**Depths in a day - A new era of rapid-response Raman-based barometry using fluid inclusions.**

Running title: Depths in a day – a new era of rapid-response barometry

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**Abstract (current 332; max 500, prefer 200-300)**

Rapid-response petrological monitoring is a major advance for volcano observatories, allowing them to build and validate models of the plumbing systems that supply eruptions in near-real-time. The depth of magma storage has recently been identified as high-priority information for volcanic observatories, yet this information is not currently obtainable via petrological monitoring methods on timescales relevant to eruption response. Fluid inclusion barometry (using micro-thermometry or Raman spectroscopy) is a well-established petrological method to estimate magma storage depths and has been proposed to have potential as a rapid-response monitoring tool, although this has not been formally demonstrated. To address this deficiency, we performed a near-real-time rapid-response simulation for the September 2023 eruption of Kīlauea. We show that Raman-based fluid inclusion barometry can robustly determine reservoir depths within a day of receiving samples - a transformative timescale that has not previously been achieved by petrological methods. Fluid inclusion barometry using microthermometric techniques has typically been limited to systems with relatively deep magma storage (>~ 0.4 g/cm3 or ~7 km) where measurements of CO2 density are easy and accurate given that the CO2 fluid homogenizes into the liquid phase. Improvements of the accuracy of Raman spectroscopy measurements of fluids with low CO2 density over the past couple of decades has enabled measurements of fluid inclusions from shallower storage systems. However, one caveat of examining shallower systems is that the fraction of H2O in the fluid may be too high to reliably convert CO2 density to pressure. To test the global applicability of rapid response fluid inclusion barometry, we compiled a global melt inclusion dataset (>4000 samples) for which we calculated fluid composition at the point of vapour saturation (XH2O). We show that fluid inclusions in crystal-hosts from mafic compositions (<57 wt% SiO2) – likely representative of recharge magmas worldwide – may trap fluids with XH2O low enough to make fluid inclusion barometry useful at many of the world’s most active and hazardous mafic volcanic systems (e.g. Iceland, Hawai’i, Galápagos, East African Rift, Réunion, Canary Islands, Azores, Cabo Verde).

**Keywords:** Fluid inclusions; Geobarometry; Raman Spectroscopy; Rapid-response; Volcano Monitoring

1. Introduction

Volcano observatories increasingly use data collected from erupted lava and tephra samples in near-real-time to obtain information about the magmatic plumbing system to help inform decision-making during volcanic crises (Gansecki *et al.*, 2019; Re *et al.*, 2021; Pankhurst *et al.*, 2022). Most work so far has focused on the chemistry of erupted lavas and crystal cargoes (Pankhurst *et al.*, 2022) to gain insight into changing melt composition and rheological properties (Gansecki *et al.*, 2019). However, up until now, petrological monitoring has been unable to address the high-priority question– *Where is the magma coming from?* (Re *et al.*, 2021). At well-monitored volcanoes, such information can be used to draw analogies to previous eruptive episodes associated with specific storage reservoirs (e.g., vigour, pathway, or length of eruption), and to help interpret geophysical signals of ongoing activity. At poorly monitored volcanoes, where there may be no prior constraints on magma storage geometry (Wieser *et al.*, 2023b), depths of storage are a vital parameter to begin interpreting unrest associated with a new episode of eruptive activity (Pritchard *et al.*, 2019). For example, the return of eruptive activity at Kīlauea in 2020 was accompanied by many questions about how the magmatic plumbing system had changed following the summit collapse in 2018 (Lynn *et al.*, 2024).

Melt inclusion barometry, a widely popular petrological method to determine storage depths from volatile contents, is slow (Re *et al.*, 2021) often taking months to complete (e.g., Lerner *et al.*, (2021) and Wieser *et al.* (2021) were both submitted ~2 years and published three years after the 2018 LERZ eruption of Kīlauea had ended). While mineral barometry can be implemented faster than this, it is imprecise (Wieser *et al.*, 2023a), and therefore can only constrain magma storage to very broad regions (e.g., crust vs. sub-Moho). It also has poor applicability at active volcanoes such as Kīlauea or Mauna Loa where the only major silicate phase in many lavas is olivine, the chemistry of which is not pressure-sensitive, and where a precision of 1–2 km is needed to distinguish between reservoirs (Baker and Amelung, 2012; Anderson and Poland, 2016).

