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1 **Degassing from magma reservoir to eruption in silicic systems:**
2 **the Li elemental and isotopic record from rhyolitic melt**
3 **inclusions and host quartz in a Yellowstone rhyolite**

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16

17 **Abstract**

18 Lithium and hydrogen are volatile elements which diffuse rapidly in crystals and melt,
19 making them powerful geochemical tools to reconstruct geological processes that take place on
20 short time scales, such as syn- and post-eruptive degassing. Although the dynamics of hydrogen
21 are fairly well understood to better constrain such processes, the assessment of Li behaviour within
22 the magma reservoir relevant for ascent-related degassing still lacks detailed evaluation. Here, the
23 first *in situ* Li concentrations and isotopic compositions (using SIMS analysis) of rhyolitic quartz-
24 hosted, naturally glassy or crystallised melt inclusions (MIs) and groundmass glass (Mesa Falls
25 Tuff, Yellowstone) are used to reconstruct Li elemental and isotopic evolution in the magma
26 reservoir. Lithium concentrations in quartz-hosted glassy MIs (10–61 ppm) from a fallout deposit
27 overlap with their groundmass glass (32–46 ppm) and their host quartz (8–15 ppm). Crystallised
28 MIs from a later erupted flow pumice clast sample have higher Li concentrations (8–190 ppm)
29 compared to the groundmass glass (32–51 ppm) and their host-quartz (15–24 ppm). Li content in
30 quartz from the early erupted sample is relatively homogenous, whereas it is up to a factor of two
31 higher in the later erupted sample and heterogeneous, with a simultaneous increase in Li versus a
32 decrease in H towards crystal rims. The $\delta^7\text{Li}$ difference (expressed as $\Delta^7\text{Li}_{\text{MI-glass}}$) between MIs
33 (–8.0‰ to +12.3‰) and groundmass glass (+9.0‰ to +20.5‰) of two pyroclastic deposits reaches
34 up to 29‰. Glassy MIs are internally heterogeneous in $\delta^7\text{Li}$ and Li abundance. The cores of the
35 glassy MIs record the $\delta^7\text{Li}$ of the least modified melt during entrapment and the data distribution
36 can be modelled by equilibrium fractionation between the melt and vapour phase during early
37 open-system degassing in the magma reservoir. Late degassing during eruption triggers Li–H
38 diffusional exchange between quartz and melt, as the degassing of H₂O and the accompanying
39 pressure change trigger H diffusion out of the host quartz and the MIs, which is charge balanced

40 by Li inward diffusion. This results in the modification of Li contents in quartz and $\delta^7\text{Li}$ values in
41 the rims of the glassy MIs. Crystallised MIs reflect the loss of H_2O from the MIs and the resulting
42 enrichment of Li during the crystallisation. Additionally, the variations of $\delta^7\text{Li}$ in the groundmass
43 glass can be explained through modelling by kinetic fractionation between the melt and vapour
44 during late stage open-system degassing linked with magma ascent.

45

46

47 **Keywords:** Lithium isotopes, melt inclusions, open system degassing, diffusion, quartz,
48 H_2O

49 **Highlights:**

- 50 • Glassy melt inclusions partially re-equilibrated with host-quartz upon degassing
- 51 • Modification of Li concentration in quartz by H–Li exchange
- 52 • Kinetic fractionation between the melt and vapour during late stage open-system
53 degassing
- 54 • Equilibrium fractionation leading to large span in $\delta^7\text{Li}$ composition between
55 different melt inclusions during early open-system degassing in magma reservoir

