Phase-equilibrium geobarometers for silicic rocks based on rhyolite-MELTS. Part 5: Principles for multiple-phase geobarometry with examples from plagioclase + orthopyroxene ± quartz ± magnetite assemblages

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Abstract

The quartz + feldspar rhyolite-MELTS phase-equilibrium geobarometer is a useful tool for calculating equilibration pressures of rhyolitic magmas. However, it is limited by requiring quartz saturation in magma. Here, we employ the principles from Parts 1-4 to move beyond modeling a specific mineral assemblage. We demonstrate methods for carefully interpreting the rhyolite-MELTS geobarometry results to constrain equilibration pressure in quartz-undersaturated dacites to rhyolites, and where quartz saturation is uncertain. We show examples of storage pressure calculations from quartz-absent rhyodacites to rhyolites from Puyehue-Cordón Caulle (PCC), Chile; and examples of equilibration between extracted rhyolitic melt compositions and unknown mush mineral assemblages from the Taupō Volcanic Zone, New Zealand. In this case, orthopyroxene + plagioclase pressures can be used. However, orthopyroxene saturation pressure results are higher at lower modelled oxygen fugacity. This can be resolved by modelling at independently constrained f_{O2}, or by modelling at a range of f_{O2} to search for orthopyroxene + magnetite + feldspar co-saturation. We show that orthopyroxene + magnetite + feldspar pressures for PCC are consistent with results from other geobarometers and occur within error of the f_{O2} calculated from Fe-Ti oxides. If quartz saturation is uncertain, quartz + feldspar pressures are a maximum and pyroxene-bearing pressures at low f_{O2} are a minimum. For uncertain mineral assemblages, the coincidence of multiple phases (≥3) saturating together at reasonable f_{O2} could be used to infer the equilibrium mineral assemblage. Careful inspection of rhyolite-MELTS geobarometry results therefore gives nuanced information about equilibration pressure, mineral assemblage, and f_{O2}.

Introduction

A fundamental problem in igneous petrology is constraining the pressure of magma storage before eruption. Pressure has critical implications for understanding the processes that drive eruption (Caricchi, et al. 2021; Gonnermann and Manga 2007). Pressures can be converted to depth assuming lithostatic conditions to estimate the depth and geometry of magma bodies (Black and Andrews 2020; Cooper, et al. 2012), and therefore the pre-eruptive architecture of magma systems (Edmonds, et al. 2019; Gualda, et al. 2018; Wieser, et al. 2023). These magma system models are useful in combination with geophysical datasets to interpret the unrest signals of modern volcanos (Giordano and Caricchi 2022; Magee, et al. 2018; Pritchard, et al. 2018).

There are many geobarometers to estimate magma pressure from compositional parameters such as mineral compositions (e.g., Hammarstrom and Zen 1986; Jorgenson, et al. 2022; Mutch, et al. 2016; Putirka 2008; Ridolfi, et al. 2010), volatile contents (e.g., Anderson Jr, et al. 1989; Burnham 1994; Liu, et al. 2005; Newman and Lowenstern 2002; Papale, et al. 2006; Wallace, et al. 1995), and melt compositions (e.g., Blundy 2022; Blundy and Cashman 2001; Gualda and Ghiorso 2013b; Gualda and Ghiorso 2014; Herzberg 2004; Voigt, et al. 2017; Weber and Blundy 2024; Wilke, et al. 2017; Yang, et al. 1996). Melt-only geobarometers search for the pressure that melt of a known composition equilibrated with mineral phases of interest. A distinct advantage of melt-only geobarometers is that major-element melt compositions are relatively easy to obtain (by X-ray fluorescence spectroscopy (XRF), wavelength dispersive X-ray spectroscopy (WDS) attached to an electron microprobe (EMP), or energy dispersive X-ray spectroscopy (EDS) attached to a scanning electron microprobe (SEM)) compared to other common geobarometry techniques (e.g., measuring H_2O-CO_2 in melt inclusions by fourier transform infrared spectroscopy or secondary ion mass spectrometry; measuring mineral rim and core compositions by WDS-EMP). Unlike geobarometers that use the composition of multiple phases (e.g., amphibole-plagioclase Holland and Blundy 1994; Molina, et al. 2021; orthopyroxene-clinopyroxene, Putirka 2008), melt-only geobarometers do not require the assumption of equilibrium between paired phase compositions. Melt-only geobarometers can either be derived from empirical relationships extrapolated from experimental datasets (Blundy 2022; Blundy and Cashman 2001; Herzberg 2004; Voigt, et al. 2017; Weber and Blundy 2024; Wilke, et al. 2017; Yang, et al. 1996), or from phase-equilibria models (Bégué, et al. 2014b; Gualda and Ghiorso 2014; Harmon, et al. 2018; Pamukçu, et al. 2015). We focus on phase-equilibrium geobarometers, which have the advantage of being grounded in thermodynamic theory and better suited to interpolation and extrapolation to unknown compositions.

In the last decade, there have been rapid advancements in using phase-equilibria to find the equilibration pressure of rhyolitic magma (Bégué, et al. 2014b; Gualda and Ghiorso 2014; Harmon, et al. 2018; Pamukçu, et al. 2015). Gualda and Ghiorso (2014) introduced a geobarometer that searches for the equilibration pressure between melt, quartz, and one or two feldspars (hereafter referred to as the “quartz + feldspar geobarometer”). They estimate pre-eruptive crystallization pressures using as input the composition of quartz-hosted melt (glass) inclusions in pyroclastic rocks from the Bishop Tuff, under the assumption that the glass compositions represent melt that equilibrated with quartz and one or more feldspars under pre-eruptive storage conditions (Figure 1). Subsequent work used matrix glass compositions to represent pre-eruptive melt (e.g., Pamukçu, et al. 2015 and others). The Gualda and Ghiorso (2014) quartz + feldspar geobarometer uses the rhyolite-MELTS version 1.0 model to calculate the equilibration pressure of quartz, feldspar, and melt. The quartz + feldspar geobarometer has been applied to many silicic systems, including the Taupō Volcanic Zone (Bégué, et al. 2014b; Gualda, et al. 2018; Gualda, et al. 2019b; Harmon, et al. 2024a; Harmon, et al. 2024b; Pamukçu, et al. 2021; Pamukçu, et al. 2020; Smithies, et al. 2024; Smithies, et al. 2023), Peach Spring Tuff, Silver Creek Caldera (Foley, et al. 2020; Pamukçu, et al. 2015), Bishop Tuff, Long Valley Caldera (Gualda and Ghiorso 2013a; Gualda, et al. 2022), the Youngest Toba Tuff, northern Sumatra (Pearce, et al. 2020); and Hokkaido, Japan (Pitcher, et al. 2021). Generally, rhyolite-MELTS quartz + feldspar geobarometry results compare well to independent volatile and amphibole geobarometry estimates on the same systems (Bégué, et al. 2014b; Gualda, et al. 2019a; Pamukçu, et al. 2015; Pamukçu, et al. 2021). Errors on quartz + feldspar geobarometry results calculated from XRF and EDS-SEM compositions are on the order of 10-20 MPa 1σ (Gualda, et al. in review; Pamukçu, et al. 2021; Pitcher, et al. 2021; Smithies, et al. 2024; Smithies, et al. 2023). These errors are equivalent to 0.4-0.8 km depth assuming a crustal density of 2.7 g cm^{-3}, making the quartz + feldspar geobarometer a useful and relatively precise estimate of pressure and depth.

Although the rhyolite-MELTS quartz + feldspar geobarometer is useful in many rhyolitic systems, it is limited to magma that is saturated in quartz. This limits its usefulness to rhyolitic compositions, and to magma where we know the equilibrium mineral assemblage with confidence. This is a potential problem, as the mineral assemblage in volcanic rocks is often a complex mixture of crystals grown in equilibrium with the surrounding melt/glass (“autocrysts”), and crystals incorporated from other parts of the magmatic system or from the country rock (“antecrysts” and “xenocrysts”) (e.g., Bachmann, et al. 2002). The rock mineral assemblage is therefore not unequivocal proof of the equilibrium mineral assemblage.

Uncertainty over whether or not quartz is saturated is also a significant limitation of using rhyolite-MELTS geobarometry to calculate the pressure that melt was extracted from the mush (hereafter “extraction pressure”, Gualda, et al. 2019b). This method assumes that the bulk composition of erupted magma represents the composition of the melt that equilibrated with the mush (Figure 1; Blundy 2022; Gualda, et al. 2019b). In this scenario, quartz saturation is uncertain as we must infer the mineral assemblage of the mush from erupted mush fragments or from the composition of the erupted magma. This leaves us with the question: how can phase-equilibria models be used to constrain pressure for systems where we are uncertain if quartz is saturated?

Harmon, et al. (2018) introduced a geobarometer that uses the same rhyolite-MELTS thermodynamic model as Gualda and Ghiorso (2014) but searches for the pressure of equilibration between feldspar (typically plagioclase) and one or two pyroxenes (hereafter the “plagioclase + pyroxene geobarometer”). Harmon, et al. (2018) tested the plagioclase + pyroxene geobarometer on basaltic-andesite compositions and found that it could find reasonable pressure estimates. Other studies subsequently applied the plagioclase + pyroxene geobarometer to dacitic to rhyolitic systems (Foley, et al. 2020; Gualda, et al. 2019b; Harmon, et al. 2024b; Pamukçu, et al. 2021; Smithies, et al. 2024; Smithies, et al. 2023). The plagioclase + pyroxene geobarometer is sensitive to oxygen fugacity (f_{O2}) due to the strong partitioning of Fe^{2+} relative to Fe^{3+} in pyroxene. Although independently estimated f_{O2} (e.g. from Fe-Ti oxides) can be used as an input into the geobarometry calculation, there is some uncertainty over whether the f_{O2} estimated from Fe-Ti oxides records pre-eruptive conditions, or whether it may have re-equilibrated during syn-eruptive conditions (Pitcher, et al. 2021; Tomiya, et al. 2013). This makes constraining pressure with the plagioclase + pyroxene geobarometer challenging.