Fluid inclusion barometry via micro-thermometry and Raman spectroscopy is a well-established technique that has regularly been applied to determine the structure of certain magma plumbing systems over the past four decades (e.g., Roedder and Bodnar, 1980; Roedder, 1983, 1984; Belkin *et al.*, 1985; Hansteen *et al.*, 1991; Andersen *et al.*, 1995; Hansteen *et al.*, 1998; Yamamoto *et al.*, 2002; Frezzotti *et al.*, 2003; Klügel *et al.*, 2005; Yamamoto *et al.*, 2007; Bali *et al.*, 2008; Hansteen and Klügel, 2008; Ladenberger *et al.*, 2009; Hildner *et al.*, 2011, 2012; Zanon and Frezzotti, 2013; Levresse *et al.*, 2016; Klügel *et al.*, 2020; Boudoire *et al.*, 2023; Dayton *et al.*, 2023; Zanon *et al.*, 2024a). Micro-thermometry – which consists of measuring the temperature at which phase changes occur in a fluid under a microscope – can determine the CO2 density of fluid inclusions with bulk densities above critical (>~0.45 g/cm3) with great accuracy (Hansteen and Klügel, 2008; Bakker, 2021). However, it is difficult to observe the evaporation of a thin liquid film in fluid inclusions that homogenize to the vapour phase (Hansteen and Klügel, 2008) and therefore the technique is limited in its applicability to estimate the shallow structure of magmatic plumbing systems (<5-7 km), except perhaps in the case of large inclusions in clear host phases such as quartz (e.g., Clocchiatti *et al.*, 1994; Zanon *et al.*, 2003). Developments in the past two decades in the accuracy and precision of Raman spectroscopy measurements of CO2 density, which uses spectral features of CO2 fluids to calculate a CO2 density using an instrument-specific calibration (e.g., Rosso and Bodnar, 1995; Kawakami *et al.*, 2003; Yamamoto and Kagi, 2006; Fall *et al.*, 2011; Wang *et al.*, 2011, 2019; Lamadrid *et al.*, 2017; Sublett *et al.*, 2020; DeVitre *et al.*, 2021; Le *et al.*, 2021), have made it possible to accurately measure lower CO2 densities, and thus identify shallow storage regions more reliably. Recent work demonstrated that Raman-based barometry of CO2-rich fluid inclusions returns the same results as melt inclusion barometry and provide much smaller uncertainties than mineral barometry, while requiring far less time and resources than melt inclusion analyses (Dayton *et al.*, 2024; DeVitre and Wieser, 2024; Lerner *et al.*, 2024). Although micro thermometry is generally more accurate than Raman spectroscopy for high-density CO2 fluids (>0.6 g/cm3; Bakker, 2021), Raman spectroscopy has the advantage of being able to easily probe nearly the entire range of geologically relevant CO2 densities (from very low to high) with reasonably consistent precision and accuracy. It is also possible to assess at the same time the composition of the fluids and/or solids in the inclusions using Raman spectroscopy. The CO2 density obtained from either technique, along with an estimate of entrapment temperature, is converted into an entrapment pressure using an equation of State (EOS, Fig. 2, either pure CO2, or CO2-H2O).

Recent studies have speculated that fluid inclusion barometry, using either micro thermometry or Raman spectroscopy, could be performed quickly enough to be useful for near-real-time volcano monitoring (Dayton *et al.*, 2023; Zanon *et al.*, 2024b). However, this has not been formally demonstrated. The CONVERSE Hawai‘i Scientific Advisory Committee (Cooper *et al.*, 2023) specifically recommended that key science questions should be identified, and pre-planning science activities performed, to facilitate more rapid implementation across a broader scientific group during hazardous eruptions. Here, we performed a near-real-time simulation to rigorously assess how quickly fluid inclusion depths can be obtained from erupted material using Raman spectroscopy, and whether these timescales are short enough to have utility as a petrological monitoring tool. We also evaluate the applicability of the method worldwide. We focus on Raman spectroscopy given that it is applicable to a wider range of storage depths than micro-thermometry and capable of easily characterizing the composition of the fluids at the same time. Performing these simulations during relatively small, low-hazard eruptions (as here) or as hypothetical simulations (e.g., (Andrews *et al.*, 2019)) is vital to iron-out bottlenecks so that we are as prepared as possible for the next large volcanic crisis (Dietterich and Neal, 2022). Importantly, this simulation revealed that rapid-response fluid inclusion work in collaboration with academic institutions was not taxing on observatory or academic staff and can be employed during future eruptions. Our work also demonstrates the utility of fluid inclusion barometry at many of the world’s most active and hazardous mafic volcanic systems.

2. Timeline of Rapid-response Simulation

The eruption onset of Kīlauea volcano on September 10, 2023 provided an unprecedented opportunity to test the validity and speed of the fluid inclusion method, given that depths of the two main magma storage regions (Halemaʻumaʻu at 1-2 km and South Caldera at 3-5 km) at this volcano have been well constrained by various independent geophysical and petrological methods, including prior fluid inclusion barometry (DeVitre and Wieser, 2024; Lerner *et al.*, 2024). Tephra samples representing the first ~14 hours of the September 2023 eruption were collected by Hawaiian Volcano Observatory (HVO) geologists on September 12 and mailed to UC Berkeley on September 15th (Fig. S1). A schematic of the workflow and detailed timeline is available in the supplement (Fig. S1).

Our simulation started on September 20 at 9 am PST (Day 1), the morning after sample receipt (Fig. S1). We used a production-line-style workflow involving two undergraduates, a 1st year graduate student, a post-doc, and an assistant professor, with stations for crushing and sieving, mineral picking, fluid inclusion preparation, sample cataloguing, and analysis. We crushed and sieved tephra, picked olivine crystals (size fractions 0.5-1 and 1-2 mm), and mounted them in CrystalBondTM\* to search for fluid inclusions. By ~2 pm PST, we collected our first Raman spectra, and by ~7 pm PST, we had calculated CO2  densities from 16 fluid inclusions using a previously established instrument-specific calibration of the relationship between CO2 density and Fermi diad splitting distance (DeVitre *et al.*, 2021; DeVitre and Wieser, 2024). All spectra processing and subsequent calculations were performed using DiadFit (Wieser and DeVitre, 2024), allowing for a conversion of raw spectra to CO2 densities within ~15 minutes. Pressures were calculated using the pure CO2 EOS of Span & Wagner (1996) implemented in DiadFit. At the time of our simulation, it was challenging to perform EOS calculations considering the possible presence of H2O in the exsolved fluid due to a lack of publicly available software running on modern operating systems. However, recent work by Yoshimura (2023) identified errors in the published equations for the H2O-CO2 EOS of Duan & Zhang (2006) and provided open-source C code meaning that such calculations can be now be performed in DiadFit. Using estimates of from previously published melt inclusion data at Kīlauea (Wieser *et al.*, 2021; DeVitre and Wieser, 2024), calculated pressures would be ~10% higher than originally reported to HVO if the CO2-H2O EOS had been used (Fig. 1d, Fig S1 in supplementary materials). This does not affect the interpretation of our results, as the shift is far smaller than the pressure offset between the Halemaʻumaʻu and South Caldera reservoir.

