**Supporting Information for**

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

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**Additional Supporting Information (Files uploaded separately)**

Data S2 and S3:

S2 is the fluid inclusion dataset

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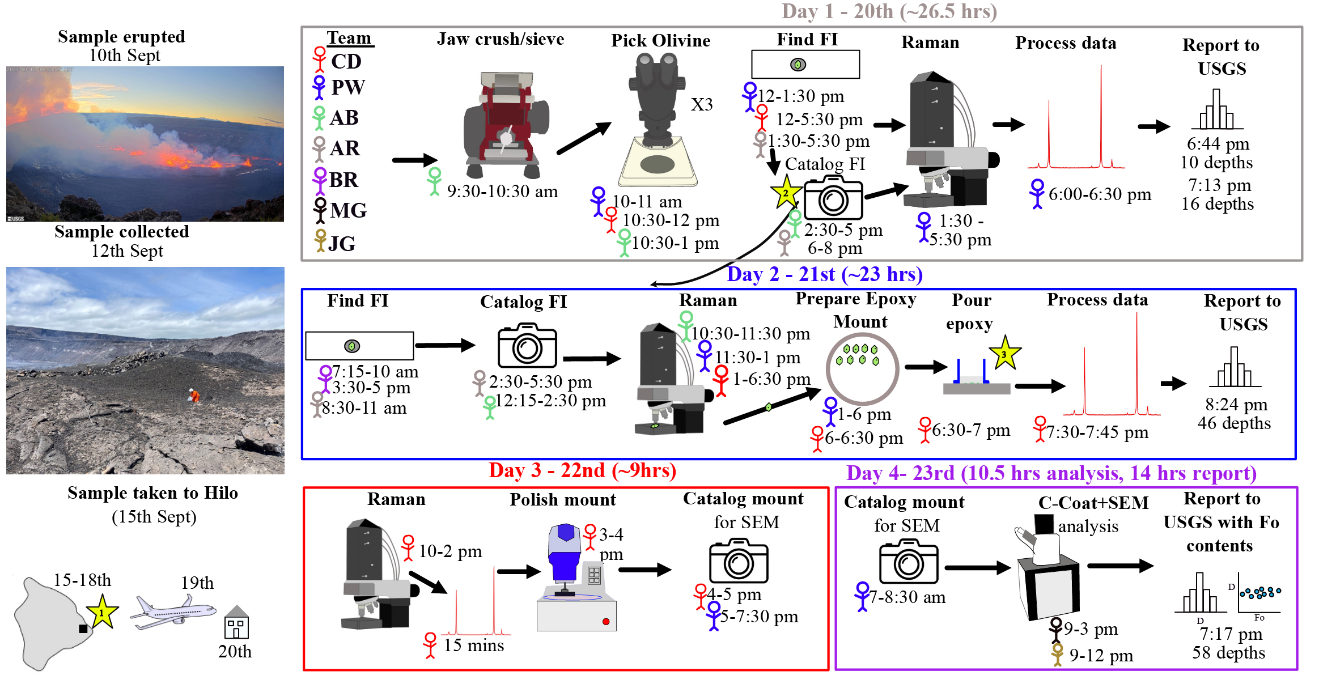
S4 FI Navigation image compilation

All other raw data (spectra, metadata, FI images) as well as raw Jupyter processing notebooks can be found on a Github repository (<https://github.com/cljdevitre/RapidresponseFI_Kilauea_Sept2023>) which will be archived at Zenodo upon acceptance.