The goal of this study is to demonstrate the efficacy of rhyolite-MELTS across a range of different observed and inferred mineral assemblages. By combining our understanding of plagioclase + pyroxene phase-equilibria geobarometry (Harmon, et al. 2018) with our understanding of quartz + feldspar phase-equilibria geobarometry (Gualda and Ghiorso 2014) to better constrain pressure in quartz-undersaturated dacites and rhyolites, we demonstrate that the principles established in this series (Bégué, et al. 2014b; Gualda and Ghiorso 2014; Harmon, et al. 2018; Pamukçu, et al. 2015) can be adapted to a wider range of igneous systems. We explore examples from two systems: extraction of rhyolitic magma from an unknown mush mineral assemblage in the Taupō Volcanic Zone (TVZ), Aotearoa New Zealand; and pre-eruptive magma storage of quartz-absent rhyodacites to rhyolites from Puyehue-Cordón Caulle (PCC), Chile. Using these case studies, we demonstrate that rhyolite-MELTS geobarometry results can be interpreted to give a more nuanced understanding of melt-only pressures in the presence or absence of quartz.

Methods

Modelling approach for determining pressure and equilibrium mineral assemblage

In Figure 2 we show an example of a quartz + feldspar geobarometry result following the method of Gualda and Ghiorso (2014). The calculations were performed on a pressure-temperature grid, calculating the equilibrium assemblage at 1°C temperature steps and 25 MPa pressure steps. The melt composition that we are interested in (in Figure 2, a whole-rock composition for extraction pressure) was input as the bulk composition of the system. The saturation surfaces represent the highest temperature that each mineral phase is present for a given pressure. The saturation surfaces were interpolated between each 25 MPa interval.

At high temperatures, the simulated magma is liquid (i.e. above the liquidus) with an exsolved fluid phase. Therefore, above the liquidus, the melt composition is the same as the bulk composition of the system. At temperatures below the liquidus, the system has liquid, solids and an exsolved fluid phase. This means that below the liquidus, crystallization of solid phases changes the composition of the melt, such that the simulated melt does not have the same composition as the bulk composition. This is an important realisation, as only the region at or above the liquidus has melt with the same composition as the bulk composition of the system, which is the measured composition input by the user (either a whole-rock or glass composition). Therefore, only pressures and temperatures in the region at or above the liquidus are acceptable for the measured melt composition, while the region below the liquidus does not yield acceptable pressure or temperature solutions for the measured melt composition. If we are searching for an equilibrium assemblage of melt (represented by the measured composition) and minerals, the only part of the diagram in Figure 2 where this is possible is the liquidus. In the example in Figure 2, if we assume that both orthopyroxene and plagioclase are in equilibrium with the input melt composition, there is only one possible pressure and temperature, at 106 MPa and 800 °C. The intersection of the orthopyroxene and plagioclase saturation surfaces therefore gives us the pressure of equilibration between orthopyroxene, plagioclase, and the melt.

The saturation surfaces are interpolated between the 25 MPa pressure intervals. To calculate the saturation surface intersections, we use the parabola-fitting procedure described by Gualda and Ghiorso (2014). The residual temperature between the saturation surfaces at each 25 MPa interval is calculated, then a parabola is fitted to the minimum residual and two points on either side of the minimum (Figure 2). This parabola-fitting procedure is only applied if the minimum is ≤ 5 °C (the minimum temperature threshold in Figure 2). Gualda and Ghiorso (2014) show that the minimum of the parabola is a satisfactory estimate of the saturation surface intersection. When the minimum of the residual curve is never ≤ 5 °C over the pressure range investigated, we conclude that the rhyolite-MELTS geobarometer finds no satisfactory pressure for the melt composition and mineral assemblage of interest.

Case study geobarometry calculations

In this study we show examples from two case studies: rhyolites of the Taupō Volcanic Zone (TVZ), Aotearoa New Zealand; and rhyodacites to rhyolites from Puyehue-Cordón Caulle (PCC), Chile. From the TVZ we show examples of extraction pressure calculations, using whole-rock compositions to model the pressure the eruptible magma was extracted from a mush with unknown mineral assemblage (Figure 1). The TVZ was selected as an example of a system where the erupted magma is quartz-bearing but we are uncertain of the mineralogy of the mush (Table 1). From PCC we show examples of pre-eruptive storage pressure calculations, using glass compositions to model the pressure the melt was in equilibrium with the phenocryst assemblage immediately prior to eruption. In contrast to the TVZ, PCC rhyolites do not have quartz in either the phenocryst mineral assemblage (Table 1) or in the co-erupted mush fragments (Winslow, et al. 2022).

In the TVZ we focus on five large (>50 km^3 dense rock equivalent), caldera-forming eruptions (Table 1). Previously published whole-rock compositions were collated from Smithies, et al. (2023). Each sample (n=53) is an individual pumice clast collected from unwelded ignimbrite deposits. Whole-rock compositions were collected by either XRF (Chimp, Pokai, Kaingaroa, and Mamaku samples) or by inductively coupled plasma optical emission spectrometry (Ohakuri samples). The pumice clasts have sparse (<8% by vol.) plagioclase + orthopyroxene + Fe-Ti oxides ± quartz ± hornblende ± clinopyroxene phenocrysts (Table 1). All the samples are rhyolitic in composition (Figure 3).

For each TVZ composition, we collated geobarometry calculations from Smithies, et al. (2023) and performed additional calculations with the same methodology to expand the range of f_{O2} values. Geobarometry calculations were performed with the rhyolite-MELTS v.1.0 model with an updated version of the MELTS_Excel interface (Gualda and Ghiorso 2015). The latest version of MELTS_Excel and supporting documentation is distributed for free from http://melts.ofm-research.org. Whole-rock compositions were input as the melt composition. Equilibration calculations were performed in a pressure-temperature grid from 500 to 25 MPa in 25 MPa steps and from 1100 °C to 700 °C in 1 °C steps. We forced fluid saturation at all pressures by setting H_2O to 15 wt.%; even though these are unrealistic H_2O contents for most crustal magmas, the presence of exsolved water does not affect the pressure calculations, and it guarantees that the melt is saturated in H_2O (see Ghiorso and Gualda 2015; Gualda and Ghiorso 2014 for full discussion). The calculations were repeated from 0.5 log units below the quartz-fayalite-magnetite (QFM) f_{O2} buffer to 2 log units above it in 0.5 log unit steps (QFM -0.5; QFM; QFM +0.5; QFM +1.0; QFM +1.5; QFM +2.0). For a small subset of samples (POK_105A, POK_112A_A, OHK302B4) we repeated the calculations at QFM -1.0, QFM -1.5, and QFM -2.0.

We include compositions from the three most recent large eruptions at PCC (Table 1). These are relatively small (0.25-1.5 km^3) eruptions, which generated both lava flows and pyroclastic deposits (Lara, et al. 2006; Pistolesi, et al. 2015; Singer, et al. 2008). Compositions were collated from Castro, et al. (2013); Schipper, et al. (2019); Seropian, et al. (2021). The samples (n=33) are individual pyroclastic clasts. Each sample composition is a mean of 9-40 spot compositions measured by WDS-EMP on fresh, unaltered glass. Phenocrysts are sparse in the pyroclastic material (<15 vol.%) with an assemblage of plagioclase + orthopyroxene + clinopyroxene + Fe-Ti oxides (Table 1). The bulk rock and glass compositions are rhyodacitic to rhyolitic (Figure 3).

For each PCC composition, we collated geobarometry calculations from Seropian, et al. (2021) and performed additional calculations with the same methodology to expand the range of f_{O2} values. The input parameters are the same as for the TVZ samples, except that glass compositions were used to result in pre-eruptive storage pressure estimates (Figure 1), and therefore the pressure-temperature grid was reduced to 400 to 25 MPa in 25 MPa steps and from 1100 °C to 700 °C in 1 °C steps. We set H_2O to 10 wt.% to force fluid saturation (see above). The calculations were repeated from 1 log unit below the nickel-nickel oxide (NNO) f_{O2} buffer to 1.5 log units above in 0.25 or 0.5 log unit steps (NNO -1.0; NNO -0.75; NNO -0.5; NNO -0.25; NNO; NNO +0.5; NNO +1.0; NNO +1.5). For three samples (D60_17, A-gr12, B-gr2) we ran additional calculations at NNO -1.5, NNO -2.0, and NNO -2.5. This is approximately equivalent to the f_{O2} range used for the TVZ samples.

Results

Geobarometry results

At the lowest f_{O2} tested (QFM-0.5), the extraction pressures for the TVZ range from 68-381 MPa with a mean of 214 MPa (Figure 4). The modelled mineral assemblages are a mixture of orthopyroxene + plagioclase (n=40), quartz + plagioclase (n=5), and plagioclase + orthopyroxene + quartz (n=8). At higher f_{O2}, the mean pressure result is higher (e.g., 291 MPa at QFM+0.5) and there are fewer plagioclase + orthopyroxene results (e.g., n=16 at QFM+0.5) and plagioclase + orthopyroxene + quartz results (e.g., n=1 at QFM+0.5) relative to the number of quartz + plagioclase results (e.g., n=36 at QFM+0.5). At the highest f_{O2} tested (QFM+2), the TVZ extraction pressures range from 122-468 MPa with a mean of 327 MPa. At high f_{O2} (QFM+2) the results are entirely quartz + plagioclase mineral assemblages (n=50).

The PCC results are dominated by a plagioclase + orthopyroxene mineral assemblage at all f_{O2} tested (Figure 4). Quartz-bearing mineral assemblages only occur in a minority of samples (n=3) at the highest f_{O2} we tested (NNO+1 and NNO+1.5). The pressure results are strongly dependent on f_{O2}. At the lowest f_{O2} tested (NNO-1.0) the pressures are relatively low, ranging from 25-123 MPa with a mean of 80 MPa. At progressively higher f_{O2}, the pressures increase. At the highest f_{O2} tested (NNO+1.5), the pressures range from 285-361 MPa with a mean of

324 MPa. At high f_{O2}, some calculations repeatedly crashed, failing to return a result (n=6 at NNO+0.5, n=9 at NNO+1, n=24 at NNO+1.5).

