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

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Abstract

Rapid-response petrological monitoring is a major advance for volcano observatories to build and validate models in near-real-time of the plumbing systems that supply eruptions. Our rapid-response analysis of tephra from the September 2023 eruption of Kīlauea shows that Raman analyses of fluid inclusions can robustly determine magma reservoir depths within a day of receiving samples – a transformative timescale for decision making that has never been achieved by petrological methods.

Main text

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[1–3]. Most work so far has focused on the chemistry of erupted lavas and crystal cargoes[3] to gain insight into changing melt composition and rheological properties (e.g., ref [1]). However, up until now, petrological monitoring has been unable to address the high-priority question– '*Where is the magma coming from?*' [2]. 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 [4], depths of storage are a vital parameter to begin interpreting new eruptive activity. Melt inclusion (MI) barometry, a widely popular petrological method to determine storage depths from volatile contents, takes months to years to complete [2]. While mineral barometry could be implemented faster (only requiring electron probe microanalysis (EPMA) measurements on eruptive minerals), it is imprecise [5,6], and therefore would only be able to constrain magma storage to very broad depths (e.g., stored in the crust vs. below the Moho). This technique has particularly

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41 poor applicability at active volcanoes such as Kīlauea or Mauna Loa, where a precision of 1–2 km is needed to

42 distinguish between storage reservoirs[7,8].

43   Recent developments have shown that Raman-based barometry of CO_2-rich fluid inclusions (FI) provides

44 an ~~exiting~~ alternative to popular petrological barometers, with much smaller uncertainties than mineral barometry,

45 and requiring far less time and resources than MI analyses [9,10]. This method uses spectral features of CO_2 fluids to

46 calculate a CO_2 density using an instrument specific calibration [11]. Along with an estimate of entrapment

47 temperature, this density is converted into an entrapment pressure using a CO_2 Equation of State (EOS). Pressures

48 are converted to depths through an estimate of crustal density. However, there has previously been no rigorous

49 assessment of ~~just~~ how quickly FI depths can be obtained from erupted material, and whether these timescales are

50 short enough to have use as a real-time monitoring tool.

51   The eruption onset of Kīlauea volcano on September 10, 2023 provided an unprecedented opportunity to

52 test the validity of this method during a response, given that depths of the main magma storage regions at this

53 volcano have been well constrained by various independent geophysical and petrological methods, including prior

54 FI barometry[10]. Tephra samples representing the first ~14 hours of the September 2023 eruption were collected by

55 Hawaiian Volcano Observatory (HVO) geologists on September 12. ~~Following discussions with HVO over the~~

56 ~~next few days, we requested samples to run a rapid-response simulation.~~

57   Our simulation started on September 20 at 9 am PST (Day 1) ~~following receipt of samples the day before~~

58 (Fig. 1). We used a production-line style workflow involving two undergraduates, a 1st year graduate student, a

59 post-doc, and an assistant professor, with stations for crushing and sieving, mineral picking, FI preparation, sample

60 cataloguing, and analysis. The first steps were to crush and sieve tephra, pick olivine crystals (size fractions 0.5-1

61 and 1-2 mm) crystals, and begin mounting crystals in CrystalBond^{TM} to search for FI. By 2 pm PST (5 hrs into the

62 simulation), we had collected our first Raman spectra. By ~7 pm PST, we had analysed and processed all data for

63 16 FI and were able to share a histogram of storage depths with HVO collaborators showing that crystals, and thus

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magma, were coming from the shallower Halemaʻumaʻu reservoir of Kīlauea (HMM on Fig. 2a–b). We also had a further ~20 FI fully prepared and catalogued for analysis. On Day 2, these 20 FI were analysed, while ~~further~~ FI were prepared and catalogued. After analysis of ~15 crystals hosting FI, these crystals were passed from the Raman to a workstation where they were removed from CrystalBond[TM] and placed on tape to make an epoxy mount. Epoxy was poured at the end of the day. By ~8:30 pm PST on Day 2, we shared an updated histogram of 46 FI pressures and depths, confirming the dominant influence of the Halemaʻumaʻu reservoir (Fig. 2a and c). On Day 3, while waiting for the epoxy to fully set, we finished analysing prepared FI. Then we polished the mount and began cataloguing the regions of crystals on which to perform energy-dispersive spectroscopy (EDS). 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. 2d).