**Text S1. Sample collection and preparation**

Tephra samples (USGS code KS33-588) representing the first ~14 hours of the September 10, 2023, eruption of Kīlauea were collected by U.S. Geological Survey Hawaiian Volcano Observatory (HVO) geologists on September 12 and shipped on Friday September 15 at ~5 pm HST (Fig. S1). This tephra was erupted from a fissure which opened at 15:36 local time on September 10 (~22 minutes after the eruption started, between 15:13 and 15:14 local time) and ceased erupting between 06:16 and 06:18 am local time on September 11. Following receipt of the samples at the University of California (UC), Berkeley, on Tuesday September 19, material was processed in a jaw crusher in the VIBE lab, which was thoroughly cleaned the week before and the morning of the simulation, and then sieved into >2, 1–2, and 0.5–1 mm size fraction. Crystals were picked from the 1–2 and 0.5–1 mm size fraction using three different binocular microscopes (one of which had the ability to cross polars). Then, crystals were individually mounted in CrystalBond™\* on glass slides and progressively polished with 1200-2500-10000 grade wet and dry paper to find fluid inclusions (FI). Grains containing FI were then passed onto a team member on a research-grade microscope to take reflected and transmitted light images to aid with Raman navigation. These images were pasted into a Google slides document so all lab personnel at UC could access them immediately (images are compiled in supplement S4 FI Image Compilation as an example).

A lava flow sample (USGS code KS33-587) was collected in a molten state and quenched with water at 6:30 AM HST on the 11 of September 2023. The sample was entirely glassy, and fragments were mounted in a 1” epoxy round and polished for microprobe analysis.



***Figure S1. Workflow of the study, all times on this figure are Pacific Standard Time (PST).*** *Stick people show the contribution of individual team members, to indicate the total time associated with each step. We note that AB was trained in these procedures during the simulation and all reports were sent to the USGS Hawaiian Volcano Observatory (HVO) prior to 5:30 pm Hawaii Standard Time (HST), thus allowing for decision-making for the following day.*

Text S2. Raman analyses

Raman spectra were acquired using a WiTec Alpha 300R Raman spectrometer at the Department of Earth and Planetary Science at the University of California, Berkeley. The relationship between CO2 density and spectral features was determined from a gas calibration cell following the methods of DeVitre and Wieser (2024). All spectra were acquired from samples heated to 37 ℃. Spectra were processed and corrected for drift using the Python tool DiadFit v0.0.73 (Wieser and DeVitre, 2024). We report ratios of SO2 to CO2 peak areas. We filtered the final dataset for SO2/CO2 ratio < 0.22 (Fig. 1d) to ensure use of the pure CO2 EOS was valid (given an instrumental efficiency of 1 for our Raman, this corresponds to <10 mol% SO2). No fluid inclusions contained carbonate peaks nor any gaseous species other than CO2. We calculated densities from the Raman-measured separation of the Fermi diad using the appropriate calibrated density equations for our instrument in DiadFit v.0.073 (Wieser and DeVitre, 2024). For the final dataset (Day 4), we took a mean of duplicate analyses, and calculated pressures using the EOS of Span and Wagner (1996) using an entrapment temperature estimated from the Fo content close to the FI (DeVitre and Wieser, 2024). Entrapment depths in Fig. 1 were calculated using a constant crustal density of 2300 kg/m3 and a normally distributed 1**σ** error of 100 kg/m3. Error in the CO2 density for each FI was determined from the error in each peak fit, the Ne line drift correction model, and the densimeter (Wieser and DeVitre, 2024). We used a 40℃ error for temperature (DeVitre and Wieser, 2024). We propagated these three sources of uncertainty in FI depths using Monte Carlo simulations implemented in DiadFit v0.0.73. We later recalculated pressures using the EOS of Duan and Zhang (2006) implemented in a newer version of DiadFit (v.0.0.85) to assess the effect of XH2O on our results (Fig. 1d “H2O effect” histogram). Further details can be found in section S6 of this supplement (“Text S6. Effect of H2O on calculated pressures”). In total we analyzed 62 FI hosted in 31 olivine crystals. Our workflow is detailed in Fig. S1. Pictures of each FI and host crystal are available in the repository linked at the beginning. We note here that the initial data reported for days 1 and 2 did not account for repeated analyses (1 repeated FI in Day 1 and 6 in Day 2; we took a mean of repetitions on Day 4), pressures were calculated using an estimated entrapment temperature of 1150˚C (Wieser *et al.*, 2021; DeVitre and Wieser, 2024), and depth was calculated using the crustal density model in Ryan (1987) and Lerner *et al.* (2021).