The effect of f_{O2} on the plagioclase + orthopyroxene results

The equilibrium mineral assemblage results (and therefore pressure results) are sensitive to f_{O2} (Figure 5). In Figure 5a-d we show geobarometry results for the same composition as Figure 2 but using different f_{O2} values. The input parameters for each calculation are identical except for f_{O2}. The effect of varying f_{O2} on the orthopyroxene saturation temperature is evident. At low f_{O2} (QFM -0.5), which results in lower Fe^{3+}/Fe^{total} in the melt, the orthopyroxene saturation temperature is high (Figure 5a). In this example, quartz is never in equilibrium with the measured melt composition. Therefore, the only acceptable pressure solution is plagioclase + orthopyroxene at 102 MPa. At more oxidising f_{O2} and higher melt Fe^{3+}/Fe^{total} (Figure 6) the orthopyroxene saturates at lower temperatures. Because the orthopyroxene saturation temperature is lower, the plagioclase + orthopyroxene intersection occurs at higher pressures. This leads to a negative correlation between f_{O2} and plagioclase + orthopyroxene pressures (Figure 6). The relationship between f_{O2} and pressure is not linear (Figure 6), given that the Fe^{3+}/Fe^{total} ratio does not vary linearly with f_{O2}. For strongly reducing f_{O2} values (e.g., <<QFM or <<NNO, Figure 6), the majority of the iron in the system is reduced to Fe^{2+}. At strongly reducing f_{O2} the pressure values therefore become less dependent on f_{O2} (Figure 6). At more oxidising f_{O2} (e.g., QFM +0.5, Figure 5c), the saturation temperature of orthopyroxene decreases, so the orthopyroxene saturation surface intersects with quartz and plagioclase on the liquidus. This means that it is possible for orthopyroxene, plagioclase, and quartz to be in equilibrium together with melt of the measured composition, resulting in a three-phase orthopyroxene + quartz + plagioclase pressure at 177 MPa. At even higher f_{O2} (QFM +1, Figure 5d), the orthopyroxene saturation temperature decreases further, such that the orthopyroxene saturation surface is below the quartz and plagioclase saturation surfaces. At this f_{O2}, orthopyroxene cannot be in equilibrium with quartz, plagioclase, and the measured melt composition. The only acceptable pressure result is therefore quartz + plagioclase at 187 MPa. Importantly, the quartz + plagioclase pressure is the same as the three-phase orthopyroxene + quartz + plagioclase pressure, within the error of the parabola curve-fitting procedure (see Figure 2). In the cases in which quartz is not present, the quartz + plagioclase pressure represents a maximum pressure, given that only at pressures below that intersection

can the melt of given composition be in equilibrium with plagioclase and not quartz – this result is independent of f_{O2}.

Discussion

Dealing with unknown f_{O2}

The strong dependence of orthopyroxene + plagioclase ± quartz pressures on f_{O2} (Figures 5 & 6) leads to a challenge: how do we constrain pressure for orthopyroxene-bearing dacites and rhyolites? Here, we discuss strategies for constraining pressure in the following scenarios: 1) we are confident that quartz is in equilibrium with the melt; 2) we are confident that quartz is NOT in equilibrium with the melt (but plagioclase and orthopyroxene are); 3) we are unsure if quartz is in equilibrium with the melt.

Scenario 1: quartz is in equilibrium with the melt

If we are confident that quartz is saturated, we can use the rhyolite-MELTS geobarometer to calculate the pressure of equilibration between the melt, quartz, and feldspar. For example, many of the Taupō Volcanic Zone rhyolites have plagioclase and quartz phenocrysts, which we are reasonably confident were in equilibrium with the surrounding melt (now quenched as glass) (Bégué, et al. 2014b; Gualda, et al. 2018; Smithies, et al. 2023). These quartz + plagioclase pressures are completely independent of f_{O2} – note that the quartz and plagioclase saturation surfaces shown in Figure 5 do not change with varying f_{O2}. Orthopyroxene is also a phenocryst phase in these rhyolites, so we could adjust f_{O2} to find a value that gives a quartz + plagioclase + orthopyroxene intersection. Importantly, the pressure of a three-phase intersection is the same as from the two-phase quartz + plagioclase intersection. The search in f_{O2} space therefore does not give us any further constraint on pressure, only on f_{O2}. This demonstrates that the quartz + feldspar geobarometer of Gualda and Ghiorso (2014) is sufficient to determine pressure in quartz-saturated systems without modelling additional phases. Nonetheless, quartz + plagioclase + orthopyroxene geobarometry could be used to find an f_{O2} that is internally consistent with the rhyolite-MELTS model.

Scenario 2: quartz is NOT in equilibrium with the melt

The rhyolites from the recent PCC eruptions have plagioclase and orthopyroxene phenocrysts, but quartz is absent (Table 1). This means that only a plagioclase + orthopyroxene ±

clinopyroxene pressure solution would be acceptable. As the pyroxenes are sensitive to f_{O2}, this makes constraining pressure more challenging. A first order approach is to use an f_{O2} value for the system that has been independently determined. Conveniently, the commonly used oxythermobarometer of Ghiorso and Evans (2008) is internally consistent with the MELTS family of thermodynamic models, so f_{O2} calculated with this oxythermobarometer are preferrable for finding pressures. For example, f_{O2} for the 2011 PCC eruption is estimated to be between NNO -0.9 and NNO -0.8 using the Ghiorso and Evans (2008) oxythermobarometer (Castro, et al. 2013; Jay, et al. 2014; Mingo 2019). The rhyolite-MELTS pyroxene + plagioclase pressure estimates at NNO -1.0 and NNO -0.75 for the 2011 PCC eruption (i.e., 25-146 MPa) are in excellent agreement with independent geobarometry and geophysical estimates of magma storage depths for the same eruption (50-140 MPa; Table 2) (Seropian, et al. 2021).

Even for eruptions where f_{O2} has not been determined, there is a limited range of f_{O2} that could be considered reasonable. Global compilations of erupted magmas from subduction systems show a limited range of f_{O2} between QFM and QFM +2 (Cottrell, et al. 2021; Ghiorso and Evans 2008; Ghiorso and Gualda 2013). The extremely reducing f_{O2} shown in Figure 6 are therefore generally implausible.

An important caveat to using f_{O2} constrained by Fe-Ti oxides is that we cannot be certain that the f_{O2} recorded by the Fe-Ti oxides was the f_{O2} of the system at the pressure recorded by the melt. Both Fe and Ti in Fe-Ti oxides can re-equilibrate rapidly (days) (Tomiya, et al. 2013; Van Orman and Crispin 2010), so they are likely to record the eruptive conditions and immediately prior to eruption rather than the longer-term pre-eruptive storage (years). During magma storage and ascent, f_{O2} is affected by complex open-system processes such as degassing (Burgisser and Scaillet 2007). If this is the case, the f_{O2} recorded by Fe-Ti oxides is not the f_{O2} of pre-eruptive storage. Using Fe-Ti oxides to estimate f_{O2} is particularly problematic for extraction pressures, as we are considering the equilibration of the melt recorded by the bulk-rock, whereas the Fe-Ti oxide phenocrysts likely equilibrated with the melt preserved as glass. (Figure 1).

In the absence of any information about f_{O2}, we make two crucial observations that can constrain a range of possible pressures. The first observation is that the plagioclase + orthopyroxene pressure must always be less than the quartz + plagioclase pressure, as orthopyroxene must saturate at a higher temperature than quartz in quartz-undersaturated magma. Therefore, we can always constrain a maximum pressure in quartz-undersaturated magma by taking the quartz + plagioclase pressure as a maximum. The second observation is that at strongly reducing f_{O2} values (e.g., <QFM-1.5, <NNO-1), as Fe^{3+}/Fe^{total} approaches 0, the orthopyroxene + plagioclase pressures approach a constant value (Figure 6). We can therefore also constrain a minimum pressure by calculating the pressure at strongly reducing conditions. These two observations give us a range of possible pressures.

<u>Scenario 3: quartz may or may not be in equilibrium</u>

There are several scenarios in which we are uncertain whether the system is quartz-saturated or not. Here, we show extraction pressures, in which we use whole-rock compositions from the TVZ to represent the theoretical melt that equilibrated with the mush mineral assemblage (Figure 1; Blundy 2022; Gualda, et al. 2019b). We are uncertain what mineral assemblage the melt was extracted from, as the mush typically does not erupt. Based on occasionally erupted mush fragments (Brown, et al. 1998; Burt, et al. 1998; Graeter, et al. 2015) and the composition of the erupted rhyolites we can reasonably assume the mush in the TVZ is either granodioritic (plagioclase + quartz + orthopyroxene) or dioritic (plagioclase + orthopyroxene). This leaves us uncertain whether magmas erupted from the TVZ were extracted from mush that is or is not quartz-saturated.

In cases in which we are uncertain of whether quartz is saturated or not, the quartz + plagioclase pressures are the maximum possible pressures (see Figure 5), with lower pressures possible for a plagioclase + orthopyroxene (Pamukçu, et al. 2021). This is also seen in Figure 4, which demonstrates that quartz + plagioclase pressures constitute a maximum bound on possible pressures. Figure 4 also shows that a range of orthopyroxene + plagioclase pressures is possible, depending on f_{O2}. If there is some information about f_{O2}, then the best estimate of f_{O2} for the system can be used to find both the likely pressure and the likely equilibrium mineral assemblage. The PCC storage pressure results are only quartz-saturated at unreasonably high f_{O2} (>NNO +1), more than one log unit higher than the estimated f_{O2} for PCC (Figure 6). We would thus conclude – based on rhyolite-MELTS geobarometry – that PCC magmas are unlikely to be quartz-saturated. This is in agreement with observations of natural rocks, given that PCC volcanic rocks are typically quartz-absent (Table 1). In contrast, the rhyolite-MELTS models show that some of the TVZ melts extracted from the mush could have equilibrated with quartz at reasonable f_{O2} (Figure 6). This agrees with evidence from mush fragments co-erupted with TVZ rhyolites, some of which are quartz-bearing (Brown, et al. 1998; Burt, et al. 1998). In this sense, our results show that – at least in some cases – the rhyolite-MELTS geobarometer can be used to constrain mineral assemblage, which is particularly useful in the case of extraction pressures (see Gualda, et al. 2019b).

