

**Supporting Information for**

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

Charlotte L. DeVitre1\*, Penny E. Wieser1, Alex Bearden1, Raela Richie1, Berenise Rangel1, Matthew Gleeson1, John Grimsich1, Kendra Lynn2, Drew Downs2, Natalia Deligne2 and Katie Mullike2

\*Charlotte L. DeVitre

Email: [cl.devitre@gmail.com](mailto:cl.devitre@gmail.com)

ORCiD (CLD): [0000-0002-7167-7997](https://orcid.org/0000-0002-7167-7997)

ORCiD (KJL): 0000-0001-7886-4376

ORCiD (DTD): 0000-0002-9056-1404

ORCiD (NID): 0000-0001-9221-8581

**This PDF file includes:**

Detailed Materials and Methods

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**Other supporting materials for this manuscript include the following:**

Dataset S1 (Excel Table attached to the submission)

All other raw data (spectra, metadata, FI image catalogue) as well raw Jupyter processing notebooks can be found on a Github repository (<https://github.com/cljdevitre/2023_Kilauea-rapid-response-simulation>) which will be archived at Zenodo upon acceptance.

# Detailed Materials and Methods

**Sample collection and preparation**

Tephra samples (USGS code KS23-588) representing the first ~14 hours of the September 10, 2023, eruption of Kīlauea volcano were collected by Hawaiian Volcano Observatory (HVO) geologists on September 12 and shipped on Friday September 15 at ~5 pm HST. 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, Berkeley on Tuesday, September 19, material was processed in a jaw crusher in Wieser’s lab which was thoroughly cleaned the morning of the simulation, and then sieved into >2 mm, 1–2 mm, and 0.5–1 mm size fraction. Crystals were picked from the 1–2 mm and 0.5–1 mm size fractions 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 FI. Grains containing FI were then passed onto a team member on a research grade scope 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.

A lava flow sample (USGS code KS23-587) 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.

**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 ref(1). All spectra were acquired at 37 ℃. Spectra were processed and corrected for drift using the Python tool DiadFit v0.0.73. We report ratios of SO2 and CO3 to CO2 peak areas and calculate approximate mol % SO2 using the equations of ref(2), implemented in DiadFit. All measured FI had SO2 mol % <10, we filtered the final dataset for SO2 mol % <5 (Fig. 2d), to ensure use of the pure CO2 EOS was valid. We calculated densities from the Raman-measured separation of the Fermi diad using the appropriate calibrated density equations for our instrument in DiadFit(3). For the final dataset (Day 4), we took a mean of duplicate analyses, and calculated pressures using the EOS of ref(4) using an entrapment temperature estimated from the Fo content(1). Entrapment depths in Fig. 2d 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 (3). We used a 40℃ error for temperature(1). Considering all this we propagated uncertainties in FI depths using MonteCarlo simulations implemented in DiadFit. In total we analyzed 62 FI hosted in 31 olivine crystals. Our workflow is detailed in Fig. 1. Pictures of each FI and host crystal are available in the repository linked at the beginning (Image Compilation). 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 (1, 5), and depth was calculated using the crustal density model in ref(6).

**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 um 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.

**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 was 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 S1). The Smithsonian-preferred Fo content (7) for the San Carlos secondary standard is 90.2 Fo, and we obtained a mean of 89.84±0.07 Fo units. For Springwater, the preferred value is 82.4 Fo, and we obtained a mean of 82.1±0.2 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 Fo units, and at the University of California, Berkeley SEM, 88.5±0.1. It should be noted that such offsets also exist between different EPMA labs (8). Considering these probable differences, we compared data acquired at Stanford University to that obtained at Cambridge University on the olivine crystals of ref(5). The difference observed amounts to ~0.62 units at ~82 Fo and 0.78 units at 90 Fo(1).

**EPMA analysis of glasses**

Major and minor element analysis of glass from USGS sample KS23-587 was done using the U.S. Geological Survey’s JEOL 8530F microprobe at the California Volcano Observatory. The samples were run over midnight between September 23 and 24th, 2023, in 1hr 37 minutes (9/23/2023 23:06 - 9/24/2023 0:43). A total of 20 total analyses were conducted, corresponding to 4 analyses per grain in 5 grains. These samples were run as part of a pre-booked session for other samples that started on September 20th. We note however that CalVO microprobe personnel later informed us that it would be possible in the future to request immediate access for eruption response if needed. This would mean that a glass mount could be prepared in 24 hrs after sample collection, shipped within 2 days to CalVO and analyzed on the probe on day 4 post field collection (calibration takes 2-3 hrs and analysis ~2 hours).

Analyses used 15 kV accelerating voltage and a 10 µm beam with a 10 nA current. Peak counting times were 45 s for S, Cl, and F, 40 s for Ti, P, and Mn, 20 s for Si, Ca, Fe, Al, and Mg, and 10 s Na and K (backgrounds were measured on both sides of the peak for half the peak counting times). Standards for glass analyses were VG2 basaltic glass (USNM 111240/52;ref (7)) for Si, Mg, and Al, Kakanui Pyrope Garnet (USNM 143968) for Fe, and Al, Wollastonite for Ca, Tiburon Albite for Na, MnO3 for Mn, TiO2 for Ti, Orthoclase OR-1A for K, Wilburforce Apatite (USGS-M105731) for P, Barite for S, Sodalite for Cl, and MgF2 for F. Two-sigma relative precision, based on two analyses of VG-2 glass (before and after lava sample was run), are 0.19 wt% for SiO2, 0.15 wt% for Al2O3, 0.003 wt% for TiO2, 0.27 wt% for FeO, 0.009 wt% for MnO, 0.006 wt% for MgO, 0.04 wt% for CaO, 0.11 wt% for Na2O, 0.02 for K2O, 0.04 for P2O5, 0.07 for SO3, 0.0001 for Cl, and 0.002 for F. X-ray intensities were converted to concentrations using standard ZAF corrections(9). Analyses with totals <99.0 wt% or >100.5 wt% were rejected. Reported analyses are an average of four replicate points on individual glass fragments. We note that if these measurements did not exist at the time of the simulation, we could have used the EDS-SEM method to get the Mg# of the host glass to calculate the equilibrium olivine Fo content shown on Fig. 2 (The only reason we need this EPMA data). EDS measurements on the matrix glass were within 1-2 Mg# units of EPMA measurements – far smaller than the uncertainty associated with choosing a KD model at Kīlauea.

**Identifying and Resolving Bottlenecks**

The yellow stars on Fig. 1 identify current bottlenecks in the process that could be easily improved.

***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 a result, 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(10). 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 Califonia 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 Fransisco 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 very hard to navigate and find FIs, particularly in volcanic crystals that are commonly coated in glass. The first 7–10 crystals were analyzed immediately after preparation, so navigation took some time. After AB had finished crushing, sieving, and picking, he began taking photos on a research-grade scope 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 in the repository linked in the beginning). 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 involved, as we almost always had one person taking photos.

***Star 3 – Epoxy impregnation***

We used EpoFixTM epoxy, which is what was available in our lab (chosen 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 a further ~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.

**Supplementary references**

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