**Text S3. Epoxy mount making and polishing**

After Raman analysis, crystals were removed from CrystalBondTM\* using a hotplate and placed in acetone. They were then mounted on double-sided sticky tape with their polished side down. EpoFixTM\* resin was used to impregnate the samples in a Cast-N-Vac vacuum pourer. After curing, the epoxy mount was polished using an EcoMet30 automatic polisher, with 9, 3, and 1 µm diamond pastes. A reflected light map and image of each crystal was taken using the Raman microscope to aid SEM sample navigation. The location within each FI in the reflected light image was cataloged so the scanning electron microscope (SEM) operator knew where to analyze to obtain an approximate Fo content for each FI.

**Text S4. EDS analysis**

Samples were carbon coated to an approximate thickness of 25–30 µm for EDS analysis. Chemical data for each host crystal in the proximity of each FI were determined using a Zeiss EVO MA-10 SEM and a single AMETEK EDAX 10 mm2 detector at the University of California, Berkeley. The beam was rastered over a 30-by-30 µm area for ~75–80s (a live time of 60 seconds with ~30% dead time). For all analyses we used an accelerating voltage of 20 kV and a 30 µm aperture, giving an approximate beam current of 5 nA. EDS data reduction was performed using an in-built standardless quantification routine (including a ZAF matrix correction), alongside pre-determined “Standardless Element Coefficients” (SECs). The SECs act as correction factors for each element in the standardless quantification routine and have been determined through several years of repeat analyses of multiple different silicate standard materials and glasses. This method returns an estimate for the relative abundance of each element in the analyzed material and, if a normalization to 100% is assumed, can be used to return semi-quantitative chemical analysis of elemental or oxide weight percent values. However, for the purposes of this study we simply focused on the relative abundance of Mg and Fe in the EDS analyses to calculate the Fo content of the olivine host crystals. Furthermore, by calculating the molar Si/(Mg+Fe) ratio of each analysis we were able to provide a stoichiometric check of data quality: we obtained an average Si/(Mg+Fe) ratio of 0.497±0.006 on Kīlauea olivine crystals, close to the ideal value of ~0.5. Precision and accuracy were determined through repeat measurements of the San Carlos and Springwater olivines, which were not used as part of the standard quantification routine. We estimate the precision and accuracy of the method using repeat analyses of secondary standards (5 at start, 5 at end of day), which have Fo contents similar to our samples (see supplementary dataset S3). The Smithsonian-preferred Fo content (Jarosewich *et al.*, 1980) for the San Carlos secondary standard is 90.2 mol% Fo, and we obtained a mean of 89.84±0.07 mol% Fo. For Springwater, the preferred value is 82.4 mol% Fo, and we obtained a mean of 82.1±0.2 mol% Fo. We also analyzed a Kīlauea olivine crystal previously measured on the USGS Menlo Park EPMA. The average Fo content obtained at Menlo Park was 87.8±0.1 mol% Fo, and at the University of California, Berkeley, SEM, 88.5±0.1. Notably, such offsets also exist between different EPMA labs (Wieser *et al.*, 2023b). Considering these probable differences, we compared data acquired at Stanford University to that obtained at Cambridge University on the olivine crystals of Wieser *et al.* (2021). The difference observed amounts to ~0.62 mol% at Fo~82 and 0.78 mol% at Fo90 (DeVitre and Wieser, 2024). Thus, EDS errors are within uncertainty of offsets between different microprobe labs.

Text S5. Identifying and Resolving Bottlenecks

The yellow stars on Fig. S1 identify current bottlenecks in the process that could be easily improved. We note that the first version of this manuscript was submitted to a journal for review on September 27th, 2023, one week after sample receipt.

***Star 1 – Shipping and receiving samples***

Distributing samples to the University of California, Berkeley was not a top priority for HVO because this simulation was being attempted for the first time, and as such, there was no guarantee of obtaining magma storage depths in a timely manner. Samples were shipped from Hilo on a Friday at ~5 pm HST. HVO was asked to ship samples to a private residence under the assumption that they might arrive over the weekend. However, no packages leave Hilo after 4pm on Friday over the weekend, so the samples started their transit to California on Monday. Had the package been taken to the courier’s office on Friday morning, it would likely have arrived on Sunday. The tracking information indicated arrival on Wednesday, which is when we planned to start the simulation. However, the samples arrived at the private residence on Tuesday morning during working hours, without notification that the package had been delivered (and no one was home).