Plagioclase, orthopyroxene, and magnetite geobarometry

An alternative approach to solving the problem of the f_{O2} sensitivity of plagioclase + pyroxene geobarometry is to add a third phase to reduce the degrees of freedom. Although the PCC magmas are quartz-absent, the erupted rocks all have magnetite phenocrysts (Table 1). In Figure 7, we therefore plot the saturation surface of magnetite in addition to plagioclase and orthopyroxene. As an Fe-bearing phase, magnetite is also sensitive to f_{O2}. The saturation temperature of magnetite increases as f_{O2} increases, the inverse relationship to orthopyroxene. This inverse relationship is expected, given that orthopyroxene predominantly incorporates Fe^{2+} into its mineral structure whereas magnetite incorporates Fe^{3+}. This means that it is possible to find a three-phase intersection of plagioclase + orthopyroxene + magnetite by incrementally adjusting f_{O2}. Magnetite is much more sensitive to f_{O2} than orthopyroxene, so smaller f_{O2} steps are necessary. From visual inspection of the example in Figure 7, the three-phase intersection must occur between NNO -1 and NNO -0.5. We therefore perform a binary search, first performing geobarometry calculations in 0.25 log intervals followed by 0.125 log intervals. We note, however, that rhyolite-MELTS is not precise to three decimal places so the significance of the second and third decimal places should not be overinterpreted. By performing this binary search, we find a three-phase intersection at NNO -0.75 for the composition shown in Figure 7.

To test this procedure, we search for plagioclase + orthopyroxene + magnetite intersections on every PCC composition. By visual inspection of the phase diagrams, we determine that the three-phase intersection must occur between NNO -1.25 and NNO for every composition (e.g., Figure 7). We therefore repeat the geobarometry calculations for each PCC composition at nine intervals between NNO -1.25 and NNO (i.e., 0.125 log steps), keeping all other model parameters the same (see Methods). Although inspection of the phase diagrams reveal three-phase intersections for most compositions (Figure 7), only 4 of the 33 compositions return a result using the parabola-fitting procedure shown in Figure 2. We therefore follow the methodology of Harmon, et al. (2018) and increase the residual temperature threshold to 10 °C. Because the magnetite saturation temperature is so sensitive to f_{O2}, a larger threshold is reasonable to avoid false negatives. With a 10 °C threshold, 24 of the 33 compositions return a result. Geobarometry results using a 5 °C, 8 °C, and 10 °C threshold are included in Online Resource 4. The overall pressure distribution is unchanged.

The plagioclase + orthopyroxene + magnetite pressures for the PCC samples are between 39 and 142 MPa, in excellent agreement with independent pressure estimates for PCC (Table 2). This suggests that the addition of magnetite improves the performance of the plagioclase + orthopyroxene geobarometer in quartz-absent magma and is an elegant solution to simultaneously constrain pressure and f_{O2}.

In addition, the f_{O2} at which these intersections occur (NNO -0.5 to NNO -1.125) overlaps with f_{O2} estimated for the PCC magma using Fe-Ti oxides with the Ghiorso and Evans (2008) oxythermobarometer (NNO -0.1 to NNO -0.9, Figure 8). The Fe-Ti oxides suggest that the 1921-1922 had the most oxidising f_{O2}, 1960 was slightly more reducing, and 2011-2012 was much more reducing (Table 2). This trend is also apparent in the f_{O2} estimated with the plagioclase + orthopyroxene + magnetite geobarometer (Figure 8). This agreement is excellent given the errors associated with each method.

Implications

Quartz + plagioclase geobarometry as maximum pressure estimates

The most important implication of the relationships between quartz, feldspar, and orthopyroxene demonstrated in Figure 5 is that the maximum possible equilibration pressure of a rhyolite is given by the quartz + feldspar intersection, regardless of whether quartz is present in the system (Pamukçu, et al. 2021). The quartz + feldspar pressure results from rhyolite-MELTS have been repeatedly shown to compare well to other geobarometers (Al-in-hornblende and H_2O-CO_2 volatile saturation; Bégué, et al. 2014b; Gualda, et al. 2019a; Pamukçu, et al. 2015). The quartz + feldspar pressures are relatively insensitive to fluid saturation (Ghiorso and Gualda 2015; Gualda and Ghiorso 2014), and, as shown in Figure 5, are insensitive to f_{O2}. Uncertainty on the quartz + feldspar geobarometer due to analytical uncertainty are on the order of 10-40 MPa 1σ, which depend on uncertainties associated with the used compositions (Gualda and Ghiorso 2014; Gualda, et al. in review; Pamukçu, et al. 2021; Pitcher, et al. 2021; Smithies, et al. 2024; Smithies, et al. 2023). The quartz + feldspar geobarometer therefore provides a useful constraint on the equilibration pressure of rhyolites, even in cases in which they are not quartz-saturated (see also Blundy and Cashman 2001; Gualda and Ghiorso 2013b).

Estimating f_{O2}

A persistent challenge to plagioclase + pyroxene geobarometry is the sensitivity of the pressure results to f_{O2} (Harmon, et al. 2018). We show that this uncertainty can be reduced with two methods: 1) using independent estimates of f_{O2} (e.g., Fe-Ti oxides) (Figure 6); and 2) searching in f_{O2} space for plagioclase + orthopyroxene + magnetite intersections (Figure 8). By adding magnetite, we can obtain more precise pressure estimates for quartz-absent systems, including systems where we have little independent information about f_{O2}. The success of the plagioclase + orthopyroxene + magnetite pressures is particularly important given that the pyroxene geobarometry results are sensitive to volatile concentrations, especially in volatile-undersaturated intermediate magma (Harmon, et al. 2018), and the pyroxene model in rhyolite-MELTS may not correctly predict the stability of clinopyroxene (see Brugman and Till 2019; Wieser, et al. 2025). The results shown in Figure 8 also demonstrate that it is possible to use the geobarometry procedure to obtain an estimate of f_{O2} from melt composition alone.

Beyond two- or three-phase rhyolite-MELTS geobarometers

In previous parts of this series (Bégué, et al. 2014b; Gualda and Ghiorso 2014; Harmon, et al. 2018; Pamukçu, et al. 2015) the quartz + feldspar, quartz + 2 feldspar, plagioclase + pyroxene, and the plagioclase + 2 pyroxene geobarometers were treated as separate entities. The methods that we have shown here, and the examples in Figures 2, 5, and 7, show how rhyolite-MELTS can be applied to search for the equilibration pressure between melt and any mineral assemblage of interest, within the constraints of the existing MELTS models.

Rhyolite-MELTS geobarometry does not need to be limited to just two or three mineral phases (Foley, et al. 2020; Gualda, et al. in review). For example, Figure 9 shows a four-phase assemblage of quartz + plagioclase + orthopyroxene + magnetite for an extraction pressure calculation for a whole-rock composition from the TVZ. As with the three-phase plagioclase + orthopyroxene + magnetite calculations, we search in f_{O2} space for the intersections of multiple phases. Although the example in Figure 9 does not give any further pressure information than a two-phase assemblage, the multiple phase assemblage reduces the degrees of freedom in compositional space and gives more confidence to the pressure calculation. If all we are interested in is pressure, searching in f_{O2} space for an orthopyroxene + quartz + plagioclase solution does not provide further pressure information. Consequentially, the quartz + feldspar geobarometer of Gualda and Ghiorso (2014) is useful for magma saturated in quartz and feldspar, without the need to add other phases (c.f. multiply saturated geobarometers, Blundy 2022). However, a multiple-phase solution has fewer degrees of freedom than a two-phase solution, so three- or four- phase pressure results will have smaller uncertainties resulting from analytical error (Gualda and Ghiorso 2014; Pamukçu, et al. 2021; Pitcher, et al. 2021; Smithies, et al. 2024; Smithies, et al. 2023).

Searching for relevant multiple phase intersections could be used to refine uncertain melt compositions and intensive parameters. In the examples presented here, we have shown that three-phase intersections that include Fe-bearing phases are useful for refining f_{O2}. It would also be informative to search within uncertainty of other parameters, for example adjusting volatile content or major element compositions within analytical uncertainty. When the composition is known, the coincidence of four or more phases increases our confidence that – in some cases – the geobarometer can be used to infer likely mineral assemblages. The Rhyolite-MELTS geobarometer is useful for more than just pressure when information from multiple phases is investigated.

Conclusions

We demonstrate how rhyolite-MELTS can be used to search for equilibration pressures between melt and any mineral assemblage of interest (within the limitations of rhyolite-MELTS), and give examples of quartz, plagioclase, orthopyroxene, and magnetite. The rhyolite-MELTS geobarometry results must be interpreted carefully as only mineral assemblages on the simulated liquidus can be in equilibrium with the melt composition input by the user. We hope this paper can be a guide to interpretation of rhyolite-MELTS results that move beyond the established geobarometry applications.

If quartz is in equilibrium with the melt, then the two-phase quartz + feldspar geobarometer is sufficient to estimate pressure; multiple saturation of additional phases does not further constraint the pressure. In quartz-undersaturated magma, a useful relationship in rhyodacites and rhyolites is that quartz + feldspar equilibration pressures are always maxima. At pressures higher than the quartz + feldspar equilibration pressure, feldspar is undersaturated, which is generally untenable for igneous rocks (e.g. Blundy and Cashman 2001; Gualda and Ghiorso 2013b). This means that even where quartz is not present, or in circumstances where we are uncertain if quartz is saturated (e.g., when modelling melt extraction from an assumed mush mineral assemblage), the rhyolite-MELTS quartz + feldspar geobarometer can still be used to calculate maximum pressures.