56

57 **1. Introduction**

58 In the last two decades an increasing number of studies have focused on the behaviour of lithium
59 (Li) in different geochemical reservoirs. This has been driven chiefly by the unique chemical
60 properties of Li, such as its typically rapid rates of diffusion in melts and crystals, its variably
61 volatile behaviour and the large relative mass difference (17%) between ${}^6\text{Li}$ and ${}^7\text{Li}$ (e.g., Richter
62 et al., 2003; Tomascak et al., 2016; Ellis et al., 2018; Beinlich et al., 2020; Neukampf et al., 2021).
63 Challenges associated with the analysis of Li and its isotopes are now largely overcome through
64 advances in modern mass spectrometry techniques (e.g., Chan and Edmond, 1988; Tomascak et
65 al., 1999a; Kasemann et al., 2005). In igneous systems, most studies have focused on Li as a proxy
66 to understand processes of crust–mantle recycling and seawater–oceanic crust interaction (e.g.,
67 Chan et al., 1992; Moriguti and Nakamura, 1998; Elliott et al., 2006; Magna et al., 2006; Tomascak
68 et al., 2008). In contrast, the behaviour of Li in more evolved, silicic magmas at mid to upper
69 crustal levels is poorly understood. Rhyolitic deposits are an important component of continental
70 volcanic systems and play an important role in the element cycles (e.g., Ellis et al., 2013). Despite
71 the fact that continental crust represents an important repository for Li (Teng et al., 2004),
72 including all known economic deposits (e.g., Hofstra et al., 2013; Benson et al., 2017), studies
73 focusing on Li elemental and isotopic compositions of pre-eruptive felsic systems are
74 comparatively infrequent (e.g., Vlastélic et al., 2011; Charlier et al., 2012; Giuffrida et al., 2018;
75 Holycross et al., 2018). Moreover, previous studies largely focused on magmatic systems along
76 arcs (e.g., Gurenko et al., 2005; Bouvier et al., 2008, 2010; Schiavi et al., 2010, 2012) whereas
77 other settings are less understood.

78 Available studies have shown that the Li concentration and isotopic composition of groundmass
79 glass and mineral phases in silicic magmatic systems can be modified by syn- (e.g., Berlo et al.,

2004; Charlier et al., 2012; Neukampf et al., 2019; Neukampf et al., 2021; Viccaro et al., 2021) and post-eruptive processes (e.g., Ellis et al., 2018; Ellis et al., 2021), and thus may not represent the intrinsic pre-eruptive Li systematics, as theoretically considered by Watson (2017). The large relative mass difference between the two Li isotopes governs isotopic fractionation and leads to ${}^7\text{Li}/{}^6\text{Li}$ variations in nature (e.g., Tomascak et al., 2016). Although large $\delta^7\text{Li}$ variations on order of $\sim 80\text{‰}$ exist among distinct reservoirs such as seawater, carbonates, granites and mantle-derived rocks, $\delta^7\text{Li}$ variability in natural igneous rocks is probably not only source-driven. High-temperature diffusive fractionation between co-existing mineral phases (e.g., olivine, clino- and orthopyroxene) and melt at magmatic temperatures (above 800°C) has been recognised as an important process resulting in the Li isotopic disequilibrium in mafic igneous systems (e.g., Jeffcoate et al., 2007, Magna et al., 2008). Moreover, Richter et al. (2009) and Holycross et al. (2018) conducted experiments at magmatic temperatures which demonstrated that ${}^6\text{Li}$ diffuses ~ 3 to 3.5% faster than ${}^7\text{Li}$ in dry and wet rhyolitic melt, respectively. The high and variable diffusivity of Li isotopes can cause large variations of Li concentration along chemical potential gradients and result in up to 40‰ kinetic fractionation of ${}^7\text{Li}/{}^6\text{Li}$ (Richter et al., 2003). The $\delta^7\text{Li}$ variations of this range can be observed within individual mineral phases at all scales, from a few microns (e.g., Jeffcoate et al., 2007; Parkinson et al., 2007; Lynn et al., 2018; Cisneros de León and Schmitt, 2019; Steinmann et al., 2020) up to several tens of meters (e.g., Lundstrom et al., 2005; Marschall et al., 2007; John et al., 2012; Beinlich et al., 2020). To provide further complexity to kinetic Li isotope behaviour, a recent study by Neukampf et al. (2021) on a flow pumice sample from the Mesa Falls Tuff (MFT; Fig. 1), Yellowstone, USA, showed that diffusive (kinetic) fractionation can lead to Li isotopic differences of $>10\text{‰}$ within single, otherwise chemically unzoned, plagioclase crystals.