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***Figure 1. Evolution of results over 4 days.*** *a) Schematic model of Kīlauea’s plumbing system, indicating reservoir depths (HMM = Halemaʻumaʻu; SC = South-Caldera). b) Day 1 fluid inclusion depths, as reported to HVO, are consistent with the estimated depths of the Halemaʻumaʻu reservoir. Kolmogorov-Smirnoff tests indicate that September 2023 fluid inclusions record significantly shallower depths than fluid inclusions (critical D = 0.22, stat = 0.24, pval=0.016) and melt inclusions (critical D = 0.22, stat = 0.41, pval=3.51e-06) from the 2018 Lower East Rift Zone (LERZ) eruption, which required a contribution from the South Caldera reservoir* (Wieser *et al.*, 2021; DeVitre and Wieser, 2024)*. 1LERZ 2018 melt inclusions* (Wieser *et al.*, 2021)*; 2LERZ 2018 fluid inclusions* (DeVitre and Wieser, 2024)*. c) Day 2 data, as reported, confirmed a likely dominant role for the Halemaʻumaʻu reservoir. A conservative degassing filter was applied (SO2/CO2 peak ratio < 0.1). d) Day 4 data, as reported. Means were taken for repeated analyses of single fluid inclusions and additional data filters (e.g., SO2/CO2 peak ratio < 0.22), fluid inclusion-specific temperatures, and a more appropriate crustal density model (~2300 kg/m3 with a normal error distribution of 100 kg/m3) were applied. Error-bars correspond to uncertainties propagated using Monte Carlo simulations and olivine Fo equilibrium field is calculated based on glass EPMA data collected on September 11, 2023 (see Supplementary Information S1 Appendix). The shifted histogram ‘*H2O *effect’ shows the effect of* H2O *corrections on pressures recalculated using inferred from melt inclusions* (Wieser *et al.*, 2021; DeVitre and Wieser, 2024)*.*

For the first and second days of the simulation, we assumed an entrapment temperature of 1150 ˚C for all fluid inclusions, based on geothermometric estimates of previously erupted liquids (Gansecki *et al.*, 2019; DeVitre and Wieser, 2024). On Day 4, we calculated entrapment temperatures for each fluid inclusion using the host forsterite content measured by Energy Dispersive Spectroscopy (EDS, DeVitre and Wieser, 2024), yielding temperatures spanning 1182–1307 ˚C. The average error induced by our initial assumption of 1150 ˚C is only ~7% (with a maximum offset of only 12 %). While crystallization temperatures at Kīlauea are well constrained relative to other volcanic systems, using similar regression methods to those employed by DeVitre and Wieser (2024) relating liquid compositions to host olivine contents, it should always be possible to constrain temperatures within ~100 K at different volcanic systems using host mineral chemistry.

On days 1 and 2, pressures were converted into depths using the crustal density model of Ryan (1987) parameterized by Lerner *et al.* (2021). We shared the resulting histogram (Fig. 1a-b) of storage depths with HVO collaborators showing that crystals, and thus magma, were likely coming from the shallower Halemaʻumaʻu reservoir of Kīlauea (Fig. 1a-b). It worthwhile to note that the number of fluid inclusions reported on Day 1 (N=16) is comparable to many melt inclusion (MI) studies, which often aim for ~20 per sample but frequently report fewer. For example, Lerner *et al.* (2021) reported only 9 MI from the 2018 eruption with sufficient data to calculate saturation pressures (counting MI with glass major element contents and H2O contents, MI with glass CO2 measurements if there was no bubble, and glass + bubble measurements if a bubble was present). Using the same criteria, Aster *et al.* (2016) only reported 13 complete measurements from Lassen Peak.

We also had an additional ~20 fluid inclusions fully prepared and catalogued for analysis by the end of Day 1. On Day 2, these 20 fluid inclusions were analysed, while additional fluid inclusions were prepared and catalogued. After analysis of ~15 samples, the crystals were removed from CrystalBondTM\* and placed on tape for epoxy mount-making. Epoxy was poured at the end of Day 2. By ~8:30 pm PST on Day 2, we shared an updated histogram of 46 fluid inclusion pressures and depths from 28 crystals, confirming the dominant contribution of the Halemaʻumaʻu reservoir (Fig. 1a and c). On Day 3, we finished analysing the remaining prepared fluid inclusions. Then we polished the epoxy mount and catalogued the regions of crystals closest to each fluid inclusion on which to perform EDS analyses. On Day 4, olivine forsterite contents (Fo = 100\*Mg/(Mg+Fe) molar) were determined by EDS, providing a framework to further interpret the plumbing system (Fig. 1d). The Fo content of an olivine is a function of MgO and FeO in the liquid and the Ol-Liq partitioning coefficient (KD). Thus, the Fo contents of the host olivine close to each fluid inclusion can be used to assess the calculated storage depth in its broader petrographic context (e.g., distinguishing high-Fo olivines which crystallize from more primitive melts from low Fo olivines forming in more evolved melts). This olivine forsterite content can also be used to estimate the likely entrapment temperature of each fluid inclusion (DeVitre and Wieser, 2024) for performing EOS calculations, rather than having to use a uniform temperature as on Day 1-2. We thus recalculated all fluid inclusion pressures on Day 4 using fluid inclusion-specific entrapment temperatures.

