cpx).

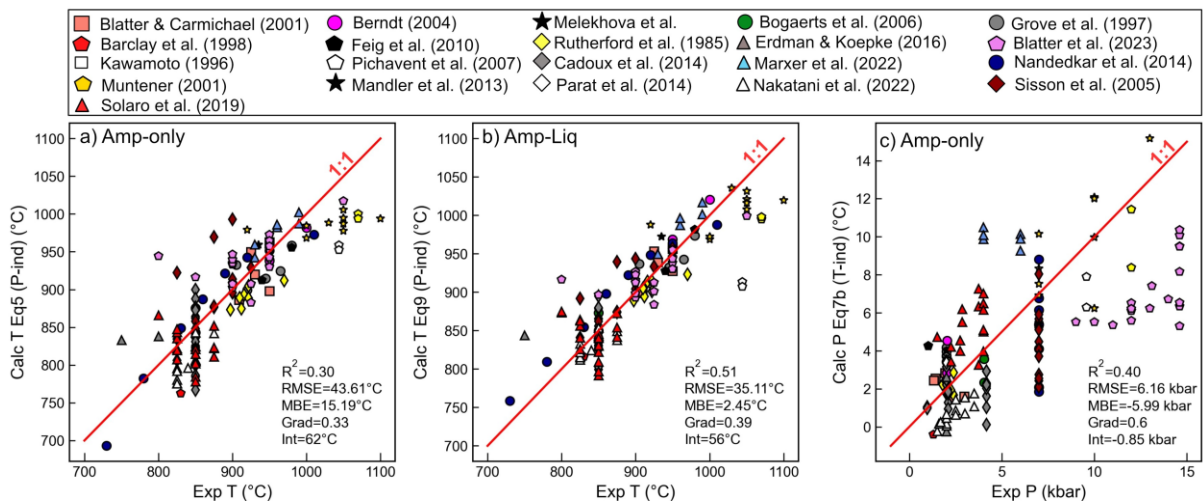
1196



1197

1198 *Figure 12. Comparison of molar volumes and volumes of fusion for Amp vs. Cpx components. a) Changes in*  
 1199 *volume following precipitation of different mineral components from the liquid ( $\Delta V$  fusion). Amphibole*  
 1200 *components show significantly smaller changes than jadeite, and the different Amp components show very*  
 1201 *similar  $\Delta V$  fusion. b) Molar volume normalized to the component of each phase with the highest molar volume*  
 1202 *(ferroactinolite for Amp, diopside for Cpx). c) Correlation between normalized molar volume and  $\Delta V$  fusion.*  
 1203 *Thermodynamic data from table 1 of Putirka (2016).*

1204 We use ArcPL data not used for calibration of the Putirka (2016) equations to test their performance and  
 1205 sensitivity to other terms present in the regression (see Supporting Figs. 6–8). The best performing Amp-only  
 1206 thermometer for this dataset is Eq5 ( $R^2=0.7$ ,  $RMSE=41.5^\circ C$ , Fig. 13a, Supporting Fig. 6), which has the advantage  
 1207 of being independent of P and  $H_2O$  in the liquid. The best Amp-Liq thermometer is Eq9 ( $R^2=0.76$ ,  $RMSE=34^\circ C$ ,  
 1208 Fig. 13b, Supporting Fig. 8), which is P independent and not very sensitive to  $H_2O$  in the liquid (Supporting Fig. 7,  
 1209  $\sim 1^\circ C$  change in T per 1 wt%  $H_2O$ ). Like Putirka (2016), we find that all three Amp-Liq barometers show  
 1210 disappointing statistics ( $RMSE=3-4$  kbar,  $Grad=0.3-0.5$ , Supporting Fig. 8, e.g., Fig. 13c). In particular, the  
 1211 pressures for the higher P experiments of Blatter et al. (2023), and Muntener et al. (2001) are greatly  
 1212 underestimated, although the barometer does a reasonable job of the lower P data, which clusters around the  
 1213 1:1 line at  $\sim 2-5$  kbar. The skew at high P means that even after the averaging suggested by Putirka (2016), Amp-  
 1214 Liq barometry can give misleading results.



1215

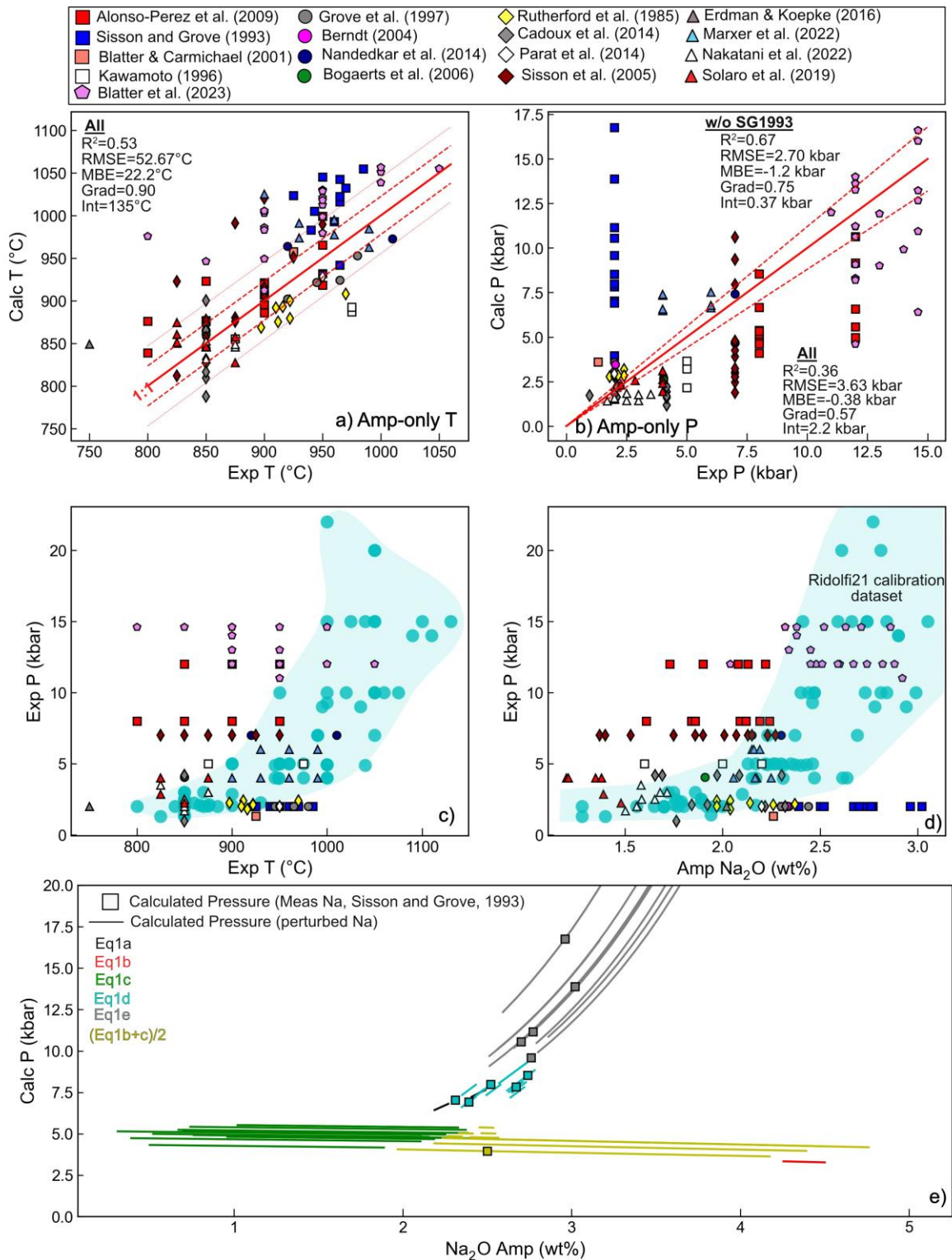
1216 *Figure 13 – Assessing Amp-Liq and Amp-only thermobarometers from Putirka (2016) using experiments not used*  
 1217 *during model calibration. Only experiments passing the  $K_D$  filter of Putirka (2016) are shown.*

1218 Ridolfi (2021) updated the Ridolfi and Renzulli (2012) amphibole-only barometer, perhaps partially in  
 1219 response to the criticism of Erdmann et al. (2014), Molina et al. (2021) and Putirka (2016), and partially because  
 1220 of an increase in the number of amphibole-bearing experiments. Using an expanded experimental dataset, they  
 1221 tweak the algorithms used to select between different P equations and add more stringent filters to give users  
 1222 warning of when the equations are being applied to amphiboles failing quality tests or outside the model  
 1223 calibration range (based on totals, unbalanced charge, low B cations, etc, low and high Ca cations, low Mg  
 1224 cations). We tested this new algorithm and quality filter on experiments from ArcPL not used during calibration



1225 (Alonso-Perez et al., 2009; Berndt, 2004; Blatter and Carmichael, 2001; Bogaerts et al., 2006; Cadoux et al., 2014;  
1226 Erdmann and Koepke, 2016; Grove et al., 1997; Kawamoto, 1996; Marxer et al., 2022; Nakatani et al., 2022;  
1227 Parat et al., 2014; Rutherford et al., 1985; Sisson et al., 2005; Sisson and Grove, 1993; Solaro et al., 2019, Blatter  
1228 et al. 2023). Of our compiled experiments (N=193), 112 pass the quality check filters of Ridolfi (2021, Fig. 14a).  
1229 For those passing the quality filters, calculated P show a moderate correspondence to experimental P, although  
1230 calculations clearly lie well outside the stated  $\pm 12\%$  error in the abstract of Ridolfi (2021, red dashed lines, Fig.  
1231 14b). The overall fit to these experiments yields  $R^2=0.36$  and  $RMSE=3.6$  kbar. The experiments conducted at 2  
1232 kbar by Sisson and Grove (1993) show particularly poor results, returning pressures which are up to 15 kbar too  
1233 high. Excluding these experiments yields  $R^2=0.67$  and  $RMSE=2.7$  kbar. Compared to the Putirka (2016) Amp-Liq  
1234 barometers, this Amp-only barometer does a much better job of recreating the high pressures of Blatter et al.  
1235 (2023), although it does still underestimate to a degree. Despite the criticism of this method in the literature, it  
1236 is noteworthy that Amp-only barometry doesn't perform any worse than Opx-Liq and Opx-Cpx based on our  
1237 dataset, but it should be noted that none of these methods are precise enough to be useful for many  
1238 volcanological questions. As amphibole-only T from Ridolfi and Renzulli (2012) require a P to be entered, we also  
1239 test how effective this thermometer is using pressures obtained from the 2021 barometer. The correlation  
1240 between calculated and experimental T is reasonably good (Fig. 14a,  $R^2=0.53$ ,  $RMSE=53^\circ\text{C}$ ), although the RMSE  
1241 is twice that stated in the abstract of Ridolfi (2021,  $22^\circ\text{C}$ , shown with dashed red lines, Fig. 14a).

1242 We examined the Sisson and Grove (1993) experiments in the context of the calibration dataset of  
1243 Ridolfi (2021) to try to understand the poor performance of the barometer. These experiments plot to  
1244 substantially higher amphibole  $\text{Na}_2\text{O}$  contents at lower pressures than any of the calibration experiments (Fig.  
1245 14d). To investigate whether this offset to higher  $\text{Na}_2\text{O}$  contents could explain the anomalously high calculated  
1246 P, for each Sisson and Grove (1993) amphibole, we perturb the  $\text{Na}_2\text{O}$  content by  $\pm 2$  wt%. Pressures for measured  
1247 amphibole compositions are shown as squares (Fig. 14e), with a line stretching from each square showing the  
1248 change in pressure as  $\text{Na}_2\text{O}$  is changed. The colors indicate the root equation from Ridolfi (2021) algorithm used  
1249 to determine P, with the rapid jumps in pressure reflect a flip to a different equation selected by the algorithm.  
1250 For the samples with high calculated P ( $>7.5$  kbar), it is very clear that Eq1e (and to a lesser extent 1d and 1a) is  
1251 highly sensitive to the  $\text{Na}_2\text{O}$  content, rapidly shooting up to extremely high pressures for very small changes in  
1252  $\text{Na}_2\text{O}$ . It may well be that these natural samples lie outside the  $\text{Na}_2\text{O}$  range used to calibrate Eq1e (the calibration  
1253 data for each specific equation is not available). The Alonso-Perez et al. (2009) experiments (red squares) where  
1254 pressure is underestimated are also clearly offset from the calibration dataset in T –  $\text{Na}_2\text{O}$  space (Fig. 14c). This  
1255 comparison emphasises the importance of ensuring that sample compositions are well represented in the  
1256 calibration dataset of the chosen model, not just in terms of P-T space, but also compositional space. It also  
1257 shows that having the correct functional form for a barometer routed in thermodynamics is essential to minimize  
1258 extrapolation issues commonly seen with empirical fits.



1259

1260 *Figure 14: Assessing Amp-only thermometers and barometers. a) Comparing experimental and calculated T using*  
 1261 *the thermometer of Ridolfi and Renzulli (2012) iterated with Ridolfi (2021). b) Comparing experimental and*  
 1262 *calculated P using the new barometer of Ridolfi (2021, T-independent). c-d) Visualizing experimental*  
 1263 *compositions relative to the calibration dataset (cyan dots and field) of Ridolfi (2021). Many of the experiments*  
 1264 *showing the largest discrepancies in calculated pressure (e.g., red and blue squares, magenta diamonds) lie*  
 1265 *outside the calibration range of Ridolfi (2021) in Pressure-Na<sub>2</sub>O space. e) To visualize the effect of Na<sub>2</sub>O on*  
 1266 *calculated pressure, we perturb the Na<sub>2</sub>O content of the experiments of Sisson and Grove (1993) by  $\pm 2$  wt%. The*  
 1267 *lines are not continuous, with jumps to a different pressure as the algorithm flips between different 'root'*

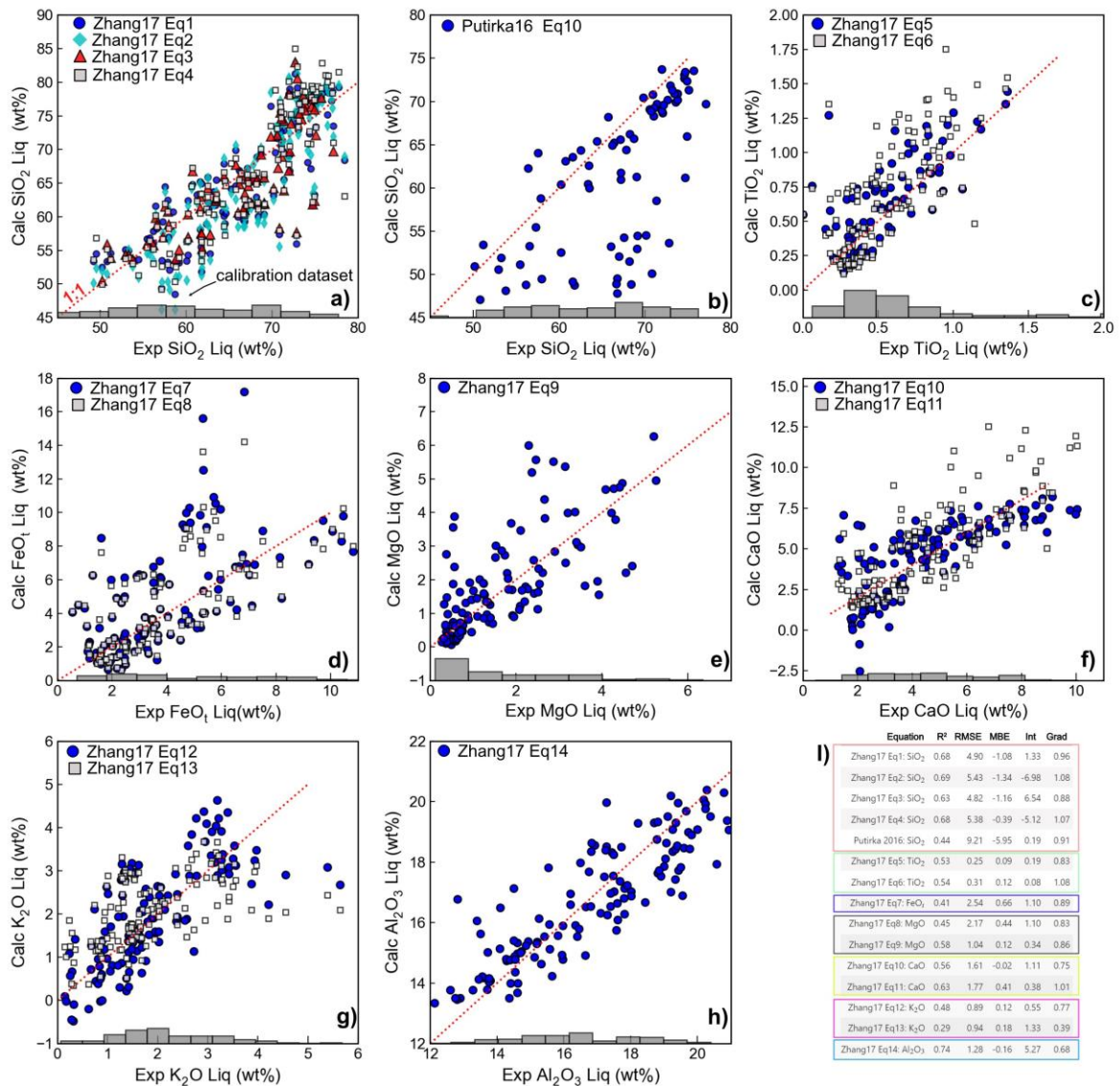
1268 equations (indicated by the color of the line). Experimental Na<sub>2</sub>O (and calculated pressures) are indicated with  
1269 squares, with the calculations following the perturbation shown as lines.

1270

## 1271 2.6.2 Amphibole Chemometry

1272 Ridolfi and Renzulli (2012) also present equations to calculate the contents of SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO<sub>t</sub>,  
1273 MgO, CaO, and K<sub>2</sub>O in the melt from which amphiboles crystallized. These equations are parameterized in terms  
1274 of amphibole composition and pressure. However, given the uncertainties discussed above calculating pressures  
1275 from amphibole compositions, these P-sensitive parameterizations can be problematic to implement in natural  
1276 systems. Erdmann et al. (2014) show that the predicted SiO<sub>2</sub> content is a reasonable match above 65 wt% SiO<sub>2</sub>,  
1277 but tends to overpredict SiO<sub>2</sub> for more mafic melts. Putirka (2016) use their newly compiled dataset to produce  
1278 an updated expression (Eq10) for melt SiO<sub>2</sub> from the amphibole using the temperature of the melt and the cation  
1279 fraction of Al in the amphibole.

1280 Zhang et al. (2017) compile a reasonably similar calibration dataset to Putirka (2016), and produce  
1281 multiple regressions to calculate melt oxide components from a variety of amphibole site positions (e.g., Si-Ti-  
1282 Mg-Fe-Ca in amphibole for predicting SiO<sub>2</sub> in the melt). These expressions are P-independent, and only Eq3 (for  
1283 SiO<sub>2</sub>) and Eq5 (for TiO<sub>2</sub>) are T-sensitive. Zhang et al. (2017) calibrate multiple equations for some melt oxide  
1284 contents (e.g., 4 equations for SiO<sub>2</sub>, 2 equations for FeO<sub>t</sub>). We test the 133 ArcLEPR amphiboles which pass the  
1285 Zhang et al. (2017) equilibrium filter ( $K_D, Fe-Mg=0.28\pm0.11$ ) and do not appear in their calibration dataset. The  
1286 calculated statistics are similar if a  $K_D$  filter isn't used. Overall, unlike many of the barometers discussed in this  
1287 review, these chemometers perform well for experiments they were not calibrated on (Fig. 15). Eq2 of Zhang et  
1288 al. (2017) does a good job of predicting melt SiO<sub>2</sub> content across a wide range, showing much better performance  
1289 than Eq10 of Putirka, 2016 (Fig. 15a vs. b). The statistics of the fit are similarly good for melt Al<sub>2</sub>O<sub>3</sub> (Eq14). There  
1290 is more scatter for other oxides, and reasonably large differences between the different provided equations, but  
1291 it is not always clear which equation is better (e.g., Fig. 15c). It is notable that the worst performance is seen for  
1292 experiments with oxide contents towards the tail end of the calibration dataset (grey histograms, Fig. 15). For  
1293 example, Eq12 and Eq13 do a good job of predicting K<sub>2</sub>O until ~3.5 wt% K<sub>2</sub>O; very few experiments in the  
1294 calibration dataset had such high K<sub>2</sub>O contents (Fig. 15g). Similarly, the fit is better at lower MgO contents, where  
1295 the calibration dataset is concentrated (Fig. 15e). In general, our tests demonstrate that amphibole compositions  
1296 can be used to estimate the melt compositions from which they grew, as long as the results are carefully  
1297 evaluated relative to the calibration range of the model.



1298

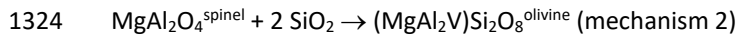
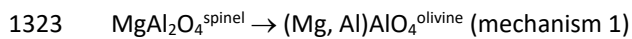
1299 *Figure 15 – Assessment of amphibole chemometers of Zhang et al. (2017, panel a, c-h) and Putirka (2016, panel*  
 1300 *b). For equation 3 and 5 of Zhang et al. (2017) and Putirka (2016) eq10, we use temperatures calculated from co-*  
 1301 *solving T from Ridolfi and Renzulli (2012) and P from Ridolfi (2021). Putirka (2016) eq10 also requires P from*  
 1302 *Ridolfi (2021) to be input. These equations have fewer datapoints on the plot, as we exclude P and Ts where*  
 1303 *Ridolfi (2021) returns an input warning. i) shows the statistics for each equation. The filtered test dataset*  
 1304 *comprises 133 experimental charges not used by Zhang et al. (2017) during calibration, and 10 experimental*  
 1305 *charges from Barclay (2004), Blatter and Carmichael (2001), and Grove et al. (1997), which were used by Zhang*  
 1306 *et al. (2017) in their test, but not calibration dataset.*

1307 We do not test predictions of H<sub>2</sub>O and fO<sub>2</sub> using amphibole-only chemometers, as there are limited  
 1308 reliable experimental data with well constrained values for these parameters that were not used during model  
 1309 calibration.

## 1310 2.7. Olivine-Spinel Aluminium-exchange thermometry

1311 The aluminium content of olivine has been used as a thermometer in the mantle (De Hoog et al., 2010),  
 1312 and Al partitioning between olivine and spinel has been used in igneous rocks (Wan et al., 2008; Coogan et al.,  
 1313 2014). Here we focus on the olivine-spinel Al-exchange thermometer, which offers an advantage over Mg-Fe  
 1314 olivine-liquid thermometry because Al in spinel and olivine and Cr in spinel are more resistant to diffusional  
 1315 modification during crystal storage and transport than Fe-Mg in olivine (Spandler & O'Neill, 2009). Additionally,  
 1316 while olivine crystals are frequently out of equilibrium with erupted liquids (Sides et al., 2014b; Wieser et al.,  
 1317 2019), the fact spinels are trapped inside olivine crystals makes it more straightforward to identify mineral-  
 1318 mineral pairs which grew together.

1319 The mechanism by which aluminium substitutes into olivine remains somewhat uncertain, despite the  
1320 fact that constraining this reaction is vital to identify which chemical parameters should appear in a  
1321 thermodynamically-constrained thermometry model. Of the possible substitutions, two mechanisms have been  
1322 the focus of the most attention:



1325 In the first mechanism there is a coupled substitution of Al into both the octahedral and tetrahedral  
1326 sites in olivine, while the second has substitution only onto the octahedral site, with charge balance maintained  
1327 by vacancies (V). It is also possible coupled substitutions could take place with Cr and Na in the octahedral site  
1328 (and Al in the tetrahedral site), or Al in the octahedral site with  $\text{Fe}^{+3}$  in the tetrahedral site (Taura et al., 1998).  
1329 Critically, if the mechanism 1 is dominant, the thermometer should depend only on the Al contents of the co-  
1330 existing olivine and spinel (in addition to any chemical parameters controlling the activity coefficient for Al in  
1331 either phase), but if mechanism 2 dominates, the thermometer will depend also on the activity of  $\text{SiO}_2$  ( $a_{\text{SiO}_2}$ ).

1332 A thermometer based on Al-exchange was first calibrated by Wan et al. (2008) using a series of  
1333 experiments at 1 bar with the bulk composition varied such that olivine and spinel co-crystallised at a range of  
1334 temperatures and Cr contents. They found that the experimental data could be adequately modelled with a  
1335 formula depending on the ratio of Al in olivine to Al in spinel, as well as the spinel Cr# ( $\text{Cr}/[\text{Cr} + \text{Al}]$ , molar). The  
1336 dependency on Cr# comes from its effect on the activity coefficient of Al in spinel. Wan et al. (2008) justified the  
1337 extrapolation of the thermometer to higher P and T than the calibration dataset by comparing temperatures  
1338 derived from the Al-exchange thermometer with temperatures calculated from the two-pyroxene thermometer  
1339 for a suite of olivine and spinel bearing mantle xenoliths. Although there was considerable scatter around the  
1340 1:1 line ( $1\sigma = 64^\circ\text{C}$ ) they found no systematic offset between the two thermometers. The behaviour of the  
1341 thermometer at 1 bar was tested with an additional set of experiments, for which experimental temperatures  
1342 were reproduced with  $1\sigma=22^\circ\text{C}$ .

1343 The thermometer was further tested and recalibrated with new experimental data by Coogan et al.  
1344 (2014), extending the calibration range to higher  $f\text{O}_2$  values ( $\Delta\text{QFM}=-0.5$  to  $\Delta\text{QFM} = +1.3$ ). They also tested the  
1345 thermometer's dependence on  $a_{\text{SiO}_2}$ . They found  $f\text{O}_2$  had no systematic effect on the performance of the  
1346 thermometer and the effect of  $a_{\text{SiO}_2}$  was within the uncertainty of the thermometer, indicating that Al  
1347 incorporation into olivine by vacancy formation (mechanism 2) is unlikely to be important in most systems. This  
1348 was corroborated by an experimental diffusion study by Zhukova et al. (2017) which found that Al incorporation  
1349 by vacancy formation was favoured only at higher  $a_{\text{SiO}_2}$  values than is found in most igneous systems where the  
1350 thermometer is applied. Further improvements have been made to both the calibration and the mathematical  
1351 formulation of the thermometer by Zhang and Namur (2022).

1352 Despite the increased calibration range of the Coogan et al. (2014) model, many natural samples  
1353 possess olivine and spinel pairs with compositions which still lie outside the calibration range. This includes the  
1354 study reporting the highest equilibration temperatures from this method ( $\sim 1570^\circ\text{C}$ , Trela et al., 2017), which  
1355 have spinels with  $\text{Cr}_2\text{O}_3$  contents higher than any of the spinel crystals used to calibrate the thermometer. Trela  
1356 et al. justified such an extrapolation based on the global correlation between the  $\text{Al}_2\text{O}_3$   $K_D$  and spinel Cr#, and  
1357 the fact that these melts also recorded extreme mantle potential temperatures and olivine liquidus  $T_s$ . However,  
1358 it has also been suggested in other locations that application of this method to spinel crystals with much higher  
1359  $\text{TiO}_2$  contents than the calibration dataset may be invalid, because these higher  $\text{TiO}_2$  may affect the activity  
1360 coefficient of Al in spinel (e.g., Jennings et al., 2019; Wong et al., 2022). Jennings et al. (2019) suggest that in the  
1361 absence of a wider calibration range, it is best to apply the thermometer only to spinel crystals that are close to  
1362 the calibration range.

1363 To robustly assess how effectively the olivine-spinel method can be extrapolated, we need a suite of  
1364 experiments with compositions lying outside the current calibration range. However, because application of the  
1365 thermometer relies on precise measurements of the low concentrations of  $\text{Al}_2\text{O}_3$  in olivine, generally only  
1366 experiments performed for the purpose of calibrating this thermometer can be used, and all such experiments  
1367 have been used during model regression (by Wan et al. 2009, or Coogan et al. 2014). Experiments conducted for  
1368 other purposes cannot be used to formulate a test dataset, because  $\text{Al}_2\text{O}_3$  concentrations in olivine were  
1369 generally not measured at all, or were measured with low precision.

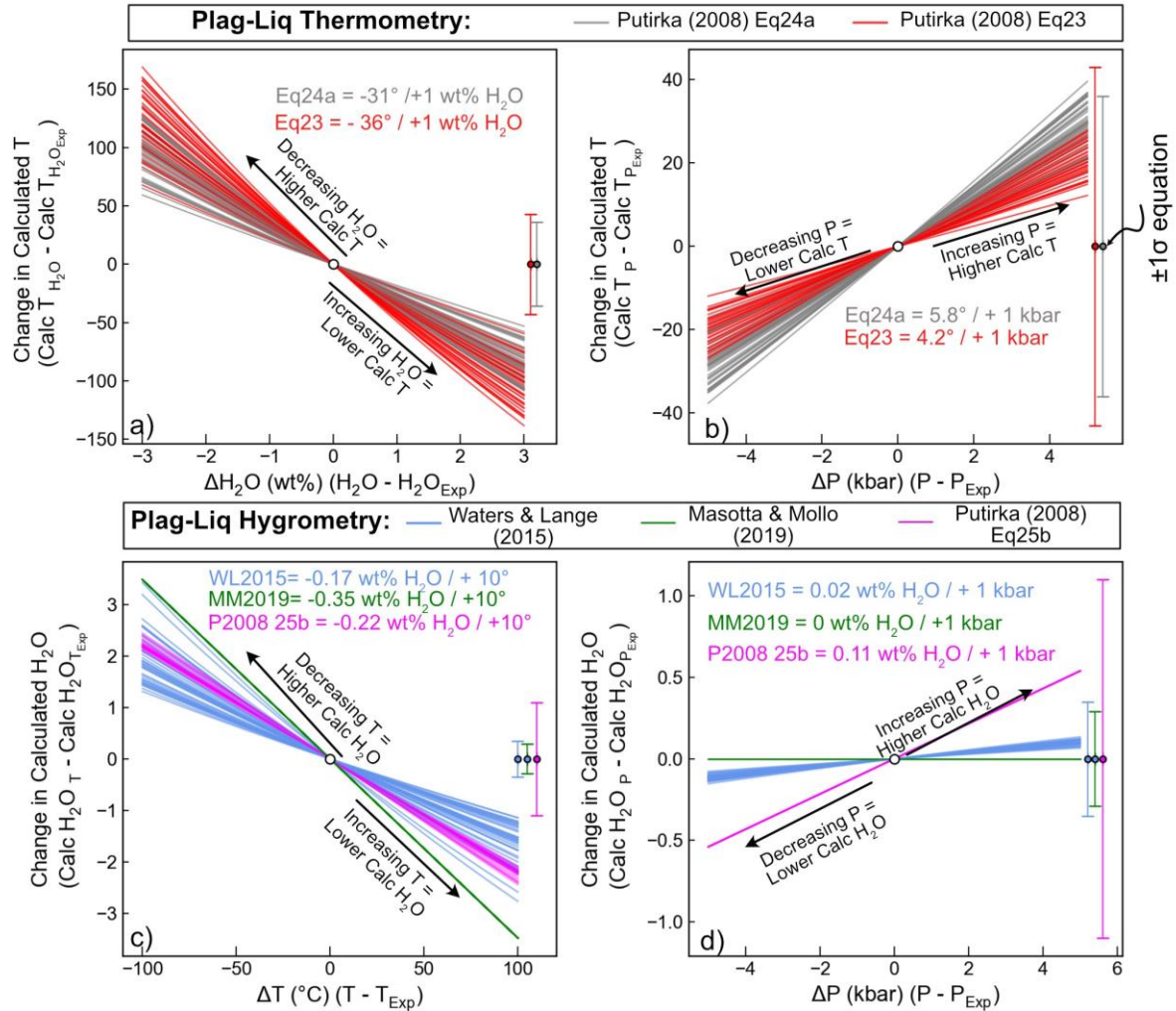
1370 The lack of an independent test dataset also makes it difficult to robustly constrain the uncertainty of  
1371 this method even when applied within the calibration range. Most studies cite the quoted standard error on the  
1372 fit for the calibration data as being a minimum estimate of the uncertainty (Matthews et al., 2021, 2016; Wong  
1373 et al., 2022), but as discussed above, statistics calculated on calibration datasets tend not to reflect the true  
1374 error when applied to data not used for calibration. A final problem with this method is that there is no  
1375 independent equilibrium test to assess whether the spinel and olivine are in equilibrium. The ubiquity of Mg-Fe  
1376 diffusive resetting means these elements are an unreliable test of equilibrium (c.f. Prissel et al., 2016). The slow  
1377 diffusion of Al in olivine (Spandler & O'Neill, 2009) means that parts of a host olivine crystal could be out of  
1378 equilibrium with their spinel inclusions if olivine crystallisation occurred over a protracted time with changing  
1379 temperature (or melt composition). Maps of the aluminium content of olivine crystals have revealed near-  
1380 ubiquitous zoning in crystals from Iceland (Matthews et al., 2021), adding complexity to identifying equilibrium  
1381 pairs. Matthews et al. (2021) and Trela et al. (2017) therefore recommended the aluminium content of olivine  
1382 crystals should be mapped with a high current electron beam before identifying locations for quantitative  
1383 analysis.