103 In this context, retrieving the primary, pre-eruptive Li isotopic signature of magmas is particularly
104 challenging. Melt inclusions (MIs) in phenocrysts are promising targets for this purpose, because
105 they are considered to preserve the pre-eruptive melt composition upon entrapment (e.g., Roedder,
106 1979). However, MIs can be modified prior to eruption (e.g., Nielsen et al., 1998; Frezzotti, 2001;
107 Rose-Koga et al., 2021). This can lead to compositional changes due to diffusive exchange
108 between inclusions and host minerals and/or between host minerals and a surrounding melt (e.g.,
109 Qin et al., 1992; Danyushevsky et al., 2000). Diffusion between a host mineral and melt inclusion
110 is deemed negligible once the sample has reached the fragmentation level in the conduit (e.g.,
111 Humphreys et al., 2008; Myers et al., 2016). Prior to eruption at rhyolitic temperatures (~800°C),
112 changes in external conditions (particularly the pressure and, associatively, H₂O fugacity) result
113 in chemical potential gradients that induce H diffusion out of MIs, leading to a loss of up to 80%
114 of their original H₂O concentration within days (Severs et al., 2007; Myers et al., 2016; Myers et
115 al., 2018; Myers et al., 2019). Because Li⁺ has a similar charge, size and diffusivity to H⁺, its
116 composition in MIs can be modified in a similar way. Zajacz et al. (2009) experimentally
117 determined that H₂O and Li contents in MIs can be modified at P–T conditions hypothesised for
118 upper crustal silicic magma reservoirs. So far, this has not been investigated for natural rhyolitic
119 samples even though Li could be used to determine decompression rates in a way similar to H₂O
120 (e.g., Myers et al., 2016).

121 Quartz phenocrysts from a basal pumice from the MFT contains MIs that experienced only minor
122 modification of their original volatile contents (Tollan et al., 2019), compared to MIs from other
123 Yellowstone eruptions such as the Huckleberry Ridge Tuff (see below) (Myers et al., 2016). The
124 MIs from the MFT are therefore ideal to investigate the behaviour of Li during pre- to syn-eruptive
125 processes in silicic systems. The H₂O and CO₂ concentrations of MIs from the MFT are consistent

126 with the entrapment pressures of ~75–100 MPa (Tollan et al., 2019), indicating a very shallow
127 upper crustal magma storage region before the final ascent. In this study, we report Li
128 concentrations and isotopic compositions of quartz-hosted MIs and associated groundmass glass,
129 complemented by Li concentrations of the host quartz from the MFT samples, previously
130 characterised for H₂O and/or Li elemental/isotope systematics in quartz, quartz-hosted MIs,
131 plagioclase, sanidine, fayalite, clinopyroxene, orthopyroxene, and groundmass glass (Tollan et al.,
132 2019; Neukampf et al., 2019; Neukampf et al., 2021). This is the first data set from a rhyolitic
133 eruptive unit which includes combined $\delta^7\text{Li}$ values, Li concentrations and H₂O concentrations of
134 quartz-hosted MIs. The new data collected in this study are used to test the extent to which
135 diffusion can modify the Li elemental and isotopic composition of MIs, and discuss the
136 implications of Li mobility in terms of degassing processes.

137 **2. Geological setting and samples**

138 The Yellowstone caldera system is located at the northern end of the Snake River Plain
139 hotspot track. It had three caldera-forming eruptions, the oldest and most voluminous Huckleberry
140 Ridge Tuff (HRT; ~2500 km³, 2.08 Ma; Christiansen, 2001; Rivera et al., 2014; Singer et al.,
141 2014), the Mesa Falls Tuff (MFT; 280 km³, 1.30 Ma; Christiansen, 2001; Rivera et al., 2016), and
142 the Lava Creek Tuff (LCT; ~1000 km³, 0.63 Ma; Christiansen, 2001; Matthews et al., 2015). The
143 HRT and LCT erupted in multiple pulses, whilst the MFT erupted in a single pulse (Christiansen,
144 2001) and formed the Henry's Fork Caldera (Fig. 1). Its eruption was a voluminous explosive
145 event with rapidly quenched fallout and pumice deposits at its base that were covered with a
146 welded ignimbrite sheet (Rivera et al., 2016). This deposit is a high-silica rhyolite containing
147 quartz, plagioclase, sanidine, fayalite, clinopyroxene, orthopyroxene, and accessory phases and

148 shows no significant chemical differences throughout the unit (Christiansen, 2001; Neukampf et
149 al., 2019).