Our results on Day 4 clearly show that the majority of fluid inclusions were entrapped at ~1–2 km below the surface (Fig. 1d), which aligns well with the depths of the Halemaʻumaʻu reservoir interpreted from geophysics (Baker and Amelung, 2012; Anderson and Poland, 2016; Anderson *et al.*, 2019), melt inclusion barometry (Lerner *et al.*, 2021; Wieser *et al.*, 2021), and fluid inclusions (DeVitre and Wieser, 2024; Lerner *et al.*, 2024). While the greater number of analyses from data processed on Day 2 and Day 4 certainly enhance the story, it is notable that depths calculated on Day 1 fall within final proposed storage reservoir depths. Rapid EDS analyses of olivine Fo contents close to each fluid inclusion reveal that olivine crystals grew from a wide range of melt compositions. It is interesting to note that fluid inclusions in the cores of high-Fo (e.g., >86) olivine crystals return pressures indicative of the shallower Halemaʻumaʻu reservoir, given that it has been suggested based on previous eruptions that these high-Fo olivine crystals predominantly grow in the deeper South Caldera reservoir (Fig. 1a) where high-MgO melts are thought to reside (Helz *et al.*, 2014; Pietruszka *et al.*, 2015, 2018; Wieser *et al.*, 2019; Lerner *et al.*, 2024). We suggest three possible scenarios to explain the relatively shallow pressures documented in high-Fo olivine crystals:

1) Fluid inclusions in high-Fo olivine crystals were entrapped within the South Caldera reservoir and then transported into the Halemaʻumaʻu reservoir, where the fluid inclusions re-equilibrated to lower pressures prior to eruption over shorter timescales than would be required to reset the host Fo content.

2) High-MgO melts were injected into the Halemaʻumaʻu reservoir, where high-Fo olivine crystallized and trapped fluid inclusions at shallow depths (Lerner *et al.*, 2024).

3) Complex skeletal growth of olivine crystals during extensive undercooling (Welsch *et al.*, 2013) could mean that high-Fo olivine cores which initially grew in the South Caldera reservoir texturally evolved and trapped lower pressure fluid inclusions in the Halemaʻumaʻu reservoir.

We think that scenario 1 is unlikely given the that fluid inclusions from the 2018 LERZ eruption appear not to have re-equilibrated despite stalling in the Halemaʻumaʻu reservoir for up to 2 years (Mourey *et al.*, 2023; DeVitre and Wieser, 2024), and our models of fluid inclusion re-equilibration indicate <10% change in pressure over ~ 2 yrs. Current data does not allow us to resolve scenario 2 vs 3, but this eruption could provide an opportunity to explore this further, such as through detailed phosphorous mapping in olivine around fluid inclusions (similar methods were applied to melt inclusions by Esposito *et al.*, 2023). Regardless of the exact mechanism, our fluid inclusion pressures indicate that erupted crystal cargo experienced storage at Halemaʻumaʻu reservoir depths prior to eruption, and thus this was the most probable reservoir supplying magma to the surface in the September 2023 eruption.

3. Advantages and limitations of fluid inclusion barometry.

Fluid inclusion barometry, using either micro thermometry or Raman spectroscopy, requires very little sample preparation. In the case of Raman spectroscopy, a single polished crystal, with FI within ~50 µm of the surface is sufficient to perform high quality analyses. For micro thermometry a doubly polished crystal or slab is needed. Data obtained from either method can quickly be converted into pressures and depths using an estimated entrapment temperature and an equation of state (EOS). One major advantage of fluid inclusion barometry is that the conversion of CO2 density to pressure is relatively insensitive to the choice of entrapment temperature, a parameter which may not be known at the onset of a new eruptive episode (Fig. 2a-b). The difference in pressure for EOS calculations considering the lower and upper limit of liquidus temperatures for olivine-saturated melts erupted at Kīlauea volcano throughout its history (~1100 and 1350 ˚C; DeVitre and Wieser, 2024) is at most ~20 %, which corresponds to an error of about ±0.1-0.2 km at depths representative of the Halemaʻumaʻu reservoir (1-2 km), and approximately ±0.3-0.5 km at the depths of the South Caldera reservoir (3-5 km; Fig. 2b and Fig. S3-S6). These errors are of similar magnitude to those associated with the conversion of pressures to depths through an estimate of crustal density (an issue affecting all petrological barometers).