We have demonstrated that this technique adds valuable quantitative depth information that expands on HVO’s routine near-real-time chemical monitoring with bulk rock ED-XRF (Gansecki *et al.*, 2019). Under ideal circumstances, HVO geologists would sample tephra or molten lava from the eruption on Day 1 (morning) and dry the samples in the lab on Day 1 (afternoon), dropping the samples for shipment on the evening of Day 1, which would go out early on Day 2 (as long as the drop-off did not occur Friday afternoon or over the weekend). Same-day shipping from Hawaii to California is not realistic, but samples shipping Monday through Thursday mornings would allow for arrival on Day 3. Additionally, it would be possible to get samples to the University of California, Berkeley, within 24 hours if someone in Hawai’i were to take a flight to San Francisco or Oakland airport with the samples, or within ~30 hours if someone based in the University of California, Berkeley, flew to Hawai’i, picked up the samples, and returned home immediately.

We note that this bottleneck can be avoided entirely if observatories rely on local research expertise (for example, in collaboration with local academic research groups) and/or establish in-house workflows for this type of work. In such a case, next-day information could readily be obtained. As this is not an option for HVO, the Hawaii-California connection will serve as the fastest way to conduct this rapid-response barometry.

***Star 2 – Sample cataloging***

The WiTec Raman microscope used in this study does not have a condenser in its optical path, which can make it difficult to navigate and find FIs directly, particularly in volcanic crystals that are commonly coated in glass. The first 7–10 crystals were analyzed immediately after preparation with no navigation photos, so finding the FI on the Raman scope added some time. After AB had finished crushing, sieving, and picking, he began taking photos on a research-grade microscope to help the Raman operator find the FIs they were supposed to be analyzing. Late on Day 2, when students were not available, Wieser began photographing crystals holding her phone to the eyepiece of the teaching-collection reflected light and transmitted light microscopes. This provided enough textural context to easily find FIs on the Raman (See Image Compilation S4 in the repository). The main advantage of using smartphones is that the person who found each FI could identify it, rather than passing it off to another person who then must work out where the FI is before photographing it. This would greatly reduce the number of people needed for the simulation, as we almost always had one person taking photos.

***Star 3 – Epoxy impregnation***

We used EpoFixTM epoxy in our laboratory because it gives low backgrounds during SIMS analysis. After pouring the epoxy at ~7 pm, it was removed from its mount at ~9 am the next morning. The epoxy was still noticeably soft (to the extent it cracked coming out of the mold). This meant that we could not start polishing immediately. Instead, we had to wait another ~5 hours for it to cure sufficiently to polish. If fast-curing epoxies were available, it is very possible that a team member could have stayed and polished and cataloged the sample overnight, allowing SEM analysis on Friday (Day 3) rather than Saturday.

Text S6. Effect of H2O on calculated pressures

The exsolved fluid phase in shallow magmatic systems like Kīlauea is not pure CO2, but rather contains a proportion of H2O. Fluid inclusion studies typically assume that H2O has been lost and therefore the measured CO2 density must be corrected based on the molar fraction of H2O and molar ratios (see Hansteen and Klügel, 2008). With this, pressures can be calculated using a mixed H2O–CO2 equation of state. Although it was not possible to implement these calculations during our simulation, a recent paper (Yoshimura, 2023) made it possible to implement these corrections starting in DiadFit v0.0.85. We recalculated pressures for our fluid inclusions using mol fractions of H2O in the exsolved fluid calculated based on the polynomial equations for Kīlauea in DeVitre and Wieser (2024). We iterated measurements 5 times and show calculated on Fig S2; the data for iteration 5 are reported are the full FI dataset (Dataset S3) and the Jupyter notebook is available in the repository. We plot the recalculated histogram of depths on Fig.1d. We note that for all 3 days, the mean and median correction factor is ~10%. Most FI have correction factors <20%. These correction factors do not shift our FI from one reservoir to another, therefore they do not affect the interpretation of our results.