Our results clearly show that the majority of FI were entrapped at ~1–2 km below the surface (Fig. 2d), which aligns well with the depths of the Halemaʻumaʻu reservoir interpreted from geophysics[7,8,12], MI barometry [13,14], and FI barometry [10]. 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 ~~as well~~. Rapid EDS analyses of olivine Fo contents close to each FI reveal that olivine crystals grew from a wide range of melt compositions. It is interesting to note that FI in the cores of high-Fo (e.g., >86) olivine crystals return pressures indicative of the shallower Halemaʻumaʻu reservoir – it has been suggested in previous eruptions that these high-Fo olivine crystals predominantly grow in the deeper South Caldera reservoir (SC on Fig. 2a), where high MgO melts are thought to reside. We suggest three possible scenarios to explain the relatively shallow pressures documented in high-Fo olivine crystals:

 1) FI in high-Fo olivine crystals were entrapped within the South Caldera reservoir and re-equilibrated at Halemaʻumaʻu pressures prior to eruption.

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86 2) High-MgO melts were injected into the Halemaʻumaʻu reservoir, where high-Fo olivine crystallized and trapped

87 FI.

88 3) Complex skeletal growth of olivine crystals during extensive undercooling (e.g., ref [15]) ~~meant~~ that high-Fo

89 olivine cores which initially grew in the South Caldera reservoir texturally evolved and trapped lower pressure FI
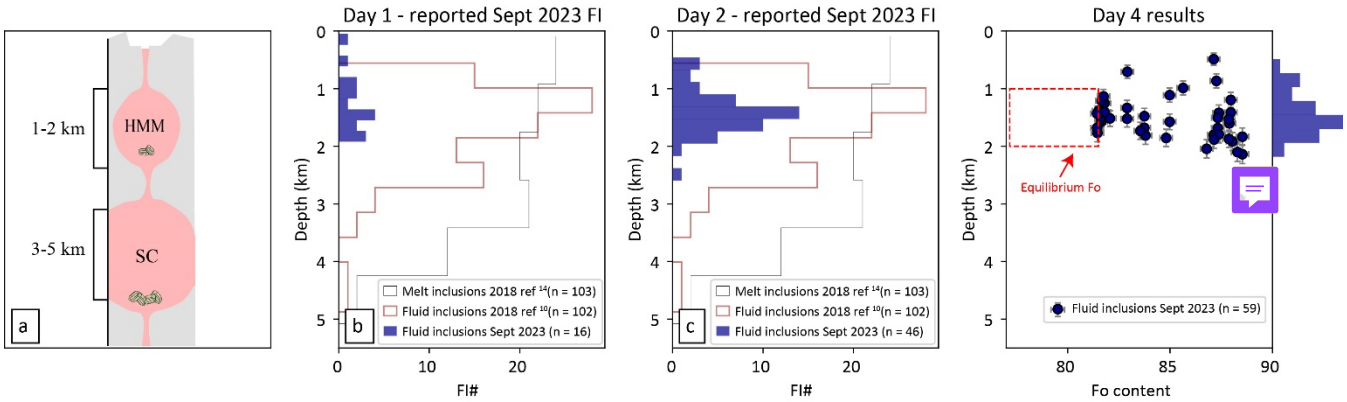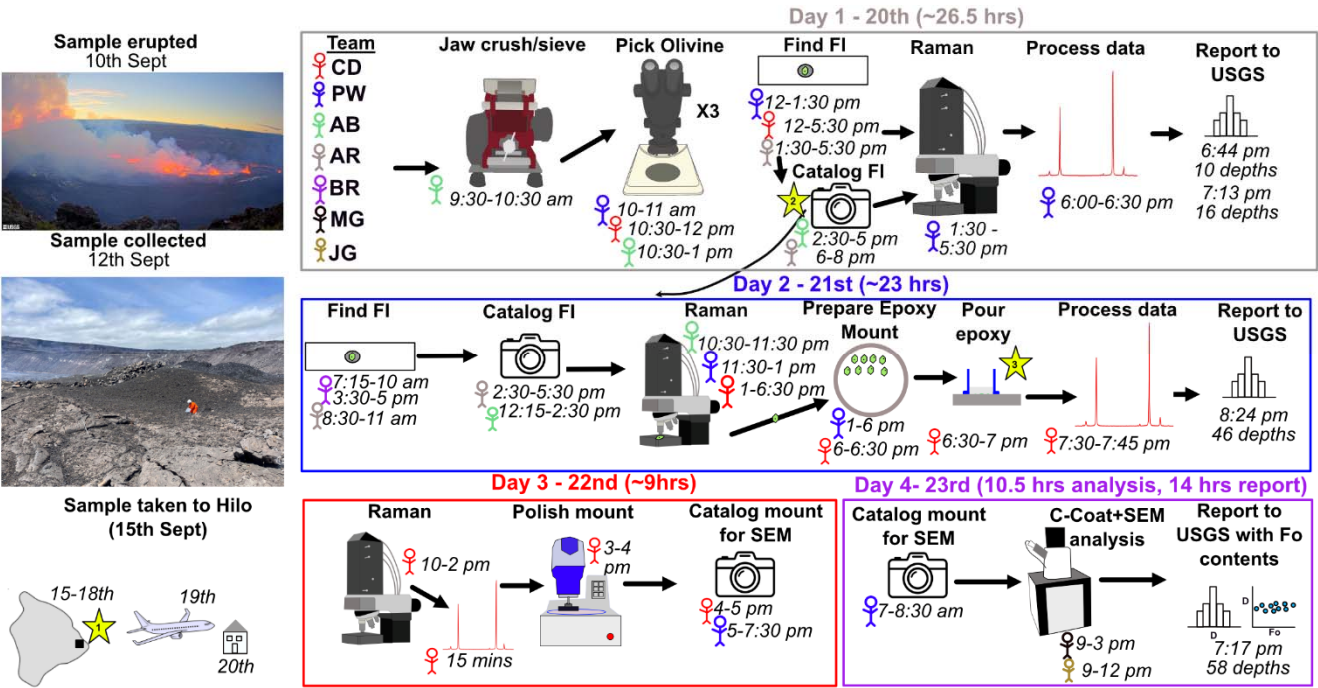
90 in the Halemaʻumaʻu reservoir.