150

151 ----INSERT FIGURE 1 Location Map----

152

153 Samples used in this study come from one sampling location (Fig. 1) and were collected
154 from a thick ash and pumice pyroclastic density current deposited at the base of MFT. The basal
155 pumice sample consists of cm-sized pumice and loose grains originating from highly vesicular
156 MFT ash and pumice deposit at the base of MFT representing the onset of the eruption. This sample
157 was previously analysed by Tollan et al. (2019) to determine H₂O and CO₂ concentrations of the
158 glassy quartz-hosted MIs. We further characterised the sample in detail for major and trace element
159 contents, and $\delta^7\text{Li}$ values. The flow pumice sample was collected from a stratigraphically different
160 horizon that represents a later stage of the eruption. This latter sample is a large piece of a highly
161 vesicular pumice clast sampled from an ash-flow sheet, deposited approximately two meters above
162 the ash and pumice deposit. This flow pumice sample has been previously studied in detail by
163 Neukampf et al. (2019) and Neukampf et al. (2021), who determined the major and trace element
164 contents and $\delta^7\text{Li}$ values of all mineral phases present in the flow pumice sample. Considering the
165 chemical and mineralogical homogeneity of the MFT and its interpretation as a single eruptive
166 unit (Christiansen, 2001), both samples likely probe the same magma reservoir. These two samples
167 were chosen to investigate the evolution of the melt and potential changes in the chemistry of the
168 melt as a consequence of degassing during an explosive eruption so that the onset of the eruption
169 can be compared with a later stage of the eruption. The choice of sampling from the non-welded

170 part of the MFT deposit was made to avoid overwhelming effects of post-eruptive processes that
171 may further modify Li and H₂O concentrations (Lloyd et al., 2013; Ellis et al., 2018).

172

173 **3. Materials and methods**

174 **3.1. Melt inclusion description**

175 Quartz crystals from both samples from MFT are subhedral and range from 1 to 5 mm in diameter.

176 The MIs occur as either naturally glassy or partly to fully crystallised. The glassy MIs types (Fig.

177 2 A–C), previously described by Tollan et al. (2019), range from transparent brown to colourless

178 or bubble-bearing, with either spherical or negative crystal shapes, and a diameter between 10 and

179 450 µm. The crystallised MIs show a thin film (a few µm) of small quartz needles (approx. 5 to

180 15 µm) along the inclusion rims, and feldspar and quartz crystallised towards the inclusion interior

181 (Fig. 2 D–F). Quartz grains from the basal pumice sample contain mostly glassy MIs with a

182 subordinate proportion of crystallised MIs. Quartz grains from the flow pumice sample contain

183 completely crystallised or opaque (partly crystallised) MIs, with only a minor population of glassy

184 MIs. Forty-three glassy and 15 crystallised quartz-hosted MIs were selected for further

185 geochemical investigation. We emphasise that the crystallised MIs were not re-homogenised as

186 laboratory-controlled reheating of the MIs can lead to modifications of their volatile budget (e.g.,

187 Nielsen et al., 1998; Zajacz et al., 2009; Gaetani et al., 2012).

188

189 ----INSERT FIGURE 2 Representative transmitted light images of double-polished quartz

190 crystals and their melt inclusion populations. ----

191

192 **3.2. Fourier transform infrared (FTIR) spectroscopy**

193 Quartz crystals with MIs were hand-picked under a binocular microscope from crushed
194 samples and mounted in 1-inch epoxy mounts. The quartz mounts were then double polished to a
195 thickness of ~350 to ~450 μm . The H_2O and CO_2 contents of 12 crystallised quartz-hosted MIs
196 were determined following the technique described in Tollan et al. (2019) where the H_2O and CO_2
197 contents of glassy quartz-hosted MIs can be found. In short, this method involves measuring MIs
198 that remain fully enclosed in the crystal and then correcting for the absorbance contribution from
199 the crystal host. First, transmitted light images of quartz crystals and their MIs were taken at the
200 University of Bern using an optical microscope, recording their position, appearance and geometry
201 (Fig. 2). The thickness of each quartz crystal was then measured using a Mitutoyo ID-S IP42 digital
202 depth gauge (3 μm precision). FTIR spectra were obtained at the University of Bern with a Bruker
203 Hyperion 3000 microscope attached to a Bruker Tensor II spectrometer. The measurements were
204 conducted in a dry air-purged measurement chamber, using non-polarised light, 15 \times magnification
205 using a Cassegrain objective and a HgCdTe detector. The light source and beamsplitter were
206 composed of SiC and KBr, respectively. Background and sample measurements were made with
207 64 scans and a resolution of 8 cm^{-1} . Three measurements with a varying spot size were made on
208 each melt inclusion, followed by the measurement immediately adjacent through the host quartz
209 (without any inclusions in the beam pathway). The host quartz exhibited limited to absent
210 interference absorption at the wavelengths of total H_2O and CO_2 in rhyolitic glass. Therefore, this
211 latter step is solely used to obtain the Si–O overtone bands of the quartz for the calculation of the
212 size of the melt inclusion, critical in the calculation of volatile abundance. The concentrations of
213 H_2O and CO_2 were calculated using the (non-integrated) absorbance of the bands centred at 5200
214 cm^{-1} , 4500 cm^{-1} and 2345 cm^{-1} , with a direct baseline correction in each case. Conversion from
215 the absorption to concentration was achieved using methods of Zhang et al. (1997) and Behrens et