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**Fig. S2**. Cumulative probability plot of the ratio of pressures from the mixed fluid EOS and pure CO2 EOS depending on the  function applied from (DeVitre and Wieser, 2024) for each day of the simulation.

Text. S7. Sensitivity of the EOS method for FI to entrapment temperature – Extended

We test the sensitivity of 3 equations of state for CO2 available in DiadFit: two are for pure CO2 (Sterner and Pitzer, 1994; Span and Wagner, 1996) and one for CO2-H2O mixtures (Duan and Zhang, 2006). For this, we calculated pressures using all three EOS at different magmatically relevant entrapment temperatures (for the mixed H2O-CO2 EOS we used  = 0.1), which encompass the entire range of measured olivine-saturated liquid temperatures at Kīlauea (1100,1150, 1240 and 1350 ˚C). Overall, none of the three equations of state are significantly sensitive to temperature at these magmatic temperatures (Fig. S3-S6). The shaded box in Fig. S3 shows storage conditions relevant to Kīlauea. In the worst case, at the depth of the HMM reservoir (1 km), the absolute uncertainty in depth due to temperature is ~0.15 km and at depths corresponding to the SC reservoir (~4 km) it is ~0.7 km. We plot in detail on Figs S4-S6 the temperature sensitivity for each of the EOS at general conditions and conditions specifically relevant to Kīlauea.

A diagram of a chemistry experiment

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Fig. S3. % Percentage difference in pressure (a) and absolute difference in depths (b) for pressures calculated at 1350and 1150˚C using two pure CO2 EOS (SW96, Span and Wagner, 1996; SP94, Sterner and Pitzer, 1994) and one mixed H2O-CO2 EOS (DZ06, Duan and Zhang, 2006). Shaded areas indicate pressures and depth relevant to Kīlauea pre-eruptive magma storage.

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Fig. S4. Temperature sensitivity of the mixed CO2-H2O equation of state at 0.1 mol% H2O (Duan and Zhang, 2006).(a) Pressure vs CO2 density calculated for various entrapment temperatures relevant at Kīlauea. 1150 ˚C was our initial fixed temperature for days 1 and 2; 1240 ˚C is the rounded mean and median of all measured temperatures in our final dataset. (b) Depth and pressure differences induced by uncertainty in temperature. Blue curves show the % difference in pressure (or depth) and maroon curves show the absolute difference in depth in km. (c) Close-up of panel a, representing relevant PT conditions for Kīlauea. Gray boxes show the depth range of the magma storage reservoirs – HMM for Halema’uma’u reservoir and SC for south caldera reservoir – inferred from FI and MI barometry as well as geophysics (DeVitre and Wieser, 2024; Lerner *et al.*, 2024). Stars show hypothetical FI trapped at HMM and SC reservoirs with error bars representing 1σ uncertainty from Monte Carlo simulations using a temperature uncertainty of ±150 K. (d) Close-up of panel b, showing depth and pressure differences induced by uncertainty in temperature for PT conditions relevant to Kīlauea. Blue curves show the % difference in pressure (or depth) and maroon curves show the absolute difference in depth in km.

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Fig. S5. Temperature sensitivity of Span and Wagner (1996) pure CO2 equation of state.

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Fig S6. Temperature sensitivity of Sterner and Pitzer (1994) pure CO2 equation of state.