91   We think that scenario 1 is unlikely given the that FI from the 2018 lower East Rift Zone eruption appear

92 not to have re-equilibrated despite stalling in the Halemaʻumaʻu reservoir for up to 2 years[10,16], and our models of

93 FI re-equilibration indicate <10% change in pressure after such a period. Current data does not allow us to resolve

94 scenario 2 vs 3, but this eruption could provide an opportunity to explore this further (e.g., through detailed

95 Phosphorous mapping in olivine around FI). Regardless of the exact mechanism, our FI pressures indicate that

96 erupted crystal cargo experienced storage ~~in the~~ Halemaʻumaʻu reservoir prior to eruption, and thus this is the most

97 probable reservoir supplying magma to the surface.

98   This simulation shows that Raman-based FI barometry has significant potential for rapid-response

99 petrological monitoring globally. It could be applied to any CO_2-rich volcanic system – which includes numerous

100 hazardous and frequently active volcanic regions worldwide (e.g., Galápagos, Réunion, Azores, Canary Islands,

101 Iceland, Cabo Verde). The resources and personnel required are modest. Sample preparation was carried out using

102 transmitted-reflected light microscopes from the University of California teaching collection, only using a research-

103 grade microscope for sample cataloguing. Raman spectrometers are widely available at many universities, given

104 that it is a popular technique in many other fields, such as material sciences, physics, chemistry, and biology, and

105 the W-filament SEM used for EDS analyses to get olivine Fo contents has been around for 15 years (See Methods).

106   This simulation also enabled us to identify several 'bottlenecks' in this rapid-response workflow which

107 could be smoothed out during future eruptions (yellow stars, Fig 1):

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108   1) No courier services ship packages out of Hilo, Hawaiʻi over the weekend, and estimated delivery days

109   are not reliable.

110   2) The epoxy took 18 hours to cure enough for polishing (vs. 8 hours on the datasheet)

111   3) We spent significant time cataloguing samples on a research-grade microscope to help navigate on the

112   Raman, but later realized that smartphone cameras with teaching microscopes would have worked

113   faster.