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***Figure 2. Sensitivity of fluid inclusion barometry to temperature and molar proportions of*** H2O ***in the exsolved fluid phase ().*** *(a) CO2 density vs Pressure for different magmatically relevant entrapment temperatures at Kīlauea using the pure CO2 EOS of* Span and Wagner, (1996)*. 1100 and 1350 ˚C are the lower and upper limit of liquidus temperatures for olivine-saturated melts erupted at Kīlauea volcano throughout its history. 1150 ˚C was the temperature used for calculations during day 1 and 2 of the simulation, 1240 ˚C is the rounded mean and median of all measured temperatures in our final dataset. (b) Panel a close-up. Grey boxes show Kīlauea magma storage inferred from fluid inclusions, melt inclusions and geophysics* (DeVitre and Wieser, 2024; Lerner *et al.*, 2024)*. HMM= Halemaʻumaʻu reservoir, SC = South Caldera reservoir. Stars show hypothetical fluid inclusions trapped at Halemaʻumaʻu and South Caldera with T=1150 ˚C and error-bars representing 1σ uncertainty from Monte Carlo simulations using a temperature uncertainty of ±125 ˚C (). (c) CO2 density vs pressure at 1150 ˚C for various using the mixed* H2O*-CO2 EOS of* Duan and Zhang (2006)*. The small discontinuity at 200 MPa is due to parameter values being switched* (see Yoshimura, 2023)*. (d) Panel c close-up. Stars show hypothetical fluid inclusions trapped at Halema’uma’u and South Caldera with T = 1150 ˚C, inferred using the -P relationship of* DeVitre and Wieser (2024)*. Error bars represent 1σ uncertainty from Monte Carlo simulations using an uncertainty of ±0.1 based on the maximum range of inferred in our dataset () when calculated using the upper limit-P relationship for Kīlauea from DeVitre and Wieser (2024).*

There are, however, a few important limitations of the fluid inclusion method. First, it requires the presence of exsolved near-pure CO2 fluids which are trapped in crystals, whether they are phenocrysts, antecrysts and/or xenocrysts entrained by an erupted magma. Erupted xenoliths have traditionally been a prime target for fluid inclusion barometry as they often contain large numbers of secondary fluid inclusions trapped due to fracture and annealing of crystals under presence of CO2-rich fluids in the wall-rocks of magmatic reservoirs (Roedder, 1965, 1984; Andersen and Neumann, 2001; Hansteen and Klügel, 2008). Although fluid inclusions are not uncommon in phenocrysts and antecrysts, they can be less frequent than melt inclusions and this vastly depends on the sample. For example, in our sample suite, we found ~1/10 crystals bore FI. In CO2-undersaturated systems, fluid inclusions will be absent, and they may be very spare in systems with a very low volume fraction of exsolved volatiles (e.g., just saturated).

In principle, fluid inclusions can only reflect the conditions at time of entrapment if they satisfy what are commonly known as “Roedder’s rules” (Roedder, 1984). At the time of entrapment, a single homogenous fluid phase must have been trapped (e.g., pure vapor/liquid CO2) and, after trapping, the inclusion must have retained its volume, and nothing must have been added or removed (Roedder, 1984; Hansteen and Klügel, 2008). Several challenges arise from natural deviations to these rules. First, magmatic fluid inclusions can often trap mixtures of fluids (e.g., H2O, CO2, SO2, N2, CO, H2S, etc). It is generally accepted that a few mol% of a different fluid does not have significant effects on fluid inclusion barometry, but it can contribute to increased uncertainty (Fig. 2c-d; Hansteen and Klügel, 2008). For example, it is not uncommon for H2O to be present in exsolved magmatic fluids trapped in fluid inclusions, making the use of a mixed H2O-CO2 equation of state necessary to calculate pressure from CO2 density. This of course requires estimating the mol% H2O in the inclusion at time of entrapment which is often not straightforward as the H2O can be lost via diffusion through the host or have reacted with the host forming carbonate crystals and/or talc. When the H2O has not been lost, the mol% H2O in the inclusion can sometimes be measured by Raman spectroscopy if the inclusion is heated > ~150 °C; (Berkesi *et al.*, 2012) where H2O and CO2 are miscible. In many cases, studies have often simply assumed the H2O has been lost, and corrected the measured density based on the molar proportion of H2O (i.e., ~10 mol% or 0.1) expressed as a percentage or a fraction (e.g., Klügel *et al.*, 2005; Hansteen and Klügel, 2008; Hildner *et al.*, 2011, 2012). From there, pressures can be calculated using a mixed H2O-CO2 equations of state. In general, <10 mol% H2O in the fluid causes a relatively small difference on the calculated pressures and depths, though the effect is more pronounced at higher CO2 densities (Fig. 2c-d). For instance, with a of 10 mol%, the difference in pressure between the pure CO2 (Span and Wagner, 1996) and the mixed H2O-CO2 (Duan and Zhang, 2006) equations of state is only ~10 % at 30 MPa (~1 km) and ~17% at 800 MPa (~35 km; Fig. 2c-d). Naturally, higher mol% H2O in the fluid can be expected in certain shallow, water-rich volcanic systems (such as those in subduction zones), which would result in much more significant error if a is not constrained and/or too high. This raises the importance of assessing the composition of fluid inclusions and constraining, at least approximately, XH2O in the fluid. Fluid inclusion barometry will only be applicable in near-pure CO2 inclusions.

As mentioned previously, to reflect entrapment conditions fluid inclusions must also have retained their volume and nothing must have been added or removed after trapping. This gives rise to another complication: After trapping and as the crystal host ascends in the magma plumbing system, strong pressure gradients will arise between the exterior of the crystals and the enclosed fluid inclusions. Large pressure gradients result in volumetric re-equilibration of the inclusions either by plastic deformation of the host (commonly referred to as “stretching”) or brittle deformation (termed “decrepitation”) (Kirby and Green, 1980; Wanamaker and Evans, 1989; Viti and Frezzotti, 2000; Yamamoto *et al.*, 2002, 2007, 2011; Bodnar, 2003; Hansteen and Klügel, 2008). This means that fluid inclusions will generally reflect minimum trapping pressures, particularly when they were originally trapped at high pressure (> 10 km depth). The higher the internal pressure of the fluid inclusion, the faster the re-equilibration will be at various levels of ascent. In the case of shallow systems like Kīlauea, if inclusions are trapped < 7 km depths, re-equilibration via plastic deformation on timescales relevant to recharge and eruption (months to a decade) is generally not of concern as the internal pressure of the inclusions is very low and the predicted change in pressure even over a decade is within the uncertainty of the measurements (< 10 %; DeVitre and Wieser, 2024). In deeper magmatic plumbing systems such as the Canary Islands, Galápagos or Cabo Verde however, significant re-equilibration will likely occur within days and fluid inclusions almost never reflect original trapping depths. However, because they are so sensitive to re-equilibration, fluid inclusions are excellent recorders of stalling events throughout a magmatic plumbing system and in particular record well the last stage of storage prior to eruption (Hansteen and Klügel, 2008), which is the most relevant to volcano monitoring efforts.