## 1384 **2.8. Plagioclase-Liquid thermometry and hygrometry**

1385 Plagioclase (Plag) is a very common mineral in a wide variety of tectonic settings (e.g., MORBs, OIBs,  
1386 Arcs), motivating the development of a number of thermometers, barometers and hygrometers parameterizing  
1387 and liquid equilibrium (Putirka, 2008, 2005; Sugawara, 2001; Waters and Lange, 2015). However, the exchange  
1388 of the anorthite (An)-albite (Ab) component between liquid and Plag is sensitive to T, P, and H<sub>2</sub>O. If none of these  
1389 variables are constrained by independent methods, there is a substantial solution space to explore. There also  
1390 isn't much consensus as to what equilibrium tests should be used to filter Plag-Liq pairs. Putirka (2008) note that  
1391 Ab-An exchange values for experiments ( $K_D^{An-Ab}$ ) are normally distributed, with experiments with T<1050°C  
1392 having values of 0.1±0.05, and experiments with T>1050°C having values of 0.27±0.1. However, plotting our  
1393 experimental data (along with the calibration dataset of Waters and Lange, 2015) shows a more continuous  
1394 variation of  $K_D$  with temperature (Supporting Fig. 9) although there is a relatively abrupt step up to higher values  
1395 between 1000–1100°C. We tentatively suggest this step up may result from the C1–I1 structural phase transition  
1396 which occurs near this temperature, and has been shown to affect plagioclase Mg partitioning behaviour (Mutch  
1397 et al., 2022). Using the criteria of Putirka (2008) would exclude a number of experiments close to the cut off  
1398 (Supporting Fig. 9)– We instead apply an exponential fit through the experimental data, excluding experiments  
1399 outside ±0.11 (Supporting Fig. 9a-b). Not applying this filter affects calculated statistics very little for the  
1400 following discussion.

1401 First, we assess sensitivity of thermometers to H<sub>2</sub>O (Fig. 16a), thermometers to P (Fig. 16b),  
1402 hygrometers to T (Fig. 16c), and hygrometers to P (Fig. 16d), by independently perturbing experimental P, T and  
1403 H<sub>2</sub>O. It is apparent from Fig. 16a that Plag-Liq temperatures are strongly sensitive to H<sub>2</sub>O; an increase of just 1  
1404 wt% H<sub>2</sub>O causes an average drop in T of ~31°C for eq24a and 36°C for eq23. This change in calculated T is  
1405 comparable to the RMSE of these thermometers. Thermometers are less sensitive to P; with the calculated  
1406 change in T only reaching the same magnitude as the RMSE for a change of ~10 kbar (Fig. 16b). Notably, the  
1407 Plag-Liq hygrometers of Masotta and Mollo (2019), Putirka (2008) and Waters and Lange (2015) are extremely  
1408 sensitive to T; calculated H<sub>2</sub>O contents drop more than the RMSE of the hygrometer for a change in T of just 10–  
1409 20°C (Fig. 16c). These hygrometers are less sensitive to P, with P changes of 10 kbar causing variations well within  
1410 the quoted RMSE (Fig. 16d).

1411



1412

1413 *Figure 16: Testing the sensitivity of Plag-Liq thermometers to H<sub>2</sub>O (a) and pressure (b), and Plag-Liq hygrometers*  
 1414 *to T (c) and P (d). 40 experiments from our new compilation were randomly selected (each represented by a*  
 1415 *colored line). We perform calculations at the experimental P, T and H<sub>2</sub>O content (0,0) on all plots, and then vary*  
 1416 *H<sub>2</sub>O by  $\pm 3 \text{ wt\%}$  (a), P by  $\pm 5 \text{ kbar}$  (b, d), and T by  $\pm 100^\circ \text{C}$  (c). We subtract the quantity calculated at experimental*  
 1417 *conditions from the quantity at these new conditions. Error bars show the quoted RMSE on each expression. We*  
 1418 *label the average perturbation for these 40 samples on the figure.*

1419

1420 Before assessing hygrometers using our new dataset, it is worth considering how well we really know the “true”  
 1421 value of H<sub>2</sub>O in each experiment. In the compiled Plag-Liq dataset, only 33% of experiments measure H<sub>2</sub>O by  
 1422 FTIR, 5% by SIMS and 4.8% by Raman spectroscopy. A further 16% report H<sub>2</sub>O using the EPMA-based water-by-  
 1423 difference method, with some mention of a calibration method. 17% have calculated H<sub>2</sub>O using a solubility  
 1424 model for a pure H<sub>2</sub>O fluid or using a measured X<sub>H<sub>2</sub>O</sub> value in the fluid (Andújar et al., 2015; Costa, 2004; Mandler  
 1425 et al., 2014), or provide enough information for us to perform these calculations using MagmaSat in VESical  
 1426 (Ghiorso and Gualda, 2015; Iacovino et al. 2019). Interestingly, Waters and Lange (2015) calibrate their  
 1427 hygrometer by calculating H<sub>2</sub>O in each experiment in their calibration dataset using the solubility model of Zhang  
 1428 et al. (2007), rather than using measured H<sub>2</sub>O contents. If they had they used MagmaSat instead, calculated H<sub>2</sub>O  
 1429 contents for these experiments would differ by an average of 0.3 wt% (the max discrepancy is 0.78 wt%), which  
 1430 would likely result in slightly different model parameters. Additionally, if the starting materials contained even  
 1431 small amounts of CO<sub>2</sub> (e.g., from contamination, Blatter et al., 2013), the amount of H<sub>2</sub>O in the melt would not  
 1432 equal that calculated using a pure H<sub>2</sub>O solubility model.

1433

1434 Ideally, we would restrict our comparison to experiments which performed FTIR, SIMS or Raman

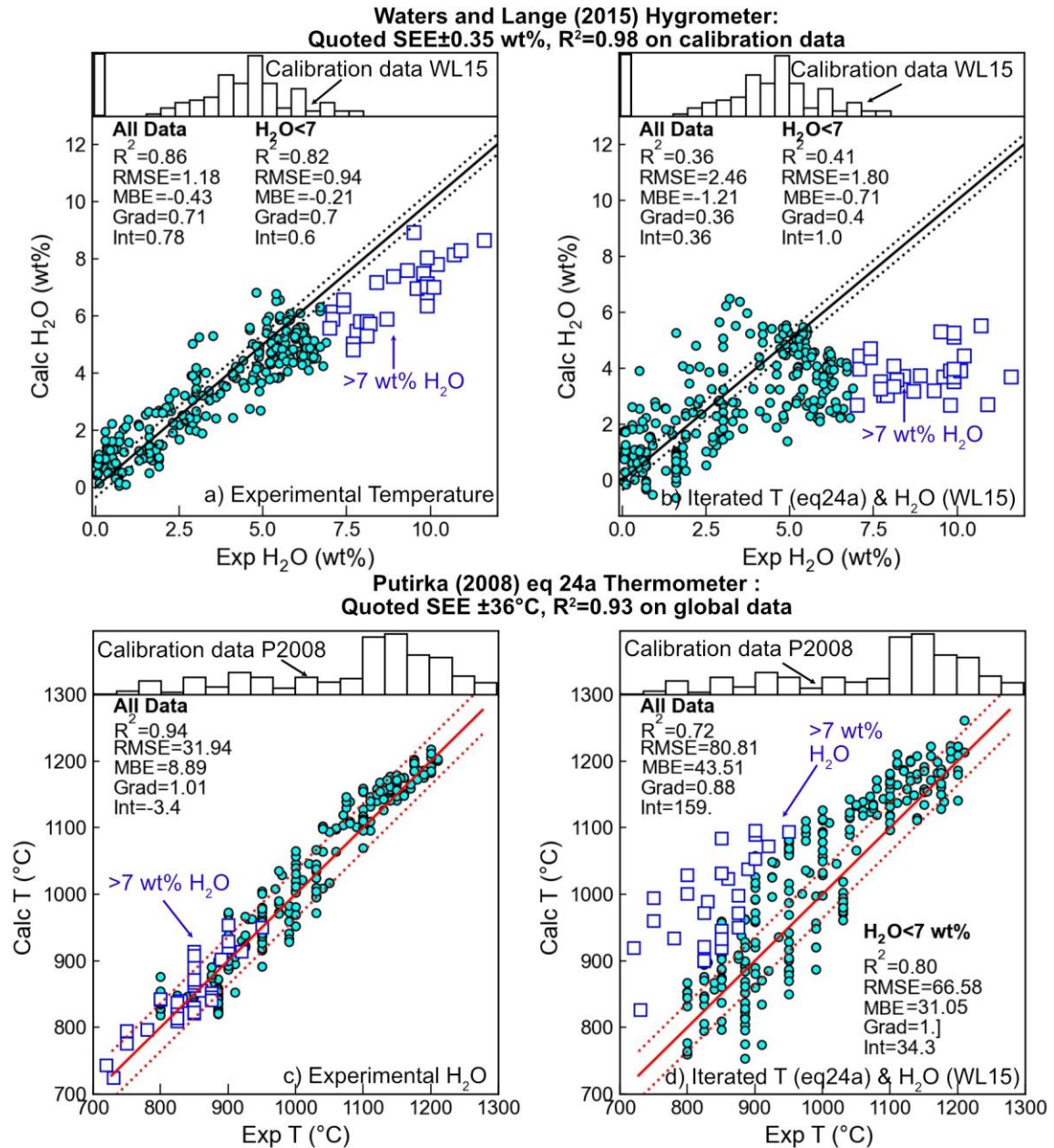
measurements of H<sub>2</sub>O. However, this results in a much smaller dataset, with N=163 vs. N=358 if calibrated VBD

1435 and solubility water contents are included. This smaller dataset also has a very restricted T range (Supporting  
1436 Fig. 10). It also seems unjustified to exclude experiments using solubility models, given that is how the H<sub>2</sub>O  
1437 contents were determined to calibrate the Waters and Lange (2015) model. Thus, we choose to proceed with  
1438 the larger experimental dataset.

1439 Using experimental T and P, the Waters and Lange hygrometer performs reasonably well on the ArcPL  
1440 dataset, with a RMSE of  $\pm 1.21$  wt% (Fig. 16a). There is a marked deviation to anomalously low calculated H<sub>2</sub>O  
1441 contents for experiments with H<sub>2</sub>O > 7 wt% (cyan squares); if these are excluded, the RMSE is 0.94 wt%, although  
1442 this is still far higher than the quoted RMSE of 0.35 wt%. The poor performance at high H<sub>2</sub>O may reflect the fact  
1443 that these super-hydrous compositions are poorly represented in the calibration dataset of this hygrometer  
1444 (white histogram, Fig. 16a-b). When using experimental H<sub>2</sub>O contents and pressures, the statistics reported for  
1445 the thermometer of P2008 Eq24a on a global dataset are very similar to those estimated from our new dataset  
1446 (we calculate RMSE=33°C vs. the stated RMSE=36°C shown as red dotted lines, Fig. 16c).

1447 As discussed in section 1.2, the extreme sensitivity of Plag-Liq thermometers to H<sub>2</sub>O content, and  
1448 hygrometers to T, means that the comparisons shown in Fig. 16a and c do not accurately represent the true  
1449 error when these equations are applied to natural systems, where in the vast majority of instances, neither H<sub>2</sub>O  
1450 nor T is known. To address this issue with many under constrained intensive variables, we investigate whether  
1451 H<sub>2</sub>O and T can be solved iteratively using a plagioclase hygrometer and thermometer, as an adaptation of the  
1452 popular workflow of iterating barometers and thermometers. Arguably, as we perform these calculations using  
1453 experimental P, we are still overestimating their performance on natural systems where H<sub>2</sub>O, T and P are all  
1454 unknown. The absence of a reliable plagioclase-liquid barometer (see Section 2.9) means that three-way  
1455 iteration will not work. However, given these equations are far less sensitive to pressure (Fig. 16), uncertainty in  
1456 pressure shouldn't hinder the model performance substantially.





1457

1458 *Figure 16. Evaluating Plag-Liquid hygrometers (a-b) and thermometers (c-d). Only experiments with H<sub>2</sub>O*  
 1459 *measured by quantitative methods are shown. a) Calculations of H<sub>2</sub>O using Waters and Lange (2015) with*  
 1460 *calculations performed using experimental T. The hygrometers performance drops substantially for H<sub>2</sub>O>7; the*  
 1461 *white histogram on top indicates that relatively few experiments used to calibrate this model had such high H<sub>2</sub>O*  
 1462 *contents. b) Iterative calculations using Waters and Lange (2015) and Putirka (2008) eq24a. c) Calculations using*  
 1463 *Putirka (2008) eq24a and experimental H<sub>2</sub>O contents, and d) Iterative calculations using Putirka (2008) eq24a*  
 1464 *and Waters and Lange (2015). 1:1 line shown with ±stated RMSE for each expression*

1465 Unsurprisingly, iteration of Plag-Liq hygrometers and thermometers yields worse statistics than  
 1466 hygrometry calculations performed using experimental T. For example, excluding experiments with H<sub>2</sub>O>7 wt%,  
 1467 the iterated RMSE is 1.77 wt% (vs. 0.94 wt% using experimental T; Fig 16a vs. b). Calculated T using the iterative  
 1468 method are also substantially worse than those obtained using known H<sub>2</sub>O contents (RMSE=66 vs. 33°C for all  
 1469 data, RMSE=58°C for H<sub>2</sub>O<7 wt%, Fig. 17c-d). The statistics for these iterative calculations are more indicative of  
 1470 the sort of precision these methods can achieve in natural system. We also suggest that such an iterative  
 1471 approach may be more accurate than calculating H<sub>2</sub>O using temperatures derived from other phases which may  
 1472 not have formed at the same temperature as Plag (e.g., Fe-Ti thermometry, Black and Andrews, 2020; Crabtree  
 1473 and Lange, 2011; Pineda et al., 2021).

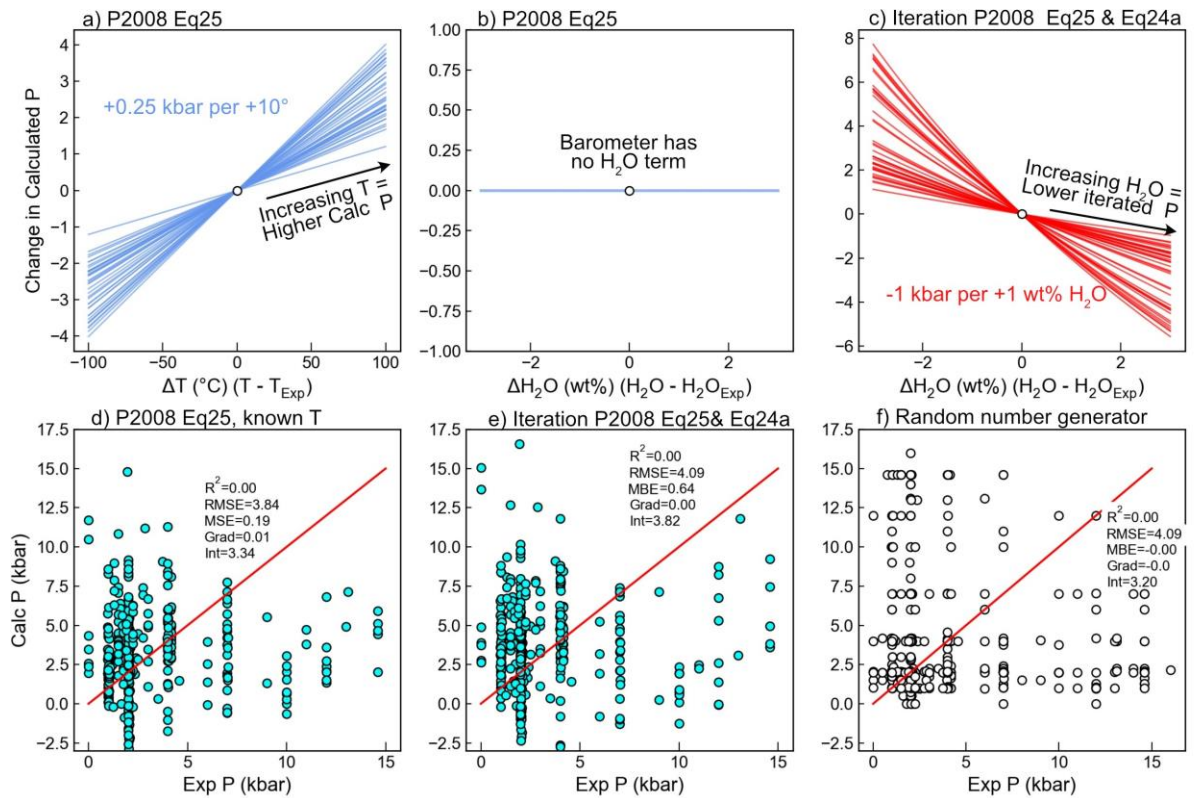
1474 The iterated thermometer has reasonable performance compared to other mineral-melt  
1475 thermometers discussed, and the hygrometer has sufficient precision to distinguish dry (0–2 wt%), moderately  
1476 wet (2–4 wt%) and wet (>4 wt%) lavas. However, when applied outside of the experimental products used for  
1477 calibration, Plag-Liq hygrometry cannot achieve anything like the <<0.5 wt% error often quoted for this method.  
1478 Future improvements would be possible with a larger dataset of experiments where H<sub>2</sub>O contents are known,  
1479 as combining different methods for estimating H<sub>2</sub>O contents in experiments undoubtedly adds uncertainty,  
1480 particularly when using volatile contents calculated using volatile solubility models (see Wieser et al., 2022a).  
1481 Additionally, given the relative success of iterating two different expressions with different underlying datasets,  
1482 we suggest that recalibrating Plag-Liq hygrometers without a T term, but with compositional terms like those in  
1483 Plag-Liq thermometers to incorporate the effect of temperature, may be more successful than having to iterate  
1484 two independently calibrated expressions.

## 1485 **2.9. Plagioclase-Liquid barometry**

1486 Putirka (2005) proposed a Plag-Liq barometer calibrated on 187 Plag-Liq pairs, which yields a RMSE of  
1487 1.8 kbar for the calibration dataset and RMSE of 2.2 kbar on N=292 test data. However, Putirka (2008) re-  
1488 evaluated this barometer using new experimental data, and found that it performed very badly, with a RMSE of  
1489 3.8 kbar excluding 1 atm data, and even worse statistics when this 1atm data was included. They tried to find a  
1490 global model to adequately predict pressures in their new dataset and found that while some regression worked  
1491 on some subsets of the database, no regression could fit all data. They suggested that new experiments with the  
1492 specific purpose of developing a Plag-Liq barometer are required to move forward. Despite their warning that  
1493 *“the status of plagioclase-liquid as a barometer is firmly in doubt”*, a concerning number of studies have  
1494 performed Plag-Liq barometry after 2008 (e.g., Budd et al., 2016; Cheng et al., 2014; Dahren et al., 2012; Geiger  
1495 et al., 2018, 2016a, 2016b; Guo et al., 2018; Jamshidi et al., 2015; Siegburg et al., 2018). The majority of these  
1496 studies quote a 2.47 kbar RMSE to justify this approach. However, this value from Putirka (2008) was only the  
1497 fit to under half the data; the full dataset gave RMSE= 3.6–3.8 kbar.

1498 As Plag-Liq barometers are still being widely used in the community, we briefly assess their sensitivity  
1499 to T and H<sub>2</sub>O, and then evaluate their performance on our new dataset. The T term in P2008 Eq25b means that  
1500 the barometer is reasonably sensitive to T, with an average increase in +0.25 kbar per +10°C increase in T (Fig.  
1501 18a). The barometer alone isn't sensitive to H<sub>2</sub>O. However, this barometer is normally used in natural systems  
1502 through iteration with the Eq24a thermometer, which is H<sub>2</sub>O-sensitive (Fig. 18b). When iterated, the barometer  
1503 is very H<sub>2</sub>O-sensitive; an increase in H<sub>2</sub>O by 1 wt% causes the P to drop by an average of ~1 kbar (Fig. 18c).

1504 We assess barometry performance on our test dataset, filtering out pairs which fail the anorthite-albite  
1505 (An-Ab) equilibrium test provided in the supporting spreadsheet of Putirka (2008). Using experimental T, the  
1506 barometer performs extremely poorly (RMSE=3.8 kbar, R<sup>2</sup> of 0, Fig. 18d). When P and T are iterated, the  
1507 performance is even worse (RMSE=4.0 kbar, Fig. 18e). It is notable that in Fig. 18d-e that experiments performed  
1508 at 2 kbar yield P>10 kbar, while experiments performed at 10 kbar yield P<0 kbar. To put the performance of  
1509 these barometers into perspective, we compare each experimental P to a random experimental pressure drawn  
1510 without replacement from the experimental dataset (Fig. 18f). The RMSE for this randomly selected number is  
1511 almost identical to that of the iterated barometer. Thus, until new experiments are done to specifically  
1512 investigate the Plag-Liq barometer, this method is only as reliable as researchers using a random number  
1513 generator spanning the crustal thickness in their location of interest than Plag-Liq barometry to estimate magma  
1514 storage pressures!

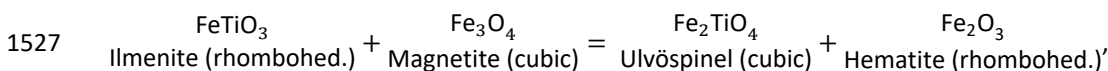


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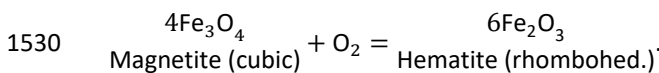
1516 *Figure 18. Assessment of the Plag-Liq barometer of Putirka (2008) Eq25. a-b) Assessing sensitivity of the*  
 1517 *barometer to T and H<sub>2</sub>O for a subset of experiments. c) Testing the sensitivity of the iterative combination of Eq25*  
 1518 *(P) and Eq24a (T) to melt H<sub>2</sub>O content. d) Testing the barometer using experimental T and H<sub>2</sub>O contents, after*  
 1519 *applying the An-Ab equilibrium test of Putirka (2008). e) As for panel d, but solving P and T iteratively (still using*  
 1520 *experimental H<sub>2</sub>O). f) Assessing the performance of a randomly selecting a P value from the experimental*  
 1521 *dataset.*

## 1522 2.10. Fe-Ti oxides

1523 The partitioning of Fe and Ti between cubic and rhombohedral oxides has been employed in estimating  
 1524 magmatic T and *f*O<sub>2</sub>. The Fe-Ti geothermobarometer is advantageous owing to the rapid cation exchange  
 1525 between the oxides, allowing equilibrium to be restored quickly following a change in magmatic conditions (days  
 1526 to weeks; Venezky and Rutherford, 1999). The exchange is described by the following reaction:



1528 where there is solid solution between ilmenite and hematite (the rhombohedral oxides), and magnetite and  
 1529 ulvöspinel (spinel series, or cubic oxides). The dependence on oxygen fugacity is described by the redox reaction:



1531 The main challenge in calibrating a Fe-Ti geothermobarometer comes from the extremely complex solid  
 1532 solution of the rhombohedral oxides. Naturally occurring rhombohedral oxides incorporate significant quantities  
 1533 of MgO, MnO, and Al<sub>2</sub>O<sub>3</sub> in addition to FeO, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, and have complex cation ordering transitions at  
 1534 lower temperatures, in addition to magnetic ordering. This means that complex expressions are required to  
 1535 accurately represent endmember activities, and multiple miscibility gaps exist. This complexity prevents simple  
 1536 empirical calibration of a geothermobarometer expression, and instead requires numerical solutions of  
 1537 expressions derived from a complex thermodynamic formulation.

1538 The first implementation of the Fe-Ti geothermobarometer was made by Buddington and Lindsley  
 1539 (1964), and improved by a number of subsequent studies as further experimental data became available (e.g.,  
 1540 Andersen and Lindsley, 1988; Spencer and Lindsley, 1981). The most recent update of the geothermobarometer  
 1541 was provided by Ghiorso and Evans (2008), building on the older thermodynamic model of Ghiorso and Sack  
 1542 (1991) using a calibration dataset with 5X more experiments (N=267 vs. N=57) and much better experimental

1543 constraints on cation ordering. In particular, the calibration range was extended to significantly higher T and  $fO_2$ ,  
1544 where previous versions of the model extrapolated poorly. Each update to the thermometer represents  
1545 increasing sophistication of the underlying thermodynamic model, and therefore more complex numerical  
1546 techniques to apply them as a geothermobarometer. An open-source implementation of the  
1547 geothermobarometer was provided by Ghiorso and Prissel (2020) through the ENKI portal.

1548 Blundy and Cashman (2008) use an independent set of experiments to estimate the uncertainty on  
1549 several versions of the Fe-Ti geothermobarometer, finding one sigma uncertainties of 44°C and 0.2–0.34 log  
1550 units  $fO_2$  for the Ghiorso and Evans (2008) model, but no systematic deviation at high or low temperatures.  
1551 However, it is likely that the uncertainty will vary across composition space, as the sensitivity of the thermometer  
1552 depends on the composition of the Fe-Ti oxides, with the best sensitivity below the NNO buffer and away from  
1553 the miscibility gap (Ghiorso and Evans, 2008).

### 1554 **2.11. Ti in Quartz (TitaniQ) thermometer**

1555 In silicic rocks where quartz is a dominant phenocryst (e.g., granites and rhyolites), there are far fewer  
1556 available thermometers relative to more mafic systems. To address this, Wark and Watson (2006) perform  
1557 experiments containing quartz and rutile at 600–1000°C at 10 kbar to produce an empirical relationship relating  
1558 the Ti content of quartz to the temperature. They state that this thermometer has an uncertainty of  $\pm 2^\circ\text{C}$  at  
1559  $>500^\circ\text{C}$  using SIMS measurements of Ti, and that this thermometer can also be applied to systems without rutile  
1560 if an independent estimate of Ti activity is obtained (e.g., from Fe-Ti equilibrium). This thermometer was  
1561 recalibrated by Kawasaki and Osanai (2008) using natural metamorphic rocks in ultrahigh temperature granulites  
1562 and Thomas et al. (2010), who perform additional experiments between 5–20 kbar, generating an expression  
1563 incorporating a term for pressure.

1564 Importantly, Thomas et al. (2010) implied that if temperature was known independently, the equation  
1565 could be inverted to solve for pressure. Wilson et al. (2012) test this inversion method on samples from the  
1566 Oruanui eruption, which has been well studied, so has independent estimates of pressure from melt inclusions,  
1567 and temperature and Ti activity from Fe-Ti oxides. They show that using Fe-Ti oxides to constrain temperature  
1568 and Ti activity, calculated pressures from Ti in quartz are 3–10X higher than those inferred from melt inclusion  
1569 saturation pressures. Similarly, if melt inclusion and Fe-Ti oxide temperatures and pressures are used, inferred  
1570 Ti activity is far too low. If pressures are used from melt inclusions and Ti activity from Fe-Ti oxide, temperatures  
1571 are well below the  $H_2O$ -saturated solidus for granite. Similar discrepancies with previously published pressures,  
1572 temperatures and Ti activities are present for calculations on the Bishop tuff. Wilson et al. (2012) suggest that  
1573 Ti activities may be highly variable in igneous systems, so activities from Fe-Ti oxides cannot be reliably used  
1574 with TitaniQ. Additionally, they suggest Ti in Qtz records complex histories that cannot be simply related to  
1575 changes in pressure and temperature over other variables, such as quartz growth conditions or melt  
1576 composition. For example, Huang and Audétat (2012) show that Ti concentrations in Qtz depend on the crystal  
1577 growth rate, so this thermobarometer should not be applied to hydrothermal fluids where growth rates are fast  
1578 and highly variable.

1579 Thomas and Watson (2012) partially rebut Wilson et al. (2012), in particular critiquing the validity of  
1580 their calculations of Ti activity (e.g., Ghiorso and Gualda, 2013) and temperature estimates from Fe-Ti oxides  
1581 (Ghiorso and Evans, 2008) in the Oruanui rhyolites that underly a lot of the arguments of Wilson et al. (2012).  
1582 Instead, Thomas and Watson (2012) use MELTS to estimate temperature and Ti activity based on the affinity for  
1583 rutile saturation from inputted melt compositions, yielding pressures similar to melt inclusions. They admit that  
1584 the approach of Wark and Watson (2006) was oversimplified in its suggestion of using a fixed value of Ti activity.  
1585 An excellent discussion of this Bishop Tuff controversy can be found in Putirka (2017), along with adjustment of  
1586 published coefficients for different equations.

1587 Acosta et al. (2020) identified that Ti in Qtz temperatures are offset  $\sim 100$ – $150^\circ\text{C}$  to lower temperatures  
1588 than other thermometers in silicic systems, particularly at  $<4$  kbar. To address the source of these offsets, they  
1589 perform hydrothermal quartz growth experiments at  $800^\circ\text{C}$  and 1 kbar with different fluid compositions. They  
1590 find that Ti in Qtz is sensitive to the Ti/Si ratio of the fluid, rather than the concentration or activity of Ti. Clearly,  
1591 significantly more experimental work is needed to determine magma storage conditions precisely and accurately  
1592 in silicic systems from Ti in Qtz.

### 1593 **3. Melt inclusion barometry**

1594 Melt inclusions (MIs) are small pockets of melt trapped during crystal growth, which become isolated  
1595 from the external melt as the surrounding crystalline host fully encloses them. MI which were trapped from a  
1596 volatile-saturated magma can be used to deduce magma storage depths because the solubility of  $\text{CO}_2$  and  $\text{H}_2\text{O}$

1597 in silicate melts is a strong function of pressure (Dixon, 1997; Goranson, 1931). If MI were trapped from a  
1598 volatile-undersaturated magma, calculated pressures are minimum estimates (Hauri et al., 2018; Matthews et  
1599 al., 2016).

1600 Numerous recent reviews have detailed the theory, methods and advances relating to melt inclusion  
1601 analysis and interpretation, as well as several specific problems associated with determination of magma storage  
1602 depths from these archives. For example, Wallace et al. (2021) present a comprehensive review of olivine-hosted  
1603 melt inclusions, describing melt inclusion formation, post-entrapment crystallization, and the wealth of  
1604 information recorded by melt inclusions (e.g., trace element contents for tracking magma batches, processes  
1605 controlling magmatic H<sub>2</sub>O contents, calculating ascent rates, and storage pressures). Rose-Koga et al. (2021)  
1606 provide a number of guidelines involving sample preparation, analysis and data reporting associated with melt  
1607 inclusion analysis and interpretation. Barth and Plank (2021) discuss the processes which can alter H<sub>2</sub>O contents  
1608 in melt inclusions after their entrapment, producing regime diagrams describing how melt inclusions can act as  
1609 hygrometers and barometers (revealing pre-eruptive H<sub>2</sub>O contents), or speedometers (revealing ascent rates  
1610 using H<sup>+</sup> diffusion). Wieser et al. (2022a) provide a detailed history of different solubility models used to calculate  
1611 melt inclusion saturation pressures and highlight the large discrepancies between different models. In particular,  
1612 they emphasize the importance of carefully examining the calibration range of each solubility model compared  
1613 to the P-T-X range of melt inclusions from a given volcano. To avoid repetition, we refer readers to these papers,  
1614 and focus our discussion on issues involving magma storage depth determinations from melt inclusions which  
1615 have not yet been reviewed in detail. We specifically focus on the growing realization that the CO<sub>2</sub> contents of  
1616 melt inclusions have been significantly underestimated, because of the presence of a substantial CO<sub>2</sub> within  
1617 vapour bubbles that were not measured in most published studies.