In quartz-undersaturated magma, plagioclase + orthopyroxene ± magnetite geobarometry gives a useful estimate of pressure, despite the sensitivity of orthopyroxene and magnetite to f_{O2}. For PCC, plagioclase + orthopyroxene pressures calculated at independently determined f_{O2} are similar to independent pressure estimates. Alternatively, we can search within f_{O2} space to find the f_{O2} at which plagioclase + orthopyroxene + magnetite saturate together. The f_{O2} and pressures estimated with this method for PCC are in excellent agreement with independent estimates. This suggests there is potential to use rhyolite-MELTS geobarometry not only to estimate pressure, but also to refine intensive parameters such as f_{O2} by searching in compositional space for multiple (≥3) mineral phase intersections.

Rhyolite-MELTS geobarometry does not need to be limited to three phases, and multiple saturation of a higher number of phases can (1) give further constraints on intensive parameters; (2) yield pressure estimates with smaller uncertainties; and (3) help determine mineral assemblages that equilibrated with a given melt composition.

Authorship contribution statement

All authors contributed to the study conception. S. Smithies performed the data analysis, wrote the first draft of the manuscript, and drafted the figures. All authors commented on and revised subsequent versions of the manuscript.

Supplementary information

Online Resource 1: Spreadsheet of compositions used in this study with geobarometry results.

Online Resource 2: Animated version of Figure 5 showing orthopyroxene saturation surface temperature decreasing as f_{O2} increases.

Online Resource 3: Animated version of Figure 7 showing magnetite saturation surface temperature increasing as f_{O2} increases.

Online Resource 4: Plagioclase + orthopyroxene + magnetite geobarometry results for PCC as in Figure 8 calculated with a residual temperature threshold of ≤8 °C and ≤5 °C.

Tables

Table 1 Characteristics of the eruptions included in this study.

Volcanic centre	Eruption	Eruption age	Volume (km^3)	Phenocryst assemblage	Crystal content	f_{O2}
Taupō Volcanic Zone (TVZ), Aotearoa New Zealand	Mamaku	240 ± 11 ka[a]	100	Plagioclase > quartz > orthopyroxene + Fe-Ti oxides > ± tr. augite ± tr. hornblende [d]	5-7 vol.% [d]	QFM 0 to +0.8 [j]
	Ohakuri	240 ± 11 ka[b]	150	Plagioclase > quartz > orthopyroxene > Fe-Ti oxides [e]	<5 vol.% [e]	QFM 0 to +0.8 [j]
	Pokai	275 ± 20 ka[a]	100	Plagioclase > orthopyroxene > quartz > Fe-Ti oxides > ± tr. clinopyroxene ± tr. amphibole [f]	2-8 vol.% [f]	QFM -0.2 to +0.6 [k, l]
	Kaingaroa	298 ± 3 ka[c]	100	Plagioclase > orthopyroxene > Fe-Ti oxides > ± tr. hornblende ± tr. augite ± tr. quartz [g]	<3.5 wt.% [g]	QFM 0 to +0.4 [m]
	Chimp	ca. 310 ka	50	Plagioclase > orthopyroxene + Fe-Ti oxides > > ± amphibole ± tr. clinopyroxene ± tr. quartz ± tr. biotite	<8 vol.% [f]	QFM +0.3 [l]
Puyehue-Cordón Caulle (PCC), Chile	1921-1922 (CCV)	1921-1922 CE	0.4	Plagioclase + orthopyroxene + clinopyroxene + spinel [h]	5-15% [h]	NNO -0.4 to -0.1 [n, o]
	1960 (CCVI)	1960 CE	0.25	Plagioclase + orthopyroxene + clinopyroxene + spinel [h]	5-15% [h]	NNO -0.5 to -0.2 [n, o]
	2011-2012	2011-2012 CE	1.5	plagioclase > orthopyroxene > clinopyroxene > magnetite + ilmenite [i]	5 vol.% [i]	NNO -0.9 to -0.8 [o, p, q]

Age references: a) Leonard (2003); b) Gravley, et al. (2007); c) Downs, et al. (2014).

Petrography references: d) Milner, et al. (2003); e) Gravley (2004); f) Karhunen (1993); g) Beresford, et al. (2000); h) Gerlach, et al. (1988) i) Castro, et al. (2013).

f_{O2} references, all calculated with the oxythermobarometer of Ghiorso and Evans (2008): j) Bégué, et al. (2014a) k) recalculated from oxide compositions reported by Deering, et al. (2010); l) recalculated from oxide compositions reported by Karhunen (1993); m) recalculated from oxide compositions reported by Beresford, et al. (2000); n) Gerlach, et al. (1988); o) Mingo (2019); p) Castro, et al. (2013); q) Jay, et al. (2014).

Table 2 Comparison of pre-eruptive storage pressure estimates for the 2011 PCC eruption using independent petrologic and geophysical techniques.

Pressure estimate method	H_2O-CO_2 geobarometer*	Petrologic experiments	Inflation source modelled from InSAR[+]	Rhyolite-MELTS plagioclase + pyroxene geobarometer at ΔNNO -1.0	Rhyolite-MELTS plagioclase + pyroxene geobarometer at ΔNNO -0.75	Rhyolite-MELTS plagioclase + pyroxene + magnetite geobarometer
	Jay, et al. (2014)	Castro, et al. (2013)	Delgado, et al. (2019); Jay, et al. (2014); Wendt, et al. (2017)	Seropian, et al. (2021); this study	Seropian, et al. (2021); this study	This study
P_{min}		50	90	25	49	39
P_{mean}	140			73	90	76
P_{max}		115	135	123	146	142

*In pyroxene glass inclusions (n=6) using the H_2O-CO_2 model of Papale, et al. (2006)
[+]Converted from depth assuming a crustal density of 2.3 g cm^{-3}.

Figures

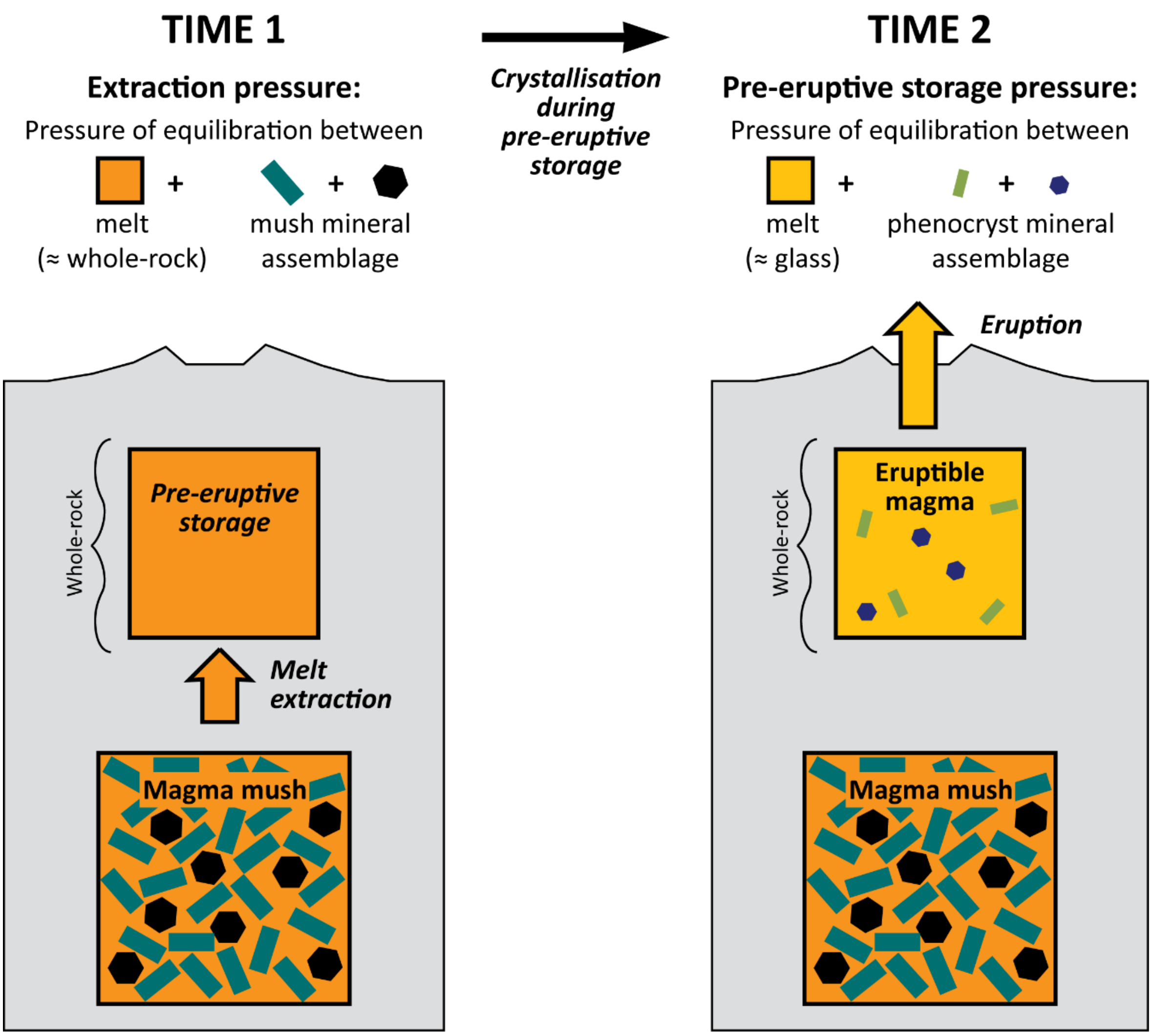


Fig. 1 Conceptual magma system model after Gualda, et al. (2019b) showing definition of extraction pressure (equilibration between bulk magma composition and the mush mineral assemblage) and pre-eruptive storage pressure (equilibration between melt and crystals immediately prior to eruption). In the case of extraction pressures, the mush mineral assemblage is unknown, whilst in the case of storage pressures the phenocrysts could be assumed to be in equilibrium with the glass composition.