216 al. (2004) for H₂O and CO₂, respectively. Three individual measurements on each melt inclusion
217 were monitored for the consistency and any significant deviation in concentration resulted in
218 discarding of the data. As noted by Tollan et al. (2019), any melt inclusion whose size was less
219 than 15% of the thickness of the host quartz typically did not yield reliable values of concentration
220 and was avoided from the H₂O and CO₂ calculations.

221 The H₂O content of the quartz crystals from the flow pumice sample was calculated based
222 on the average core and rim measurements from 17 crystals. For each crystal, the OH bands in the
223 wavenumber region 3600–3000 cm⁻¹ were integrated, normalised to 1 cm and converted to H₂O
224 using the integrated absorption coefficient of Thomas et al. (2009). Since the measurements
225 consisted of non-polarised light and non-oriented crystals, the total absorbance was multiplied by
226 a factor of 3 (Jackson et al. 2018). In addition to the melt inclusion measurements, high-resolution
227 FTIR imaging and profiles of several quartz crystals were conducted to investigate the distribution
228 of H throughout the quartz lattice. These FTIR images and profiles were obtained using a focal
229 plane array (FPA) detector coupled to the FTIR setup described above. The measurements were
230 conducted at a resolution of 8 cm⁻¹ using a total of 128 scans. Pixels were binned three times,
231 resulting in a spatial resolution of approximately 22×22 μm.

232

233 **3.3. Secondary Ionization Mass Spectrometry (SIMS) measurements**

234 Following the FTIR measurements, selected single MIs were exposed, polished and the
235 quartz crystals hosting the MIs were excavated from the epoxy mount and mounted into a 1-inch
236 indium mount for measurements of Li isotope compositions. Additionally, groundmass glass was
237 hand-picked under a binocular microscope from crushed samples and mounted in 1-inch epoxy
238 mounts for the measurements. Prior to the measurements backscattered electron (BSE) and

239 cathodoluminescence (CL) images of the MIs, host quartz and groundmass glass were acquired
240 using a JEOL JSM-6390 LA scanning electron microscope (SEM), housed at the Institute of
241 Geochemistry and Petrology, ETH Zürich. The BSE images of groundmass glass and quartz
242 crystals were acquired with 15 kV acceleration voltage and CL images used 20 kV acceleration
243 voltage. Additionally, the quartz grains from the basal pumice sample with glassy MIs studied by
244 Tollan et al. (2019) for the contents of H₂O and CO₂, were included in the following geochemical
245 analysis.

246 Lithium isotope compositions were determined using a CAMECA ims1280-HR secondary
247 ionization mass spectrometer, housed at the SwissSIMS laboratory (University of Lausanne).
248 Samples were mounted in indium together with a reference material (either NIST SRM 612 or
249 BHVO-2G; Jochum et al., 2011). Prior to the analysis samples were coated with a 35 nm thick
250 gold layer. Sample surfaces were bombarded using an O⁻ beam generated by a Hyperion RF
251 source. The analyses were performed in three separate SIMS sessions; the intensity of the primary
252 O⁻ ion beam was ~2 nA in the first session whereas it was ~5 nA in the second and third session.
253 The ⁶Li⁺ and ⁷Li⁺ ion beams were collected in multi-collection mode using two opposing electron
254 multipliers. The mass resolution was set to 2400, using an entrance slit width of 121 μm and multi-
255 collector slits 1. The field aperture was closed to 1360, in order to avoid possible surface
256 contamination. Prior to each analysis, the surface was pre-sputtered for 200 s using a 15-μm raster
257 to remove the gold layer and any potential Li surface contamination. Automatic centring of the
258 field aperture and contrast aperture deflectors were conducted at the end of the pre-sputtering.
259 Measurements were performed using a 5-μm rastered primary beam. Each Li measurement
260 consisted of 70 cycles, with each cycle 12 s long. One to four measurements per inclusion were