### 1618 **3.1 Vapour bubble growth systematics**

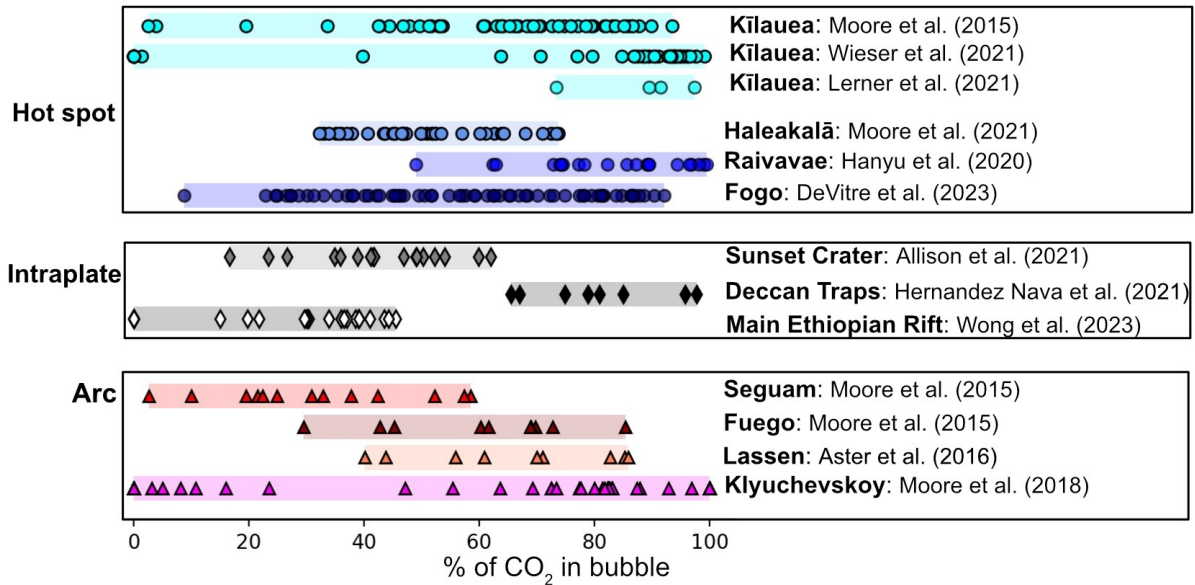
1619 The vast majority of studies have used olivine-hosted melt inclusions to determine magma storage  
1620 depths (e.g., Aster et al., 2016; Moore et al., 2015; Ruscitto et al., 2010; Sides et al., 2014; Wallace et al., 2021).  
1621 This focus on olivine may reflect the fact that it is one of the first crystallizing phases (important for studies  
1622 focusing on the most primitive melt compositions), it is relatively abundant, and tends to have melt inclusions  
1623 which are larger than those in other phases from the same sample suite (Bennett et al., 2019, Wieser et al.  
1624 2022c). It has also been suggested that the absence of cleavage in olivine makes leakage less likely than in say  
1625 pyroxene, which has a strong cleavage (Kress and Ghiorso, 2004). Finally, the simple chemistry of olivine, well-  
1626 constrained  $K_{D,Fe-Mg}$ , and low partition coefficients for REE and other trace elements of geological interest means  
1627 that correcting melt inclusions for post-entrapment crystallization (PEC) is more straightforward than in  
1628 plagioclase and pyroxene (Danyushevsky and Plechov, 2011; Kress and Ghiorso, 2004; Neave et al., 2017; Wieser  
1629 et al., 2022c).

1630 However, as a consequence of the fact that olivine is often the first phase to crystallize in a magma,  
1631 there is significant potential for melt inclusions to experience substantial amounts of cooling prior to eruption  
1632 (e.g., ~150–170°C in high forsterite olivines from the 2018 eruption of Kīlauea, Lerner et al., 2021; Wieser et al.,  
1633 2021). This results in a large amount of PEC. Crystallization of denser olivine from less dense silicate melt,  
1634 combined with differential contraction of the melt and host during cooling, causes the pressure in the inclusion  
1635 to drop, driving the growth of a vapour bubble (often termed a shrinkage bubble, Kress and Ghiorso, 2004;  
1636 Steele-Macinnis et al., 2011; Wallace et al., 2015). Because the solubility of CO<sub>2</sub> is strongly dependent on  
1637 pressure, if there is sufficient time between bubble growth and syn-eruptive quenching, a significant proportion  
1638 of the total CO<sub>2</sub> content of the melt inclusion will diffuse into the vapour bubble (Fig. 19, Maclennan, 2017,  
1639 Wieser et al. 2021). Rapid diffusive re-equilibration of H<sub>2</sub>O between the melt inclusion and a more H<sub>2</sub>O-poor  
1640 carrier melt as a result of fast H<sup>+</sup> diffusion rates in olivine can also drive the growth of a vapour bubble (Aster et  
1641 al., 2016; Gaetani et al., 2012).

### 1642 **3.2 Raman measurements of vapour bubbles**

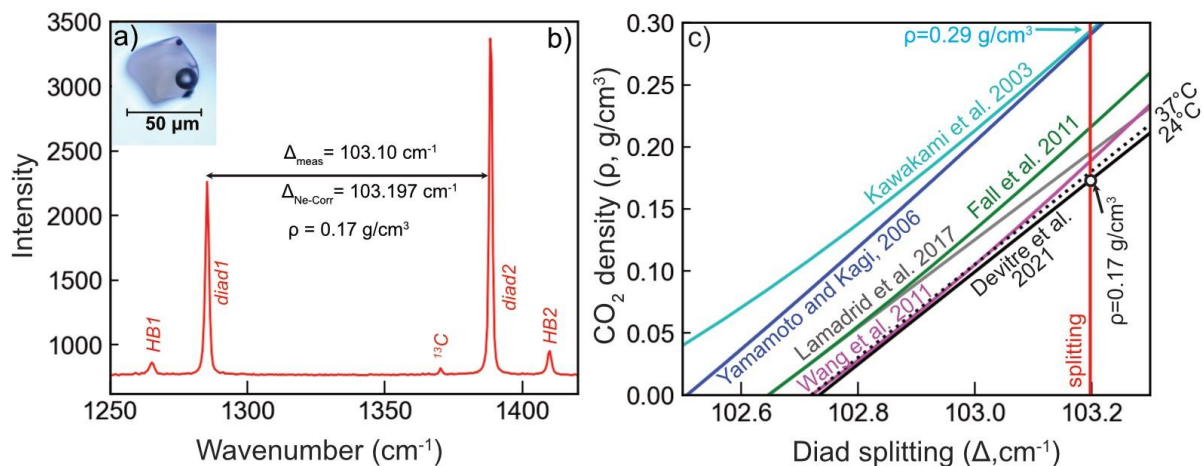
1643 In situ Raman spectroscopic measurements of vapour bubbles over the last decade have demonstrated  
1644 that a large and often dominant proportion of the total CO<sub>2</sub> content of melt inclusions is held within the bubble  
1645 (Fig. 19, Allison et al., 2021; Aster et al., 2016; DeVitre et al., 2023a; Hanyu et al., 2020; Hernandez et al., 2018;  
1646 Lerner et al., 2021; Moore et al., 2015, 2018, 2021; Wieser et al., 2021). To our knowledge, the first Raman  
1647 analyses of a melt inclusion vapour bubble were made by Steele-Macinnis et al. (2011) in samples from Solchiaro  
1648 Volcano, Italy. They found a distinctive signal consisting of two strong peaks which is indicative of the presence  
1649 of a CO<sub>2</sub> fluid (Fig. 20b). This contradicted the dominant hypothesis at the time that these bubbles were vacuums  
1650 or voids. In two almost concurrent papers, Hartley et al. (2014) and Moore et al. (2015) present Raman  
1651 measurements in melt inclusion vapour bubbles from Laki, Kīlauea, Fuego and Segouam, demonstrating that 40

1652 to >90% of the total CO<sub>2</sub> is held within the bubble. More recent work has found similar proportions spanning a  
 1653 range of tectonic settings (Fig. 19).



1654  
 1655 *Figure 19 – Percent of the total melt inclusion CO<sub>2</sub> content held in the vapour bubbles from studies which have*  
 1656 *used an instrument-specific Raman calibration. Refs: Allison et al., 2021; Aster et al., 2016; DeVitre et al., 2023a;*  
 1657 *Hanyu et al., 2020; Hernandez Nava et al., 2021; A. H. Lerner et al., 2021; Moore et al., 2021, 2018, 2015; Wong*  
 1658 *et al., 2023.*

1659 Raman spectroscopic analyses of CO<sub>2</sub> in vapour bubbles rely on the strong correlation between the  
 1660 density of CO<sub>2</sub> and the distance between the two strong CO<sub>2</sub> spectral peaks collectively termed the Fermi diad.  
 1661 This distance is commonly called the splitting, diad splitting, or diad separation ( $\Delta$ , Fig. 20b). However, the  
 1662 relationship between density and diad splitting has been shown to vary as a function of instrument hardware  
 1663 and acquisition parameters (Lamadrid et al., 2017, Fig. 20c). This means that the relationship between the diad  
 1664 splitting and CO<sub>2</sub> density must be determined for the acquisition parameters and specific data processing  
 1665 strategy used by each Raman laboratory. The absolute differences in CO<sub>2</sub> densities for a measured diad splitting  
 1666 on different Raman instruments are very large (Fig. 20c). For example, the vapour bubble shown in Fig. 20a yields  
 1667 a splitting of 103.10 cm<sup>-1</sup> on the Cornell WITEC Alpha300R (Fig. 20b). Following the protocol of Lamadrid et al.  
 1668 (2017), this splitting is corrected based on the measured distance between two peaks from the atomic spectra  
 1669 of Ne to give a splitting of 103.197 cm<sup>-1</sup>. Using the densimeter calibrated for this exact instrument, acquisition  
 1670 parameters and Ne correction regime (DeVitre et al. 2021), the density of this bubble is  $\rho=0.17$  g/cm<sup>3</sup> (Fig. 20c).  
 1671 However, if the densimeter of Kawakami et al. (2003) was instead used, the calculated density would be nearly  
 1672 twice as high ( $\rho=0.29$  g/cm<sup>3</sup>, Fig. 20c).



1673  
 1674 *Figure 20 – Determining CO<sub>2</sub> density using Raman Spectroscopy. a) Image of an olivine-hosted melt inclusion*  
 1675 *from the Twin Lakes Crater, OR. b) Raman spectra showing the strong Fermi diad (peaks at ~1285 and 1388 cm*  
 1676 *<sup>-1</sup>) with hot bands on either side. The distance between the peaks is the diad splitting ( $\Delta=103.10$  cm*

1677 *correction for the measured splitting of the Ne emission spectra (Lamadrid et al. 2017), this corresponds to a CO<sub>2</sub>*  
1678 *density of 0.17 g/cm<sup>3</sup> using the splitting-density relationship developed on this specific instrument (DeVitre et al.*  
1679 *2021). c) The relationship between density and splitting is different on each Raman instrument (e.g., DeVitre et*  
1680 *al., 2021; Fall et al., 2011; Kawakami et al., 2003; Lamadrid et al., 2017; Rosso and Bodnar, 1995; Wang et al.,*  
1681 *2019; Yamamoto and Kagi, 2006). If the Kawakami et al. (2003) densimeter was used for this vapour bubble, it*  
1682 *would give a density of 0.29 g/cm<sup>3</sup>.*

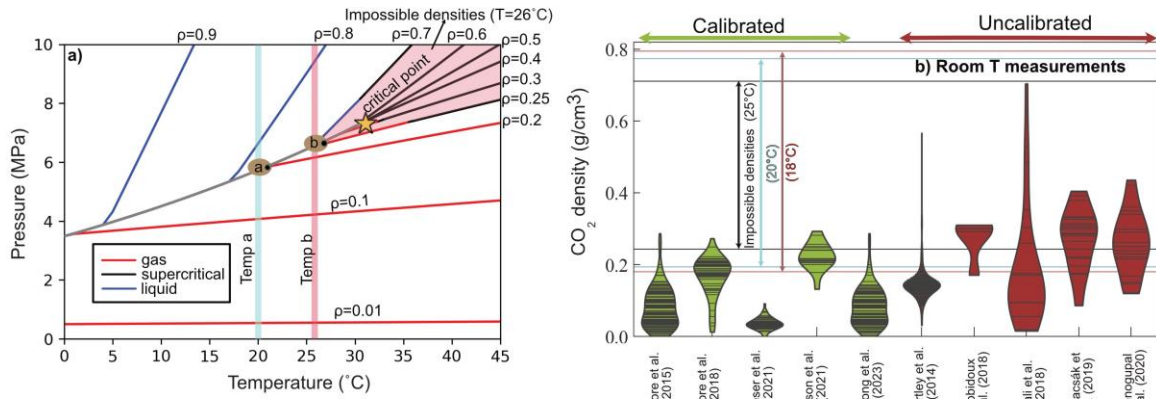
1683  
1684 The most robust way to calibrate a specific Raman spectrometer for a given analytical protocol is to measure  
1685 the diad splitting for ultra-pure CO<sub>2</sub> gas held at a variety of pressures (and thus densities). This is often achieved  
1686 using a high-pressure optical cell (HPOC) or a fluid density calibration apparatus (FDCA). These apparatus feed  
1687 pure CO<sub>2</sub> gas into a chamber where the pressure is tightly controlled, and ideally the temperature too. The  
1688 measured P and T in the cell can be converted into a CO<sub>2</sub> density using the CO<sub>2</sub> equation of state (EOS, e.g., Span  
1689 and Wagner, 1996). Raman measurements are made on this trapped fluid with known density, and the splitting  
1690 is determined for each Raman acquisition. The relationship between the measured diad splitting and CO<sub>2</sub> density  
1691 is often parameterized over a number of discrete density windows, as the shape of the curves vary (DeVitre et  
1692 al., 2021).

1693 Despite the importance of measuring CO<sub>2</sub> in melt inclusion vapour bubbles being recognised in ~2014–2015  
1694 (Hartley et al., 2014; Moore et al., 2015) and the calibration issue being highlighted in 2017 (Lamadrid et al.,  
1695 2017), only published melt inclusion vapour bubble measurements made at Virginia Tech and Cornell have  
1696 calibrated their Raman using a gas cell apparatus.

1697 Only the Cornell calibration closely controls and measures the T of the CO<sub>2</sub> gas, which is required to convert  
1698 pressure into density with high accuracy and precision (DeVitre et al., 2021). A few more laboratories have used  
1699 lower cost methods, where samples with known CO<sub>2</sub> densities are measured in a manner analogous to primary  
1700 standards for EPMA calibration. For example, Allison et al. (2021) developed a calibration line by measuring the  
1701 splitting-density relationships for fused silica capillary capsules (FSCC). The CO<sub>2</sub> density in these capsules was  
1702 calculated from the mass of loaded CO<sub>2</sub> and the volume of the capillary, which allowed the calibration line to be  
1703 determined at low densities (FSCCs ranged from 0.008–0.133 g/cm<sup>3</sup>). Wieser et al. (2021) calibrated their Raman  
1704 at low densities using 19 synthetic fluid inclusions (SFI) in quartz standards (0.04–0.14 g/cm<sup>3</sup>) which were  
1705 measured on the calibrated Virginia Tech Raman, with the same calibration being used by Wong et al. (2023).  
1706 Mironov et al. (2020) use a similar approach, developing a calibration line using 8 melt inclusion vapour bubbles  
1707 measured at Virginia Tech with densities between 0.013–0.22 g/cm<sup>3</sup>.

1708 Other studies measuring vapour bubbles have converted measured diad splitting into densities using a  
1709 published calibration line developed in a different laboratory (e.g., Bali et al., 2018; Hartley et al., 2014; Taracsák  
1710 et al., 2019; Venugopal et al., 2020). The choice of densimeter in these studies varies widely, and the choice of  
1711 one densimeter instead of another is not justified. For example, Hartley et al. (2014) using Kawakami et al. (2003,  
1712 cyan line on Fig. 19c), Taracsák et al. (2019) and Venugopal et al. (2020) using Wang et al. (2011, salmon line),  
1713 and Bali et al. (2018) and Robidoux et al. (2018) using Fall et al. (2011, green line). The offset of their densities  
1714 from the true value is not known, although a correction could be applied retrospectively if samples with known  
1715 CO<sub>2</sub> densities were analysed on the same instrument with the same analytical conditions.

1716 Thermodynamic limits on the density of CO<sub>2</sub> at ambient conditions reveal a possible issue with the  
1717 selection of a densimeter from the literature developed for a different instrument. The CO<sub>2</sub> phase diagram shows  
1718 that at room T (20–26°C), the maximum possible density of CO<sub>2</sub> gas is ~0.2–0.26 g/cm<sup>3</sup> (Fig. 21a). A vapour  
1719 bubble with a higher bulk density will consist of an inner sphere of CO<sub>2</sub> gas of  $\rho=0.2\text{--}0.26\text{ g/cm}^3$ , and a coexisting  
1720 outer shell of CO<sub>2</sub> liquid with  $\rho>0.7\text{ g/cm}^3$  (see inclusion at Temp b on Fig. 21a). It is not thermodynamically  
1721 possible for densities between these values to be measured by Raman spectroscopy unless the sample is heated  
1722 above the critical point of CO<sub>2</sub> at 31°C (supercritical CO<sub>2</sub> can have any density, Span and Wagner et al. 1996).  
1723 While laser heating may occur during Raman analysis, which can account for the small number of measurements  
1724 above 0.26 g/cm<sup>3</sup> on calibrated instruments (Fig. 21b, DeVitre et al., 2023b; Dubessy et al., 2012; Hagiwara et  
1725 al., 2021), the presence of a significantly larger number of measurements with  $\rho>0.26\text{ g/cm}^3$  in studies which did  
1726 not perform an instrument specific calibration may indicate that these densities have been overestimated  
1727 through selection of an inappropriate literature calibration. For example, had the Kawakami et al. (2003)  
1728 densimeter been used for the melt Inclusion in Fig. 20a, an impossible density of 0.29 g/cm<sup>3</sup> would have been  
1729 obtained.



1730  
 1731 *Figure 21 – a) Phase diagram of CO<sub>2</sub>, drawn using the NIST webbook with the Span and Wagner (1996) EOS. At*  
 1732 *Temp a (20°C), a CO<sub>2</sub> fluid with  $\rho > 0.2 \text{ g/cm}^3$  will comprise of a vapour with  $\rho = 0.194 \text{ g/cm}^3$ , and a liquid with*  
 1733  *$\rho = 0.773 \text{ g/cm}^3$ . At Temp B (26°C), the liquid will have a density of  $\sim \rho = 0.7 \text{ g/cm}^3$  and the vapour will have a density*  
 1734 *of  $\sim \rho = 0.25 \text{ g/cm}^3$ . Impossible densities at 26°C are shown in pink. b) Compilation of the densities of room T melt*  
 1735 *inclusion vapour bubble measurements by Raman spectroscopy, shown as a Violin plot where each horizontal*  
 1736 *line represents 1 measurement. Studies which used an instrument-specific calibration are colored green, those*  
 1737 *which did not are colored dark red. The maximum density of a vapour and minimum density of a liquid phase at*  
 1738 *three temperatures are shown with horizontal lines. Even with a room T of 25°C, many of the densities reported*  
 1739 *by uncalibrated studies are thermodynamically impossible. Refs: (Allison et al., 2021; Bali et al., 2018; Hartley et*  
 1740 *al., 2014; Moore et al., 2018, 2015; Robidoux et al., 2018; Taracsák et al., 2019; Venugopal et al., 2020; Wieser*  
 1741 *et al., 2021; Wong et al., 2023).*

1742 Once the relationship between measured splitting and CO<sub>2</sub> density for a specific Raman instrument and data  
 1743 reduction strategy is determined, the amount of the CO<sub>2</sub> held in the vapour bubble (in ppm equivalent in the  
 1744 glass) is calculated using mass balance:

1745  
 1746 
$$CO_2(\text{ppm equivalent}) = 10^4 \frac{Vol\%_{VB} \times \rho_{CO_2}}{\rho_{melt}} \text{ [Equation 9]}$$

1747  
 1748 Where  $Vol\%_{VB}$  is the vol% of the vapour bubble,  $\rho_{CO_2}$  is the density of the CO<sub>2</sub> fluid (determined by  
 1749 Raman spectroscopy), and  $\rho_{melt}$  is the density of the silicate melt (e.g., using DensityX, Iacovino and Till, 2019).  
 1750 Equation 9 can be used to demonstrate the large effect of the choice of densimeter on calculated CO<sub>2</sub> contents.  
 1751 For example, using a typical melt density (e.g., 2.7 g/cm<sup>3</sup>) and a bubble volume percent of ~3.9% (as in the melt  
 1752 inclusion shown in Fig. 20a), the true vapour bubble CO<sub>2</sub> density of 0.17 g/cm<sup>3</sup> means the bubble contributes  
 1753 2455 ppm CO<sub>2</sub> to the melt inclusion. However, if a literature densimeter was randomly chosen from those in Fig.  
 1754 20b, the amount of CO<sub>2</sub> contributed by the bubble could be as high as 4188 ppm. These discrepancies in Raman  
 1755 calibration propagate to large uncertainties in magma storage depths. Wieser et al. (2021) show that for a typical  
 1756 Kīlauea melt inclusion with a vapour bubble occupying 5% of the inclusion volume, different densimeters could  
 1757 yield storage depths ranging from 4 to 18 km. Thus, constraining the splitting to CO<sub>2</sub> density relationship for  
 1758 each individual instrument is vital to avoid the introduction of very large systematic errors on calculated storage  
 1759 pressures (and therefore depths). Arbitrary choice of a Raman calibration is likely the largest source of  
 1760 systematic error in many published melt inclusion studies, only overshadowed by studies which didn't measure  
 1761 the bubble at all. Raman analyses without an instrument-specific calibration must be considered as qualitative.  
 1762 They are useful to determine whether CO<sub>2</sub> is present in vapour bubbles in any given system, but systematic  
 1763 errors spanning a factor of 3 are unacceptable when it comes to determining magma storage depths.

1764  
 1765 **3.3 Other uncertainties reconstructing vapour bubbles**

1766 Once a Raman instrument is calibrated, there are four additional major sources of uncertainty affecting  
 1767 estimates of the amount of CO<sub>2</sub> held in vapour bubbles, discussed below.

1768 **3.3.1. Volume proportions of vapour bubbles**

1769 The first source of uncertainty is associated with determining the relative volume of the vapour bubble  
 1770 and melt inclusion (i.e. the  $Vol\%_{VB}$  term in Equation 9). The vast majority of melt inclusion studies estimate  
 1771 volumes using transmitted light images, where a best fit ellipse is fitted to the 2D outline of the melt inclusion  
 1772 and vapour bubble, and the third (z) dimension is estimated either as an average of the two visible axes, or the



1773 minimum of the two measured axes. Tucker et al. (2019) simulate the uncertainty associated with 2D sectioning  
1774 of 3D ellipsoids, concluding that the best estimate is obtained when the third (z) dimension is calculated from  
1775 the average of the 2 visible dimensions. They quantify the  $1\sigma$  uncertainty of this method (-48% to +37%), which  
1776 translates into a significant error in calculated storage depths where vapour bubbles contain a large proportion  
1777 of the total inclusion  $\text{CO}_2$ .

1778 However, in many cases, melt inclusions have faceted faces (e.g., Fig. 20a) or more complex shapes that  
1779 can deviate significantly from a perfect ellipsoid. A best fit ellipse fitted to a more cubic shape may result in the  
1780 melt volume being overestimated, and by extension, the bubble volume and  $\text{CO}_2$  content underestimated  
1781 (Hanyu et al., 2020). Mironov et al. (2020) compared methods of calculating the z dimension using the measured  
1782 x-y dimensions to direct measurements of the 3<sup>rd</sup> dimension using a vertically calibrated microscope, or by  
1783 polishing two orthogonal faces so the x-y and z direction can be measured. They find that volume measurements  
1784 using z from a vertically calibrated microscope or by polishing an orthogonal plane were in good agreement ( $\pm 10$   
1785 %) with each other, but differed from the z-axis assumption methods by up to 45%. Thus, they suggest that  
1786 researchers should measure the 3<sup>rd</sup> axis using these relatively low-cost methods, rather than inferring it from 2D  
1787 measurements.

1788 The most accurate and precise approach to determine the volume of each phase is to use x-ray  
1789 tomography (i.e. nanoCT,  $\mu\text{CT}$ ; Richard et al., 2019; Hanyu et al., 2020; Jorgenson et al., 2021). Hanyu et al.  
1790 (2020) showed that optical methods fitting ellipses tend to overestimate MI volumes by  $\sim 20\%$ , even in fairly  
1791 ellipsoidal shaped MI (they did not assess the effect of strong asymmetry or faceting). Attempts have been made  
1792 to constrain volumes using 3D confocal Raman imaging (Aradi et al., 2021; Schiavi et al., 2020). There are  
1793 additional complications associated with the fact that the different refractive indices of the host crystal, melt and  
1794 vapour can cause vertical distortion (Everall, 2010). This can make vapour bubbles appear oblate (Schiavi et al.,  
1795 2020). Raman mapping is also significantly slower than  $\mu\text{CT}$ , and data segmentation is even more time  
1796 consuming.

1797 Most recently, DeVitre et al. (2023a) perform nano-CT scans for MI of various shapes and sizes,  
1798 including those with extreme asymmetry or faceting. They compare these CT volumes to those calculated using  
1799 2D methods (measuring x-y, calculating z), and 3D methods where z is measured using a vertically calibrated  
1800 microscope, or by polishing an orthogonal surface. For relatively ellipsoidal shapes, the median offset between  
1801 2D and CT methods is  $\sim \pm 15\text{--}20\%$  (similar to Hanyu et al. 2020), although for certain melt inclusion morphologies,  
1802 the offsets can be  $\sim \pm 50\%$ , similar to the uncertainty estimated from slicing simulations of Tucker et al. (2019) of  
1803  $1\sigma = -48\%$  to +37%. For the most faceted or complex shaped MI, the systematic mis-prediction of volume inflicted  
1804 using averaging or minimum axis 2D methods results in an uncertainty of up to  $\sim 3$  kbar in the saturation  
1805 pressures (meaning MI could have been trapped at crustal levels at 7–8 km, or in the mantle, 17–18km). For  
1806 regular, relatively ellipsoidal-shaped melt inclusions, DeVitre et al. (2023a) find that measuring the 3<sup>rd</sup> dimension  
1807 (via microscope, motorized-z stage Raman, or on an orthogonal plane) returns values within  $\pm 10\%$  of CT  
1808 measurements, although the offsets are larger for more irregularly shaped inclusions. Overall, DeVitre et al.  
1809 (2023a) suggest that the orthogonal plane method is the most time- and cost-effective way to reduce uncertainty  
1810 associated with bubble volumes. While CT is clearly superior, these measurements cost  $\sim 100\$/\text{hr}$ , with high  
1811 quality scans needing several hours. Data reduction is also time consuming and computationally expensive. At  
1812 the moment, the CT method has not been scaled up to datasets typical of melt inclusion studies (e.g.,  $N > 100$ ) in  
1813 a time or cost-effective manner. We suggest that it makes more sense to constrain the volumes of all melt  
1814 inclusion to within  $\pm 20\%$  of the true value for all melt inclusions (and published studies), compared with a smaller  
1815 number of super precise CT scans, and a larger number of imprecise 2D optical methods. Developing fast,  
1816 inexpensive, and precise ways to estimate vapour bubble volumes is an important frontier to address to optimize  
1817 melt inclusion barometry.

1818

### 1819 **3.3.2. Secondary phases in vapour bubbles**

1820 Another major source of uncertainty when reconstructing bubble  $\text{CO}_2$  comes from the presence of  
1821 carbon-bearing phases on the wall of the bubble, which may sequester 100s-1000s of ppm of  $\text{CO}_2$  (Aster et al.,  
1822 2016; Moore et al., 2015; Schiavi et al., 2020; Tucker et al., 2019; Venugopal et al., 2020). These phases can be  
1823 identified optically in larger bubbles (Tucker et al., 2019), and produce distinctive peaks in Raman spectra,  
1824 particularly if the laser is focused near the bubble wall or line scans and 3D maps are used (Fig. 22d, Moore et  
1825 al., 2015; Robidoux et al., 2018; Schiavi et al., 2020). Secondary phases can also be identified using BSE, SE and/or  
1826 EDS imaging on an SEM of an exposed bubble walls (Robidoux et al., 2018; Schiavi et al., 2020; Tucker et al.,  
1827 2019; Wieser et al., 2020).

1828           The occurrence of secondary phases on bubble walls is highly variable, and their genesis is poorly  
1829 understood. It appears that carbonate species (e.g., Mg, Fe, Na, and Ca carbonates) are more common in more  
1830 H<sub>2</sub>O-rich melt inclusions (e.g., arcs and wet OIBs like Fogo vs. dry OIBs such as Kīlauea). Even at a given volcano,  
1831 some eruptions may have a reasonable proportion of melt inclusions containing carbonate (e.g., 1960 Kīlauea,  
1832 Moore et al., 2015; Tucker et al., 2019), while other eruptions have no carbonate (e.g., 2018 Kīlauea, Lerner et  
1833 al., 2021; Wieser et al., 2021). Most intriguingly, even within a single crystal, some melt inclusions contain  
1834 carbonate while others do not, and within a single melt inclusion with multiple bubbles, some have all their CO<sub>2</sub>  
1835 as carbonate, some have a mix of carbonate and CO<sub>2</sub> fluid, and some consist only of CO<sub>2</sub> fluid (Fig. 23). It has  
1836 been suggested that solid phases form on bubble walls as a paragenetic sequence during cooling of the vapour  
1837 bubble, with sulfide precipitation at 500–700 °C, magnesite (MgCO<sub>3</sub>) precipitation at <350 °C, and carbonate and  
1838 sulfide precipitation from liquid H<sub>2</sub>O at <150 °C (Robidoux et al., 2018).  
1839

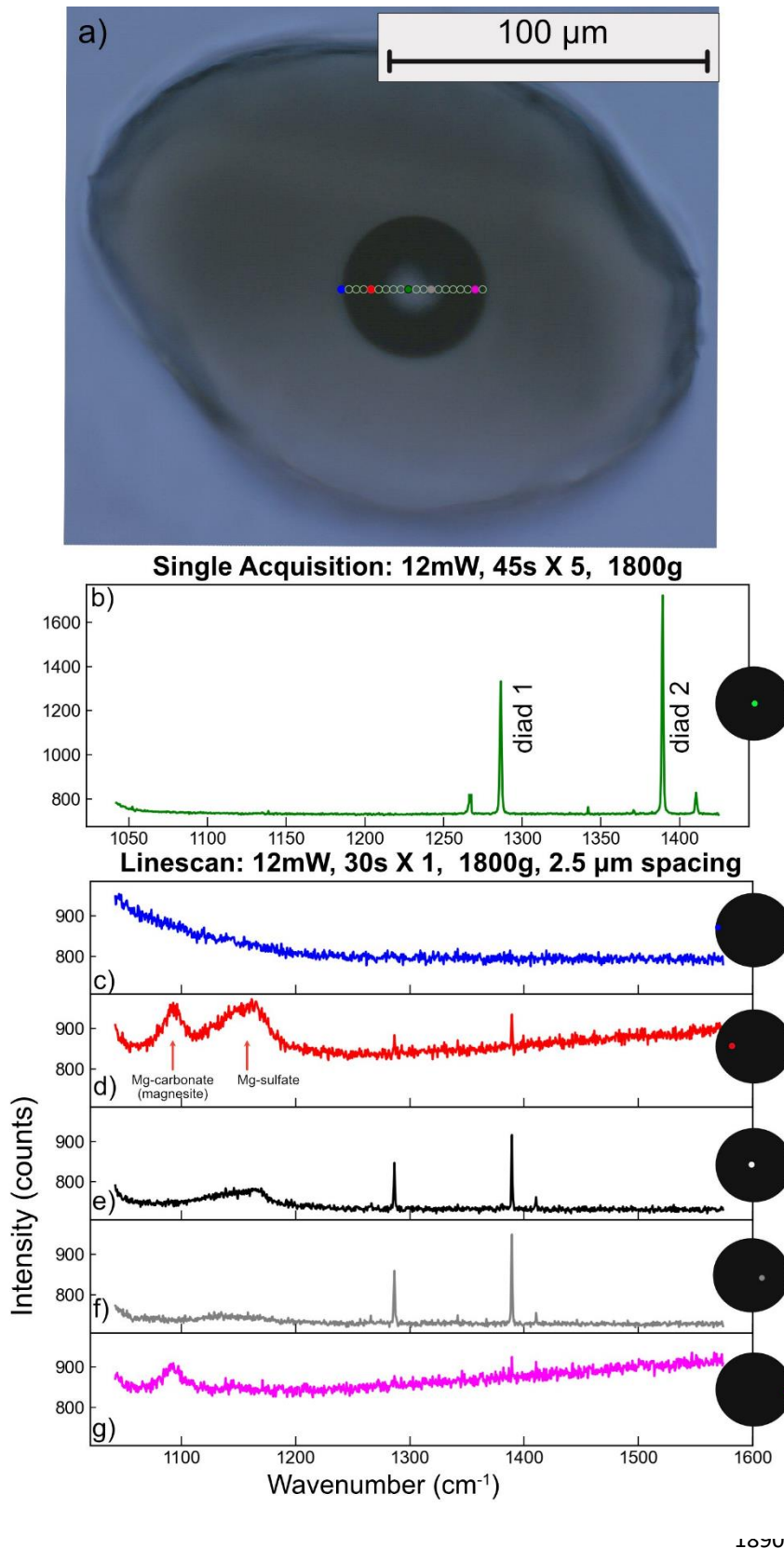


Figure 22 – Comparing a Raman acquisition in the centre of a melt inclusion vapour bubble (scan b) with individual acquisitions taken as part of a line scan across the bubble (c-g). A carbonate and sulfate peak is only apparent at specific locations near the bubble edge, and does not appear in the central acquisition.