114   Overall, we have demonstrated that a modest-sized research group with prior teaching and class

115 commitments working without overnight shifts can obtain pressures on ~~game-changing~~ timelines for understanding

116 volcanic plumbing systems during periods of unrest. This technique adds valuable quantitative storage depth

117 information that expands on HVO's routine near-real-time chemical monitoring with bulk rock ED-XRF[1]. In a true

118 eruptive crisis, magma storage depths could be obtained even faster by removing bottlenecks 1–3, implementing

119 overnight shift work, and requesting teaching release and class absences for students.

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Figure 1: 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. We note that all reports were sent to HVO prior to 5:30 pm Hawaii Standard Time (HST), thus allowing for decision making for the following day.

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Figure 2: Evolution of results over 4 days. a) Schematic model of Kīlauea's plumbing system, indicating reservoir depths determined by geophysics and prior petrological work (HMM- Halemaʻumaʻu; SC – South Caldera). b) By the end of Day 1, FI revealed that the crystals were supplied from the Halemaʻumaʻu reservoir. KS tests show that within 5% confidence this is significantly shallower than depths indicated by FI (critical D = 0.22, stat = 0.24, pval=0.016) and MI (critical D = 0.22, stat = 0.41, pval=3.51e-06) from the 2018 lower East Rift Zone eruption, which required a contribution from the South Caldera reservoir. c) By the end of Day 2, depths from 46 FI were sent to HVO, confirming a very dominant role of the Halemaʻumaʻu reservoir. On Day 2 we applied a conservative degassing filter (SO_2 mol% < 2.5) d) By the end of Day 4, after taking a mean of repeated analyses of single FI, applying more stringent data filters, using FI-specific temperatures, and a more appropriate crustal model (density of ~2300 kg/m^3 with a normal error distribution of 100 kg/m^3), entrapment depths with uncertainties were linked to crystal chemistry. Olivine Fo equilibrium field is calculated based on Glass EPMA data (see Methods). We note here that initial data for Days 1 and 2 did not filter out repeated analyses (1 repeated FI in Day 1 and 6 in Day 2), pressures were calculated using an estimated entrapment temperature of 1150°C, and depth was calculated using the model of ref[17] described in ref[13] for crustal density.

Methods (Online)

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, and then

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150   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

151   size fractions using three different binocular microscopes (one of which had the ability to cross polars). Then,

152   crystals were individually mounted in CrystalBond™ on glass slides and progressively polished with 1200-2500-

153   10000 grade wet and dry paper to find FI. FI were then passed onto a team member on a research grade scope to

154   take reflected and transmitted light images to aid with Raman navigation. These images were pasted into a Google

155   slides document so all lab personnel at UC could access them immediately.

156   Glass compositions were measured on USGS sample KS23-587, a lava flow sample collected in a molten

157   state and quenched with water at 06:30 HST on 11 September 2023. The sample was entirely glassy, and fragments

158   were mounted in epoxy in a 1" round and polished for microprobe analysis.

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160

161   **Raman analyses**

162   Raman spectra were acquired using a WiTec Alpha 300R Raman spectrometer at the Department of Earth

163   and Planetary Science at the University of California, Berkeley. The relationship between CO_2 density and spectral

164   features was determined from a gas calibration cell following the methods of ref[10]. All spectra were acquired at 37

165   °C. Spectra were processed and corrected for drift using the Python tool DiadFit v0.0.73[18]. We report ratios of SO_2

166   and CO_3 to CO_2 peak areas and calculate approximate mol % SO_2 using the equations of ref[19], implemented in

167   DiadFit. All measured FI had SO_2 mol % <10, we filtered the final dataset for SO_2 mol % <5 (Fig. 2d), to ensure

168   use of the pure CO_2 EOS was valid. We calculated densities from the Raman-measured separation of the Fermi

169   diad using the appropriate calibrated density equations for our instrument in DiadFit[18]. We then calculated pressures

170   using the EOS of ref[20] and an entrapment temperature estimated from the Fo content[10]. We propagated uncertainties

171   in FI ~~depths~~ using MonteCarlo simulations implemented in DiadFit. Entrapment depths in Fig. 2d were calculated

172   using a constant crustal density of 2300 kg/m^3 and a normally distributed 1σ error of 100 kg/m^3. Error in the CO_2

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173 density for each FI was determined from the error in each peak fit, the Ne line drift correction model, and the