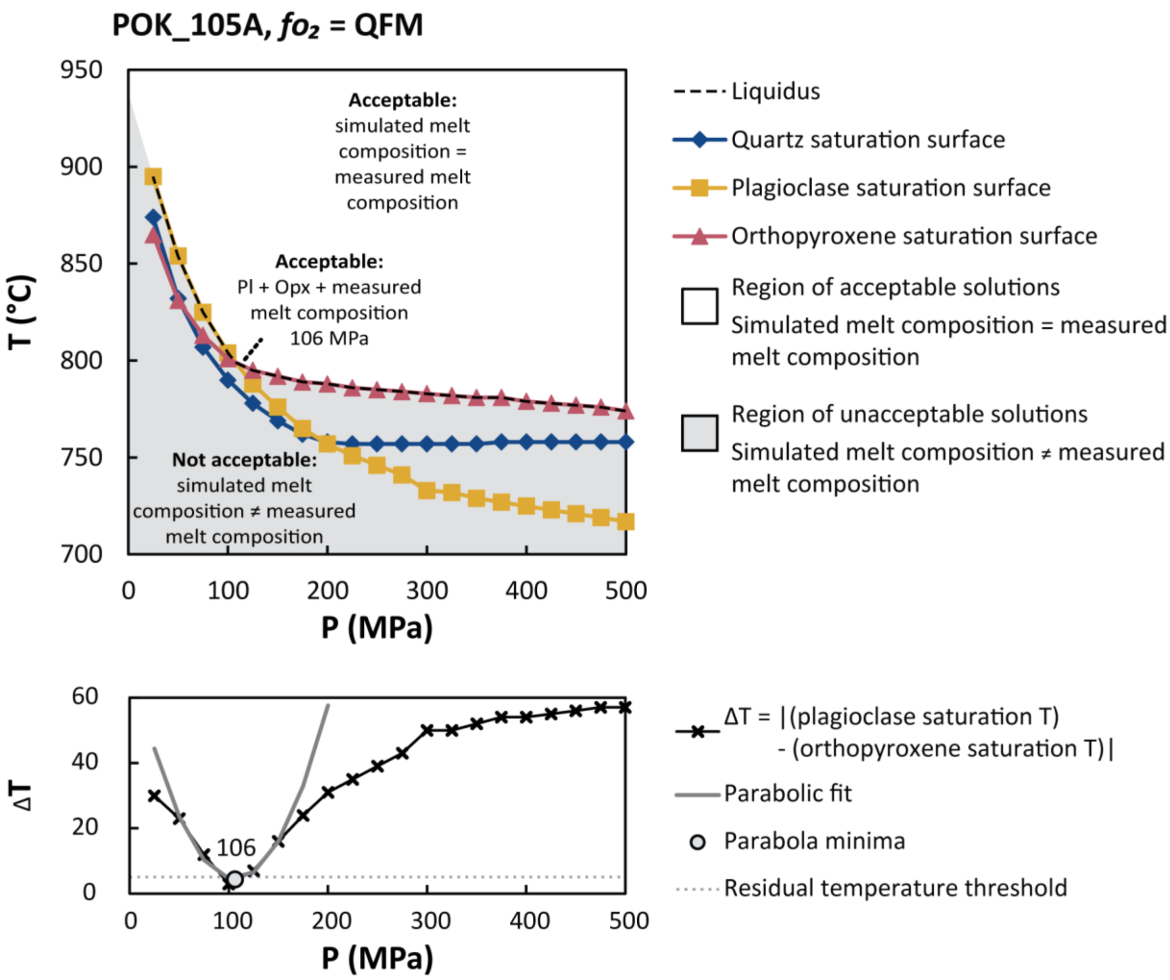


Fig. 2 Top: pressure-temperature phase diagram result from a typical rhyolite-MELTS geobarometry calculation (sample POK_105A at the QFM buffer). Above the liquidus (dashed line) the melt composition simulated by rhyolite-MELTS is the same as the bulk composition of the system input by the user (i.e. the measured composition, a whole-rock pumice composition in this case). Below the liquidus the simulated melt is fractionated, so the simulated melt does not have the same composition as the measured melt composition. This means that pressure solutions for the measured melt composition must be on or above the liquidus. If both plagioclase and orthopyroxene are in equilibrium with the measured melt composition, the only possible pressure is at the intersection of the plagioclase and orthopyroxene saturation surfaces at 106 MPa. Bottom: illustration of parabola-fitting procedure to determine the pressure that the plagioclase and orthopyroxene saturation surfaces intersect. A parabola is fit along the lowest temperature difference and the temperature differences two pressure steps either side of the lowest temperature difference. The parabola-fitting procedure is only performed if $\Delta T \leq 5$ °C (the residual temperature threshold). This ensures that pressures are only calculated if there is a true intersection.

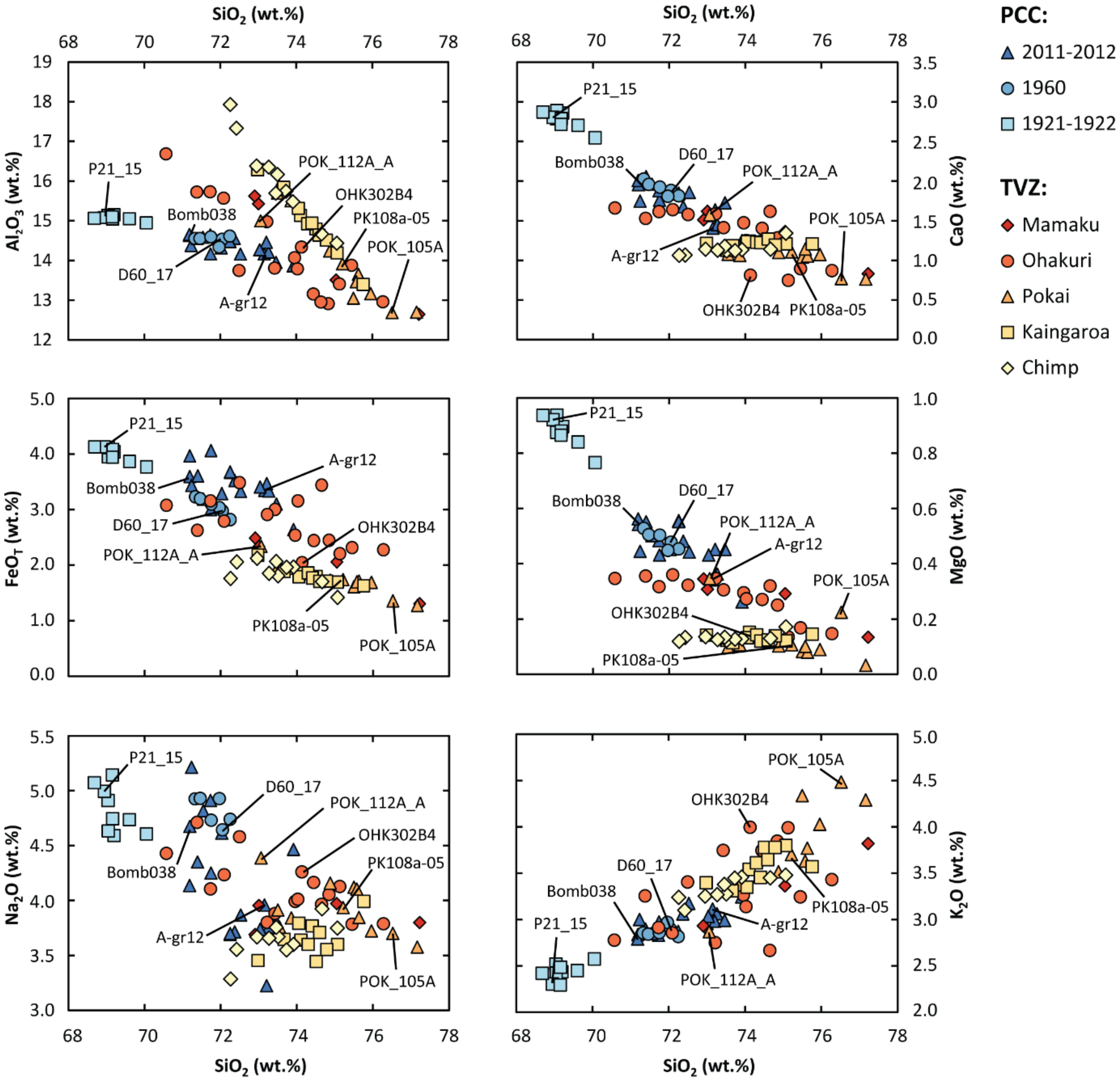


Fig. 3 Major-element compositions from PCC (blue symbols) and TVZ (yellow-red symbols) samples used for the geobarometry calculations in this study. Compositions used as examples in Figures 2, 5, 6, 7, and 9 are labelled. All compositional data is included in Online Resource 1.