Clearly, the carbonate forming reactions are subject to very local variations in condition (on the scale of the diameter of a single melt inclusion), and significant further work is required to understand them further. Quantifying the amount of CO<sub>2</sub> present within carbonate is non-trivial. Tucker et al. (2019) do preliminary mass balance calculations based on optical observations, considering different thicknesses of carbon on the wall of bubbles. Schiavi et al. (2020) determine the volume of carbonate and S-bearing species using 3D Raman mapping, showing that solid phases can account for 21–50% and 16–60% of the C and S budget respectively. Several experimental approaches have been developed for bubble-bearing melt inclusions as an alternative to mass balance reconstructions using Raman Spectroscopy (see below), some of which can help to resolve the carbonate problem.

### 3.3.2.1 Experimental homogenization approaches

Two broad homogenization strategies have been used to account for carbonate in vapour bubbles. The ‘in situ’ strategy involves reheating of individual

1891 crystals in a Linkam or Vernadsky heating stage in an  $fO_2$  controlled Ar or He atmosphere, making observations  
 1892 of the melt inclusion of interest under an optical microscope. The crystal is heated until the vapour bubble and  
 1893 other secondary phases redissolve, and then the sample is rapidly quenched to obtain a single-phase melt  
 1894 inclusion. This method allows the operator to view the melt inclusion and quench the crystal just after the  
 1895 inclusion homogenizes, meaning a different reheating path can be used for each crystal. The ‘bulk’ strategy heats  
 1896 crystals in batches in various experimental apparatus. This had the advantage of being far less time consuming

1897 and allowing reheating at different pressures (see below), but has the disadvantage of meaning crystals trapped  
1898 at a range of temperatures may be overheated or underheated (e.g., Esposito et al., 2012).

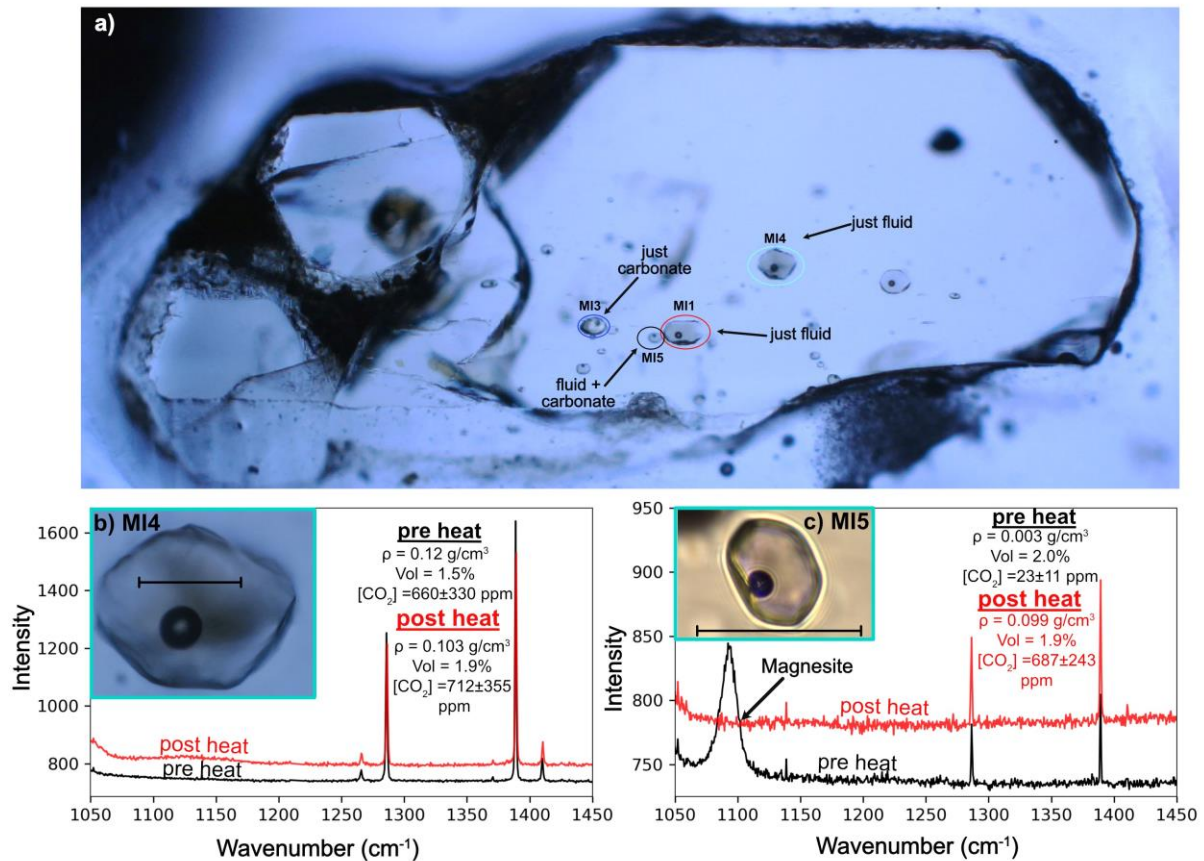
1899       Regardless of whether a single crystal or a batch of crystals is heated, performing reheating experiments  
1900 at atmospheric pressure often results in vapour bubbles not fully redissolving, or dissolving at spuriously high  
1901 temperatures. For example, Le Voyer et al. (2017) individually heat melt inclusions from Mt. Shasta in the  
1902 Cascade Arc using a Vernadsky-type heating stage, noting that many inclusions retain their vapour bubble, even  
1903 if they are heated up to 1500°C. The failure to homogenize the bubble has been attributed to the fact that at  
1904 atmospheric pressure, the host exerts less pressure on the melt inclusion than was present during natural  
1905 cooling at depth in the magmatic system (Danyushevsky et al., 2002; Esposito et al., 2012). Additionally, if  
1906 sufficient time passes between post-entrapment crystallization and syn-eruptive quenching, chemical changes  
1907 such as FeO or H<sup>+</sup>-loss through the host crystal may occur, which cannot be reversed by reheating (Aster et al.,  
1908 2016; Bucholz et al., 2013). To account for the excess bubble growth resulting from these irreversible changes,  
1909 the inclusion must be overheated, often by many hundreds of degrees to get the bubble to disappear. This is  
1910 concerning because overheating results in extensive re-equilibration between the melt inclusion and host,  
1911 erasing important chemical information (e.g., major element zoning preserving quench rate, Newcombe et al.,  
1912 2014; information on the amount of PEC; Wieser et al., 2021). An additional problem with heating at 1  
1913 atmosphere is that melt inclusions may rupture/decrepitate (Tuohy et al., 2016). This is a particular problem for  
1914 melt inclusions closer to the polished surface or the crystal, inclusions trapped at high pressures in the plumbing  
1915 system, and more H<sub>2</sub>O-rich inclusions.

1916       Crystals can also be heated at elevated pressures (e.g., Piston cylinder apparatus, Rasmussen et al.,  
1917 2020, internally heated gas pressure vessel, Skirius, 1990). The confining pressure exerted around the crystal  
1918 can help prevent decrepitation, and aid bubble dissolution. To get around the issue that reheating can cause H<sup>+</sup>  
1919 loss, and to try to resorb bubbles which have experienced extensive H<sup>+</sup> loss, Mironov et al. (2015) homogenize  
1920 melt inclusions in an internally heated pressure vessel (IHPV) under high H<sub>2</sub>O pressure achieved through a  
1921 hydrated silicate melt matrix. Specifically, they heat melt inclusions from lavas which are thought to have  
1922 diffusively lost 3 wt% H<sub>2</sub>O (such extensive H<sub>2</sub>O-loss favours near-ubiquitous bubble growth). They find that  
1923 bubbles remain after heating under dry and damp conditions, but a large proportion disappear at higher H<sub>2</sub>O  
1924 pressures where the melt inclusion is rehydrated. This indicates that, at least in wet arc magmas, diffusive H<sub>2</sub>O  
1925 loss can account for the observation that bubbles often persists after heating (rather than resulting from a lack  
1926 of confining pressure during heating in 1 atm apparatus). This reheating method was adapted by Rasmussen et  
1927 al. (2020), who use a piston cylinder apparatus with KBr and Mg(OH)<sub>2</sub> as the hydrated matrix to achieve a higher  
1928 experimental success rate.

1929       One limitation of these hydrated experimental reheating methods is that the initial H<sub>2</sub>O content of the  
1930 system must be estimated when preparing the hydrated matrix, and melt inclusion water contents will be reset  
1931 to this value (Buso et al., 2022). While Rasmussen et al. (2020) use unheated melt inclusion volatile contents as  
1932 a guide, there is still the risk of adding too much or too little H<sub>2</sub>O to any specific inclusion. Additionally, while an  
1933 approximate estimate of initial H<sub>2</sub>O contents can be placed based on the point of homogenization, there is a  
1934 non-unique play off between the confining P, T and H<sub>2</sub>O content required to obtain complete homogenization  
1935 of the bubble (e.g. Mironov et al., 2015 show that instead of increasing H<sub>2</sub>O by 1 wt%, P could be increased by  
1936 6.5 kbar, or T increased by 100°C). Thus, as with the techniques mentioned above, a limitation of these bulk  
1937 homogenization experiments is that the same experimental conditions must be applied to all melt inclusions in  
1938 a given capsule, even if they formed on different P-T-H<sub>2</sub>O paths in nature (Rasmussen et al., 2020).

1939       All the methods discussed so far attempt to redissolve the bubble entirely, so measurements only need  
1940 to be performed on a single homogenous glass phase. In contrast, DeVitre et al. (2023a) developed a reheating  
1941 method where the aim is to redissolve the carbonate phase back into the vapour bubble where it can be  
1942 measured using Raman spectroscopy, rather than redissolve the bubble into the melt. They heat individual  
1943 crystals using a Linkam TS1400XY stage which heats from room T to 1400°C at up to 200 °C/min, and quenches  
1944 using Ar or He flow combined with a water-cooled plate at 240 °C/min. Heating is conducted in an fO<sub>2</sub> controlled  
1945 Ar atmosphere to prevent oxidation of the melt and olivine. As the melt inclusion is progressively heated under  
1946 a microscope, it passes through the glass transition temperature, and goes dark. The liquidus temperature is  
1947 estimated from the major element composition of the system and a reasonable range of volatile contents (using  
1948 MELTS, or a liq thermometer). As the liquidus temperature is reached, the melt inclusion clears to a brown glass,  
1949 and the inclusion is held at this temperature for ~8–10 minutes to redissolve any carbonate on the walls of the  
1950 bubble back into the fluid phase, before being rapidly quenched on a water-cooled plate. The advantage of this  
1951 method is that it only heats the inclusion to the liquidus, rather than to higher temperatures needed to resorb  
1952 the bubble. Heating to the lowest possible T is advantageous, because it limits olivine dissolution, and preserves  
1953 the major element information held in the melt and olivine. Raman acquisitions collected before and after

1954 heating indicate that the carbonate is effectively redissolved back into the bubble (Fig. 23e), and that inclusions  
 1955 experience minimal H<sub>2</sub>O-loss. After heating, bubbles without carbonate return CO<sub>2</sub> contents within uncertainty  
 1956 of pre-heating estimates (CO<sub>2</sub> contents change by ~±10% accounting for slight changes in bubble volume, or  
 1957 errors associated with measuring the same bubble proportion using 2D images). The main disadvantage of this  
 1958 method over complete homogenization methods is the fact that Raman is used to measure the bubble after  
 1959 heating, which requires accurate estimates of the relative volume of the vapour and melt phase.



1960  
 1961 *Figure 23: Olivine crystal with numerous melt inclusions with variable carbon partitioning between fluid and solid*  
 1962 *phases. A) Two melt inclusions (MI1, MI4) have a strong fermi diad but no carbonate phases (see spectra b),*  
 1963 *while MI5 has a fermi diad and a carbonate peak (see spectra c), and MI3 has just a carbonate peak b) pre and*  
 1964 *post-heating, MI4 has very similar densities and volumes, with CO<sub>2</sub> contents within error. c) pre-heating, MI5 has*  
 1965 *a prominent magnesite peak, and weak Fermi diads. After reheating using the method of DeVitre et al., 2023a,*  
 1966 *the amount of CO<sub>2</sub> increases substantially, and the magnesite peak completely disappears. Scalebar on b-c shows*  
 1967 *50 μm*

1968  
 1969 **3.3.3. Theoretical vapour bubble reconstruction methods**

1970 A variety of methods have also been developed to reconstruct the CO<sub>2</sub> content of a vapour bubble  
 1971 theoretically, although there have been relatively few comparisons with Raman approaches on a single inclusion  
 1972 basis (e.g. Aster et al., 2016, Wieser et al. 2021). Anderson and Brown (1993) investigated bubble CO<sub>2</sub> in a suite  
 1973 of melt inclusions from Kīlauea Iki, calculating an internal pressure for each melt inclusion using the measured  
 1974 CO<sub>2</sub> content in the melt phase of the inclusion. This internal pressure was then used to calculate the density of  
 1975 CO<sub>2</sub> in the coexisting vapour phase using an equation of state. To convert these densities into CO<sub>2</sub> amounts, they  
 1976 assumed all bubbles occupied 0.5 vol% prior to syn-eruptive quenching, which is the point at which CO<sub>2</sub> diffusion  
 1977 and bubble growth become decoupled. Riker (2005) adapt this method for Mauna Loa, calculating the pre-  
 1978 quench bubble volume as a factor of the T drop experienced by each melt inclusion, accounting for the fact  
 1979 different melt inclusions experience different amounts of cooling, and therefore PEC. Aster et al. (2016) further  
 1980 adapt this method for melt inclusions from Lassen Volcanic Centre, tracking the volume of a growing vapour  
 1981 bubble using phase volume and density information from Rhyolite-MELTS, and vapour compositions to partition

1982 elements into the bubble using the volatile solubility model of Iacono-Marziano et al. (2012). This method was  
1983 also used in the Cascade Arc by Johnson and Cashman (2020) and Walowski et al. (2016).

1984 In contrast to these methods reconstructing the vapour bubble volume *prior* to bubble expansion  
1985 accompanying syn-eruptive quenching, Tucker et al. (2019) use the equation of state method outlined by  
1986 Anderson and Brown (1993) to calculate CO<sub>2</sub> density in the bubble, and then calculate the amount of CO<sub>2</sub> in the  
1987 bubble using the measured bubble volume. This measured-volume method generates extremely high CO<sub>2</sub>  
1988 estimates (and therefore storage pressures) for Hawaiian melt inclusions (4000–10,000 ppm). Using the  
1989 measured bubble volume assumes that the vapour bubble and melt continue to exchange CO<sub>2</sub> until the glass  
1990 transition T (~725°C), such that the bubble is always in equilibrium with the measured melt composition.  
1991 However, vapour bubbles experience two distinct phases of growth. The first phase of bubble growth at high T  
1992 accompanies PEC or diffusive H<sub>2</sub>O loss. High temperatures mean that CO<sub>2</sub> can easily diffuse from the melt into  
1993 the growing vapour bubble. The second phase of bubble growth occurs during syn-eruptive quenching, where  
1994 CO<sub>2</sub> becomes diffusion-limited as the temperature drops, but the bubble volume continues to grow until the  
1995 temperature cools below the glass transition temperature (Maclennan, 2017). Wieser et al. (2021) compare the  
1996 Tucker EOS method to Raman measurements at Kīlauea and show that the Tucker method overestimates bubble  
1997 CO<sub>2</sub> by a factor of 10–20X compared to the Raman method for melt inclusions which grew most their bubble  
1998 during syn-eruptive quenching (where CO<sub>2</sub> migration was diffusion limited). The measured-volume EOS method  
1999 results in calculated magma storage depth of 5–20 km for melt inclusions while the Raman method and  
2000 geophysics indicate magmas were stored at 1–5 km. For melt inclusions contained in high-Fo olivines, where  
2001 most of the bubble grew during PEC at high temperatures, EOS methods are still 1.5–2X too high, as the method  
2002 still neglects a non-negligible increase in bubble volume upon quench which is not accompanied by CO<sub>2</sub> diffusion.

2003 To unravel the relative importance of these two stages of vapour bubble growth, good estimates are  
2004 required of the amount of PEC, the amount of H<sub>2</sub>O-loss, the quench rate, and the glass transition T (Maclennan,  
2005 2017; Rasmussen et al., 2020). Rasmussen et al. (2020) produce a Python3 tool, MIMiC (Melt Inclusion  
2006 Modification Corrections), which calculates bubble CO<sub>2</sub> using empirical parametrizations of volume and density  
2007 changes, with uncertainties quantified by Monte-Carlo techniques. However, while constraining the amount of  
2008 PEC is relatively straightforward in systems with a well-defined liquid line of descent where the initial FeO  
2009 content can be easily estimated (e.g., Kīlauea Volcano, Wieser et al., 2021), it can be very challenging in systems  
2010 with a large amount of scatter in FeO at a given MgO number (e.g., Rasmussen et al., 2017; Walowski et al.,  
2011 2019), perhaps because of variability in primary FeO contents and/or mixing of diverse melt compositions (e.g.,  
2012 Maclennan, 2008). Reconstructing initial H<sub>2</sub>O contents can also be very challenging, and the arc magmas at the  
2013 point of melt inclusion entrapment may be substantially more hydrous than the amount of H<sub>2</sub>O measured in  
2014 the melt inclusion (Gavrilenko et al., 2019; Goltz et al., 2020).

2015

#### 2016 **3.3.4. Co-entrapped vapour bubbles**

2017 All the methods discussed thus far rely on the assumption that vapour bubbles formed after melt  
2018 inclusion entrapment, through some combination of PEC, cooling, and H<sup>+</sup> loss. However, it has been long  
2019 recognised that bubbles may also become trapped at the point of melt inclusion formation. These are termed  
2020 co-entrapped bubbles. In fact, determining magma storage depths from melt inclusion saturation pressures  
2021 *requires* that the melt was volatile saturated at the point of melt inclusion formation. This assumption  
2022 necessitates that there is an excess volatile phase available to co-entrap. If co-entrapped bubbles are added  
2023 back in by mass balance techniques, the amount of CO<sub>2</sub> could be drastically overestimated.

2024 Many studies simply select a threshold volume above which bubbles are assumed to be co-entrapped  
2025 (e.g., 5%, Lowenstern, 2003; Robidoux et al., 2018, or 10%, Buso et al., 2022; Moore et al., 2015). However, the  
2026 maximum vapour bubble volume that can form without requiring co-entrapment is a function of the amount of  
2027 cooling, and the amount of diffusion H<sup>+</sup> loss, and varies greatly between different eruptions (Tucker et al., 2019).  
2028 Tucker et al. (2019) examine distributions of bubble volumes from Hawai'i, discarding outliers which clearly lie  
2029 outside the main distribution of bubble volumes (8 vol%+). In suites where there are abundant fluid inclusions  
2030 in crystals addition to bubble-bearing melt inclusions, co-entrapped bubbles can often be identified based on  
2031 the fact that they have larger relative volumes than other vapour bubbles, and CO<sub>2</sub> densities more similar to  
2032 fluid inclusions (Lerner et al., 2021, Hanyu et al., 2020).

2033 Alternatively, co-entrapped bubbles can be identified by comparing bubble volumes to variables such  
2034 as H<sub>2</sub>O content, CO<sub>2</sub> density, and PEC amount. For example, Wieser et al. (2021) show that there is a correlation  
2035 between the amount of PEC (0–33%) and the volume of the vapour bubble (1–6 vol%) at Kīlauea. The 5% cut off  
2036 from Lowenstern (2003) would clearly be inappropriate in this instance. Instead, samples lying significantly off  
2037 the observed PEC-volume trend were classified as co-entrapped. While bubble growth in H<sub>2</sub>O-poor, CO<sub>2</sub>-rich

2038 systems can be relatively well predicted based on the amount of PEC and the cooling path alone (Maclennan,  
2039 2017; Riker, 2005; Wieser et al., 2021), it is more complicated in H<sub>2</sub>O-rich magmas which have the potential to  
2040 experience large amounts of bubble growth following H<sub>2</sub>O loss. In these situations it is more robust to use bubble  
2041 growth models, and any bubbles which exceed even the most extreme model scenarios were likely co-entrapped  
2042 (e.g., Allison et al. 2021, DeVitre et al. 2023a). For example, Ruscitto et al. (2011) report the presence of bubbles  
2043 with volumes spanning 6–16 vol % in high Mg olivines from Mt. Shasta, and conclude that these bubble volumes  
2044 can grow through a combination of PEC and H<sub>2</sub>O loss, so were not necessarily co-entrapped. In contrast, Allison  
2045 et al. (2021) found that melt inclusions at Sunset Crater, Arizona, with bubbles >3.5 vol% were likely to be co-  
2046 entrapped. These two contrasting scenarios highlight the issue with selecting a single universal volume % as a  
2047 cut off.

2048 Even using bubble growth models, the details of specific inclusion must be considered, else co-  
2049 entrapped bubbles with volumes within the range predicted by the growth model could be overlooked, even if  
2050 they were co-entrapped. Allison et al. (2021) subdivide bubble-bearing melt inclusions from Sunset Crater, AZ,  
2051 into 2 groups based on bubble volumes, densities, offset trends in Olivine forsterite-total CO<sub>2</sub> space, and bubble  
2052 growth models. They conclude that group 2 inclusions (>3.5 vol%) co-entrapped a bubble. To more robustly  
2053 identify co-entrapped vapour bubbles, we are in desperate need of a forward-model of bubble growth,  
2054 accounting for both H<sub>2</sub>O and CO<sub>2</sub>. The model of Maclennan (2017) only considered CO<sub>2</sub> (not H<sub>2</sub>O) and is not  
2055 publicly available. While the Monte-Carlo methods incorporated in the model of Rasmussen et al. (2020) have  
2056 huge potential for this problem, currently this code only works to correct melt inclusions, and cannot be run  
2057 forward for a hypothetical P-T-X path post-entrapment. In summary, it is becoming very clear that the CO<sub>2</sub>  
2058 contents of bubbles must be accounted for to obtain reliable storage depths, and that as a community,  
2059 substantially more work is required to a) develop reliable bubble growth models to ensure co-entrapped bubbles  
2060 don't result in spurious CO<sub>2</sub> contents b) calibrate individual Raman instruments and perform measurements at  
2061 >33°C and appropriate laser powers c) improve methods to determine relative volumes d) further investigate  
2062 experimental homogenization methods.

### 2063 **3.4. Decrepitation**

2064 Another issue affecting melt inclusion saturation pressures is the process of decrepitation, where the  
2065 internal pressure of the inclusion exceeds the strength of the host mineral, and cracks open. Decrepitation  
2066 commonly occurs during magma ascent, as the confining pressure exerted by the surrounding liquid drops.  
2067 Maclennan (2017) compile a global dataset of melt inclusions from MORBs, OIBS, and continental settings,  
2068 noting that 95% yield saturation pressures <2 kbar, which is close to the experimental decrepitation threshold  
2069 of Wanamaker et al. (1990). Using their model of P-T-V-X evolution of melt inclusions, they conclude that  
2070 pressure difference between olivine and melt causes decrepitation in most tectonic settings, so preserved CO<sub>2</sub>  
2071 contents are minimum estimates. They note that decrepitation can be partially mitigated if the melt inclusion is  
2072 trapped from a significantly undersaturated melt, so the melt inclusion experiences significant cooling and PEC  
2073 at depth before it ascends, which reduces the internal pressure of their inclusion. Similarly, sequestration of CO<sub>2</sub>  
2074 in a vapour bubble can also help to reduce the pressure of the liquid below the decrepitation threshold. The  
2075 modelling of Maclennan (2017) suggested that entrapment pressures up to twice the decrepitation threshold  
2076 (i.e., ~4 kbar) could be preserved if ascent conditions allow for bubble formation while remaining below the  
2077 decrepitation threshold.

2078 However, a number of studies have been published since 2017 yielding significantly higher saturation  
2079 pressures than those in compilation of Maclennan (2017), and their inferred decrepitation thresholds. In the  
2080 glass phase alone, DeVitre et al. (2023a) measure CO<sub>2</sub> contents of up to 1.3 wt%, corresponding to glass-only  
2081 saturation pressures of ~1-7 kbar. Once CO<sub>2</sub> in the vapour bubble is included, pressures rise to ~2-11 kbar.  
2082 Similarly high glass CO<sub>2</sub> contents (1.2 wt%) are reported by Buso et al. (2022) in melt inclusions from the French  
2083 Massive Central, corresponding to entrapment depths of >10 kbar. Once bubbles are dissolved using  
2084 homogenization methods, saturation pressures in these samples extend to 15–25 kbar. Glass-only  
2085 measurements from Haleakala, HI, cluster at 1–3 kbar, and extend to 2–6 kbar after accounting for the bubble  
2086 (Moore et al., 2021). Melt inclusions from Isla Floreana in the Galápagos record glass-only saturation pressures  
2087 of 1.1–7.2 kbar (median=5 kbar, bubbles not measured). Critically, one bubble-free inclusion records a glass-only  
2088 saturation pressure of ~7 kbar, where the lack of decrepitation cannot be attributed to the presence of a bubble  
2089 keeping the inclusion below the decrepitation threshold. This high pressure overlaps with the pressure  
2090 calculated from Cpx-based barometry, indicating it is not an outlier (Gleeson et al., 2022, 2021). There are  
2091 numerous other examples of saturation pressures calculated from the glass phase only yield saturation  
2092 pressures >2 kbar from many alkali ocean island settings (e.g., French Polynesia, Hanyu et al., 2020; El Hierro,

2093 Taracsák et al., 2019), and studies accounting for the glass and bubble exceeding 2-4 kbar (e.g., Sunset Crater,  
2094 AZ, at 3-5 kbar, Allison et al., 2021, Deccan Traps between ~ 2–7 kbar, Hernandez Nava et al., 2021, Pico Volcano,  
2095 Azores, 2.2-6.6 kbar, Van Gevre et al. 2023).

2096 The existence of melt inclusions with glass-only saturation pressures of >>2-4 kbar and glass + bubble  
2097 saturation pressures of >4 kbar suggests decrepitation may not be as important a process as Maclennan (2017)  
2098 suggests. While Maclennan (2017) conclude that “*decrepitation of melt inclusions, where the inclusion ruptures*  
2099 *and loses CO<sub>2</sub> to the external melt, is the dominant process that controls the observed distribution of CO<sub>2</sub> in the*  
2100 *compiled data set*”. We suggest that the paucity of alkaline, CO<sub>2</sub>-rich settings in the compilation of Maclennan  
2101 (2017), combined with the fact most studies did not measure the vapour bubble, led to a dataset that was  
2102 skewed to anomalously low pressures.

### 2103 **3.5. Melt inclusions hosted in other mineral species**

2104 While storage depths calculated from olivine-hosted melt inclusions have dominated the literature in  
2105 the past few decades, there are a growing number of studies measuring melt inclusions in plagioclase (Bennett  
2106 et al., 2019; Blundy et al., 2010; Drignon et al., 2019; Koleszar et al., 2012; Neave et al., 2017; Wieser et al.,  
2107 2022c), ortho- and clinopyroxene (Araya et al., 2019; Koleszar et al., 2012; Wieser et al., 2022c), and amphibole  
2108 (Koleszar et al., 2012). In more silicic systems, quartz-hosted inclusions are also commonly examined (Bégué et  
2109 al., 2015; Quinn, 2014; Wallace et al., 1999), along with plagioclase (Bacon et al., 1992, Wright et al., 2012) and  
2110 ortho- and clinopyroxene (Wright et al., 2012). Saturation pressures from inclusions in other phases often  
2111 overlap with those determined from olivine (Wieser et al., 2022c), and may even yield deeper saturation  
2112 pressures (Bennett et al. 2019) indicating that the “rupture resistance” of these other mineral phases may have  
2113 been underestimated. Also, to gain an unbiased understanding of storage condition in a wide range of melt  
2114 compositions, it is certainly advantageous to consider more than one mineral phase, particularly as in many  
2115 systems olivine is restricted to a relatively narrow range of melt compositions (if present at all). However,  
2116 significantly more work is needed to understand bubble growth and post-entrapment processes in these other  
2117 phases, as well as rates of diffusive H<sub>2</sub>O-loss.

2118

### 2119 **4. Fluid inclusion Barometry**

2120 Crystals growing in a fluid-saturated magma trap pockets of melt and exsolved fluid in varying  
2121 proportions, varying from pure melt (melt inclusions), melt and varying proportions of fluids (melt inclusions  
2122 with co-entrapped vapour bubbles), and pockets of pure fluid with little or no attached melts (fluid inclusions –  
2123 FIs, Steele-Macinnis et al., 2011). In CO<sub>2</sub>-rich, H<sub>2</sub>O-poor volcanic systems such as mid-oceanic ridge basalts and  
2124 ocean island basalts (OIBs), the exsolved vapour phase (and thus the fluid being trapped) is almost pure CO<sub>2</sub> at  
2125 pressures >200 bars (Gerlach and Graeber, 1985). In these relatively anhydrous systems, the density of FIs can  
2126 act as an excellent barometer, because the density of a CO<sub>2</sub>-rich fluid, along with an estimate of its entrapment  
2127 temperature, can be converted into a pressure using the pure CO<sub>2</sub> equation of state (e.g., Span and Wagner,  
2128 1996).

2129 Despite clear potential, a Web of Science search demonstrates that FI barometry has been  
2130 underutilized by igneous petrologists in the last 10 years relative to other petrological barometers (Fig. 24c-d).  
2131 Conventionally, the densities of FIs have been determined by observing phase changes during heating and  
2132 cooling in a temperature-controlled microscope stage (microthermometry, Sorby, 1858). The relatively small  
2133 number of existing studies in volcanic settings that use microthermometric techniques to obtain FI densities  
2134 show the enormous potential of this method (Fig. 24c, see Hansteen and Klügel, 2008 and refs within). For  
2135 example, FI in quartz-rich xenoliths from volcanoes in the Aeolian arc yield densities corresponding to both deep  
2136 (~16–20 km) and shallow (4–6 km) pressures within the crust (Frezzotti et al., 2003). The deeper regions likely  
2137 represent the primary magma storage zones, with shallower depths recording re-equilibration of FI during  
2138 temporary residence at shallower levels during ascent towards the surface. The ability of FI to identify multi-  
2139 stage ascent has also been demonstrated at Mt Etna (Frezzotti et al., 1991) at Mt. Etna, Cabo Verde (Klügel et  
2140 al., 2020), Azores (Zanon and Frezzotti, 2013) and the Canary Islands (Hansteen et al., 1998).

2141 It has long been established that Raman spectroscopy can be used as an alternative to  
2142 Microthermometry to determine the density of CO<sub>2</sub>-rich fluid inclusions (e.g., Rosso and Bodnar, 1995). This has  
2143 been aided by recent improvements in the spatial and spectral resolution of confocal Raman spectroscopy, along  
2144 with the development of precise ways to calibrate the relationship between peak parameters and CO<sub>2</sub> density  
2145 for different Raman instruments (e.g., DeVitre et al., 2021; Kawakami et al., 2003; Lamadrid et al., 2017, see  
2146 section 3.2). Raman analyses have many advantages over Microthermometry:



2147 1. Confocal Raman spectrometers are becoming increasingly common in universities, where they are  
2148 widely used in other subdisciplines within the Earth Sciences (e.g., paleontology, mineral physics). In contrast,  
2149 the use of heating-cooling stages and the associated expertise to conduct microthermometry is more restricted.