174 densitimeter [18]. We used a 40°C error for temperature. In total we analyzed 62 FI hosted in 31 olivine crystals. Our

175 workflow is detailed in Fig. 1. Pictures of each FI and host crystal are available in the supplement (Image

176 Compilation S2).

177

178 **Epoxy mount making and polishing**

179 After Raman analysis, crystals were removed from CrystalBond^{TM} using a hotplate and ~~placed~~ in Acetone.

180 They were then mounted on double-sided sticky tape with their polished side down. EpoFix^{TM} resin was used to

181 impregnate the samples in a Cast-N-Vac vacuum pourer. After curing, the epoxy mount was polished using an

182 EcoMet30 automatic polisher, with 9, 3, and 1 um diamond pastes. A reflected light map and image of each crystal

183 was taken using the Raman microscope to aid SEM sample navigation. The location within each FI ~~within~~ the

184 reflected light image was cataloged so the Scanning Electron Microscope (SEM) operator knew where to analyze

185 to obtain an approximate Fo content for each FI.

186

187 **EDS analysis**

188 Samples were carbon coated to an approximate thickness of 25–30 μm for EDS analysis. Chemical data

189 for each host crystal in the proximity of each FI was determined using a Zeiss EVO MA-10 SEM and a single

190 AMETEK EDAX 10 mm^2 detector at the University of California, Berkeley. The beam was rastered over a 30-by-

191 30 μm area for ~75–80s (a live time of 60 seconds with ~30% dead time). For all analyses we used an accelerating

192 voltage of 20 kV and a 30 μm aperture, giving an approximate beam current of 5 nA. EDS data reduction was

193 performed using an in-built standardless quantification routine (including a ZAF matrix correction), alongside pre-

194 determined "Standardless Element Coefficients" (SECs). The SECs act as correction factors for each element in

195 the standardless quantification routine and have been determined through several years of repeat analyses of

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196 multiple different silicate standard materials and glasses. This method returns an estimate for the relative abundance

197 of each element in the analyzed material and, if a normalization to 100% is assumed, can be used to return semi-

198 quantitative chemical analysis of elemental or oxide weight percent values. However, for the purposes of this study

199 we simply focused on the relative abundance of Mg and Fe in the EDS analyses to calculate the Fo content of the

200 olivine host crystals. Furthermore, by calculating the molar Si/(Mg+Fe) ratio of each analysis we were able to

201 provide a stoichiometric check of data quality: we obtained an average Si/(Mg+Fe) ratio of 0.497±0.006 on Kīlauea

202 olivine crystals, close to the ideal value of ~0.5. Precision and accuracy were determined through repeat

203 measurements of the San Carlos and Springwater olivines, which were not used as part of the standard

204 quantification routine. We estimate the precision and accuracy of the method using repeat analyses of secondary

205 standards (5 at start, 5 at end of day), which have Fo contents similar to our samples (see supplementary dataset

206 S1). The Smithsonian-preferred Fo content [21] for the San Carlos secondary standard is 90.2 Fo, and we obtained a

207 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

208 Fo. We also analyzed a Kīlauea olivine crystal previously measured on the USGS Menlo Park EPMA. The average

209 Fo content obtained at Menlo Park was 87.8±0.1 Fo units, and at the University of California, Berkeley SEM,

210 88.5±0.1. It should be noted that such offsets also exist between different EPMA labs [5]. Considering these probable

211 differences, we compared data acquired at Stanford University to that obtained at Cambridge University on the

212 olivine crystals of ref[14]. The difference observed amounts to ~0.62 units at ~82 Fo and 0.78 units at 90 Fo[10].

213

214 **EPMA analysis of glasses**

215 Major and minor element analysis of glass from a 11 September 2023 lava (sampled molten, water

216 quenched) was done using the U.S. Geological Survey's JEOL 8530F microprobe at the California Volcano

217 Observatory. Analyses used 15 kV accelerating voltage and a 10 µm beam with a 10 nA current. Peak counting

218 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

11

219 (backgrounds were measured on both sides of the peak for half the peak counting times). Standards for glass

220 analyses were VG2 basaltic glass (USNM 111240/52;ref [21]) for Si, Mg, and Al, Kakanui Pyrope Garnet (USNM

221 143968) for Fe, and Al, Wollastonite for Ca, Tiburon Albite for Na, MnO_3 for Mn, TiO_2 for Ti, Orthoclase OR-1A