261 performed depending on the inclusion size. In this study 43 glassy MIs in 21 quartz crystals and
262 15 crystallised MIs in 14 quartz crystals were analysed.

263 Calibration was made using StH, ATHO and TI MPI-DING reference glass materials
264 (Jochum et al., 2006). NIST SRM 612 and BHVO-2G were used to monitor the instrumental
265 stability during the analytical sessions. Analyses of MIs were bracketed every four to five analyses
266 by either NIST SRM 612 or BHVO-2G.

267 The measured data were corrected for an instrumental drift for each analytical session
268 (typically 2–3‰ over an eight-hour period) using the Li isotopic composition of NIST SRM 612
269 or BHVO-2G measured throughout each session (Supplementary data – Table S13). The long-
270 term reproducibility of the reference materials (2SD) after a drift correction is $\pm 1.6\%$ for NIST
271 SRM 612 and $\pm 2.3\%$ for BHVO-2G. The internal error for each measurement is dependent on the
272 Li content; it varied between ± 0.3 and $\pm 1.5\%$ (2SE) during the course of this study. Lithium
273 isotopic compositions are reported relative to the L-SVEC reference material (Flesch et al., 1973)
274 and calculated as $\delta^7\text{Li} (\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000$.

275

276 **3.4. Electron microprobe analyses (EPMA) measurements**

277 Major and trace element contents of the MIs were measured following the SIMS analyses
278 to minimise potential modifications of their Li isotopic composition. The major element
279 compositions (Si, Na, Mg, Al, Ca, K, Ti, Fe, P, Cl, Cr, Mn, F) of the exposed MIs and the
280 groundmass glass were determined with a Jeol JXA-8230 electron microprobe, housed at the
281 Institute of Geochemistry and Petrology, ETH Zürich. All analyses were measured with 15 kV
282 acceleration voltage. The beam diameter was either 2 μm with a beam current of 2 nA, 5 μm with
283 a beam current of 4 nA, or 20 μm with a beam current of 10 nA, depending on the size of the MIs.

284 The beam diameter for the groundmass glass was 5 μm with a beam current of 4 nA. For Na, Si,
285 Al, Mg, Ca and P, a counting time of 30 s on peak was used whereas a counting time of 20 s on
286 peak was employed for K, Ti, Cl, Fe, Mn and Cr. Two to five individual measurements per melt
287 inclusion were obtained. To ensure the reliability of the technique, the rhyolitic reference material
288 VG-568 from the Smithsonian Institution (Supplementary TableS 9) was used as a secondary
289 standard with the reproducibility better than 5% (SD).

290

291 **3.5. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)**

292 Trace element concentrations in host quartz and quartz-hosted MIs were determined using
293 the ETH prototype of the GeoLas laser ablation system equipped with a Compex Pro 102F
294 (Coherent) Excimer 193 nm (ArF) laser source and coupled to a Nexion2000 (Perkin Elmer) fast-
295 scanning quadrupole ICP-MS, housed at the Institute of Geochemistry and Petrology, ETH Zürich.
296 The on-sample energy density of the laser beam was set to $20 \text{ J}\cdot\text{cm}^{-2}$ and the repetition rate was
297 10 Hz. Quartz crystals were measured with a spot size of $40 \mu\text{m}$; for the glassy MIs the spot size
298 was 10 to $40 \mu\text{m}$, and one to seven measurements per inclusion were performed depending on the
299 inclusion size. For crystallised MIs, one to nine measurements with a spot size of $40 \mu\text{m}$ was
300 performed to account for the inherent compositional heterogeneity in the MI. The ablation was
301 performed in an in-house cell designed for 1-inch mounts, using ca. $1.0 \text{ l}\cdot\text{min}^{-1}$ He as carrier gas
302 flow and ca. $1.0 \text{ l}\cdot\text{min}^{-1}$ Ar make-up gas admixed downstream of the ablation chamber. All
303 concentrations were quantified against the NIST SRM 610 glass wafer as the primary reference
304 material (Jochum et al., 2011). The raw data were reduced using the Matlab-based SILLs program
305 (Guillong et al., 2008) by using Si as internal standard for quartz (stoichiometric value), glassy
306 MIs (as determined by EMPA) and crystallised MIs (average Si of glassy MIs). A natural quartz