2150 2. Raman analyses are faster (2–4 mins) compared with the 10s of minutes required to conduct a single  
2151 heating and cooling experiment. This is particularly true if there is only one fluid inclusion within the field of view  
2152 at high magnification. Microthermometry can be faster on fluid inclusion trails as phase changes in multiple  
2153 inclusions can be observed in one experiment.

2154 3. Raman analyses only require only one surface to be ground down to within ~50–100  $\mu\text{m}$  of the fluid  
2155 inclusion, with a good enough polish to be able to visualize the FI on the Raman microscope. Normally, all that  
2156 is required to achieve this is relatively fine wet-and-dry paper (2000–7000 grade) and a quick 30 s polish on 1  
2157  $\mu\text{m}$  Aluminium polishing paper, while microthermometry requires a crystal to be prepared into a double polished  
2158 wafer, with a good enough polish to see phase changes in detail.

2159 4. Raman spectroscopy can be used on  $\text{CO}_2$  fluid inclusions with a very wide range of densities (e.g.  
2160 0.01–1.24  $\text{g}/\text{cm}^3$ ) densities. In contrast, it is very hard to observe the homogenization temperature of a fluid  
2161 inclusion with a density less than the critical density of  $\text{CO}_2$  ( $< \sim 0.47 \text{ g}/\text{cm}^3$ ) or a density higher than the triple  
2162 point ( $> 1.18 \text{ g}/\text{cm}^3$ ) using microthermometry (Kobayashi et al., 2012).

2163 5. Raman spectroscopy can be applied on FIs with diameters down to  $\sim 1 \mu\text{m}$  (Frezza et al., 2012,  
2164 Dayton et al., 2023), while it is very difficult to observe phase changes during microthermometry for inclusions  
2165  $< 3\text{--}10 \mu\text{m}$  (Kobayashi et al., 2012). This is of particular importance in volcanic systems, where many fluid  
2166 inclusions are very small (and smaller inclusions are more resistant to decrepitation during ascent, Bodnar et al.,  
2167 1989; Campione et al., 2015; Wanamaker et al., 1990).

2168 Relative to melt inclusion analyses and mineral barometry, estimates of magma storage depths from  
2169 FIs are significantly more precise than both melt inclusions and mineral barometry, and have fewer sources of  
2170 systematic uncertainty relating to the conversion of the measured quantity (density) to pressure (Dayton et al.,  
2171 2023). Unlike the complex relationships relating pressure to mineral components (e.g., Jd in Cpx) or dissolved  
2172  $\text{H}_2\text{O}$  and  $\text{CO}_2$  concentrations in silicate melts, the  $\text{CO}_2$  equation of state is extremely well constrained, with very  
2173 little offset between different parameterizations ( $\sim 3\%$  at 7 kbar, Span and Wagner, 1996; Sterner and Pitzer,  
2174 1994; Wieser and DeVitre, 2023). Additionally, unlike many mineral-melt barometers which are very  
2175 temperature sensitive, the P calculated from the EOS is not all that sensitive to T (Fig. 24a). To demonstrate the  
2176 high precision of this method, we propagate a  $\pm 30 \text{ K}$  uncertainty in trapping temperature and a Raman analytical  
2177 error of  $\pm 0.02 \text{ g}/\text{cm}^3$  using Monte-Carlo methods (Wieser and DeVitre, 2023), which yields a 12%  $1\sigma$  error at 0.6  
2178 kbar, a 7% error at 2.2 kbar, and a 5% error at 5.2 kbar. These errors are significantly smaller than other  
2179 petrological barometers (Fig. 24b). A final advantage over melt inclusion barometry is that far fewer analytical  
2180 steps are required to obtain FI pressures (no  $\mu\text{CT}$ , FTIR/SIMS, EPMA measurements of glass), increasing the  
2181 speed at which depths can be determined, at a far lower cost (Dayton et al., 2023). This speed is aided by open-  
2182 source Python3 packages which help to automate data processing and  $\text{CO}_2$  equation of state calculations, which  
2183 were previously one of the slower aspects of the Raman fluid inclusion method (Wieser and DeVitre, 2023).

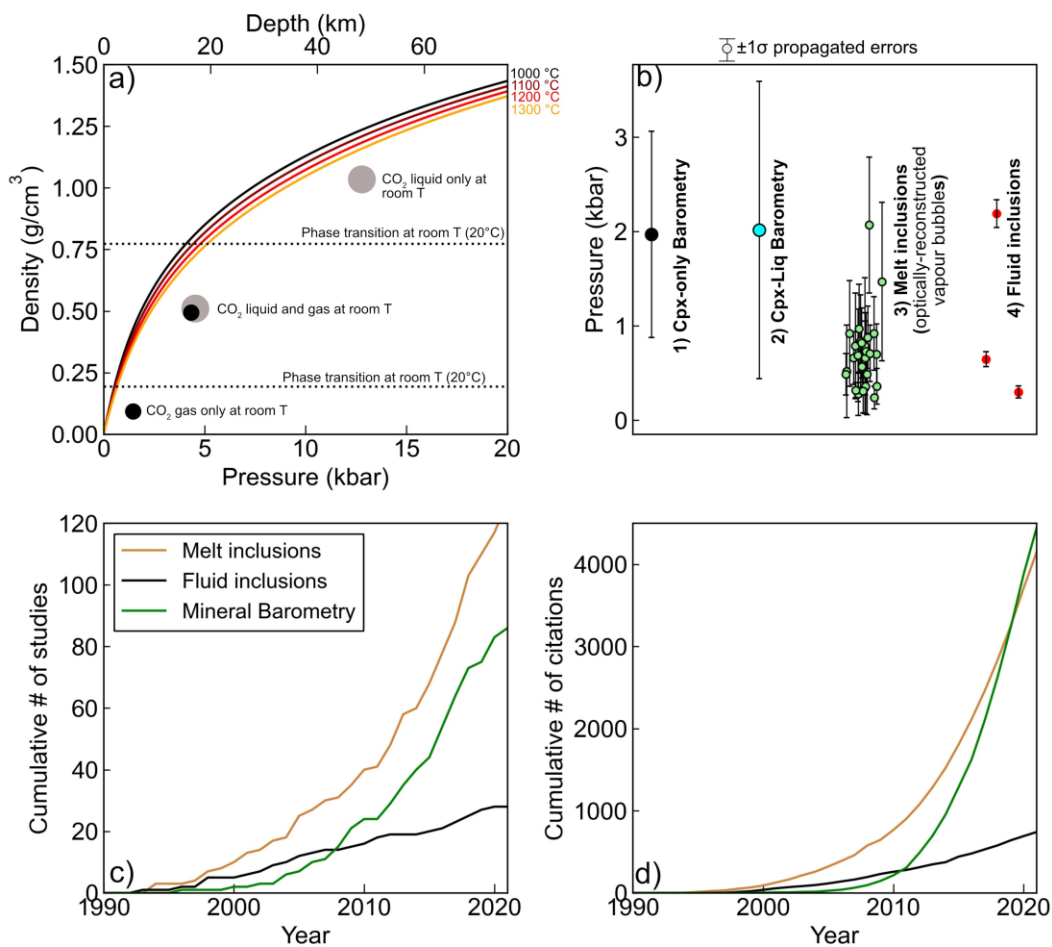
2184 Several sources of systematic error must still be considered when interpreting fluid inclusion pressures.  
2185 First, like melt inclusions, fluid inclusions may experience decrepitation upon ascent, which can yield  
2186 anomalously low pressures, sometimes without clear textural evidence for  $\text{CO}_2$ -loss because of reheating during  
2187 ascent. Second, the pressure the inclusion exerts on the host can also cause deformation of the host through  
2188 the movement of dislocations, increasing the inclusion volume. These two processes are captured by two of the  
2189 three 'Roedders' rules of fluid inclusions: '2) *the inclusion represents a constant volume*, 3) *nothing has been*  
2190 *added or lost from the inclusion*' (Bodnar, 2017; Roedder, 1984). Namely, fluid inclusion barometry assumes that  
2191 a fixed mass of  $\text{CO}_2$  was trapped in the crystal, with a fixed volume, meaning the inclusion has a fixed density, so  
2192 the density measured in the laboratory is the same as the density at which the inclusion was trapped.  
2193 Decrepitation violates rule 3 (and possibly 2 as well), while re-equilibration violates rule 2. While numerous work  
2194 has been conducted to determine re-equilibration processes for quartz-hosted fluid inclusions (Bakker, 2017;  
2195 Boullier et al., 1989; Pecher, 1981; Qin et al., 1992), to our knowledge, the only experimental constraint on  
2196 olivine re-equilibration was performed by Wanamaker and Evans (1989). They re-equilibrate fluid inclusions  
2197 within San Carlos olivine by holding crystals at  $1400^\circ\text{C}$  and atmospheric pressure for several days. We suggest  
2198 that further experimental work is required to confidently predict how fluid inclusions in common mafic phases  
2199 (olivine, pyroxenes etc) re-equilibrate when subject to a specific P-T-t path, with the aim of having models which  
2200 can be run for a given set of samples similar to those used to model  $\text{H}^+$  loss from melt inclusions (E.g., Barth and  
2201 Plank, 2021). However, it is clear from analyses of fluid inclusions in mantle xenoliths that return crustal  
2202 pressures that re-equilibration should be taken as the norm rather than the exception, and fluid inclusions will

2203 normally be reset to the pressures corresponding to the final region of prolonged magma stalling prior to  
2204 eruption (Hansteen and Klugel, 2008).

2205 The presence of fluid species other than CO<sub>2</sub> can also influence the accuracy of calculated pressures by  
2206 both Raman spectroscopy and microthermometry. In igneous systems, the most common species present in the  
2207 exsolved fluid phase are H<sub>2</sub>O, SO<sub>2</sub>, Cl, F, H<sub>2</sub>S, N<sub>2</sub>, CH<sub>4</sub>, CO, and He. While some species are strongly Raman active  
2208 with peaks that are close enough to the CO<sub>2</sub> diad to be visible in most high resolution acquisitions (e.g. SO<sub>2</sub>  
2209 produces a sharp peak at 1151 cm<sup>-1</sup>, Frezzotti et al., 2012), others will require a separate acquisition centered at  
2210 higher wavenumbers (e.g. the N<sub>2</sub> peak is at 2331 cm<sup>-1</sup>, CH<sub>4</sub> at 2917, Frezzotti et al., 2012). Monoatomic gases  
2211 (e.g. He) are Raman inactive, meaning they don't produce any peaks. Molar proportions can be estimated from  
2212 peak area ratios and knowledge of scattering cross sections for different Raman-active gases (Burke, 2001).  
2213 Some fluid species can also be identified (and sometimes quantified) from changes in the freezing and melting  
2214 temperatures by microthermometry (Hansteen and Klugel, 2008; Van Den Kerkhof, 1990), although in many  
2215 cases, the relevant phase diagram has not been constrained (e.g. C O<sub>2</sub>-He).

2216 Mixed H<sub>2</sub>O-CO<sub>2</sub> fluids present a particularly challenging problem to fluid inclusion barometry, because  
2217 H<sub>2</sub>O is so ubiquitous in the exsolved vapour phase in igneous systems. In arc magmas H<sub>2</sub>O will be present in non  
2218 negligible molar proportions at all crustal levels (>>10 mol%, Wieser et al. 2023d). Even in CO<sub>2</sub> dominated  
2219 systems (e.g. Hawai'i), exsolved fluids will have substantial proportions of H<sub>2</sub>O in the vapour phase as magmas  
2220 ascend towards the surface. H<sub>2</sub>O can be identified by microthermometry through the appearance of clathrate  
2221 phases, and by Raman spectroscopy through identification of the O-H stretching band at ~3600 cm<sup>-1</sup> (Azbej et  
2222 al., 2007). However, at room temperatures, H<sub>2</sub>O will be present as a thin film of liquid along the edge of the  
2223 inclusion. This can make it very hard to identify by Raman spectroscopy, unless the inclusion is heated to the  
2224 point at which H<sub>2</sub>O dissolves into CO<sub>2</sub> (e.g., to ~150°C, Esposito et al., 2016). It has also been demonstrated that  
2225 this H<sub>2</sub>O film can react with the host crystal or a thin film of melt around the fluid inclusion (Andersen et al.,  
2226 1984; Esposito et al., 2016; Frezzotti et al., 2002), and/or be lost through diffusive re-equilibration with a  
2227 degassed carrier melt (Mackwell and Kohlstedt, 1990). This means it can be hard to identify which FIs had non  
2228 negligible quantities of H<sub>2</sub>O at the time of entrapment.

2229 The presence of other fluid species complicates calculations of pressure in two ways. First, CO<sub>2</sub> densities  
2230 obtained by Raman spectroscopy or microthermometry are normally converted into an entrapment pressure  
2231 using a pure CO<sub>2</sub> EOS, which will deviate from the true relationship defined by a mix of the species of interest.  
2232 Secondly, the reaction of secondary phases to form precipitates on walls, solid crystals, or liquid films means  
2233 that the measured density represents only that of the residual CO<sub>2</sub> fluid phase, not the initial trapped fluid.  
2234 Hansteen and Klugel (2008) discuss possible corrections for mixed fluids in their review (e.g. estimating H<sub>2</sub>O/CO<sub>2</sub>  
2235 ratios, then using a mixed H<sub>2</sub>O-CO<sub>2</sub> EOS). Looking forward, we suggest that further work into mixed fluid  
2236 equation of states and phase diagrams, as well as experiments of fluid inclusion re-equilibration, is required to



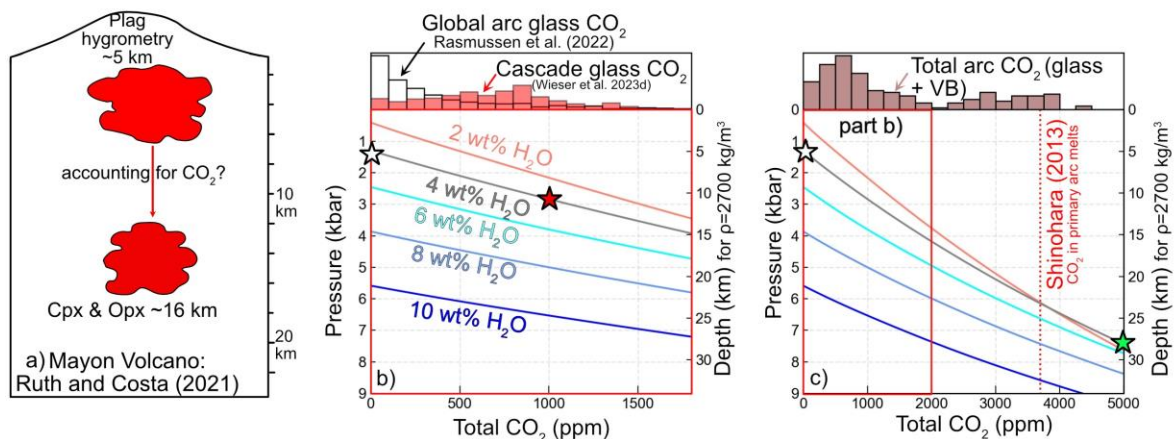
2238  
 2239 *Figure 24: a) Relationship between pressure and the density of a pure CO<sub>2</sub> fluid (calculated using the Span and*  
 2240 *Wagner, 1996 EOS implemented in CoolProp, Bell et al., 2014). Storage depths shown for crustal densities of*  
 2241  *$\rho=2700 \text{ kg/m}^3$ . b) Monte Carlo simulations of  $1\sigma$  errors for different barometry methods resulting from analytical*  
 2242 *uncertainty. Uncertainties calculated using Putirka (2008) eq32d-32b for Cpx-only and eq3 3–30 for Cpx-Liq*  
 2243 *arising from the EPMA analytical uncertainties of Neave et al. (2019, see Wieser et al. 2023b). Melt inclusion*  
 2244 *uncertainties show propagated errors in melt inclusions with vapour bubbles from the 2018 eruption of Kilauea*  
 2245 *(Wieser et al. 2021). The large relative errors ( $\pm 50\%$ ,  $\sim 1\text{--}1.5 \text{ kbar}$ ) arise from reconstructions of the volume of*  
 2246 *the vapour bubble using optical microscopy (with  $z=(x+y)/2$ , after Tucker et al. 2019).  $1\sigma$  errors on calculated*  
 2247 *pressures for 3 FIs trapped at different crustal pressures, assuming an analytical error of  $0.02 \text{ g/cm}^3$  from Raman*  
 2248 *spectroscopy, and uncertainty in  $T$  of  $1\sigma=30 \text{ K}$ . c) Web of Science search for number of articles using each method*  
 2249 *for barometry (full search criteria given in supporting information), and d) number of citations to these articles.*

2250 **5. Can hygrometers be used as barometers?**

2251 At the opposite end of the spectra to determining pressures from fluid inclusions in CO<sub>2</sub>-rich systems,  
 2252 many studies have used melt H<sub>2</sub>O contents to estimate pressures using a pure H<sub>2</sub>O solubility model, either  
 2253 through direct measurements in melt inclusions (e.g., Blundy and Cashman, 2005, Rutherford et al., 1985) or  
 2254 calculated H<sub>2</sub>O contents from mineral and mineral-melt hygrometers (e.g., Amphibole Mg#s – Goltz et al., 2020,  
 2255 Krawczynski et al., 2012, Plag-Liq hygrometry – Ruth and Costa, 2021). For example, Ruth and Costa (2021)  
 2256 conduct thermobarometry on a variety of phases from Mayon Volcano (Fig. 25a). Cpx-Liq, Opx-Liq and Cpx-Opx  
 2257 pressures show a prominent peak at  $\sim 4 \text{ kbar}$  (16 km). In contrast, they invoke a shallower magma reservoir at  $\sim$   
 2258 5 km based on H<sub>2</sub>O-only saturation pressures calculated from plagioclase-liquid hygrometry (and H<sup>+</sup> in  
 2259 pyroxene). However, it is well established that primary arc magmas have non-negligible quantities of CO<sub>2</sub>  
 2260 (Shinohara, 2013; Wallace, 2005). While such H<sub>2</sub>O-only calculations are often quoted as minimum estimates, it  
 2261 is worth questioning whether such minimum estimates are even useful, given that uncertainty in the amount of

2262 CO<sub>2</sub> can change the calculated pressure by up to an order of magnitude (Black and Andrews, 2020; Wieser et al.,  
2263 2022a).

2264 Using a global compilation of CO<sub>2</sub> in the glass phase of melt inclusions (Rasmussen et al., 2020, white  
2265 histogram, Fig. 25b) and a compilation from the Cascade arc (red histogram, Fig. 25b, Wieser et al., 2023d), it is  
2266 apparent that arc magmas have, at the very minimum, several hundred to a thousand ppm of CO<sub>2</sub>. These  
2267 quantities of CO<sub>2</sub> have a very significant effect on the calculated saturation pressures. For example, the H<sub>2</sub>O-only  
2268 saturation pressure of a typical arc basalt with 4 wt% H<sub>2</sub>O (Plank et al., 2013) is ~ 1.3 kbar (white star on grey  
2269 line), while the saturation pressure accounting for 1000 ppm CO<sub>2</sub> is 2.8 kbar (red star on grey line, Fig. 25b). In  
2270 reality, it is becoming apparent that glass-only melt inclusion measurements have substantially underestimated  
2271 the CO<sub>2</sub> content of arc magmas. A compilation of CO<sub>2</sub> contents in arc magmas for studies accounting the vapour  
2272 bubble extends up to ~5000 ppm (Fig. 25c). For a magma with 4 wt% H<sub>2</sub>O, a H<sub>2</sub>O-only saturation pressure  
2273 underestimates the true storage depth of a magma with 5000 ppm CO<sub>2</sub> by a factor of 5.7X (Fig. 25c, white star  
2274 vs. green star). While H<sub>2</sub>O depths are indeed minimum estimates, this example shows just how misleading they  
2275 can be. Even for a magma with 10 wt% H<sub>2</sub>O, H<sub>2</sub>O-only pressures underestimate by factors of ~1.8X if there is  
2276 5000 ppm CO<sub>2</sub>. Thus, we speculate in many cases that accounting for CO<sub>2</sub> will push hygrometry estimated magma  
2277 storage pressure substantially deeper, perhaps more in line with other barometry estimates (Fig. 25a).



2278  
2279 *Figure 25: Sensitivity of saturation pressures to CO<sub>2</sub> contents. a) Schematic model of plumbing system at Mahon*  
2280 *Volcano, adapted from Ruth and Costa (2021), where the depth of the shallower reservoir was calculated using*  
2281 *a H<sub>2</sub>O-only solubility model. b-c) Increase in saturation pressure with CO<sub>2</sub> for 5 different H<sub>2</sub>O contents (for a*  
2282 *typical mafic Cascade melt composition, SiO<sub>2</sub>=54.3 wt%), calculated using the solubility MagmaSat (Ghiorso and*  
2283 *Gualda, 2015) in VESical (Iacovino et al., 2021). The histograms in b) show a global compilation of arc CO<sub>2</sub>*  
2284 *contents just measuring the glass phase (Rasmussen et al., 2022), and a compilation from the Cascade Arc. c)*  
2285 *Expanded x scale (region shown in b) indicated in the red box) up to 5000 ppm CO<sub>2</sub>. Histogram shows a compilation*  
2286 *of total arc CO<sub>2</sub> accounting for the vapour bubble through Raman spectroscopy or homogenization (from Mironov*  
2287 *et al., 2015; Moore et al., 2018, Rasmussen et al., 2020). We overlay the estimate of primitive arc magma CO<sub>2</sub>*  
2288 *contents from Shinohara (2013).*

2289 Therefore, we suggest that H<sub>2</sub>O-only saturation pressures should only be used in systems where it has been  
2290 demonstrated that very little CO<sub>2</sub> is present, in the same way that fluid inclusion barometry using the pure CO<sub>2</sub>  
2291 EOS can only be used in systems where there is very little H<sub>2</sub>O in the fluid phase. In more CO<sub>2</sub>-rich systems,  
2292 saturation pressure calculations should be performed for a wide range of possible CO<sub>2</sub> contents to determine  
2293 the uncertainty associated with H<sub>2</sub>O-only saturation pressures.

## 2294 6. Elastic Thermobarometry/Thermoba-Raman-try

2295 While the thermobarometric methods discussed thus far rely on changes in the chemistry of minerals,  
2296 melts and fluids as a function of P and T, elastic thermobarometry relies on relative changes in the physical  
2297 properties of inclusions and their hosts with changing P and T (Kohn et al. 2023, Cisneros and Befus, 2021). At  
2298 the time of mineral growth and entrapment, a host-inclusion pair have the same pressure. However, after  
2299 entrapment, the different thermal expansivity (change in volume with T) and compressibility (change in volume  
2300 with P) of the two mineral species means that a residual pressure develops as the pair cool and/or ascend to the  
2301 surface. This pressure can be deduced from the band/peak positions of minerals measured by Raman  
2302 Spectroscopy, leading Kohn (2014) to term this method Thermoba-Raman-try! The magnitude of the residual

2303 pressure depends on the P-T path taken (see Fig. 1 from Kohn, 2014). The final stress measured in the inclusion  
2304 is a function of the initial P-T conditions of trapping, and the influence of differential contraction of the host-  
2305 mineral pair, which can be modelled using knowledge of expansivity and incompressibility of different mineral  
2306 species (Kohn, 2014). The most effective barometers are those where there is a large difference between the  
2307 isothermal compressibility of the inclusion and host (i.e., changes in volume during pressure changes), while the  
2308 most effective thermometers are those with the largest variations in isobaric expansivity (i.e., changes in volume  
2309 during temperature changes, Kohn, 2014, Kohn et al. 2023).

2310 Useful host-inclusion pairs are those with large differences in physical properties. There are a number  
2311 of barometers using quartz inclusions, because these have a very different compressibility to host minerals such  
2312 as zircon, lawsonite, and garnet (Kohn et al. 2023). Diamond is another popular host (e.g. Smith et al. 2022),  
2313 along with garnet and zircon (e.g. olivine inclusions in diamond, coesite-in-diamond, and coesite-in-zircon, Kohn,  
2314 2014, Cisneros and Befus, 2020). Thermobarometry techniques can be remarkably precise; the estimated  
2315 error in calculated pressure for Qtz-in-Gt inclusions is 0.3–0.5 kbar, resulting from uncertainty in the Raman  
2316 band position of  $0.5 \text{ cm}^{-1}$  (Kohn, 2014). However, in general this technique has been applied to higher pressure  
2317 systems where these phases are common (e.g. mantle rocks, metamorphic systems, xenoliths). Less attention  
2318 has been paid to typical phases present in samples used to address volcanological research questions.

2319 Befus et al. (2018) state that they provide the first elastic thermobarometer in igneous systems, by  
2320 performing diamond anvil experiments on feldspar from atmospheric pressure to 3.6 GPa, and characterising  
2321 the Raman bands. They find a clear shift of peak positions to higher pressure from 0 to  $\sim 30$  kbar, with Raman  
2322 shifts of the band at  $\sim 485 \text{ cm}^{-1}$  of  $\sim 0.42 \text{ cm}^{-1}$  per kbar for Albite,  $0.45 \text{ cm}^{-1}$  per kbar for andesine, and  $0.31 \text{ cm}^{-1}$   
2323 per kbar for anorthite. Their calibrations relating peak position with pressure could be applied to natural  
2324 feldspar inclusions (e.g. Fsp in Cpx, Fsp in Ol, etc.) with known compositions, using models of host-inclusion  
2325 relaxation along a PT path. They suggest that the main limitation of applying this technique to shallower crustal  
2326 systems where peak shifts are rather small is the limited spectral resolution of many Raman spectrometers ( $\sim 1$   
2327  $\text{cm}^{-1}$ ). However, the most recent generation of Raman spectrometers have improved spectral resolution ( $0.1$ –  
2328  $0.4 \text{ cm}^{-1}$ ). Additionally, Befus et al. (2018) fit a cubic spline to the Raman data. If the peak shape can be  
2329 determined (i.e. a Lorentzian or Gaussian), peak fitting can achieve significantly higher precision than the spectra  
2330 resolution (Yuan and Mayanovic, 2017). This increase in spectral resolution accompanying peak fitting is vital for  
2331 precise quantification of  $\text{CO}_2$  densities using Raman spectroscopy. For example, a WITTEC alpha300R Raman has  
2332 a spectra resolution of  $0.57 \text{ cm}^{-1}$  using the 1800 grating. However, the peak fitting error on the  $\text{CO}_2$  peaks using  
2333 a pseudovoigt ranges from  $0.002$ – $0.05 \text{ cm}^{-1}$  (error quantified in lmfitt implemented in DiadFit, Newville et al.,  
2334 2016; Wieser and DeVitre, 2023).

2335 To further broaden the scope of the elastic thermobarometry method, Kohn (2014) evaluate 48  
2336 inclusion-host pairs and Cisneros and Befus (2020) consider  $>5000$  pairs, highlighting a number of inclusion-host  
2337 pairs that may provide useful P-T constraints in volcanic systems (e.g., magnetite in olivine, feldspar in pyroxene,  
2338 feldspar in olivine). Despite the potential of this method, in the 5 years that have passed since Befus et al. (2018)  
2339 and 3 years since Cisneros and Befus (2020), none of the citing studies are focused on volcanic rocks. Kohn et al.  
2340 (2023) and Cisneros and Befus (2020) identify numerous roads for improvement of the elastic thermobarometry  
2341 method, including the need for measurements of elastic properties at the P-T conditions of interest, calibrations  
2342 of Raman shift as a function of pressure, models for inelastic processes, nonideal geometries, and a better  
2343 understanding of the effects of anisotropy on ideal P. Hopefully, the recent proliferation of interest and expertise  
2344 in Raman spectroscopy by igneous petrologists measuring vapour bubbles should aid such efforts.

2345

## 2346 7. Experimental Petrology

2347 Experimental petrology fundamentally underpins the melt inclusion, mineral-melt thermobarometry,  
2348 and elastic thermobarometry methods discussed so far, because the composition of experimental products are  
2349 used to calibrate models. However, experimental petrology can also be used directly to investigate magma  
2350 storage conditions in a specific system. Generally, such experiments use a starting composition characteristic of  
2351 a specific volcanic system or eruption, and perform experiments at a range of P, T,  $\text{H}_2\text{O}$  and  $f\text{O}_2$  conditions. Then,  
2352 experimental phase compositions are compared to natural samples to determine the most probable storage  
2353 conditions (e.g., comparing glass compositions, mineral core and rim conditions, occurrence of breakdown  
2354 reactions; First et al., 2021; Rutherford et al., 1985; Weber and Castro, 2017).

2355 For example, Voigt et al. (2022) perform experiments at  $0.25$ – $5$  kbar and  $850$ – $1100^\circ\text{C}$  on natural starting  
2356 materials from the 1257 Samalás eruption. They observe plagioclase and amphibole in their samples, so the PT  
2357 space between amphibole breakdown and plagioclase instability places constraints on pre-eruptive PT  
2358 conditions. Generally, once a stability region is identified, additional constraints are required to narrow down

2359 the magma storage conditions (Bohrson and Clague, 1988). For example, Cadoux et al. (2014) overlay Fe-Ti oxide  
2360 temperatures on their phase diagrams, concluding that the observed phase assemblage at Santorini is recreated  
2361 experimentally at 2 and 4 kbar.

2362 When performing experiments to deduce magma storage conditions at a given volcano, there can be a  
2363 very large solution space to explore, in terms of pressure, temperature, and  $fO_2$ . If a natural Cpx has  
2364 compositional similarities to one grown experimentally at a specific set of conditions, it is difficult to quantify  
2365 the true uncertainty on storage conditions without exploring a very large number of experimental conditions to  
2366 determine whether a very similar composition may appear at a different set of P-T- $fO_2$  conditions, particularly  
2367 from a slightly different bulk composition). It is also vital to consider the composition of the fluid phase, which  
2368 is often described in terms of the partial pressure of  $H_2O$  ( $P_{H_2O}$ ) or the mole fraction of  $H_2O$  in the starting  
2369 composition or exsolved fluid phase ( $X_{H_2O}$ ). In order to reduce the size of one variable of the solution space,  
2370 many experiments are performed at water-saturated conditions (i.e.,  $X_{H_2O}=1$ , Blatter and Carmichael, 2001; First  
2371 et al., 2021; Grove et al., 1997; Nakatani et al., 2022; Sisson and Grove, 1993; Voigt et al., 2022). However, many  
2372 natural systems do not contain enough  $H_2O$  to be volatile saturated at high pressures, or contain relatively large  
2373 amounts of  $CO_2$ , meaning the system is volatile saturated in a fluid with  $X_{H_2O}<1$ . Experiments with  $H_2O$  below the  
2374 quantity required for  $H_2O$  saturation have been performed (e.g., Kawamoto, 1996), as have experiments in  
2375 equilibrium with mixed  $CO_2$ - $H_2O$  fluids (e.g., Alonso-Perez et al., 2009; Cadoux et al., 2014), although these are  
2376 less common than pure  $H_2O$ -saturated experiments.

2377 Interestingly, there are many reports in the literature of phase stability being affected by  $X_{H_2O}$ . For  
2378 example, Keppler (1989) investigate solidus temperatures in the haplogranite system, and find that the solidus  
2379 position varies as a function of the fluid phase composition for a mix of  $H_2O$  and  $CO_2$ . However, if  $X_{H_2O}$  is reduced  
2380 by the addition of  $N_2$  instead, this relationship is not seen. These experiments indicate that at  $X_{H_2O}$  close to 1,  
2381  $CO_2$  is not just acting as an inert component to reduce the activity of  $H_2O$ , but is modifying the structure of the  
2382 melt. Rutherford et al. (1985) also note that experiments where  $X_{H_2O}$  is reduced by the presence of  $H_2$  are not  
2383 directly comparable to those where it is reduced by  $CO_2$  (e.g., the addition of  $CO_2$  is not simple Henry's law  
2384 behaviour).

2385 It has been shown numerous times that  $CO_2$  affects the stability of amphibole. Given the increasing  
2386 amounts of  $CO_2$  being measured in melt inclusions in mafic arc magmas (Fig. 19), it is highly likely that the  
2387 majority of high Mg# amphiboles examined at the surface formed in a system with  $X_{H_2O} \ll 1$ . For example, Ridolfi  
2388 et al. (2010) suggested that large amounts of  $CO_2$  in a relatively high T igneous system with relatively low  
2389 amounts of  $H_2O$  stabilizes OH- bearing phases such as amphibole. They suggest this may occur because of  
2390 increasing solubility of OH- in the melt with increasing  $CO_2$  dissolution (King and Holloway, 2002 suggest a  
2391 reaction where molecular  $CO_2$  and  $H_2O$  react to form carbonate and OH<sup>-</sup>). Ridolfi et al. (2010) note that the  
2392 paucity of magnesiohastingsite amphiboles in predominantly  $H_2O$ -saturated experiments may indicate that  
2393 these compositions only form at high T and high  $CO_2$  contents. Krawczynski et al. (2012) also find amphibole is  
2394 stabilized at a higher temperature, with a lower Mg# in experiments with more  $CO_2$ .