222 for K, Wilburforce Apatite (USGS-M105731) for P, Barite for S, Sodalite for Cl, and MgF_2 for F. Two-sigma

223 relative precision, based on two analyses of VG-2 glass (before and after lava sample was run), are 0.19 wt% for

224 SiO_2, 0.15 wt% for Al_2O_3, 0.003 wt% for TiO_2, 0.27 wt% for FeO, 0.009 wt% for MnO, 0.006 wt% for MgO, 0.04

225 wt% for CaO, 0.11 wt% for Na_2O, 0.02 for K_2O, 0.04 for P_2O_5, 0.07 for SO_3, 0.0001 for Cl, and 0.002 for F. X-ray

226 intensities were converted to concentrations using standard ZAF corrections[22]. Analyses with totals <99.0 wt% or

227 >100.5 wt% were rejected. Reported analyses are an average of four replicate points on individual glass fragments.

228

229 **Identifying and Resolving Bottlenecks**

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

231

232 *Star 1 - Shipping and receiving samples*

233   Distributing samples to the University of California, Berkeley was not a top priority for HVO because this

234 simulation was being attempted for the first time, and as a result, there was no guarantee of obtaining magma

235 storage depths in a timely manner. Samples were shipped from Hilo on a Friday at ~5 pm HST. HVO was asked to

236 ship samples to a private residence under the assumption that they might arrive over the weekend. However, no

237 packages leave Hilo after 4pm on Friday over the weekend, so the samples started their transit to California on

238 Monday. Had the package been taken to the courier's office on Friday morning, it would likely have arrived on

239 Sunday. The tracking information indicated arrival on Wednesday, which is when we planned to start the

240 simulation. However, the samples arrived at the private residence on Tuesday morning during working hours,

241 without notification that the package had been delivered (and no one was home).

12

242   We have demonstrated that this technique adds valuable quantitative depth information that expands on

243   HVO's routine near-real-time chemical monitoring with bulk rock ED-XRF[1]. Under ideal circumstances, HVO

244   geologists would sample tephra or molten lava from the eruption on Day 1 (morning) and dry the samples in the

245   lab on Day 1 (afternoon), dropping the samples for shipment on the evening of Day 1, which would go out early

246   on Day 2 (as long as the drop off did not occur Friday afternoon or over the weekend). Same-day shipping from

247   Hawaii to Califonia is not realistic, but samples shipping Monday through Thursday mornings would allow for

248   arrival on Day 3. Additionally, it would be possible to get samples to the University of California, Berkeley within

249   24 hours if someone in Hawai'i were to take a flight to San Fransisco or Oakland airport with the samples, or within

250   ~30 hours if someone based in the University of California, Berkeley flew to Hawai'i, picked up the samples, and

251   returned home immediately.

252   We note that this bottleneck can be avoided entirely if observatories rely on local research expertise (for

253   example, in collaboration with local academic research groups) and/or establish in-house workflows for this type

254   of work. In such a case, next-day information could readily be obtained. As this is not an option for HVO, the

255   Hawaii-California connection will serve as the fastest way to conduct this rapid-response barometry.

256

257   ***Star 2 – Sample cataloging***

258   The WITEC Raman microscope used in this study does not have a condenser in its optical path, which can

259   make it very hard to navigate and find FIs, particularly in volcanic crystals that are commonly coated in glass. The

260   first 7–10 crystals were analyzed immediately after preparation, so navigation took some time. After AB had

261   finished crushing, sieving, and picking, he began taking photos on a research-grade scope to help the Raman

262   operator find the FIs they were supposed to be analyzing. Late on Day 2, when students were not available, Wieser

263   began photographing crystals holding her phone to the eyepiece of the teaching-collection reflected light and

264   transmitted light microscopes. This provided enough textural context to easily find FIs on the Raman (Fig. S1 and

13

265   S2). The main advantage of using smartphones is that the person who found each FI could identify it, rather than

266   passing it off to another person who then must work out where the FI is before photographing it. This would greatly

267   reduce the number of people involved, as we almost always had one person taking photos.

268

269   ***Star 3 – Epoxy impregnation***

270   We used EpoFix^{TM} epoxy, which is what was available in our lab (chosen because it gives low backgrounds

271   during SIMS analysis). After pouring the epoxy at ~7 pm, it was removed from its mount at ~9 am the next morning.