Text S8. Global Melt inclusion compilation

We compiled melt inclusion datasets with published major element data, H2O and CO2 concentrations in the glass from EarthChem (https://www.earthchem.org/), Georoc (https://georoc.eu/), Rasmussen *et al.* (2022), DeVitre *et al.* (2023) and Wieser *et al.* (2023c) as well as other MI datasets from the literature (Harris and Anderson Jr, 1983; Anderson and Brown, 1993; Roggensack *et al.*, 1997; Roggensack, 2001a, 2001b; Saal *et al.*, 2002; Cervantes and Wallace, 2003; Wade *et al.*, 2006; Benjamin *et al.*, 2007; Sadofsky *et al.*, 2008; Vigouroux *et al.*, 2008; Auer *et al.*, 2009; Famin *et al.*, 2009; Johnson *et al.*, 2009; Kelley and Cottrell, 2009; Koleszar *et al.*, 2009; Roberge *et al.*, 2009; Zimmer, 2009; Cooper *et al.*, 2010, 2022; Kelley *et al.*, 2010; Ruscitto *et al.*, 2010, 2011; Shaw *et al.*, 2010; Zimmer *et al.*, 2010; Esposito *et al.*, 2011; Head *et al.*, 2011; Helo *et al.*, 2011; Mormone *et al.*, 2011; Schipper *et al.*, 2011; Berlo *et al.*, 2012; Bouvet de Maisonneuve *et al.*, 2012; Field *et al.*, 2012; Rose-Koga *et al.*, 2012; Wanless and Shaw, 2012; Wysoczanski *et al.*, 2012; de Moor *et al.*, 2013; Lloyd *et al.*, 2013; Brounce *et al.*, 2014; Hartley *et al.*, 2014; Métrich *et al.*, 2014; Myers *et al.*, 2014; Sides *et al.*, 2014; Wanless *et al.*, 2014, 2015; Cassidy *et al.*, 2015; Colman *et al.*, 2015; Hudgins *et al.*, 2015; Moore *et al.*, 2015, 2018, 2021; Plechov *et al.*, 2015; Ribeiro *et al.*, 2015; Wallace *et al.*, 2015; Aster *et al.*, 2016; Druitt *et al.*, 2016; Ruth *et al.*, 2016; Venugopal *et al.*, 2016, 2020, 2020; Walowski *et al.*, 2016, 2019; Donovan *et al.*, 2017; Hauri *et al.*, 2017, 2021; Longpré *et al.*, 2017; Rasmussen *et al.*, 2017; Robidoux *et al.*, 2017, 2018; Allison, 2018; Bali *et al.*, 2018; Bennett *et al.*, 2019; Gennaro *et al.*, 2019; Manzini *et al.*, 2019; Miller *et al.*, 2019; Taracsák *et al.*, 2019; Iddon and Edmonds, 2020; Allison *et al.*, 2021; Hernandez Nava *et al.*, 2021; Lerner *et al.*, 2021; Rasmussen and Plank, 2021; Wieser *et al.*, 2021; Gleeson *et al.*, 2022; DeVitre *et al.*, 2023; Wong *et al.*, 2023).