From the perspective of choosing suitable samples for fluid inclusion work, it has been suggested that fluid inclusions found in lava flow samples may re-equilibrate more readily than those found in tephra (Hildner *et al.*, 2012) as they cool slower upon eruption, however, this effect is more likely to be significant for fluid inclusions trapped at high-pressures. In shallower systems, no significant difference is observed between naturally quenched lava flow samples and those rapidly quenched in water (DeVitre and Wieser, 2024). For a given fluid inclusion density, size, and ascent path, it is possible to model the predicted re-equilibration scenario using a plastic deformation model, allowing assessment of the possible influence of equilibration on the measured density (Wanamaker and Evans, 1989; Yamamoto *et al.*, 2011; DeVitre and Wieser, 2024).

4. Broader applicability of the method

As mentioned previously, the use of a pure CO2 EOS results in an underestimate of the entrapment pressure of fluid inclusions if there was H2O in the fluid at the time of inclusion entrapment (Fig. 1 and 2). At Kīlauea, melt inclusion data indicates that the exsolved fluid phase is ~90% CO2 at pressures corresponding to the Halema’uma’u reservoir, and >95% CO2 at pressures indicative of the South Caldera reservoir (Wieser *et al.*, 2021; DeVitre and Wieser, 2024). This means that the effect of is very small on calculated pressures presented here (Fig. 1d). Given that re-equilibration is also not a significant concern on timescales relevant to pre-eruptive storage and syn-eruptive transport at Kīlauea (DeVitre and Wieser, 2024), we can conclude that FI barometry is a useful and reliable technique at Kīlauea. But from this alone, it is hard to determine whether the technique could be applicable elsewhere.

To assess the utility of the method for rapid-response petrology globally, it is necessary to evaluate contents, and their effect on fluid inclusion pressures. To do this, we compiled published melt inclusion data from all over the world, spanning many different tectonic settings (see supplement for compilation details). We calculate using the solubility model MagmaSat (Ghiorso and Gualda, 2015), implemented in VESIcal (Iacovino *et al.*, 2021) using a custom multiprocessing routine in Python (supplement for details). For each volcano, there is a clear correlation between and pressure, with increasing drastically at shallow pressures (Fig. 3 and Fig. S9a-i), perhaps as melt inclusions are trapped during enhanced degassing of H2O upon ascent. Thus, in this compilation, the median and 25th percentiles are likely most representative of in the main magma storage region. For this reason, we show the distribution, median, 25th and 75th percentiles of calculated for 4069 melt inclusions with SiO2 < 57 wt%, MgO < 16 wt% and saturation pressure > 20 MPa on Fig. 4b-c, coloured by tectonic setting. We stress the importance of considering the possible range of values when determining the suitability of this method to a particular system, and the fact that the pressure correction tends to be more significant at higher entrapment pressures. For example, if we consider a value of 0.1 (the median of our fluid inclusion dataset at Kīlauea and a commonly assumed in deep storage systems), the pressure correction goes from < 15% at pressures < 220 MPa (~10 km) to ~20% at 700 MPa (~30 km). Naturally, the correction is even more significant if is greater than 0.1 (e.g., for =0.2, the correction is 25-30% at P<150 MPa and ~50% at P = 700 MPa; Fig. 2).

A group of images of different types of pressure

Description automatically generated

***Figure 3. Examples of pressure vs for some recently active mafic volcanic systems (a-c) and the East-African rift (d) where fluid inclusion barometry could be used as a monitoring tool.*** *Data shown for melt inclusions with reconstructed total CO2 using Raman spectroscopy (supplement information for extended details on the compilation). Outlined symbols represent data collected using a Raman with an instrument specific calibration. Filled symbols with no outline are data that did not use an instrument specific calibration. The supplementary information contains similar plots for every location in the compilation, including glass-only melt inclusion volatile data (Fig. S9a-i).*

A map of the world with different colored graphs and charts

Description automatically generated

*Figure 4.* ***Global compilation of in the exsolved fluid phase from melt inclusion data for continental rift, continental intraplate, alkalic and tholeiitic ocean island basalt (OIB, see Fig S7), mid-ocean ridge and subduction zone volcanoes (details and references in the supplement*** *(a) World map coloured by median of the melt inclusion suites. Circles indicate glass-only MI data and stars those for which CO2 has been constrained by Raman. (b) Boxplot of for melt inclusion suites plotted on panel a. Boxplots show the median, Q1 (25th percentile), Q3 (75th percentile) and whiskers mark the last datapoint before Q3+1.5\* (Q3-Q1) and the first datapoint after Q1-1.5\*(Q3-Q1). Violin plots show the density distribution of all the data and are coloured according to tectonic setting. (c) Boxplot of showing only MI suites which constrained total CO2 by Raman spectroscopy. EAR – East African Rift, GSC – Galápagos Spreading Center, NAR – North Atlantic Ridge, JdFR – Juan de Fuca Ridge, GR – Gakkel Ridge, MAR – Mid-Atlantic Ridge, EPR – East Pacific Rise, IBM – Izu Bonin Mariana. Data are filtered to SiO2 < 57 wt%, MgO < 16 wt% and saturation pressure >20 MPa (supplement for details).*