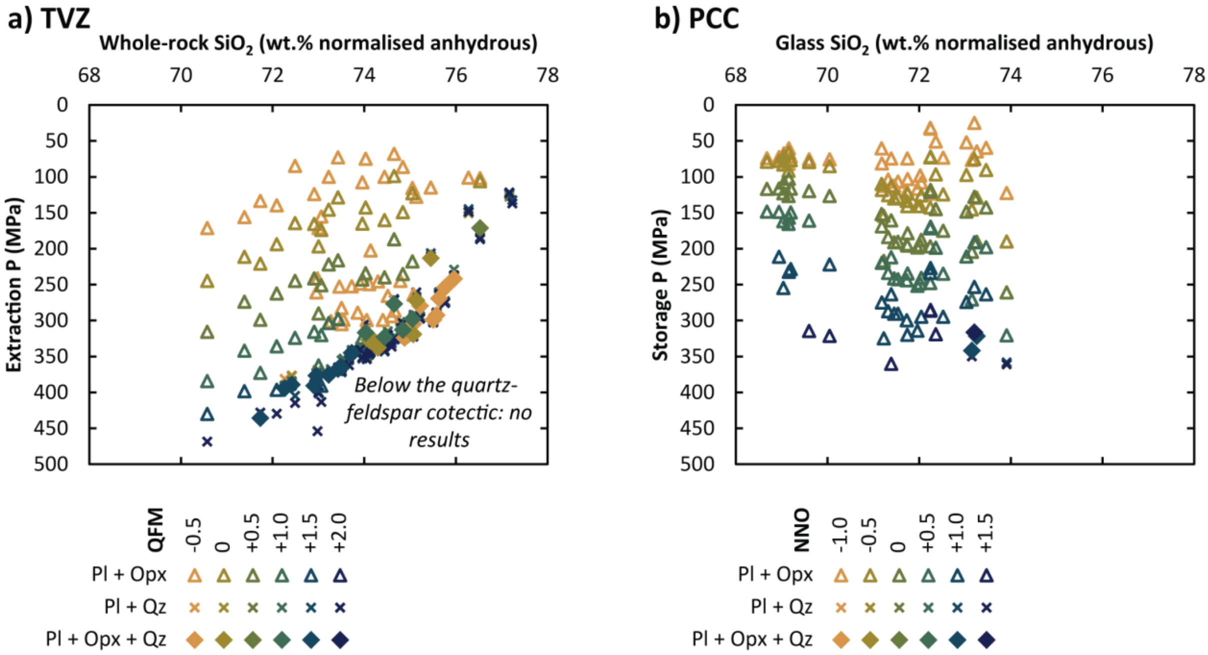
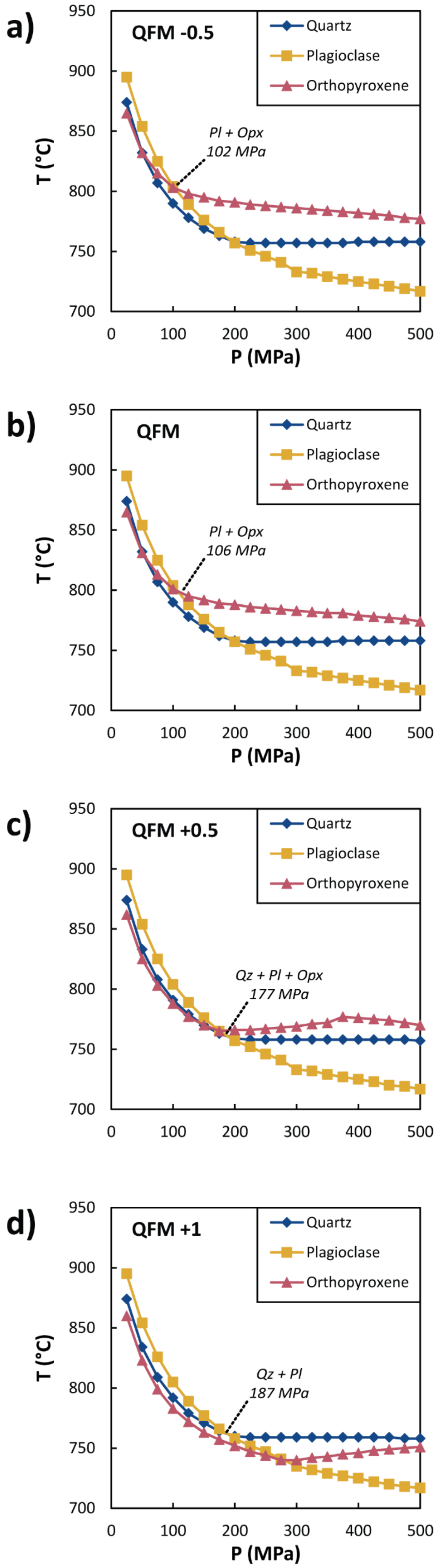


Fig. 4 Geobarometry results for all compositions at various f_{O2} (Online Resource 1). Symbol shape shows acceptable mineral assemblage as in Figure 6, symbol shading shows f_{O2} as in Figure 6. In the high-silica rhyolites of the TVZ (a) there is a region below the quartz-feldspar cotectic where no pressure solutions are possible. This demonstrates that the quartz + feldspar geobarometer can be used to constrain maximum pressure.


a)
QFM -0.5
Quartz
Plagioclase
Orthopyroxene
Pl + Opx
102 MPa
T (°C)
P (MPa)
b)
QFM
Pl + Opx
106 MPa
c)
QFM +0.5
Qz + Pl + Opx
177 MPa
d)
QFM +1
Qz + Pl
187 MPa

591

Fig. 5 Example of quartz + plagioclase + orthopyroxene saturation surfaces for the same model inputs (sample POK_105A) but varying f_{O2}. The quartz and plagioclase saturation temperatures and pressures are invariable with f_{O2}, whilst the orthopyroxene saturation temperature decreases as f_{O2} increases. At low f_{O2} (QFM -0.5 and 0; a, b) the only acceptable pressure results are plagioclase + orthopyroxene. At moderate f_{O2} (QFM +0.5; c) there is a three-phase plagioclase + orthopyroxene + quartz pressure solution. At high f_{O2} (QFM +1; d) orthopyroxene is no longer saturated on the liquidus so only quartz + plagioclase pressure solutions are possible. An animated version of this figure showing an extended range of f_{O2} is available in Online Resource 2.

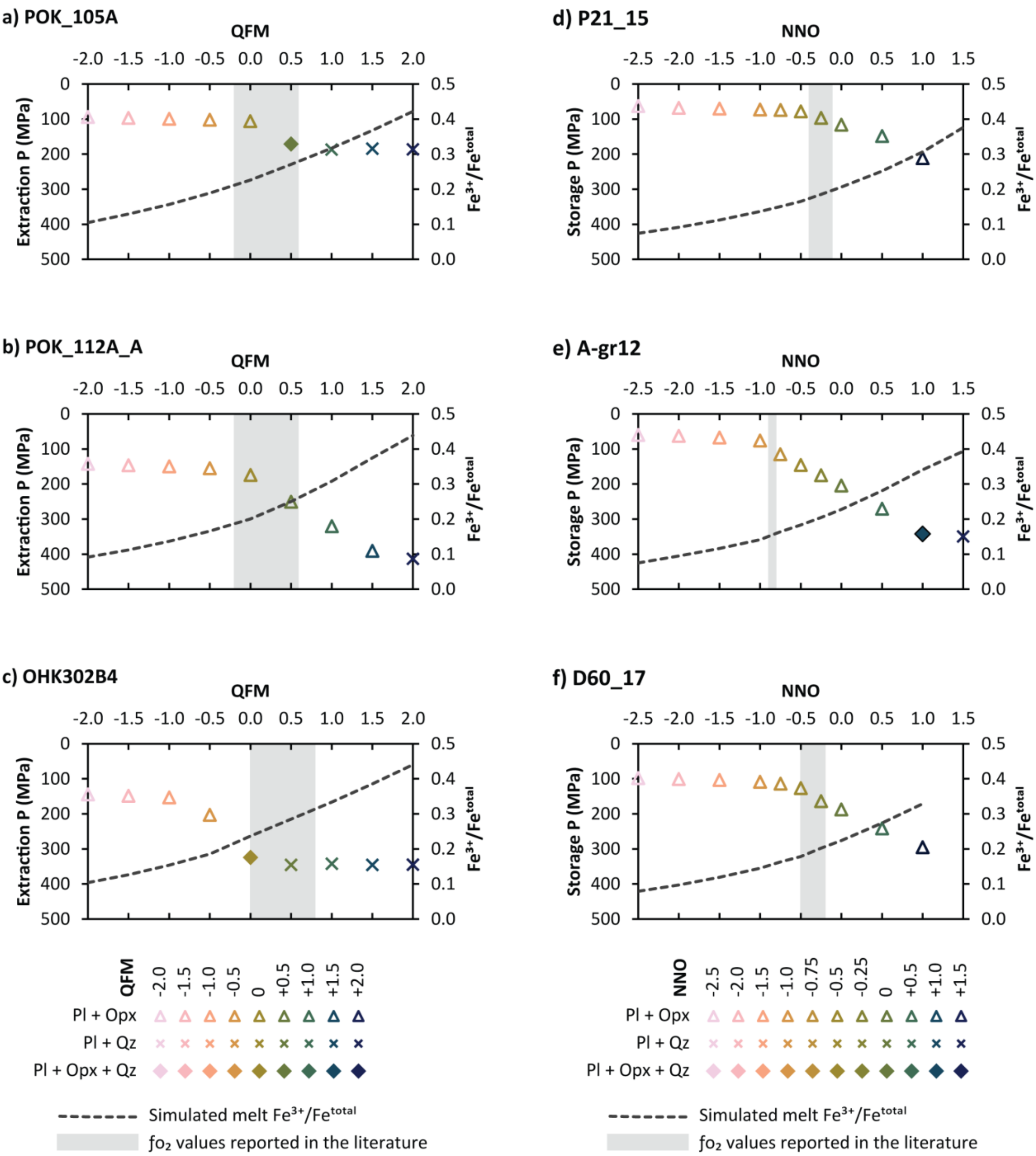


Fig. 6 Three examples of geobarometry results from the TVZ (a-c) and PCC (d-f) as a function of f_{O2}. Note that a) shows the same calculations as Figure 5. Symbol shape shows acceptable mineral assemblage as in Figure 4, symbol shading shows f_{O2} as in Figure 4. Acceptable mineral assemblage shown with symbols. At low f_{O2} the results are plagioclase + orthopyroxene (triangles), as f_{O2} increases some compositions return quartz + plagioclase + orthopyroxene (diamonds), and at high f_{O2} some compositions return quartz + plagioclase (crosses). The dashed line shows Fe^{3+}/Fe^{total} in the simulated liquid modelled by rhyolite-MELTS, this is

correlated with f_{O2} leading to the sensitivity of pyroxene to f_{O2}. The grey boxes show the range of f_{O2} reported for that eruption based on Fe-Ti oxides (see Table 1).