307 crystal characterised by Audéat et al. (2015) was employed as a secondary reference material for
308 quartz analyses (see Supplementary Table S8). The average 2 SD reproducibility of concentrations
309 in the secondary quartz reference material for all analytical sessions was used to determine the
310 uncertainties on the concentrations of unknown samples (5% relative for Li). For other element
311 contents, the reproducibility on glassy MIs concentrations were on average 5% relative (2 SD) and
312 for crystallised MIs 20% relative (2 SD).

313 In this study, we observed an offset of 20–50% in Li concentrations for LA-ICP-MS versus
314 SIMS in the analysed MIs. In the following, we only use the Li concentrations determined by LA-
315 ICP-MS for the interpretations, because the Li concentrations estimated by SIMS are less accurate.
316 This is due to using ^7Li and primary intensity as a proxy for the yield and the relationship between
317 yield and Li concentration can be non-linear depending on the matrix of the unknown sample
318 (Hoover et al., 2021). When only the Li concentrations estimated by SIMS was available for our
319 MIs, we have corrected the data using this above given offset.

320

321 **4. Results**

322 **4.1. Major and trace element composition in melt inclusions**

323 The MFT glassy MIs from the basal pumice sample have a chemical composition of a high-silica
324 rhyolite (> 75 wt.% SiO_2 , recalculated to a volatile-free basis) with Al_2O_3 , K_2O and Na_2O ranging
325 11.5–12.6 wt.%, 5.2–5.9 wt.% and 1.6–3.5 wt.%, respectively (Supplementary Table S1).
326 Furthermore, they are similar in their trace element composition compared to data for groundmass
327 glass from the same sample (Neukampf et al., 2019) and similar MFT samples (Pearce et al., 1996;
328 Perkins and Nash, 2002). However, the glassy MIs show a variability in trace element
329 concentrations between different crystals (Table 1). Notably, Li shows larger relative variations

330 than most other elements in the population of glassy MIs, with Li concentrations from 10 to 61
331 ppm (basal pumice sample, average: 34 ppm; n = 104; n includes multiple analyses on single
332 inclusions). Furthermore, seven out of the forty-three measured inclusions show a zonation in Li
333 concentration (Fig. 3B) with up to 4 ppm higher Li concentration in their rims. The other MIs for
334 which core-to-rim data was acquired were homogenous in their Li concentrations. There is no
335 correlation between Li concentrations and the MI size, MI type or position in the quartz crystal.

336

337 ----INSERT FIGURE 3 and TABLE 1 Lithium concentration in groundmass glass and melt
338 inclusions. ----

339

340 Crystallised MIs from the flow pumice sample show a wider range in their trace element
341 compositions compared to the glassy MIs from the basal pumice sample. They have higher Li
342 concentrations (8–190 ppm; average 74 ppm; n = 44), overlapping those of the previously studied
343 crystallised MIs from the same flow pumice sample from MFT (70–397 ppm, average: 244 ppm;
344 n = 29; Neukampf et al., 2019). The differences between the Li concentrations measured in this
345 study compared to the results of Neukampf et al. (2019) may be related to differences in the
346 analytical method (exposed MIs, this study, versus unexposed MI bulk measurement, Neukampf
347 et al., 2019). In contrast, the concentrations of other trace elements match well those of the glassy
348 MIs (Table 1). Similar to the glassy MIs, there is no relationship between MI size and Li
349 concentration. Only a few MIs show an increase of Li concentration towards their rims.