2395 In their experiments on the Mt. St. Helens dacite, Rutherford et al. (1985) find radical changes in the  
2396 crystallization temperature of different phases as  $CO_2$  is added, reducing  $P_{H_2O}$  at a constant  $P_{total}$ ; Plag, Px and  
2397 Fe-Ti oxides crystallization temperatures increase, while the amphibole liquidus temperatures decrease.  
2398 Additional experiments by Rutherford and Devine (1988) confirm that the observed phase stability is produced  
2399 experimentally at 920°C,  $P=220$  Mpa, and  $X_{H_2O}=0.67$ . Rader and Larsen (2013) perform experiments on low MgO  
2400 basaltic-andesites to constrain the impact of small amounts of  $CO_2$ , running experiments at a range of T (90–  
2401 1200°C) and P (0.001–1.8 kbar) at both  $X_{H_2O}=1$  and  $X_{H_2O} \sim 0.7$ . They found that the plagioclase stability curve was  
2402 the most sensitive to  $X_{H_2O}$ , shifting 25°C for  $X_{H_2O} \sim 0.7$ . They also observe shifts in amphibole stability. Finally,  
2403 Cadoux et al. (2014) found that at 850°C and 4 kbar, there was more amphibole present when  $X_{H_2O}$  was 0.9 than  
2404 1. They also find changes in the stability of both pyroxenes, ilmenite and plagioclase, as well as the liquidus phase  
2405 with changes in  $X_{H_2O}$ . In particular, they find that orthopyroxene is generally not stable where  $X_{H_2O}=1$  at 2–4 kbar.

2406 In summary, these experiments show that  $X_{H_2O}$  is clearly a very important variable to investigate in  
2407 further experiments, and comparison of natural samples to experimental products should factor in possible  
2408 differences in  $X_{H_2O}$ . We believe this avenue of investigation is particularly important given the last decade of  
2409 Raman work has clearly demonstrated that mafic arc magmas, have substantially more  $CO_2$  (and thus a lower  
2410  $X_{H_2O}$  ratio) than previously thought.

2411

## 2412 **8. Thermobarometers based on thermodynamic modelling**

2413 Thermodynamic modelling is a powerful tool in igneous systems for exploring various hypotheses, such as  
2414 whether the chemical variations in a suite of lavas can be produced by equilibrium or fractional crystallization  
2415 alone, or whether processes such as crustal melting/assimilation are required (Heywood et al., 2020). However,  
2416 in addition to general hypothesis testing, thermodynamical models have also been used to place quantitative  
2417 constraints on magma storage conditions. Two main methods are discussed below, matching liquid lines of  
2418 descent to erupted lava compositions, and multiphase saturation methods.

### 2419 **8.1 Liquid lines of descent**

2420 One method to determine magma storage conditions compares fractional crystallization models  
2421 conducted at different conditions (e.g.,  $P$ ,  $fO_2$ , melt  $H_2O$  content) to observed liquid lines of descent (LLD, e.g.,  
2422 whole-rock XRF, glass EPMA data). Magma storage conditions in the system of interest are inferred from the  
2423 model conditions providing the best fit to natural data. Comparison of observed and modelled LLDs have been  
2424 used to deduce storage conditions in explosive silicic eruptions (e.g., the Campanian Ignimbrite, Campi Flegrei,  
2425 Fowler et al., 2007, Bishop Tuff, Long Valley Caldera, Fowler and Spera, 2010), in trachytes and pantellerites of  
2426 the East African Rift (Gleeson et al., 2017; Hutchison et al., 2018; Peccerillo, 2003; Ronga et al., 2010), in  
2427 peralkaline rhyolites from Atlantic Ocean hotspots (Jeffery et al., 2017, 2016), and in basalts from Mauna Loa  
2428 (Gaffney, 2002).

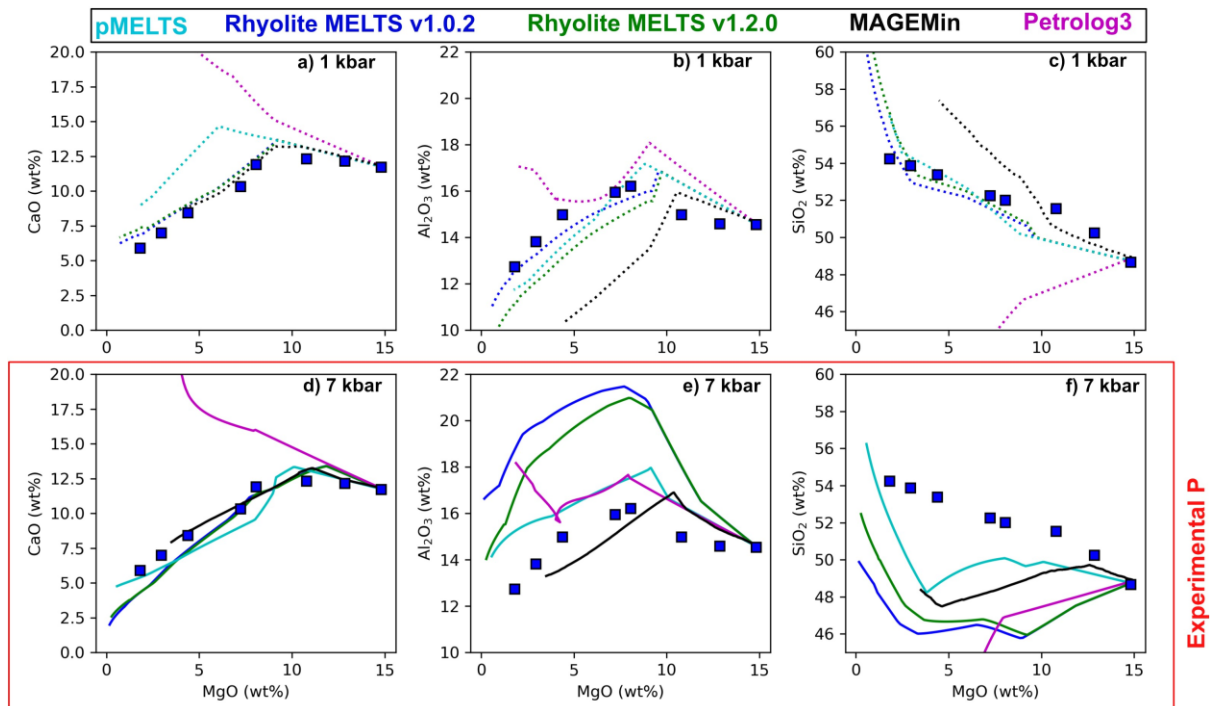
2429 LLD methods are typically performed in MELTS, but other tools for modelling fractional crystallization  
2430 such as COMAGMAT or Petrolog3 could also be used (Ariskin et al., 1993; Danyushevsky and Plechov, 2011). The  
2431 best fit model is often determined by visual comparison between model outputs and natural samples (e.g.,  
2432 Fowler et al. 2007), although statistical methods have also been used. For example, Gleeson et al. (2017) develop  
2433 an algorithm to calculate the smallest misfit between each datapoint and the modelled LLD path for each MELTS  
2434 model. They combine the residuals of all individual samples into a weighted RMSE offset for each model.

2435 In certain situations, storage conditions determined by LLD methods are supported by independent  
2436 lines of evidence. For example, there is a close agreement between the depths of magma storage estimated by  
2437 MELTS modelling and geophysical estimates of magma storage depths in the East African Rift (Hutchison et al.  
2438 2016; Gleeson et al. 2017), and between MELTS-estimated  $fO_2$  and experiment constraints (Scaillet and  
2439 Macdonald, 2001). However, as pointed out by Gleeson et al. (2017), even the best-fit models display systematic  
2440 offsets between the MELTS predictions and the natural data for certain oxides (e.g., CaO,  $P_2O_5$ ). These offsets  
2441 indicate that there are several inaccuracies or omissions in the MELTS thermodynamic models (e.g. absence of  
2442 amphibole or biotite in calc-alkaline magmas) that present severe limitations for the use of MELTS-based  
2443 crystallisation models as a thermobarometric technique.

2444 In most cases, MELTS correctly identifies the directionality caused by changing  $P$ ,  $H_2O$ , or  $fO_2$  on the LLD  
2445 (e.g. enhancing or suppressing the stability of a given mineral). However, it is unclear whether the predicted  
2446 mineral stability for a given value of  $P$ ,  $H_2O$ , or  $fO_2$  is correct, or whether it is just relative differences that are  
2447 trustworthy. While MELTS modelling may be able to distinguish a dry vs. wet LLD, it may not be able to determine  
2448 whether a magma has 0.1 or 0.6 wt%  $H_2O$ . It has been shown that MELTS models at Kilauea Volcano must be  
2449 run with melt  $H_2O$  contents below those measured in melt inclusions to recreate the MgO content at which  
2450 plagioclase and Fe-Ti oxide crystallize (Garcia, 2003; Wieser et al., 2022c). If  $H_2O$  contents were not  
2451 independently constrained, such models could lead to incorrect inferences about the hydration state of magmas  
2452 at this volcano.

2453 To assess LLD methods further, we compare the measured composition of experimental liquids  
2454 produced during fractional crystallisation experiments on a  $H_2O$ -poor tholeiitic basalts to MELTS crystallisation  
2455 models (Villiger et al., 2007). We run a fractional crystallization model at the specified experimental pressure (7  
2456 kbar),  $fO_2$  and  $H_2O$  content. We also run models at pressures of 1, 4 and 10 kbar (Fig. 26a, Supporting Figs. 11–  
2457 13). We use three different MELTS versions (pMELTS, rhyolite-MELTS v1.0.2 and v1.2.0), Petrolog3  
2458 (Danyushevsky and Plechov, 2011), and MAGEMin (Riel et al., 2022) using the Holland et al. (2018)  
2459 thermodynamic database. Both versions of rhyolite-MELTS show a very poor fit at the experimental pressure,  
2460 predicting extensive  $Al_2O_3$  enrichment and  $SiO_2$  depletion relative to the experimental products (dark blue and  
2461 green lines, Fig. 26e-f). The fit is far better at 1 kbar, which could lead to anomalous inferences of magma storage  
2462 pressures using LLD methods. pMELTS (which has a different liquid model to rhyolite-MELTS) doesn't show such  
2463 extreme  $Al_2O_3$  enrichment at the experimental pressure, but the fit for  $Al_2O_3$  is still better at 4 kbar than 7 kbar,  
2464 and the fit for  $SiO_2$  is best at 1–4 kbar (cyan lines). Petrolog3 shows anomalous  $SiO_2$  depletion at all pressures  
2465 (magenta lines, Fig. 26), and none of the 4 pressures used here provide a satisfactory fit to most elements

2466 (Supporting Fig. 11). The Holland et al. (2018) database, implemented through MAGEMin, certainly does the  
 2467 best job of recreating Al<sub>2</sub>O<sub>3</sub> systematics at experimental pressures (Fig. 26e), although the fit to SiO<sub>2</sub> is far better  
 2468 at 4 kbar than 7 kbar (black lines, Fig. 26, Supporting Fig. 11).

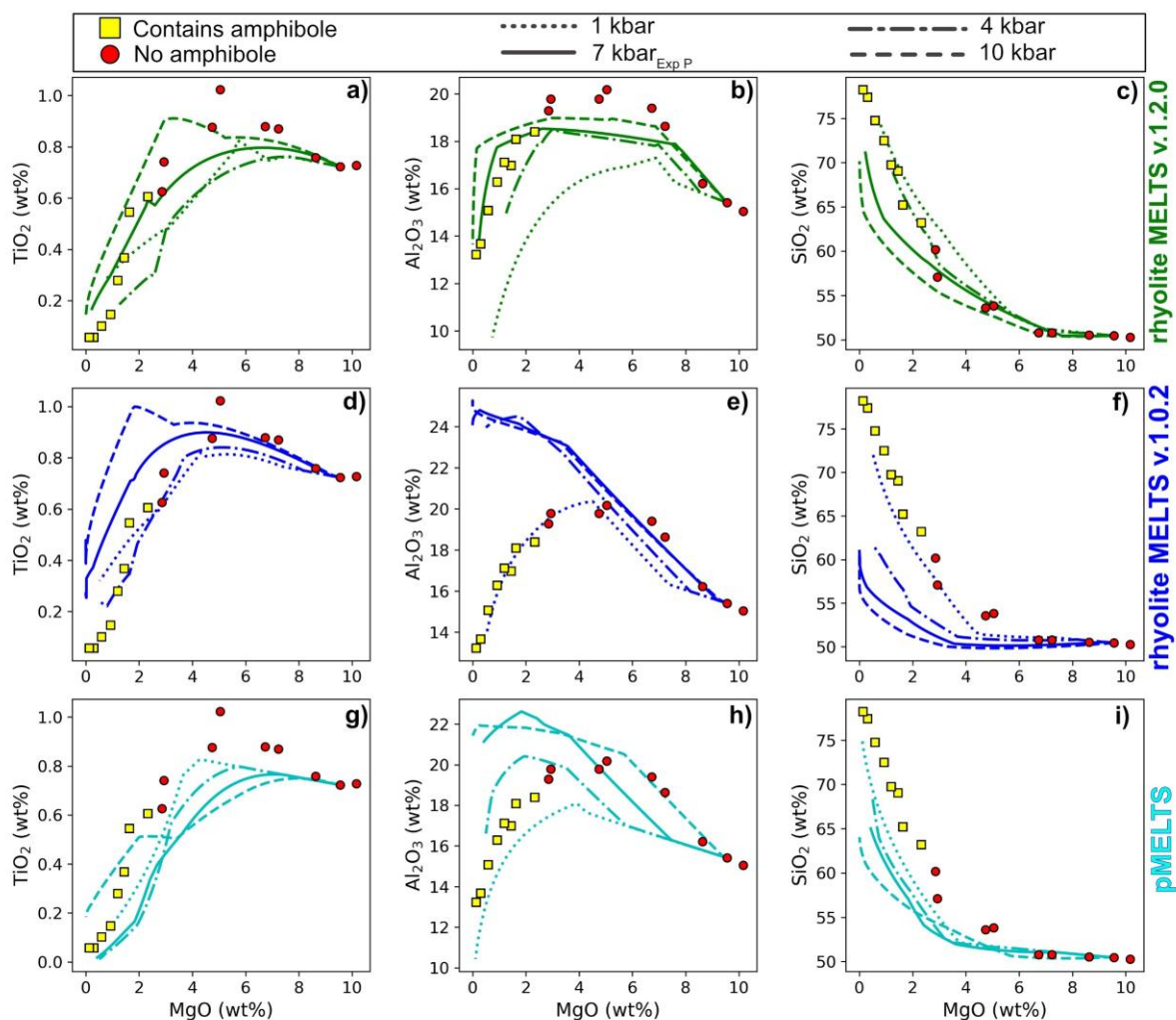


2469  
 2470 *Figure 26 – Comparison of fractional crystallisation models run in rhyolite-MELTS, pMELTS, Petrolog3 and*  
 2471 *MageMin (using the Holland et al. 2018 database) to fractional crystallization experiments from a nominally*  
 2472 *anhydrous, tholeiitic basalt from Villiger et al. (2007). MELTS calculations are performed at the experiment  $f_{O_2}$*   
 2473 *(NNO), with  $H_2O=0.2$  wt% (i.e. nominally anhydrous). While experiments were conducted at 7 kbar (solid lines),*  
 2474 *models run at 1–4 kbar provide a much better fit (particularly regarding the onset of plagioclase). Other pressures*  
 2475 *shown in Supporting Fig. 11.*

2476 To further assess LLD methods, we use all three MELTS versions to model the fractional crystallization  
 2477 experiments of Nandedkar et al. (2014) conducted on a hydrous arc basalt (Fig. 27). The hydrous nature of these  
 2478 experiments means that the differences between rhyolite-MELTS v1.2.0 and v1.0.2 are far more noticeable  
 2479 compared to the H<sub>2</sub>O-poor experiments of Villiger et al. (2007). Using v1.2.0, models run at 4 to 10 kbar provide  
 2480 a reasonable match to observed oxide contents. In contrast, using v1.0.2, models run at 1 kbar provide the best  
 2481 fit to both SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It is concerning that these models give such different results, given they are used  
 2482 somewhat interchangeably in the literature, and obviously, any studies conducted prior to the release of v1.2.0  
 2483 in 2015 must have used v1.0.2. pMELTS shows behaviour between the two rhyolite-MELTS models, with trends  
 2484 best recreated at 1–4 kbar.

2485 These comparisons to two experimental studies demonstrate that the pressure you would deduce from LLD  
 2486 methods is very sensitive to both the choice of model and the oxides used for assessment of the ‘best model’.  
 2487 In neither comparison does the experimental pressure stand out as the best model fit. It is also worth noting  
 2488 that for both these examples, we are using known  $f_{O_2}$  and H<sub>2</sub>O contents. In reality, it is likely that P,  $f_{O_2}$ , and  
 2489 H<sub>2</sub>O are all uncertain, which leaves a very large solution space to explore (and can result in even greater  
 2490 ambiguity regarding the best fit model). Overall, we conclude that in their current state, LLD methods are not a  
 2491 reliable way to deduce storage pressure, particularly given the result can differ so much simply based on the  
 2492 choice of fractional crystallization model. It may be that an update of the MELTS liquid model, and/or tweaks to  
 2493 the thermodynamic data controlling the mineral stability fields (as performed for the qtz-2 fspar ternary) can  
 2494 revive this method. These comparisons also demonstrate that it is absolutely vital for papers to state the version  
 2495 of MELTS that they used.





2496

2497 *Figure 27 – Comparison of fractional crystallization experiments from Nandedkar et al. (2014) at 7 kbar to MELTS*  
 2498 *fractional crystallization models run using three different versions. Experiments containing amphibole are shown*  
 2499 *in yellow, those without amphibole in red. Models were run at the experimental  $fO_2$  and  $H_2O$  contents, at 1, 4, 7*  
 2500 *(Exp P) and 10 kbar. MELTS models run in pyMELTScalc using alphaMELTS for Python (Gleeson et al., 2023,*  
 2501 *Antoshechkina and Ghiorso, 2018).*

## 2502 8.2 Multi-phase saturation

2503 As discussed in Section 2.2, pressure influences the location of mineral cotectics and eutectics. Under  
 2504 the assumption that the measured composition of a multi-phase saturated melt might contain information  
 2505 about the pressure of the system, rhyolite-MELTS has been used to address the crystallisation pressure of silicic  
 2506 and intermediate magmas that are co-saturated in quartz+feldspar (Bégué et al., 2014; Gualda et al., 2019;  
 2507 Gualda and Ghiorso, 2014; Pamukcu et al., 2015), feldspar+orthopyroxene±quartz (Pamukcu et al., 2021) or  
 2508 plagioclase+clinopyroxene+orthopyroxene (Harmon et al., 2018).

2509 Specifically, these methods work by performing crystallisation calculations at several discrete pressures  
 2510 (and a specified  $H_2O$  and  $fO_2$  value). T is progressively dropped from the liquidus, and the appearance of different  
 2511 phases is tracked. Mineral saturation curves (see Fig. 28a-b) are determined from these individual isobaric  
 2512 crystallization calculations. A residual is defined as the maximum temperature difference between the  
 2513 saturation curves of the phases of interest ( $\Delta T$ , Fig. 28c). In many cases, the mineral saturation curves never  
 2514 intersect exactly at a single point, so the best fit pressure is calculated from the minimum point on the residual  
 2515 curve. A solution is only considered valid if the residual T gets within a pre-specified threshold value of a perfect  
 2516 intersection (e.g., 5°C for quartz – plagioclase – alkali-feldspar equilibrium; Gualda and Ghiorso, 2014). This  
 2517 threshold varies - in their application of this method to Plag-Opx-Cpx equilibrium, Harmon et al. (2018) compare  
 2518 experimental pressures to calculated pressures with minimum residuals from 16–121°C.

2519 One complication of these methods is that the position of saturation curves is not just influenced by  
2520 pressure, but also  $fO_2$  and melt  $H_2O$  content. This means for natural samples; calculations must be repeated at  
2521 different melt  $fO_2$  and  $H_2O$  contents to identify the location of the minimum T offset in multivariate P- $fO_2$ - $H_2O$   
2522 space. In an ideal world, this would mean that MELTS could be used simultaneously as a barometer,  
2523 oxybarometer, and hygrometer. However, in reality, this very large solution space can result in substantial errors  
2524 which do not reproduce the true conditions for P,  $fO_2$ , or  $H_2O$ .

### 2525 **8.2.1 Quartz – 2 Feldspar MELTS barometry**

2526 Interest in using the co-saturation of quartz, plagioclase and alkali feldspar to help constrain pressure  
2527 (Gualda and Ghiorso, 2014) led to a substantial update to the MELTS algorithm in 2012. To recreate the near  
2528 invariant behaviour of pumice and melt inclusion compositions from the early erupted Bishop Tuff which have  
2529 major and trace element systematics indicating a low degree of freedom, Gualda et al. (2012) tweaked the  
2530 enthalpy of formation of quartz and the potassic endmember in the alkali-feldspar solid-solution (Gualda et al.  
2531 2012, rhyolite-MELTS v1.0.2). Using this new model, and the residual T method described above, Gualda and  
2532 Ghiorso (2014) estimated storage pressures for a variety of quartz-saturated rhyolites. They compared these  
2533 MELTS pressures to  $H_2O$ - $CO_2$  saturation pressures from the Bishop Tuff (Anderson et al., 2000), the Younger  
2534 Toba Tuff (Chesner and Luhr, 2010) and the Mamaku Ignimbrite (Bégué et al., 2014), and found a close  
2535 agreement. Based on the results in Fig. 10 of Gualda and Ghiorso (2014), we calculate an  $R^2$  of 0.75 and RMSE  
2536 of 0.38 kbar for N=30 melt inclusions when performing a linear regression between the two pressure methods.  
2537 However, it is worth noting N=17 of these inclusions are from the Bishop Tuff, which was used as a reference  
2538 point for the tweaking of the rhyolite-MELTS model calibration (Gualda et al. 2012).

2539 The rhyolite-MELTS quartz-feldspar barometers have since been applied to several other systems  
2540 worldwide. This includes the application of quartz-plagioclase barometry to rhyolitic eruptions of the Taupo  
2541 Volcano Zone, New Zealand (Bégué et al., 2014), and quartz - 2 feldspar barometry on the matrix glass of the  
2542 Peach Spring Tuff, USA (Pamukcu et al., 2015). Results indicate spatial and/or temporal variations in the magma  
2543 storage conditions beneath the Taupo Volcanic Zone, as well as correlations between rhyolite  $SiO_2$  contents and  
2544 pressure (Bégué et al., 2014; Pamukçu et al., 2020). However, these papers have been the subject to a number  
2545 of comment-reply articles (e.g., Wilson et al., 2021, Pamukçu et al., 2021). Most notably, Wilke et al. (2017)  
2546 question the accuracy of the rhyolite-MELTS barometer following comparison of the results of the rhyolite-  
2547 MELTS geobarometer with their new empirical expression for the pressure of quartz+feldspar saturated liquids.  
2548 The Wilke et al. (2017) method, termed DERP (Determining Rhyolitic Pressures), is based on experiments on  
2549 haplogranitic compositions which examine the influence of melt  $H_2O$  content (or activity) and the normative  
2550 melt An content (largely determined by the CaO content of the liquid) on the quartz+feldspar saturation surface.  
2551 Comparison of rhyolite-MELTS and DERP barometric results for melt-inclusions and matrix glasses from the  
2552 Taupo Volcanic Zone and Peach Spring Tuff revealed a large offset between the two methods, with DERP typically  
2553 returning pressures around twice as large as those from rhyolite-MELTS. The pressure discrepancy between the  
2554 two methods correlates with the normative melt An content (a key part of the new DERP parameterisation).  
2555 Thus, Wilke et al. (2017) suggest that rhyolite-MELTS may underestimate magma storage pressures in Ca-bearing  
2556 rhyolites.

2557 The relative performance of DERP and rhyolite-MELTS was revisited by Gualda et al. (2019b), who  
2558 argued that the use of multi-linear fits in DERP to determine the influence of P, An content and  $H_2O$  on the quartz  
2559 – 2 feldspar thermal minimum results in a functional form that is thermodynamically impossible. As a result,  
2560 extrapolation of the DERP barometer outside the range of the calibration data could lead to systematic errors.  
2561 Gualda et al. (2019b) also question the use of TitaniQ as an independent barometer to compare to the results  
2562 from DERP in Wilke et al. (2017), as the Ti content in quartz is influenced by a wide number of parameters,  
2563 including the mineral growth rate and melt Ti activity, which may limit its use as a geobarometer (see section  
2564 2.11). To assess the performance of the 2 barometers in natural systems, Gualda et al. (2019b) compare the  
2565 results derived from the DERP and rhyolite-MELTS barometers to independent pressure estimates from  $H_2O$ -  
2566  $CO_2$  saturation in melt inclusions and amphibole thermobarometry. In general, the barometric estimates  
2567 provided by rhyolite-MELTS are in good agreement with the independent pressure estimates. DERP-derived  
2568 pressures are typically more scattered and often higher than those derived from melt inclusion or amphibole  
2569 thermobarometry. However, given the issues with amphibole barometry discussed in section 2.6, such  
2570 comparisons should perhaps be interpreted with caution.

2571 Wilke et al. (2019) responded by stating that the large range of pressured estimated by the DERP  
2572 barometer in Gualda et al. (2019b) result from its sensitivity to glass  $Na_2O$  and  $K_2O$  contents, which are used to  
2573 calculate the normative Qz, Or, and Ab values. Wilke et al. (2019) suggest that in hydrous rhyolitic glasses where

2574 alkali migration during analysis is a serious issue, DERP should only be used to estimate storage pressures when  
2575 data quality is assured. Furthermore, Wilke et al. (2019) note that the experimental compositions used to  
2576 calibrate the DERP barometer all contain normative corundum, meaning that all CaO in the glass is used to  
2577 calculate the normative An content. In many natural samples, such as the Peach Spring Tuff used by Pamukcu  
2578 et al. (2015), lower Al<sub>2</sub>O<sub>3</sub> contents lead to the presence of Wollastonite in the normative mineral assemblage,  
2579 complicating the determination of the normative melt An content. As normative Wollastonite is not accounted  
2580 for in the DERP calibration, this could explain the offset between the two barometers and indicates that DERP  
2581 should only be used in systems where Corundum appears in the normative mineral assemblage.

2582 Therefore, for most natural samples where Wollastonite is present in the normative mineral  
2583 assemblage, the rhyolite-MELTS geobarometer might be more reliable than empirically calibrated alternatives  
2584 like DERP. Nevertheless, questions regarding the application of the rhyolite-MELTS barometer to natural systems  
2585 still remain, especially as the test datasets used to evaluate this barometer have largely relied on data from the  
2586 Bishop Tuff (part of the 2012 recalibration). In addition, inclusion of the updated H<sub>2</sub>O-CO<sub>2</sub> model of Ghiorso and  
2587 Gualda (2015) in the rhyolite-MELTS calculations (i.e., rhyolite-MELTS v1.2.0) shifts the quartz and sanidine  
2588 stability field to such an extent that 3-phase saturation cannot be simulated at any pressure for the compositions  
2589 of Gualda and Ghiorso (2014) and Pamukcu et al. (2015). This indicates a further update to the quartz + sanidine  
2590 ± plagioclase thermodynamic properties is necessary to align with the most recent volatile solubility model, so  
2591 that users do not need to perform calculations for magmas that are typically saturated in a mixed H<sub>2</sub>O-CO<sub>2</sub> fluid  
2592 phase using an outdated H<sub>2</sub>O solubility model (Ghiorso et al. 1995). We are not aware of any new experiments  
2593 that can be used as an independent test dataset for resolving the rhyolite-MELTS vs. DERP debate, and to gain a  
2594 better understanding of the errors involved. Further experiments in this compositional range will be vital to  
2595 move this approach forward in a rigorous manner.

#### 2596 **8.2.2 Plagioclase – 2 pyroxene MELTS barometry**

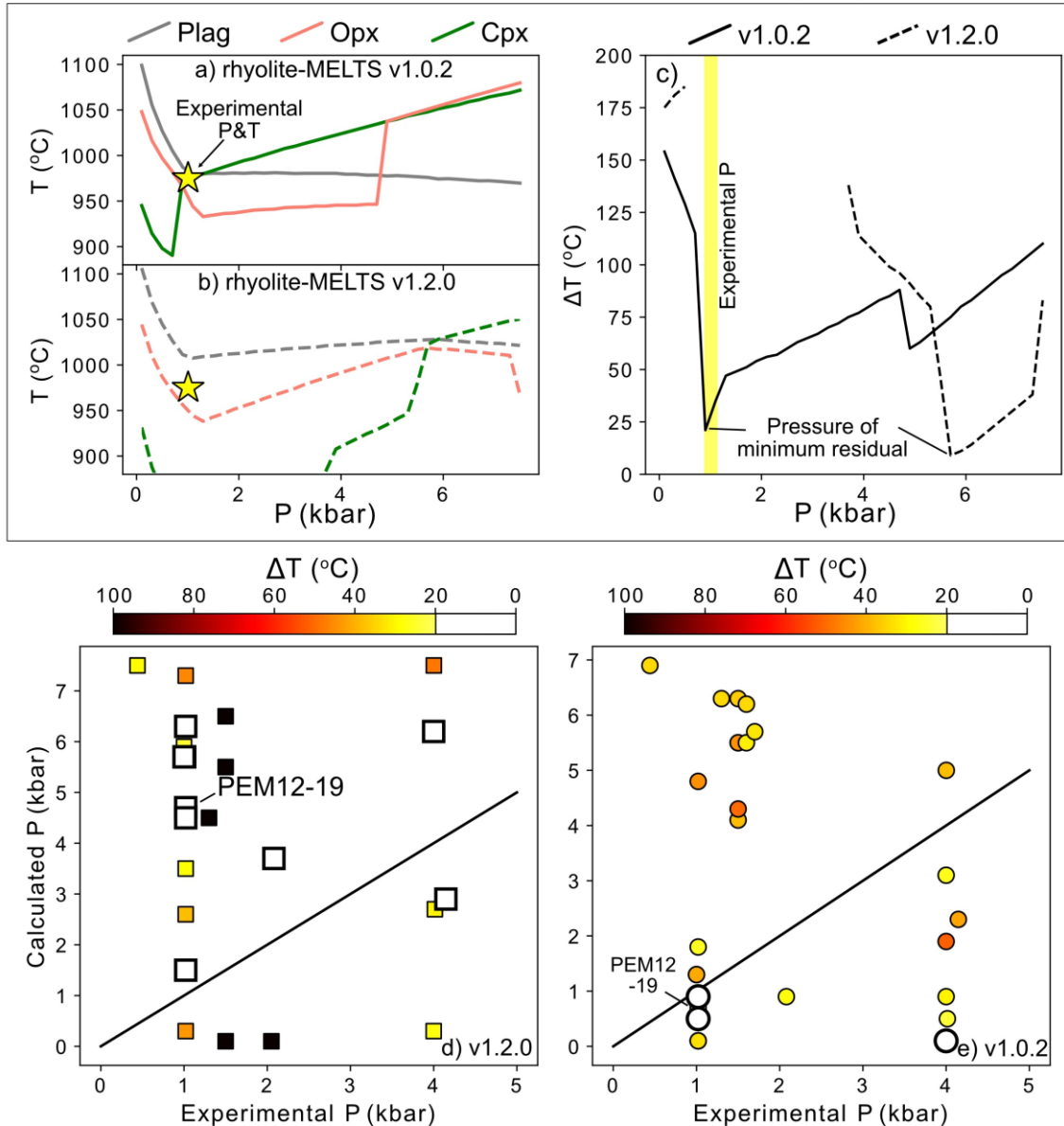
2597 Since the inception of the rhyolite-MELTS geobarometer in 2014, the general method developed by  
2598 Gualda and Ghiorso (2014) has been expanded to examine the cosaturation of other phases. Harmon et al.  
2599 (2018) suggest that the rhyolite-MELTS thermodynamic models could be used to provide pressure estimates for  
2600 intermediate magmas saturated in plagioclase, clinopyroxene and orthopyroxene.