Notably, most melt inclusion suites in our global compilation did not measure CO2 in the vapour bubble, meaning that the total CO2 content has been underestimated, and overestimated. This can be demonstrated by comparing values at volcanoes where there are some studies with Raman measurements and some without (Fig. S9c EAR; Fig. S9h Kamchatka, and Cascades). Thus, Fig. 4c shows a compilation only using melt inclusions where bubble CO2 was measured by Raman spectroscopy. Both compilations demonstrate that subduction zones record much higher globally than mid-ocean ridge basalts, ocean island basalts, continental rifts and intraplate volcanoes. It is also interesting that within hotspot and intraplate settings, regions with tholeiitic compositions (e.g. Iceland, Hawai’i, Galápagos, Réunion, Deccan Traps) generally have lower values than regions with more alkalic magmas (e.g., Canary Islands, Azores, Cabo Verde, Fig. 5). This likely represents the lower melt extents in alkalic settings, and the possibility of more volatile-rich sources (e.g., DeVitre *et al.* 2023). This observation is useful when tackling different volcanoes in specific tectonic settings. For example, even if there is no pre-exiting volatile data for a specific volcano in an OIB setting, a first approximation of the expected can be made from this compilation and some knowledge of the chemistry of the erupted magma. One could fit a general polynomial for an alkalic or tholeiitic OIB type magma with a generous error window encompassing available data from different volcanoes and perform a reasonable correction on fluid inclusion pressures.

A diagram of different types of chemical elements

Description automatically generated with medium confidence

*Figure 5.* ***TAS diagram (a) and pressure vs for tholeiitic and alkalic ocean island volcanoes.***

Thus, while rapid-response fluid inclusion barometry is highly applicable to active volcanic regions such as Hawai’i, Iceland, East African Rift, Galápagos, Réunion, Cabo Verde, and the Canary Islands (Fig. 5), it is not appropriate in subduction zones such as Alaska, Kamchatka, or Central America. Interestingly, although there are only two studies with Raman data in the Cascades (Aster *et al.*, 2016; Venugopal *et al.*, 2020), the inclusions with highest pressures have values <0.2. This may indicate that in drier subduction zones, fluid inclusions may have some utility for the most mafic, CO2-rich magmas.

Of course, at many volcanoes worldwide, detailed melt inclusion measurements may not be available to accurately calculate XH2O, particularly given the paucity of studies worldwide measuring both the bubble and glass phase of melt inclusions (Wieser *et al.*, 2024). However, this does not mean rapid-response fluid inclusion barometry cannot be used in these systems. Clearly, unless detailed melt inclusion measurements have been performed demonstrating high CO2, low H2O magmas, fluid inclusion barometry should not be applied to arc volcanoes during an eruptive crisis. However, excluding arcs, we believe the knowledge of the tectonic setting, major element chemistry, and phase abundances (which are often available, or easily constrained, even if there is no volatile data) will allow an informed guess of the likely range of XH2O values. For example, our global compilation shows a clear pattern, where more alkalic systems have higher XH2O values at a given pressure (Fig. 5). Thus, by conducting rapid XRF, EPMA, or EDS analyses, an informed guess would be possible. Using these general trends (Fig. 5), we would feel comfortable applying the rapid-response fluid inclusion method to any OIB or intraplate volcano erupting mafic compositions. Calculations would be conducted with a wide range of XH2O values informed by local studies/our global database, and the associated uncertainties propagated when calculating pressures. As more data become available (e.g. post eruption), these estimates could be revised within uncertainty to better pinpoint magma storage depths. For volcanoes that are not currently erupting but have had historic eruptions, an informed guess on a likely XH2O range can be made using chemical information from such previous eruptive events. For instance, one could easily determine the chemical tendency of a volcano from already existing major element data (e.g., Fig. 4a). In many cases, even when no chemical data is available for a specific volcano, analogy may be possible to draw from neighbouring volcanoes. For example, during the 2022 eruption of Mauna Loa, no detailed melt inclusion measurements accounting for the vapour bubble were available. However, as a first estimate, the P-XH2O relationships from neighbouring Kīlauea could be used. We note that once arc magmas are excluded from the compilation, even if is entirely unconstrained, fluid inclusion barometry is still more accurate than other methods such as mineral-melt thermobarometry in recovering magma storage pressures.

Looking forward, to increase the accuracy of rapid-response petrological monitoring during future eruptions, it should be a priority to perform melt inclusion studies accounting for vapour bubble CO2 in more volcanic systems worldwide, given the large offsets between studies accounting for bubbles and those which do not in space (Fig. 4), and to determine approximate trends in -pressure space for a given volcanic system or region during times of quiescence. This will allow assessment of the suitability of the fluid inclusion method for a given volcano and permit appropriate corrections for the complexities of mixed fluids without requiring melt inclusion work during each eruptive episode. In systems with no prior constraints, our observations of correlations between alkalinity and can provide a first order assessment of appropriate values to use. Better constraining is also vital for other petrological workflows, such as calculating phase stabilities, performing experiments, and modelling vapour saturation and eruption triggering.