272   The epoxy was still noticeably soft (to the extent it cracked coming out of the mold). This meant that we could not

273   start polishing immediately. Instead, we had to wait a further ~5 hours for it to cure sufficiently to polish. If fast-

274   curing epoxies were available, it is very possible that a team member could have stayed, and polished and cataloged

275   the sample overnight, allowing SEM analysis on Friday (Day 3) rather than Saturday.

276

Author contributions

278   Author contributions for lab work are shown on Fig. 1. CD and PW wrote the paper. CD, PW, AR, BR,

279   and AB prepared tephra, picked olivine, found FIs, catalogued them, mounted them, and Raman-ed them. CD and

280   PW performed all spectral fitting, data processing, and figure making, with schematic illustrations shown in Fig. 1

281   from AB. JG developed the Mg/Fe calibration for the EDS detector and MG performed EDS analyses with help

282   from JG. KJL, DTD, NID and KMM collected samples, processed them in Hilo, and provided eruption context.

283   KJL and DD prepared the glass mount and did the EMPA analyses.

284

Acknowledgements

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Data availability

All data are made available with the publication. All data and Jupyter notebooks are also stored on Github (https://github.com/cljdevitre/2023_Kilauea-rapid-response-simulation). The Github repository will be archived on Zenodo upon acceptance.

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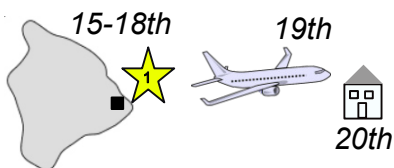
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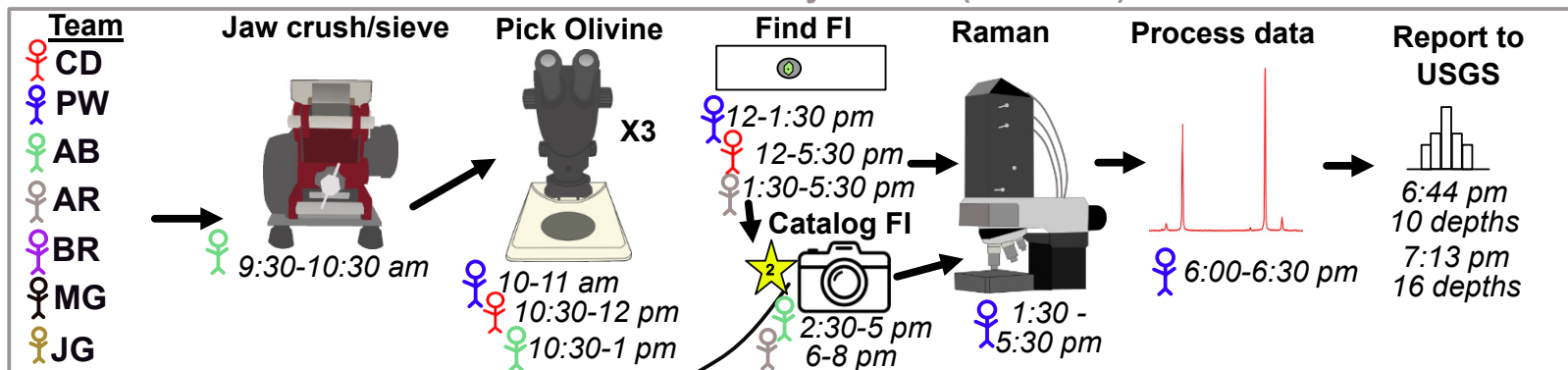**a** — Schematic cross-section showing magma chamber geometry with HMM (1-2 km) and SC (3-5 km) regions.

b Day 1 - reported Sept 2023 FI

- Melt inclusions 2018 ref [14] (n = 103)
- Fluid inclusions 2018 ref [10] (n = 102)
- Fluid inclusions Sept 2023 (n = 16)

c Day 2 - reported Sept 2023 FI

- Melt inclusions 2018 ref [14] (n = 103)
- Fluid inclusions 2018 ref [10] (n = 102)
- Fluid inclusions Sept 2023 (n = 46)

Day 4 results

- Equilibrium Fo
- Fluid inclusions Sept 2023 (n = 59)