2601 To test the plagioclase – 2 pyroxene geobarometer, Harmon et al. (2018) apply their method to N = 8  
2602 experiments from the LEPR database that are saturated in 2 or more of the phases of interest. As the plagioclase  
2603 - 2 pyroxene geobarometer is significantly more sensitive to *f*O<sub>2</sub> and H<sub>2</sub>O content than the quartz - 2 feldspar  
2604 barometer, they use experimental *f*O<sub>2</sub> and melt H<sub>2</sub>O contents for these comparisons to eliminate the multi-  
2605 dimensional aspects of mineral stability, allowing the best fit pressure to be found. Of the 8 experiments they  
2606 use, only one returned a ΔT between the 3 mineral saturation curves of <20°C, with the minimum T offset for  
2607 other experiments stretching up to 121°C (i.e., the saturation curves never intercept close to one another).

2608 The single experiment with a minimum T offset <20°C (1140mf #27 from Grove et al. 1997) returns a  
2609 predicted P only 0.2 kbar offset from the true experimental P. If the threshold for the minimum T offset is  
2610 relaxed, experiments with minimum T offsets between 20 and 40°C also return P estimates within ~0.25 kbar of  
2611 their experimental P. However, convergence of only 4 experiments conducted at 0.00 1–1 kbar where *f*O<sub>2</sub> and  
2612 melt H<sub>2</sub>O contents are known makes it difficult to robustly assess the accuracy of the geobarometer in natural  
2613 systems when applied up to the 5 kbar limit suggested by Harmon et al. (2018).

2614 We investigate this method further using experiments from variably hydrous magmas cosaturated in  
2615 plagioclase, orthopyroxene and clinopyroxene present in the ArcPL dataset conducted within the pressure range  
2616 suggested by Harmon et al. (2018, 0–5 kbar, N=39). As for LLD methods, we find that the version of MELTS used  
2617 for these calculations drastically affects calculations of storage conditions. Based on the flowchart provided on  
2618 the MELTS-OFM website (<https://melts.ofm-research.org/MELTS-decision-tree.html>), rhyolite-MELTS v1.2.0  
2619 should be used for these calculations, as these experiments contain dissolved H<sub>2</sub>O (±CO<sub>2</sub>). However, Harmon et  
2620 al. (2018) use rhyolite-MELTS v.1.0.2. For experiment PEM12–19 from Moore and Carmichael (1998), rhyolite-  
2621 MELTS v.1.0.2 shows very good convergence at pressures very close to the experimental pressure (Fig. 28e).  
2622 However, if rhyolite-MELTS v1.2.0 is used, the clinopyroxene stability curve intersects plagioclase and  
2623 orthopyroxene at significantly higher pressures (Fig. 28a-b), leading to an estimated pressure of ~ 6 kbar (~5  
2624 kbar higher than the experimental pressure, Fig. 28c).

Experiment PEM12-19; Moore and Carmichael (1998)



2625

2626 *Figure 28: Assessing the Rhyolite-MELTS Plagioclase 2-pyroxene barometer of Harmon et al. (2018). a-b*  
 2627 *Constructing mineral stability curves for Exp. PEM1 2–19 from Moore and Carmichael (1998) at the experimental*  
 2628  *$fO_2$  ( $\Delta NNO=+1.1$ ) and  $H_2O$  contents (3.6 wt%) using two different versions of MELTS. c) Calculating the maximum*  
 2629  *$T$  offset at each pressure between the three mineral stability curves. The MELTS barometer takes the minimum*  
 2630 *residual as the best-fit  $T$  ( $\sim 1$  and  $\sim 6$  kbar depending on the MELTS version). d-e) Testing the barometer using*  
 2631 *experiments saturated in Plag-2 pyroxene from ArcPL. Calculated pressure using the residual method plotted*  
 2632 *against the experimental pressure (calculations performed at experiment  $fO_2$  and  $H_2O$  contents). Experiments*  
 2633 *with residuals  $<20^\circ\text{C}$  are colored white, and larger residuals are colored based on this value. Calculations*  
 2634 *performed in pyMELTSCalc (Gleeson et al., 2022) using alphaMELTS for Python (Antoshechkina and Ghiorso,*  
 2635 *2018).*

2636

2637 Using rhyolite-MELTS v.1.0.2 for all  $N=39$  experiments,  $N=10$  do not stabilize all 3 phases at any pressure  
 2638 within  $200^\circ\text{C}$  of the liquidus, which is well below the experimental temperature in all cases. Of the remaining  
 2639  $N=29$ , models converging with a residual  $<20^\circ\text{C}$  are shown in white on Fig. 28d-e. These produce a very poor fit  
 2640 to experimental pressures. If we take solutions produced at larger temperature residuals (following Harmon et  
 2641 al. 2018), there is no improvement. Using rhyolite-MELTS v1.2.0,  $N=23$  experiments converge, and the fit is  
 2641 similarly bad, regardless of the temperature residual used. The poor performance of this barometer supports

2642 previous criticism of the ability of MELTS to correctly predict the stability of these phases, pointing to the need  
2643 for better solution models (e.g., Klein et al., 2023; Nandedkar et al., 2014; Villiger, 2004).

## 2644 **9. Other methods**

2645 There are of course, numerous methods to determine magma storage conditions which we do not address in  
2646 detail, both in the interest of relative(!) brevity, and because there is insufficient experimental data that wasn't  
2647 used during calibration to independently test models.

2648 Additional thermometers have been developed based on:

- 2649 • REE exchange between Opx-Cpx (Liang et al., 2013) and Plag-Cpx (Sun and Liang, 2012).
- 2650 • Mg-Fe exchange between Ol and Cpx (Loucks, 1996).
- 2651 • Ni partitioning between Ol-Liq (resulting in a H<sub>2</sub>O-independent thermometer, Pu et al., 2021, 2017).
- 2652 • NaSi-CaAl exchange between Amp-Plag (e.g., Holland and Blundy, 1994; Molina et al., 2021).
- 2653 • Mg exchange between Plag-Cpx (Sun and Lissenberg, 2018).

2654 Hygrometers based on:

- 2655 • Cpx-Liq major element equilibrium (e.g., Armienti et al., 2013; Perinelli et al., 2016).
- 2656 • Ca exchange between Ol-Liq (Gavrilenko et al., 2016).
- 2657 • The highest amphibole Mg# found in a given volcanic system (Krawczynski et al., 2012).
- 2658 • The H<sub>2</sub>O contents of nominally-anhydrous minerals (NAMs) combined with models of mineral-melt  
2659 partition coefficients (Demoucy et al., 2006; Towbin et al., 2023; Wade et al., 2008).
- 2660 • Projections of the Ol, Cpx and Plag cotectics (Klein et al. 2023).

2661 Barometers based on:

- 2662 • Sr/Y contents of erupted lavas (Profeta et al., 2016).
- 2663 • 'Multi-reaction' thermodynamic models relying on underlying thermodynamic models (e.g., Holland  
2664 and Powell, 2011), where predicted and observed mineral compositions and phase fractions are  
2665 compared to constrain storage conditions (E.g., Ziberna et al. 2017, Nicoli and Matthews, 2019).
- 2666 • Al-Si partitioning between Plag and Amp (Molina et al., 2015).
- 2667 • CaO-Mg# systematics of mid-oceanic ridge magmas (Villiger et al., 2007).

2668 Of course, these lists are by no means exhaustive.

## 2669 **10. Future developments should be guided by FAIR principles**

2670 It is becoming increasingly recognised that science needs to shift to a framework where research  
2671 products are findable, accessible, interoperable, and reusable (FAIR; Wilkinson et al., 2016). In the context of  
2672 this review, this applies not only to research data such as analyses of experimental products and natural samples,  
2673 but also the tools and workflows used to perform calculations. There have already been a few advances in this  
2674 regard, but there is still lots of work to do.

2675 From a data availability perspective, a major advance came in 2008 when Hirschmann et al. (2008)  
2676 created a web-hosted database of 6,600 experiments (The Library of Experimental Phase Relationships – LEPR),  
2677 which has been widely used to calibrate thermobarometers and chemometers (e.g., Jorgenson et al., 2022;  
2678 Petrelli et al., 2020). This compilation represented a massive team effort, requiring most phase compositions  
2679 and experimental contents to be hand typed from data tables in journal pdfs. However, the dataset is still  
2680 incomplete in many aspects, stemming from missing data in the underlying publications, compounded with  
2681 missing information during digitization. For example, in the LEPR download of Cpx-Liq pairs used by Petrelli et  
2682 al. (2020) and Putirka (2008), 66% of experiments do not have a glass H<sub>2</sub>O content. In some cases, this represents  
2683 the fact that the experiment was anhydrous, in others the fact that authors didn't report water, and sometimes  
2684 because H<sub>2</sub>O is often presented in a different table from other chemical information, so may have been missed  
2685 during digitization. Similarly, with few exceptions, the number of analyses used to produce the reported average  
2686 for each phase (e.g., N=5 Cpx analyses, N=8 amphibole analyses) is not present in LEPR. This makes filtering out  
2687 experiments with compositions defined by small numbers of analyses challenging, despite the importance of  
2688 this given the influence of analytical error on minor, pressure-sensitive components (e.g., Cpx, Wieser et al.  
2689 2023b).

2690 A bigger challenge is that there is no framework by which LEPR is regularly updated as new experimental  
2691 studies are published. This has led to individual authors digitizing data from new experimental papers to use in  
2692 their studies (Jorgenson et al., 2022, Wieser et al. 2023a-b). However, individual researchers who compile data

2693 may not have time to format the data for inclusion in the database, because under the current academic  
2694 publishing model, they would gain no credit for this activity (citations for use of the database would go to the  
2695 original author team from 2008). One option moving forwards may be for LEPR to frequently publish new short  
2696 articles or Zenodo dois with an author team consisting of anyone who has contributed to the curation of the  
2697 database (as for open-source tools such as Numpy; e.g., Dubois et al., 1996; Harris et al., 2020). Alternatively,  
2698 the responsibility could be placed on people generating experimental data, where journal editors do not allow  
2699 a paper to be accepted before the experimental data is included in these databases. However, in many cases,  
2700 journals do not mandate authors submitting data to a specific repository. Community guidelines for exactly how  
2701 such data should be presented and archived are clearly needed, as well as ways for data curation to be valued  
2702 when hiring and promoting researchers (e.g., Klöcking et al., 2023).

2703 From a modelling perspective, there has been a rapid increase in the number of open-source, easy to  
2704 use tools to perform calculations, making workflows more user-friendly, faster, more reproducible, and less  
2705 susceptible to user-error and version control issues. In general, calculation tools have evolved from GUIs, macro-  
2706 enabled spreadsheets and web apps, many of which require users to type every single composition by hand, to  
2707 python or R packages where calculations can be run on any number of rows in a user-supplied spreadsheet using  
2708 Jupyter Notebooks or web apps built on top of underlying code (e.g., Iacovino and Till, 2019; Weber and Blundy,  
2709 2023). One major contribution towards more automated workflows for thermodynamic calculations has been  
2710 the development of the ENKI ThermoEngine (Thermoengine Code Contributors, 2022), allowing the MELTS  
2711 thermodynamic models and algorithms to be accessed through Python. This allows creation of modelling  
2712 workflows or complete packages based on the underlying MELTS models. For example, the Fe-Ti oxybarometer  
2713 and thermometer of Ghiorso and Evans (2008) was originally released as a web-app where users had to hand-  
2714 type major element values for each Fe-Ti oxide pair. Ghiorso and Prissel (2020) produced a Jupyter Notebook  
2715 using Thermoengine which allows users to upload an excel file of matching Fe-Ti oxide pairs, and all calculations  
2716 are performed automatically. The open-source Python3 package VESlcal (Iacovino et al., 2021) relies on  
2717 Thermoengine to perform calculations using the solubility model Magmasat (which requires MELTS, Ghiorso and  
2718 Gualda, 2015), as well as 6 other popular solubility models. Prior to VESlcal, saturation pressure calculations  
2719 were performed using different tools for each solubility model in a myriad of different environments (Excel  
2720 macros, web apps, web servers). The MELTS thermodynamic models can also be accessed using the alphaMELTS  
2721 for MATLAB/Python packages (Antoshechkina and Ghiorso, 2018). As the alphaMELTS for MATLAB/Python  
2722 packages (and Thermoengine) requires some familiarity with the underlying language, easy-to-use, wrapped  
2723 functions for common workflows have been released through the pyMELTScalc package (used for calculations  
2724 in Section 8, Gleeson et al., 2023).

2725 Calculations using the thermodynamic models/databases developed by Holland and Powell (e.g.,  
2726 Holland and Powell, 1998; Holland et al. 2018), which represent the main thermodynamic alternative to MELTS  
2727 in igneous petrology, have traditionally performed using a variety of different software packages, including  
2728 THERMOCALC, Perple\_X (Connolly, 2009, 2005) and Theriak-Domino (de Capitani and Petrakakis, 2010). The  
2729 learning curve for these tools is typically quite steep, and it remains challenging to integrate the thermodynamic  
2730 calculations with common coding languages such as MATLAB, Python3 or Julia. Development of MAGEMin, a C-  
2731 based Gibbs Free Energy minimization software with a Julia interface (Reil et al. 2022), improves the ease with  
2732 which thermodynamic calculations can be performed using the Holland et al. (2018) thermodynamic database.  
2733 This is because the Julia MAGEMin functions can also be used outside of the main GUI and integrated with  
2734 Python3 functions. This allows the pyMELTScalc package to perform the same calculations (e.g. LLD, phase  
2735 stability, phase diagrams) using MELTS or the Holland et al. (2018) thermodynamic models. Such advances are  
2736 vital for model intercomparison (e.g., Fig. 26).

2737 For mineral-melt thermobarometry and chemometry, calculations using 100s of different popular  
2738 equations can be performed in Thermobar (Wieser et al., 2022b). This tool replaces a very large number of  
2739 separate Excel spreadsheets, R and Matlab code released by individual thermobarometry papers, and allows  
2740 more complex functions such as assessing all possible pairs for equilibrium, error propagation etc. For  
2741 thermobarometers applicable to determining the conditions of mantle melting, Python package meltPT (McNab  
2742 and Ball, 2023) can perform calculations using twelve published expressions.

2743 These open-source python tools allow investigation of science questions that were almost impossible to address  
2744 using existing tools requiring extensive manual data input. For example, Wieser et al. (2022a) use VESlcal to  
2745 perform detailed comparisons of solubility models, including their sensitivities to different parameters. Wieser  
2746 et al. (2023a-b) use Thermobar to propagate thermobarometry uncertainties using Monte Carlo methods. Open-  
2747 source packages also have the advantage that the source code is version-controlled, and hosted in a public

2748 repository (e.g., on GitHub) for anyone to inspect and adapt. This means even if the authors stop supporting the  
 2749 packages (perhaps moving from academia into industry), packages could be updated by a third party, although  
 2750 as a community we need to develop clear guidelines as to how academic credit can be allocated for such an  
 2751 activity. This is in stark contrast with numerous tools which have simply become unusable with age. For example,  
 2752 the volatile solubility model of Duan (2014) is no longer available at the website listed in the paper, requiring  
 2753 authors to rely on archived downloads (e.g., Allison et al., 2022 rely on a version archived in 2017).

2754 **11. Conclusions**

2755 A wide diversity of methods have been used to determine the pressures, temperatures, H<sub>2</sub>O contents and  $fO_2$   
 2756 conditions at which magmas are stored and staged as they transit from the mantle to the surface. Many  
 2757 thermometry methods work very well, indicating that silicate melt ( $\pm$ mineral) compositions are sensitive to  
 2758 temperature. However, it becomes more challenging to determine temperatures in subsolidus or highly evolved  
 2759 systems. In contrast, many mineral-based and thermodynamical barometers perform extremely poorly,  
 2760 struggling to reliably distinguish between different storage regions in the crust within ~10–20 km. This partially  
 2761 results from thermodynamic limitations; mineral compositions are not overly sensitive to the relatively narrow  
 2762 range of crustal pressures in the vast majority of tectonic settings on Earth. This fundamental limitation is not  
 2763 helped by sources of analytical and experimental uncertainty (e.g., poor analytical precision for minor  
 2764 components, missing elements such as Cr, Wieser et al. 2023b). Melt inclusion barometers have the potential to  
 2765 be more precise, because the dissolution of CO<sub>2</sub> and H<sub>2</sub>O is highly sensitive to pressure. However, extensive work  
 2766 is required to resolve discrepancies between solubility models, as well as evaluate the influence of the vapour  
 2767 bubble CO<sub>2</sub> in many published datasets. Raman-based fluid inclusion has great potential in specific systems,  
 2768 although further work is needed to investigate the influence of decrepitation, elastic relaxation, and the  
 2769 influence of other fluid species (e.g. SO<sub>2</sub>, H<sub>2</sub>O etc). Thermobar-Raman-try also shows great promise, but further  
 2770 work is required. We propose a number of key frontiers to address in the pursuit of better thermobarometers,  
 2771 hygrometers and oxybarometers:

- 2772 1) The development of higher quality experimental and thermodynamic datasets with precisely constrained  
 2773 mineral compositions, fluid compositions, dissolved volatile contents, and experimental  $fO_2$  for recalibration of  
 2774 thermodynamic models (e.g., MELTS), mineral-melt thermobarometers, and volatile solubility models. Sufficient  
 2775 experiments need to be performed to allow full isolation of a test dataset during model calibration. More  
 2776 experiments using mixed H<sub>2</sub>O-CO<sub>2</sub> fluids are needed to understand phase stability in relatively CO<sub>2</sub>-rich arc  
 2777 magmas.  
 2778 2) Development of more robust infrastructure for compiling experimental and thermodynamic data, alongside  
 2779 sufficient metadata to assess data quality. This will ensure that application of new and exciting machine learning  
 2780 techniques will not suffer from the old computer science adage: ‘garbage-in, garbage-out’.  
 2781 3) Further development of open-source methods to perform calculations, allowing easy intercomparison  
 2782 between models, error propagation, and model updates as new data becomes available.

2783 **12. Author Contributions**

2784 PW coordinated the review and was responsible for writing and coding for all sections except those listed below.  
 2785 MG was responsible for the OPAM, MELTS and MAGEMin sections with edits from PW, and SM for OI-Sp and Fe-  
 2786 Ti oxide sections. CD contributed text to the MI and FI section, and provided edits throughout. CD and EG  
 2787 contributed to analytical work. All authors reviewed and edited the text.

2788 **13. Acknowledgements**

2789 PW thanks Iris Buisman for extracting the Cpx counting statistics shown in Fig. 8, and Keith Putirka for many  
 2790 useful conversations on thermobarometry and the formulation and calibration of his equations. PW  
 2791 acknowledges support from NSF EAR 2217371, the Rose Hills Innovator Program, and start up funds to UC  
 2792 Berkeley for computing resources. EG acknowledges support from NSF EAR 2216738.

2793 **13. Useful websites and open-source tools**

<b>Tools for petrologists</b> – Contains Excel workbooks and python scripts for a number of petrographic workflows.	<a href="http://www.kaylaiacovino.com/tools-for-petrologists/">http://www.kaylaiacovino.com/tools-for-petrologists/</a>
<b>VESical GitHub, Read The Docs and YouTube pages:</b> Code, documentation and worked examples for calculations using VESical	<a href="https://github.com/kaylai/VESical">https://github.com/kaylai/VESical</a> , <a href="https://vesical.readthedocs.io/en/latest/">https://vesical.readthedocs.io/en/latest/</a>
<b>Thermobar read the docs page:</b> Code, documentation and worked examples for thermobarometry and hygrometry calculations using Thermobar	<a href="https://github.com/PennyWieser/Thermobar">https://github.com/PennyWieser/Thermobar</a>

	<a href="https://thermobar.readthedocs.io/en/latest/">https://thermobar.readthedocs.io/en/latest/</a>
<b>Putirka spreadsheet compilation:</b> Contains Excel spreadsheets for different thermobarometry calculations	<a href="https://sites.google.com/mail.fresnostate.edu/keithputirka/home">https://sites.google.com/mail.fresnostate.edu/keithputirka/home</a>
<b>MELTS resources:</b> Links to download different MELTS calculation tools (Matlab, python, GUI, excel).	<a href="https://magmasource.caltech.edu/gitlist">https://magmasource.caltech.edu/gitlist</a>
<b>MAGEMin:</b> Gibbs free energy minimisation solver package	<a href="https://github.com/ComputationalThermodynamics/MAGEMin">https://github.com/ComputationalThermodynamics/MAGEMin</a>
<b>PyMageMinCalc:</b> Python package for common petrological workflows using MAGEMin.	<a href="https://github.com/gleesonm1/pyMAGEMINcalc">https://github.com/gleesonm1/pyMAGEMINcalc</a>
<b>PyMELTScalc:</b> Python package for easier calculations using Melts for Python	<a href="https://github.com/gleesonm1/pyMELTScalc">https://github.com/gleesonm1/pyMELTScalc</a>
<b>ENKI server:</b> Allows calculations to be performed using ThermoEngine infrastructure without the need for local installation.	<a href="http://enki-portal.org/">http://enki-portal.org/</a>
<b>NIST Web Book:</b> Phase data for CO <sub>2</sub> and calculations using the CO <sub>2</sub> equation of state.	<a href="https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&amp;Mask=1">https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&amp;Mask=1</a>
<b>DiadFit:</b> Code, documentation and worked examples using DiadFit for fitting Raman data and performing EOS calculations for CO <sub>2</sub> .	<a href="https://github.com/PennyWieser/DiadFit">https://github.com/PennyWieser/DiadFit</a> , <a href="https://diadfit.readthedocs.io/en/latest/">https://diadfit.readthedocs.io/en/latest/</a>
<b>CoolProp:</b> A python package for calculating thermodynamic properties of gases using different equation of states.	<a href="http://www.coolprop.org/">http://www.coolprop.org/</a>

2794

#### 2795 **14. Data Availability**

2796 Jupyter Notebooks and Excel workbooks used to make each figure are available on GitHub  
2797 ([https://github.com/PennyWieser/Thermobarometry\\_Review\\_2023](https://github.com/PennyWieser/Thermobarometry_Review_2023)).

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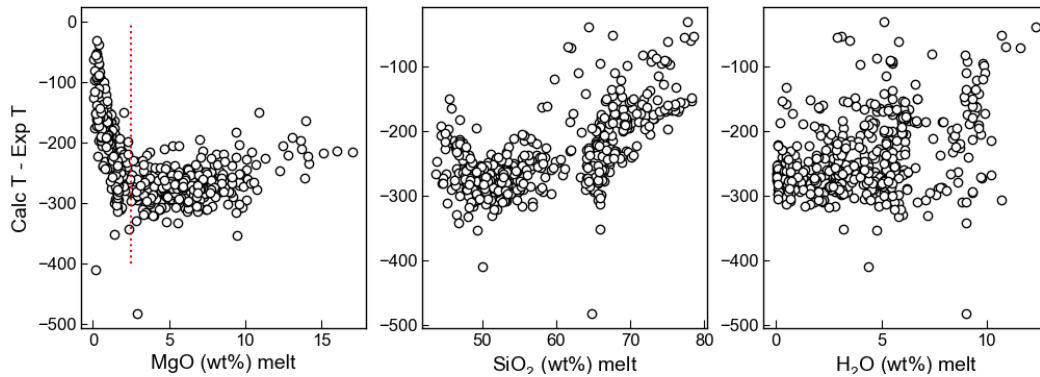
### Supporting Information: P-T-X conditions of magmas

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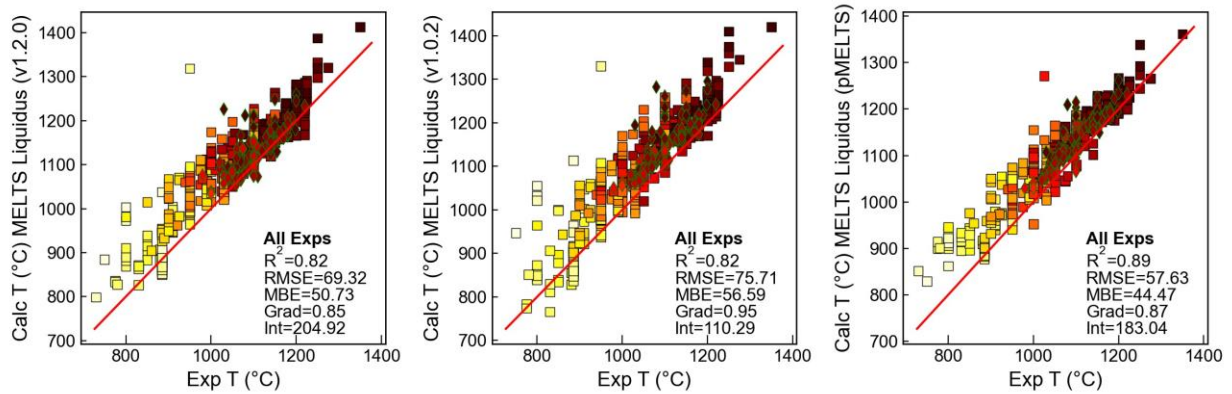
1. Earth and Planetary Sciences, UC Berkeley

2. Earth Science Department, University of Cambridge

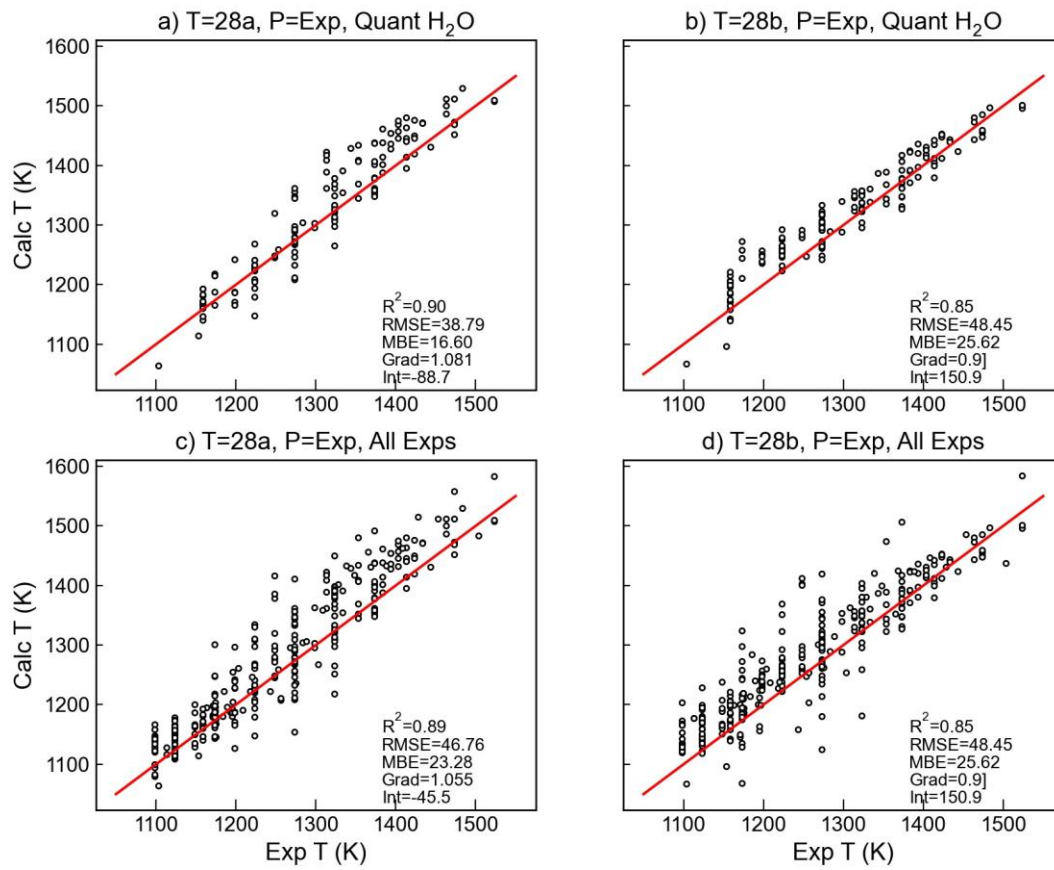
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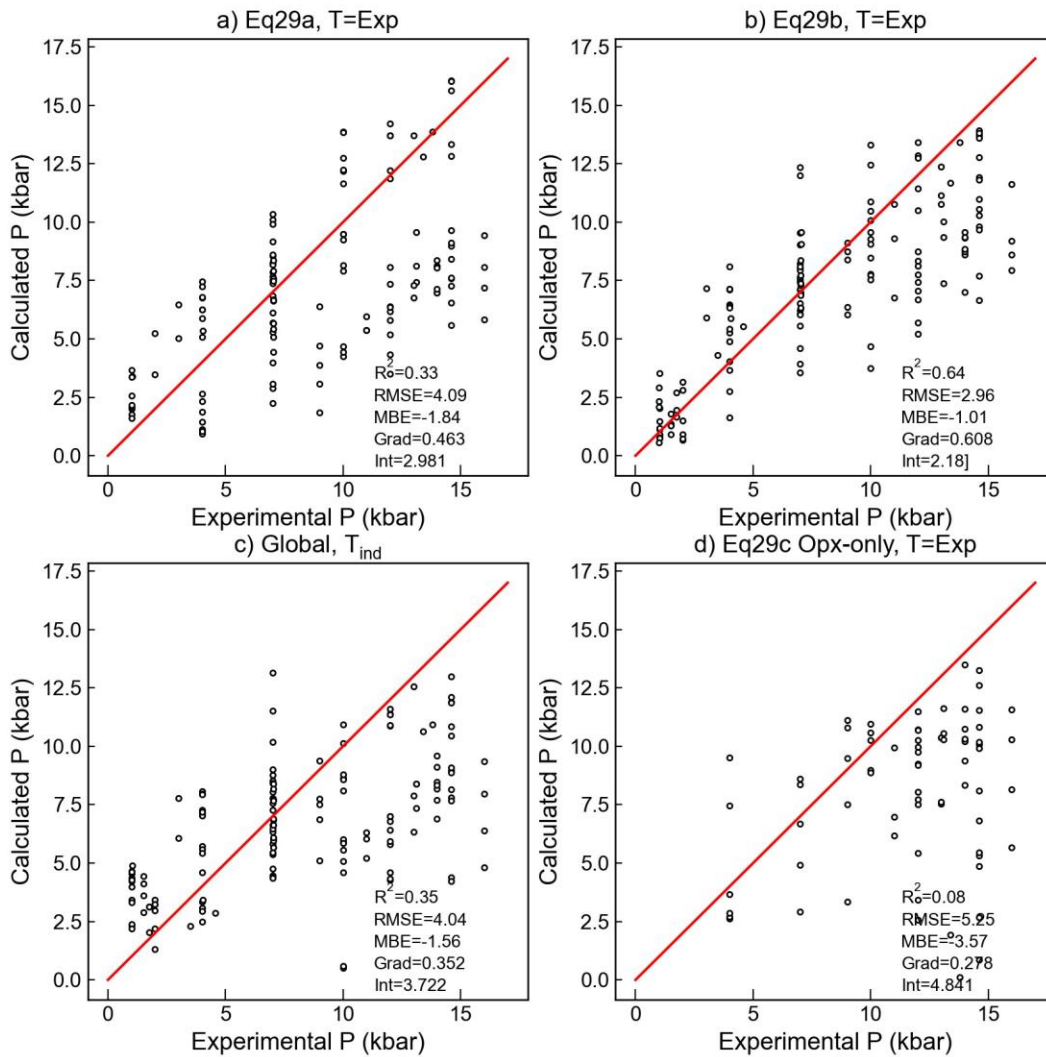
**Supporting Fig. 1** – Offset between calculated temperature using Shi et al. (2021) and experimental temperature shows a strong relationship with MgO content.



**Supporting Fig. 2** – Liquidus calculations performed with different versions of MELTS for comparison with the main text.