4. Conclusion

Our simulation shows that magma storage depths can be determined within a day of receiving samples, with modest resources and personnel requirements (e.g. no overnight shift work, with normal semester teaching and class schedules). For example, sample preparation was carried out using transmitted-reflected light microscopes from the University of California teaching collection, only using a research-grade microscope for sample cataloguing. Raman spectrometers are widely available at many universities, given that it is a popular technique in many other fields, such as material sciences, physics, chemistry, and biology, and the W-filament SEM used for EDS analyses to measure olivine Fo contents has been around for 15 years (S1 Appendix).

Importantly, this simulation showed that rapid-response work in collaboration with universities was not taxing on observatory or academic staff, particularly considering the usefulness of information provided. This means this methodology can be employed during future eruptions to help observatories deduce the geometry of the plumbing system supplying magma, adding a crucial information for interpreting activity (Re *et al.*, 2021), without detracting from other essential duties during eruption responses. For example, during the 2018 LERZ Kīlauea eruption, HVO’s near-real-time chemical monitoring with bulk rock ED-XRF identified the appearance and disappearance of many magma batches (Gansecki *et al.*, 2019). Fluid inclusion barometry could have linked these distinct chemical signatures to different storage regions, addressing the questions of scientists and residents alike. Similarly, the return of eruptive activity at Kīlauea in 2020 was accompanied by many questions about how the magmatic plumbing system had changed following the summit collapse in 2018 (Lynn *et al.*, 2024). Fluid inclusion barometry would have allowed been a critical addition to understanding the eruption and the system.

The case study presented here intentionally targeted a low-hazard eruption as a testbed for implementing near-real-time fluid inclusion barometry as a monitoring tool. This type of work, on low-hazard, short-lived eruptions, has a few advantages. First, it allows observatories to iron-out bottlenecks to implement the tool for future events. Second, it enables researchers to establish baselines that can be used for routine monitoring, which is fundamental to notice changes and trends in systems as volcanoes like Kīlauea continue their eruptive activity and evolve over human perceptible timescales. Although this eruption was short-lived, one can also imagine how such data could be useful in the context of a much longer eruption (e.g., Kīlauea 2018 LERZ). For instance, if FI barometry indicated depths of ≥5km within 48 hours, this data would be used by HVO to inform discussions with partners about the potential for a deeper source than seen in previous events and therefore an expectation for greater volume, increased duration, or potential waxing and waning if magma transport involves shallow sources along the way. In terms of regular near-real-time monitoring of a longer-lived eruption, FI barometric data could aid in understanding pre-eruptive deformation and unrest. Specifically, such data could be used to identify the reservoir being tapped by the eruption and how associated stresses could change. In the case of Kīlauea, if pressurization was observed in both the South Caldera and the Halema‘uma‘u reservoirs, but the eruption primarily taps Halema‘uma‘u, this could mean that the South Caldera reservoir could be primed to support eruption. This can change the expectations for developing activity at the volcano.

Our global compilation of values shows that fluid inclusion barometry has utility as a rapid-response petrological monitoring method at many of the world’s most active and hazardous basaltic volcanoes (e.g., Hawai’i, Galápagos, Réunion, Azores, Canary Islands, Iceland, Cabo Verde, EAR). As our understanding of exsolved fluid compositions improves as more studies account for CO2 held within vapour bubbles, it is likely that the applicability of rapid-response fluid inclusion barometry method may expand to even more volcanic systems (e.g. to drier arc magmas such as in the Cascades).

Overall, fluid inclusion barometry is broadly applicable, and adds valuable quantitative storage depth information that provides a key advancement for volcano observatories that utilize near-real-time geochemical monitoring to better understand eruptions as they unfold (see overview–(Re *et al.*, 2021); Hawai‘i–(Gansecki *et al.*, 2019); La Palma–(Pankhurst *et al.*, 2022); Fuego–(Liu *et al.*, 2020); Italy–(Corsaro and Miraglia, 2022)).

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Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

**5.1. Author contributions**

Author contributions for lab work are shown on Fig. S1. CD and PW wrote the paper. CD, PW, AR, BR, and AB prepared tephra, picked olivine, found fluid inclusions, catalogued them, mounted them, and conducted Raman analyses. CD and PW performed all spectral fitting, data processing, and figure making, with schematic cartoons shown in Fig. S1 from AB. JG developed the Mg/Fe calibration for the EDS detector and MG performed EDS analyses with help from JG. KJL, DTD, NID and KMM collected samples, processed them in Hilo, provided eruption context and edited the manuscript. KJL and DD prepared the glass mount and did the EPMA glass analyses.

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**5.3. Competing interests**

Authors declare that they have no competing interests.

6. Data availability

All data are made available in the Supplementary Information associated with the publication. We include detailed materials and methods (S1 Appendix), complete processed fluid inclusion dataset (S2 Dataset), the global melt inclusions dataset (S3 Dataset), a compilation of microphotographs of the fluid inclusions and crystals that were used for navigation only during the simulation (S3 FI Image Compilation) and a record of emails reporting results to HVO and tracking receipts related to sample shipment (S4 Email and tracking record). All raw data and Jupyter notebooks are stored on Github at the following link: [https://github.com/cljdevitre/2023\_Kīlauea-rapid-response-simulation](https://github.com/cljdevitre/2023_Kilauea-rapid-response-simulation). The Github repository will be archived on Zenodo upon acceptance.

**7. References**