We calculated saturation pressures and the fraction of H2O in the exsolved fluid phase () using the MagmaSat solubility model (Ghiorso and Gualda, 2015) implemented in VESIcal (Iacovino *et al.*, 2021). Whenever measurements were available, we used total CO2 contents calculated from mass balance for Raman-measured MI bubbles, otherwise we use glass-only CO2. When possible, we use post-entrapment crystallization corrected MI concentrations. As a first approximation, temperatures were calculated from major element data using the CaO liquid-only thermometer of Helz and Thornber (1987) implemented in Thermobar (Wieser *et al.*, 2022) as it is not pressure sensitive. From there we calculated saturation pressures using MagmaSat in VESIcal (Iacovino *et al.*, 2021). We then used these approximated pressures to recalculate temperatures with the more appropriate ol-liq equation 22 of Putirka (2008) implemented in Thermobar (Wieser *et al.*, 2022)). As we did not have access to olivine-host chemistry, we used the Thermobar function “T\_Put2008\_eq22\_BeattDMg,” which couples a theoretical calculation of the DMg from Beattie (1993) to calculate equilibrium olivine compositions so that equation 22 of Putirka (2008) can be used as a liquid-only thermometer. Equation 22 of Putirka (2008) has recently been identified as the most robust liquid-only thermometer across a wide range of compositions (Wieser *et al.*, 2023a). Lastly, we recalculated saturation pressures using MagmaSat and our refined temperatures. We did not recalculate saturation pressures, temperatures or  for MI in the Cascades compilation of (Wieser *et al.*, 2023c) or for (Dayton *et al.*, 2024) except for Ruscitto *et al.* (2010). It is a known issue that MagmaSat may fail to converge and/or crash during saturation pressure calculations, which can be problematic when calculating saturation pressures on large datasets such as our >4000 MI compilation. To circumvent crashing issues, we implemented a Python multiprocessing routine along with a try-except block using the Python package “multiprocessing.” The dataset is divided into chunks corresponding to 5 times the number of cores available (e.g., for a laptop with 8 logical core processors, the dataset is divided into chunks of 40 samples) to limit the overhead on the processors which can cause memory saturation and crashing. Each chunk is assigned to a processor and run simultaneously. In the case of this study a Dell Inspiron 15 with i7 8 core processor 16 GB memory was used, which limited to a maximum of 8 chunks run simultaneously. Within each chunk, the MI were run one by one within a try-except block such that whenever an error occurred, NaN values were returned along with the error message from VESIcal (Iacovino *et al.*, 2021). Any MI for which MagmaSat did not converge were filtered out in the final dataset. The notebook is included in the data repository. We provide both the complete unfiltered compilation, and the compilation filtered for MagmaSat errors, SiO2 < 57 wt% and MgO < 16 wt%. As discussed in previous sections, our method is not applicable to systems and magmas where is very high, like for example in high-silica magmas where H2O is concentrated due to fractional crystallization and CO2 is lost due to extensive degassing. Therefore, to identify locations in the world where the rapid-response fluid inclusion barometry technique could be relevant, we plot only mafic MI with SiO2 <57 wt% (Fig. S7). Such magmas are likely representative of recharge magmas regardless of tectonic setting. Interestingly, it is evident that  tends to be higher at alkaline intraplate volcanoes than their tholeiitic counterparts at similar pressures (Fig. 3 main text, Fig. S9).

We then plot against pressure at each unique location, grouped by tectonic settings (Fig. S8a-e). It is notable that there is a marked increase in at very low pressures (<50 MPa). We filter the dataset presented on Fig 4, and Fig S10 considering a pressure cutoff of 20 MPa, where is very high regardless of setting.

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Figure S7. Total Alkalis vs Silica diagram for all the MI <57 wt% SiO2 and MgO <16 wt% in our compilation. Larger black edged symbols indicate the medians of specific locations. (a) Intraplate (oceanic and continental) volcanoes in the compilation. We separate OIB-tholeiitic and OIB-alkaline locations based on the medians on this plot. (b) Subduction zone volcanoes. (c) Mid-ocean ridges. (d) Continental rifts.

A group of graphs showing different types of pressure

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Figure S8a. Pressure vs at tholeiitic OIB locations.

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Figure S8b. Pressure vs at alkaline OIB locations and Sunset Crater (an alkaline continental intraplate volcano).

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Figure S8c. Pressure vs at continental rift locations.

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Figure S8d. Pressure vs at mid-ocean ridge locations (Part 1). JdFR – Juan de Fuca Ridge, GSC – Galápagos Spreading Center, EPR – East Pacific Rise.

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Figure S8e. Pressure vs at mid-ocean ridge locations (Part 2). NAR – North Atlantic Ridge, MAR – Mid-Atlantic Ridge, GR – Gakkel Ridge.

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Figure S8f. Pressure vs at subduction zones (Part 1).

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Figure S8g. Pressure vs at subduction zones (Part 2).

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Figure S8h. Pressure vs at subduction zones (Part 3).

A comparison of different types of subduction zones

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Figure S8i. Pressure vs at subduction zones (Part 4).

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Figure S9. Boxplots and violin plots of H2O and CO2 contents of melt inclusions in the compilation. Filtered to SiO2 < 57 wt%, MgO < 16 wt% and saturation pressure > 20MPa.

Data S2. (separate file)

Fluid inclusion dataset for this study.

Data S3. (separate file)

Global melt inclusion compilation (described in previous sections).

**Image Compilation S4 (separate file)**

Compilation of images used for navigation during the simulation. These are presented as they were used during the simulation as an example of what is necessary for the technique.

**Supplementary references**

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