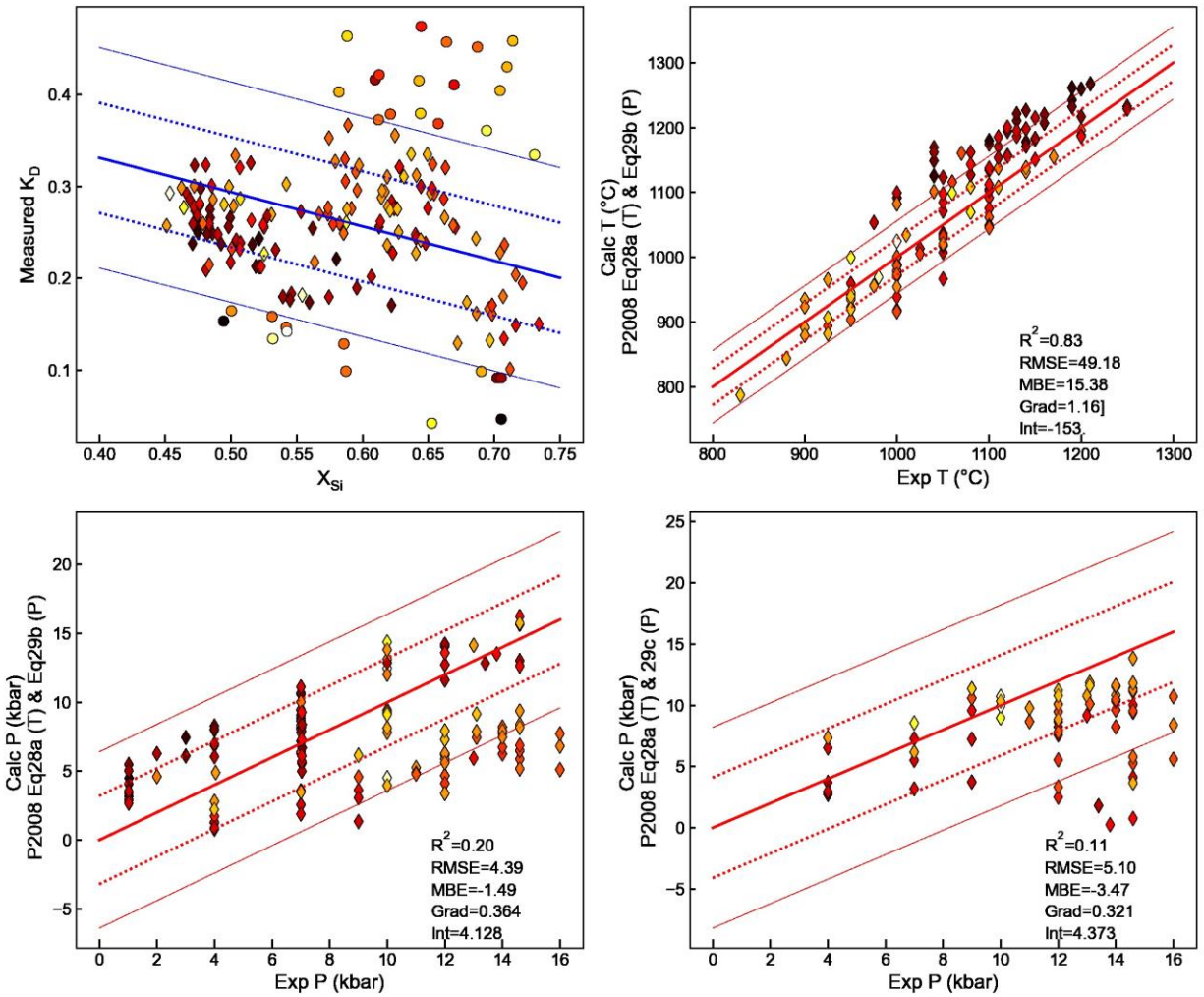


**Supporting Fig. 3**– Comparison of different Opx-Liq thermometers. a-b) uses only experiments where H<sub>2</sub>O was measured using a quantitative method, while c-d shows all experiments.

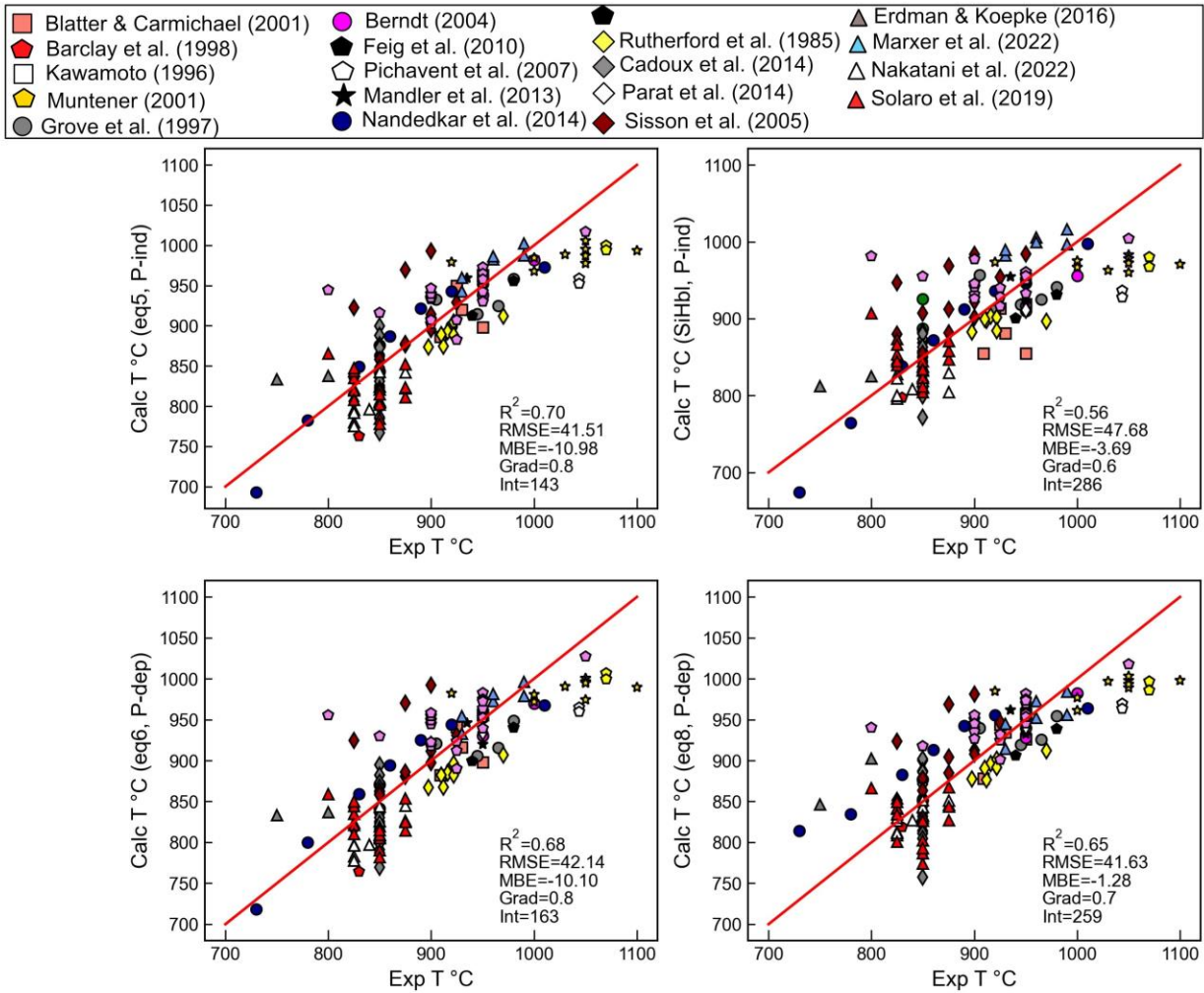


**Supporting Fig. 4:** Comparison of 4 different Opx-Liq and Opx-only barometers using experimental temperatures and H<sub>2</sub>O contents. Eq29b provides the best match.

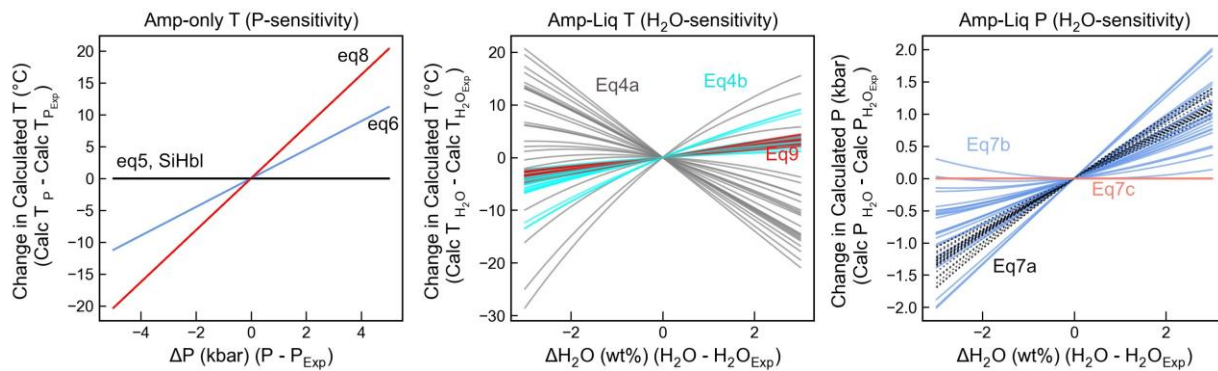




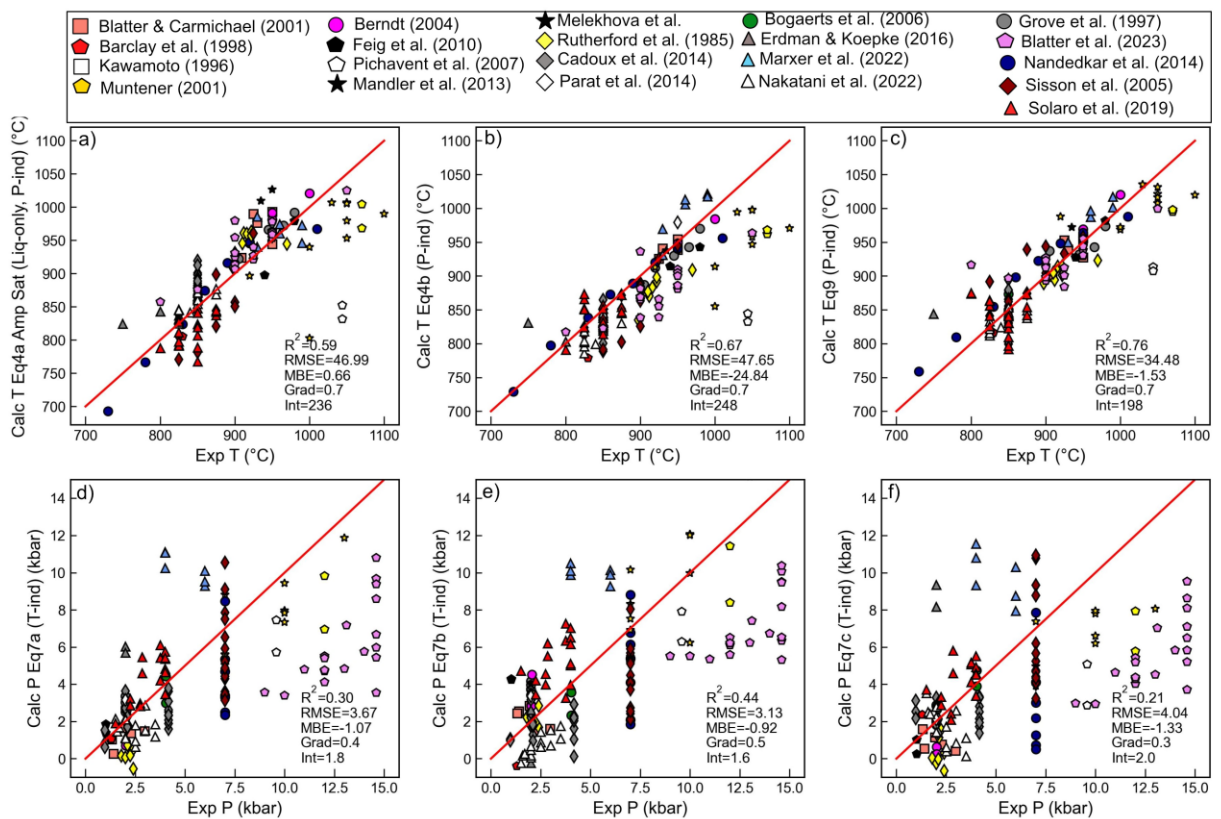
**Supporting Fig. 5** – As for Fig. 9 in the main text, but only using experiments where H<sub>2</sub>O was reported using a quantitative method.



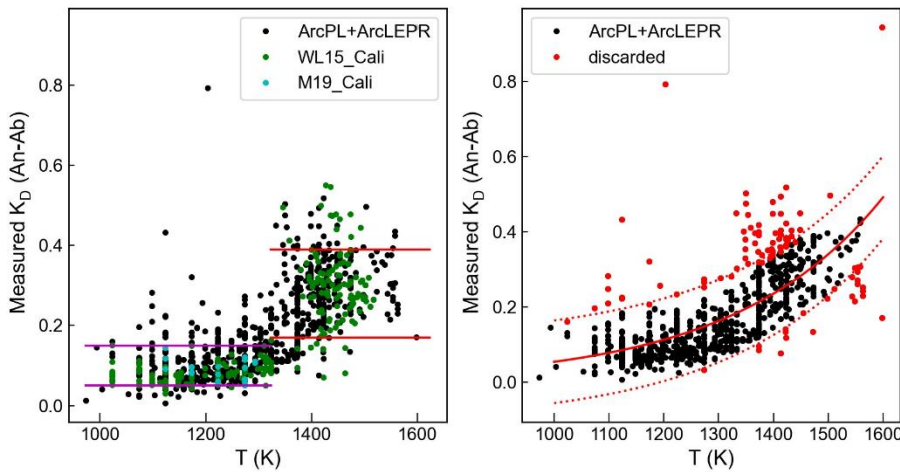
**Supporting Fig. 6** – Assessment of Amp-only thermometers from Putirka (2016) on data not used during equation calibration.



**Supporting Fig. 7** – Sensitivity testing of Putirka (2016) Amp expressions to unknowns in each equation.

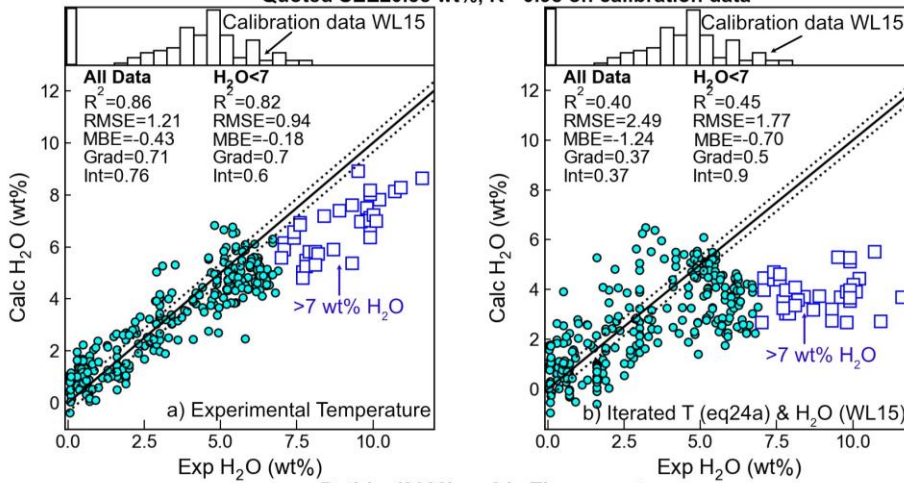


**Supporting Fig. 8** – Assessment of Amp-Liq thermometers and barometers from Putirka (2016) on data not used during equation calibration.

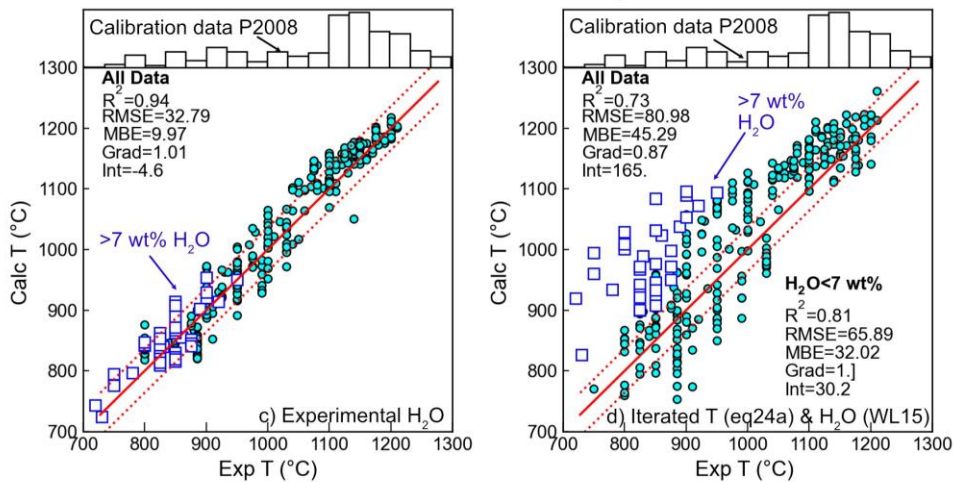


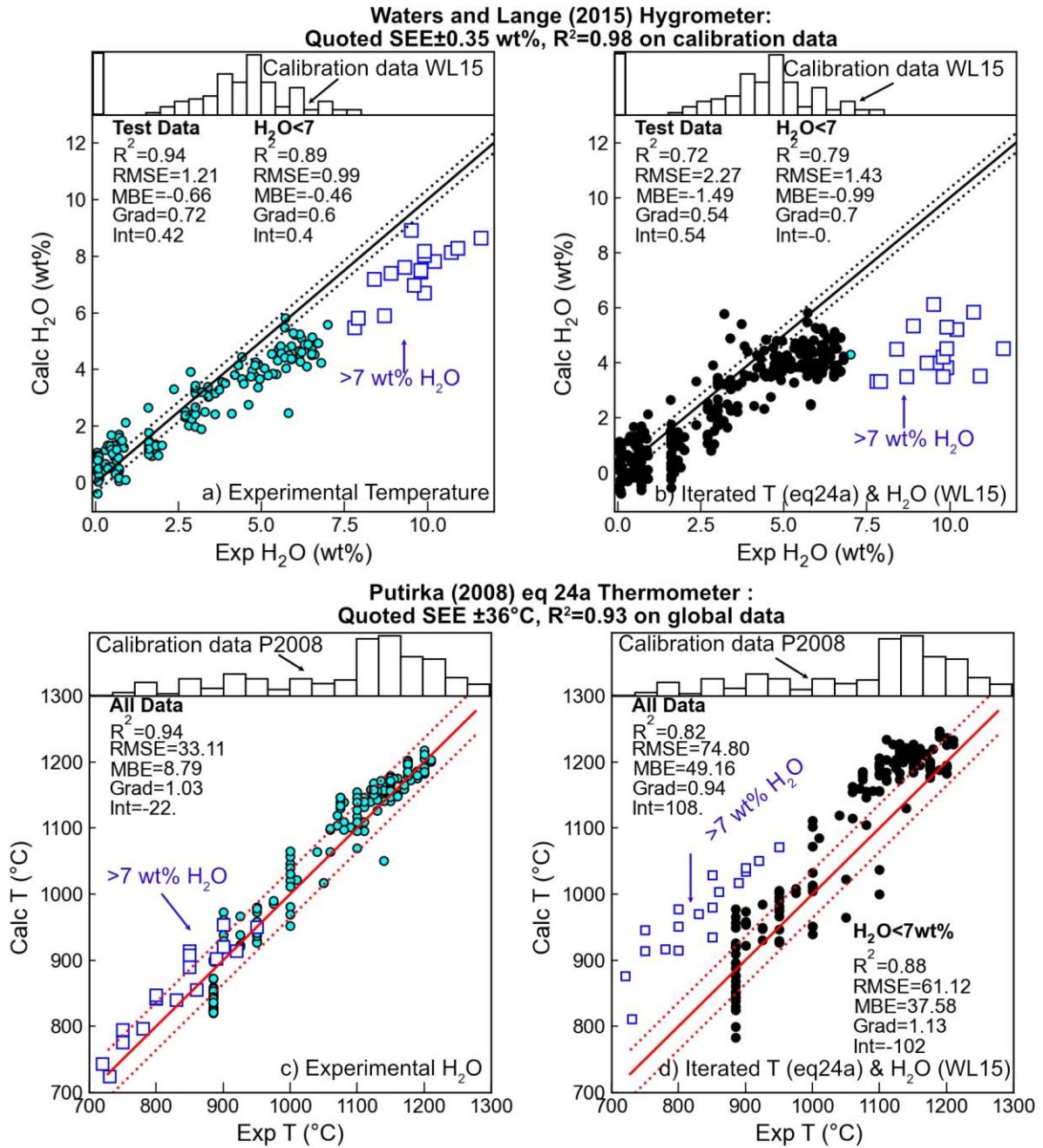
**Supporting Fig. 9 –**  
 Assessing Plag-Liquid equilibrium tests using our new dataset. WL15 – Waters and Lange (2015) calibration dataset. M19- Masotta et al. (2019) calibration dataset. Lower plots are the same as Fig 16 in the main text, but without application of any equilibrium filters.

**Waters and Lange (2015) Hygrometer:**  
 Quoted SEE±0.35 wt%, R<sup>2</sup>=0.98 on calibration data

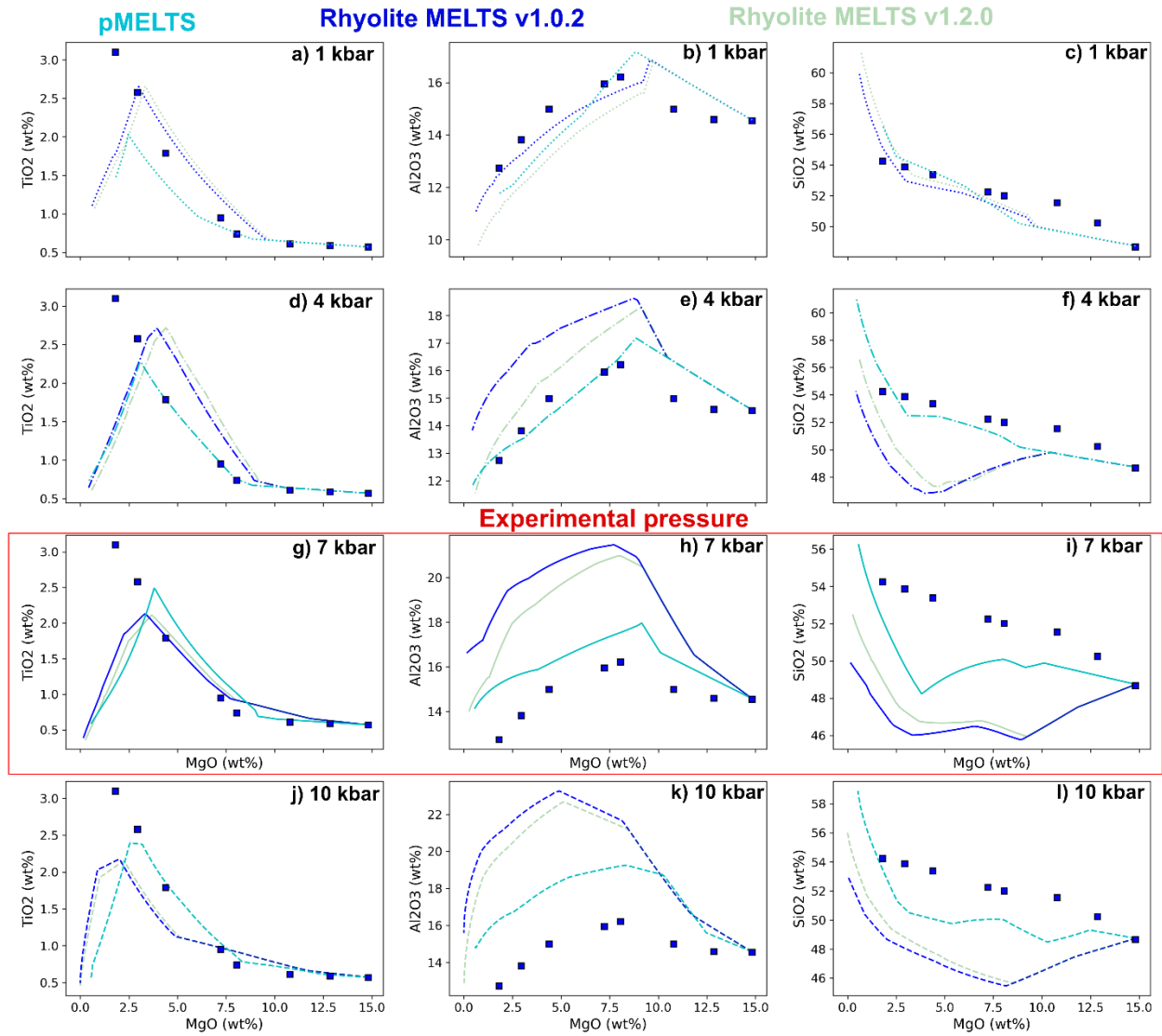


**Putirka (2008) eq 24a Thermometer :**  
 Quoted SEE ±36°C, R<sup>2</sup>=0.93 on global data

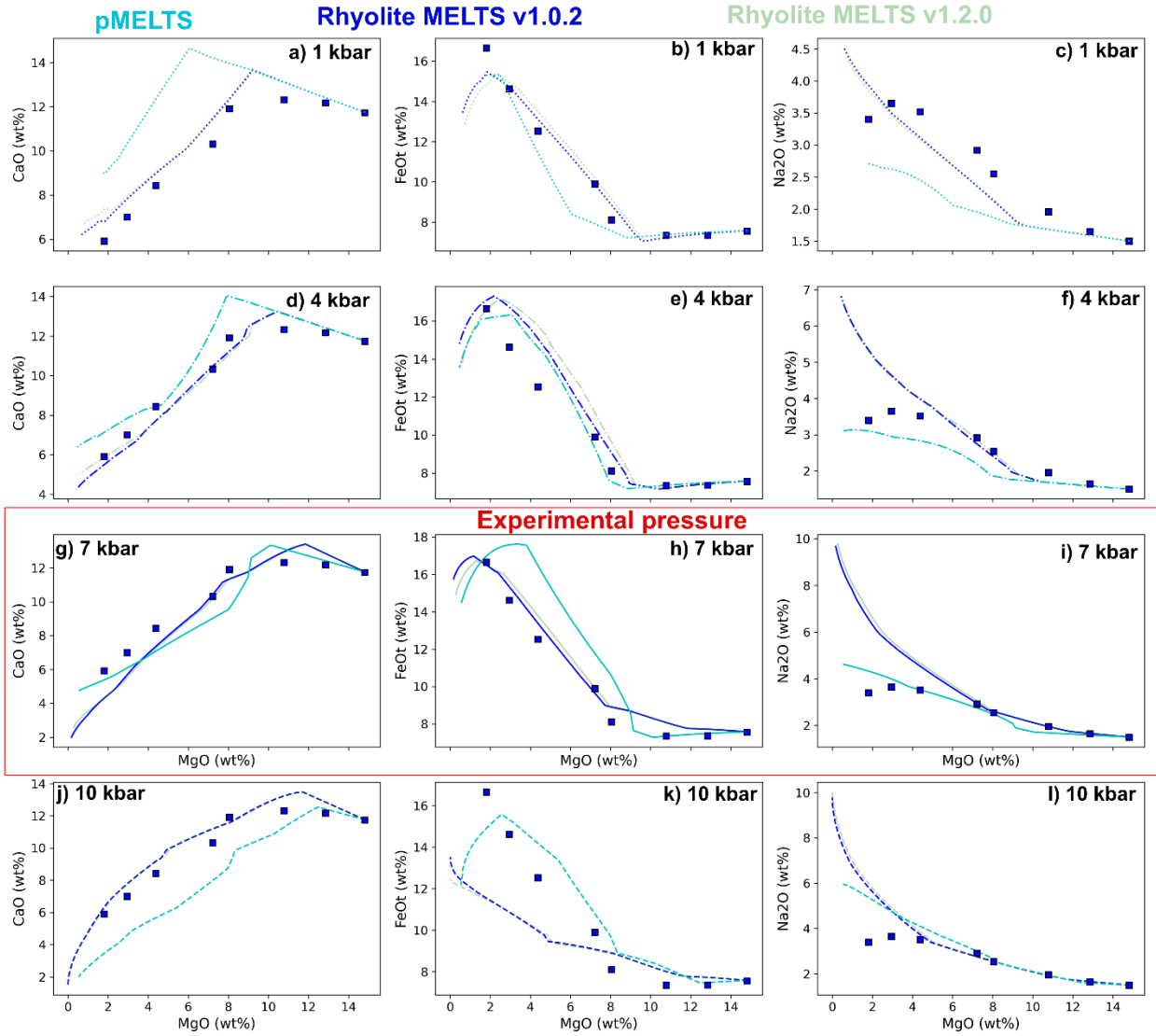




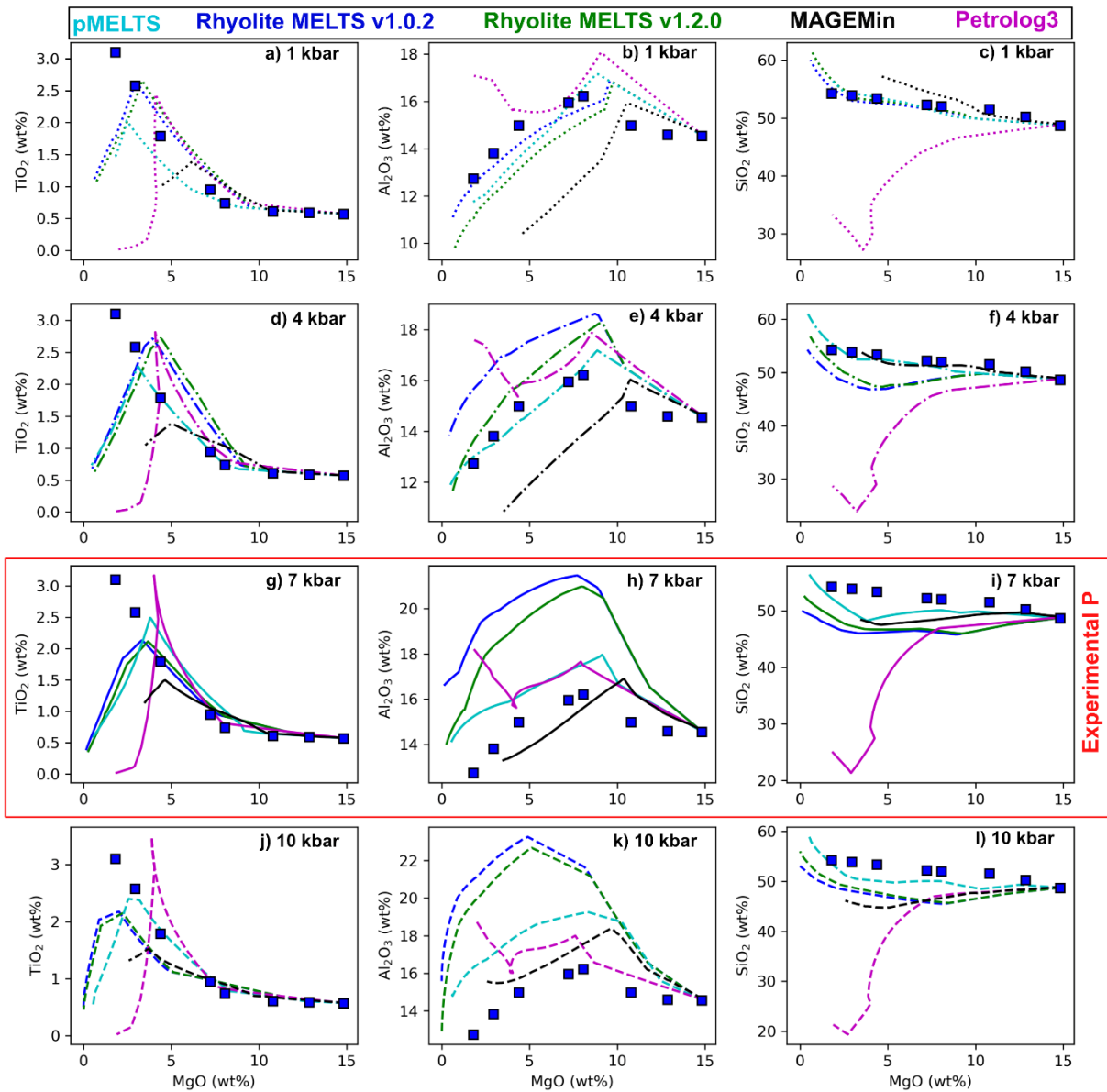
**Supporting Fig. 10** – As for Fig. 16 in the text, but only using experiments where H<sub>2</sub>O was measured using Raman, FTIR or SIMS.



**Supporting Fig 11** – As for main text, but showing different MELTS models against the experimental data of Villiger et al. (2007).



Supporting Fig 12 – As for Fig. 11, but for different major elements



**Supporting Fig. 13** – Models at 4 pressures for the Villiger et al. (2007) experiments, showing MageMin and Petrolog3