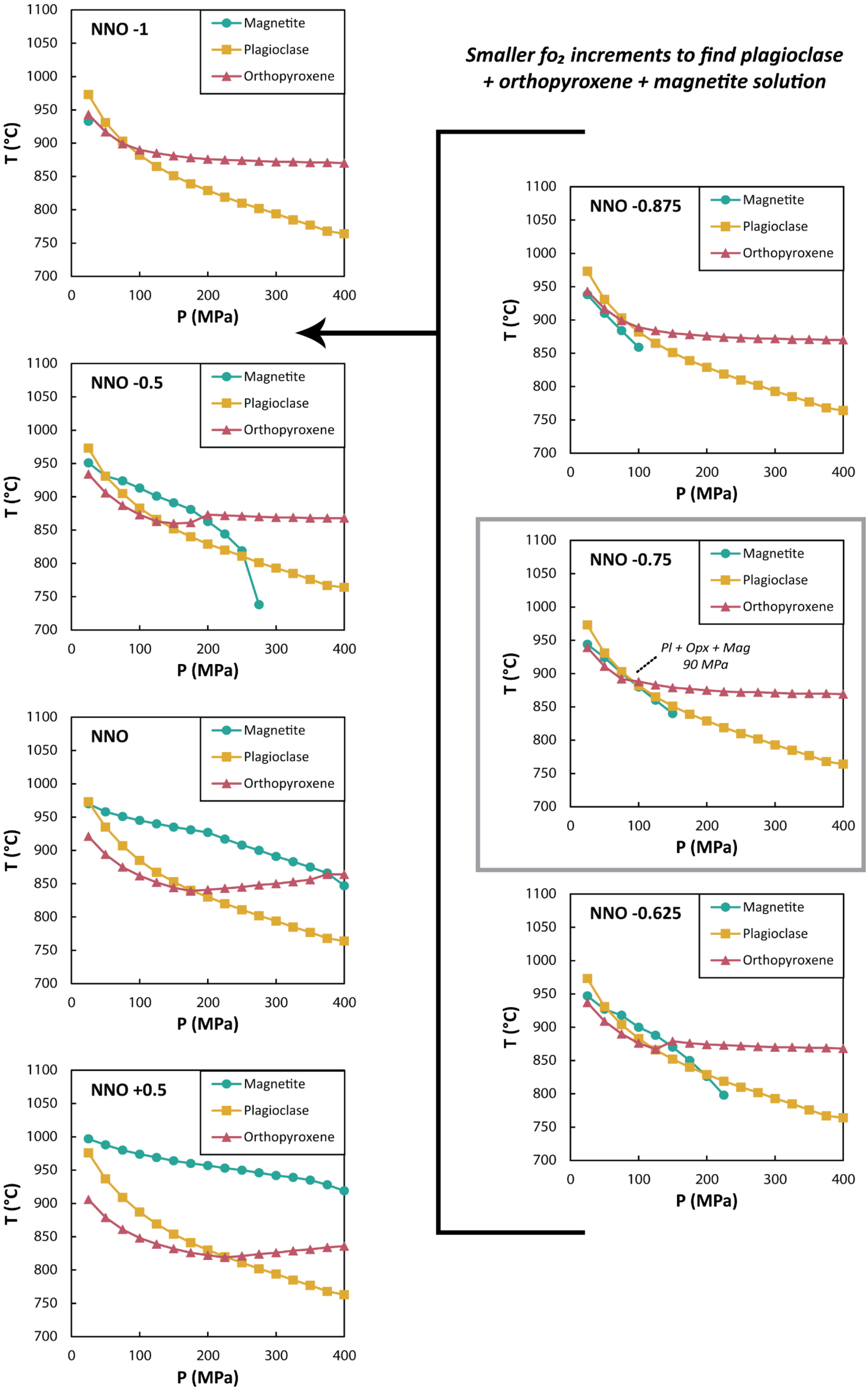

Smaller fo₂ increments to find plagioclase + orthopyroxene + magnetite solution
NNO -1
NNO -0.5
NNO
NNO +0.5
NNO -0.875
NNO -0.75
NNO -0.625
Magnetite
Plagioclase
Orthopyroxene
Pl + Opx + Mag
90 MPa
T (°C)
P (MPa)

Fig. 7 Example of plagioclase + orthopyroxene + magnetite saturation surface intersections at varying f_{O2} (sample Bomb038, PCC). The left column shows calculations performed at 0.5 log interval f_{O2} steps. The orthopyroxene saturation temperature moves down as f_{O2} increases, conversely, magnetite saturation temperature moves up as f_{O2} increases. This means it is possible to find a three-phase intersection by adjusting f_{O2}. As magnetite is very sensitive to f_{O2}, small increments are necessary. In this example, the three-phase intersection must occur between NNO -1 and NNO -0.5 (arrow). The right column therefore shows small 0.125 log increment f_{O2} steps between this interval. A three-phase solution is found at NNO -0.75, giving a pressure of 90 MPa. An animated version of this figure showing saturation surfaces moving with f_{O2} is available in the Online Resource 3.

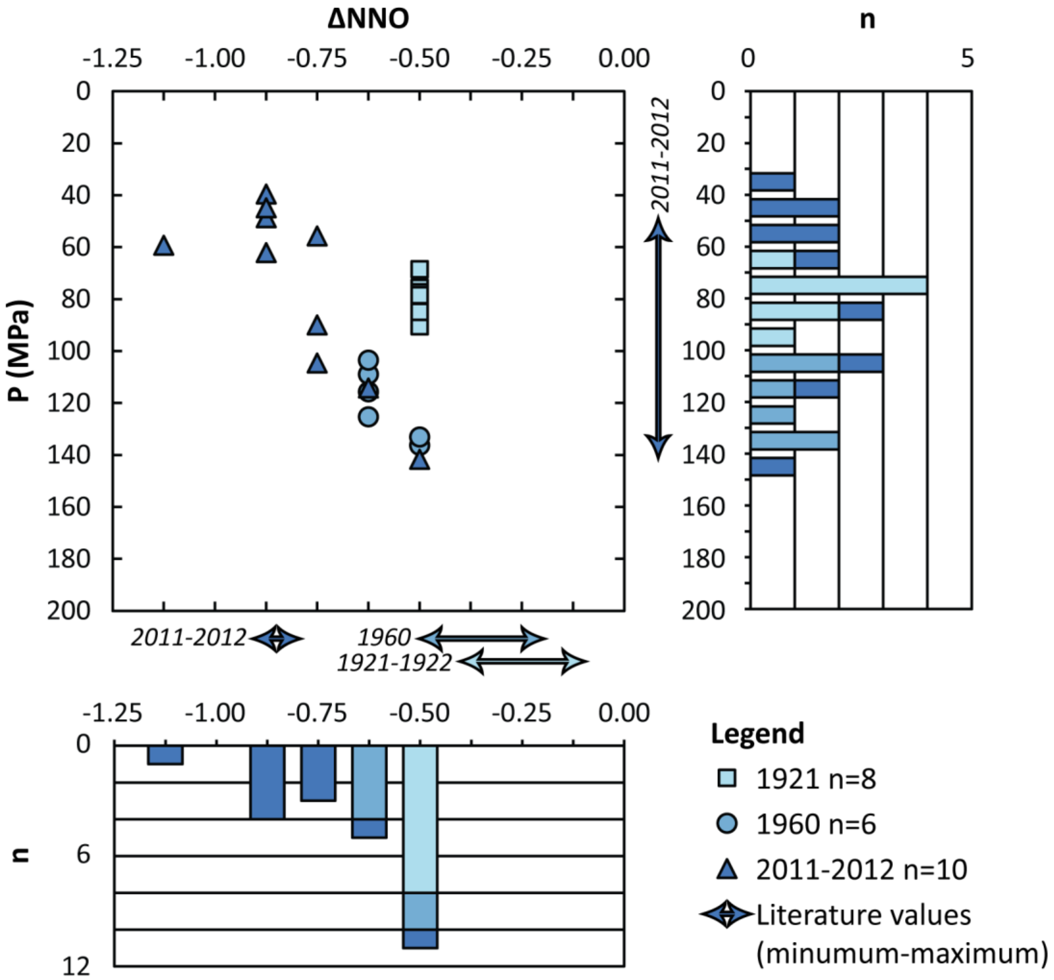


Fig. 8 Plagioclase + orthopyroxene + magnetite geobarometry results for PCC compositions, showing both the pressure result and the f_{O2} at which the three-phase intersection occurred. Results are calculated with a residual temperature threshold of ≤10 °C, see Online Resource 4 for results with ≤8 °C and ≤5 °C thresholds. The arrows show the range of P and f_{O2} for each eruption reported in the literature (see Table 2). There is excellent agreement between these independent P and f_{O2} estimates and both the P and f_{O2} results of the plagioclase + orthopyroxene + magnetite geobarometer.

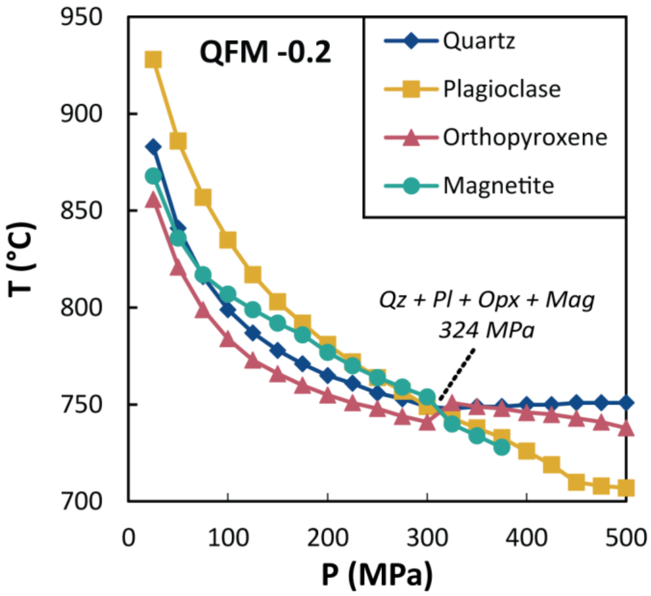


Fig. 9 Examples of a four-phase intersection (plagioclase + quartz + orthopyroxene + magnetite) from sample PK108a-05 at QFM -0.2. This intersection does not provide any further pressure constraint than a two- or three-phase intersection, but by reducing the degrees of freedom we can constrain f_{O2} (QFM -0.2) and the likely mineral assemblage (quartz-bearing in this example).

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