350

351 **4.2. Trace element composition of quartz**

352 The CL images of the quartz crystals from the two investigated samples show growth zones
353 with no coherent patterns of internal zoning across the quartz populations (Fig. 4A–B;
354 Supplementary Table S1 and S3). In quartz crystals from the flow pumice sample (Fig. 4A, 4C,
355 4E), P concentrations (8.8–19.2 ppm) are relatively homogeneous whereas Al (93–147 ppm) and
356 Ti (60–151 ppm) show more substantial variations. Lithium concentrations in the flow pumice
357 sample increase from the cores (15–24 ppm; n = 106) towards the rims (22–24 ppm; n = 7). All
358 measured element patterns are in good agreement with the previously published values (Neukampf
359 et al., 2019).

360 Quartz crystals from the basal pumice sample are compositionally similar to quartz from
361 the flow pumice sample in most trace elements (e.g., Al = 88–117 ppm, Ti = 63–126 ppm) (Fig.
362 4.B, 4D, 4F), except Li. They indeed show more homogenous Li concentration from rims to cores
363 compared to the flow pumice sample, but, at the same time, shifted to lower Li concentrations (8–
364 15 ppm, average: 10 ppm; n = 184) by a factor of two. Thirteen trace element profiles were
365 measured within five crystals from the basal pumice sample. Of the measured profiles six show an
366 increase in Li concentration (10–30% relative) towards the MIs (Supplementary Table S3).
367 Additionally, four trace element profiles indicate an increase of up to 3 ppm in Li abundance
368 towards the crystal rims (Supplementary Table S3).

369

370 ----INSERT FIGURE 4 Host quartz ----

371

372 **4.3. Major and trace element composition in groundmass glass**

373 The major element chemistry of the groundmass glass from the flow pumice sample
374 resembles that of the composition of a high-silica rhyolite (> 75 wt.% SiO₂, recalculated to a

375 volatile-free basis) with Al₂O₃, Na₂O and K₂O ranging 11.7–12.9 wt.%, 2.1–3.3 wt.% and 5.3–6.3
376 wt.% (n= 94), respectively. All measured element contents are in good agreement with the
377 previously published values from the same sample (Neukampf et al., 2019).

378 The groundmass glass from the basal pumice sample has a similar high-silica rhyolitic
379 major element composition with Al₂O₃ ranging from 12.2 to 12.5 wt.%, Na₂O from 3.0 to 3.3 wt.%
380 and K₂O from 5.5 to 5.7 wt.% (n= 23). The trace element abundances of groundmass glass in the
381 two investigated samples are overlapping (Table 1). Lithium concentrations in groundmass glass
382 from both samples are also overlapping, ranging from 32 to 51 ppm in the flow pumice sample
383 (average 41 ppm; n = 66) and from 32 to 46 ppm in the basal pumice sample (average 41; n = 88;
384 Fig. 3A).

385

386 **4.4. H₂O and CO₂ in melt inclusions and host quartz**

387 The calculated H₂O and CO₂ concentrations in crystallised MIs range from 2.2–3.8 wt.%
388 and 120–470 ppm, respectively (Supplementary Table S1). The content of dissolved H₂O and CO₂
389 in the glassy MIs was investigated by Tollan et al. (2019). These authors determined that H₂O and
390 CO₂ contents in the colourless MIs range from 2.8–2.9 wt.% and from 332–416 ppm (n=2),
391 respectively, they ranged from 2.8–3.2 wt.% and 191–319 ppm (n=3) in brown MIs, respectively,
392 and the bubble-bearing MI had 3.7 wt.% H₂O and 68 ppm CO₂. In the present study, no additional
393 H₂O and CO₂ in glassy MIs was determined.

394 The FTIR spectra of quartz from the flow pumice sample are typical for magmatic quartz,
395 with the absorbance dominated by bands centred at 3373 cm⁻¹ and 3294 cm⁻¹. These features are
396 interpreted to reflect H charge balancing Al (Stalder and Konzett, 2012). Single point
397 measurements reveal that, for the flow pumice sample, crystal cores contain an average of 5 ± 1

398 ppm H₂O and rims have an average of 3 ± 1 ppm H₂O. Almost all of this difference in absorption
399 is accounted for by the decreased intensity of the band at 3373 cm^{-1} (factor of 3 reduction in
400 integrated absorbance at the rim), while the 3294 cm^{-1} band only shows a factor of 1.3 reduction
401 at the rim, despite being typically considered as part of the same crystallographic defect (Stalder
402 and Konzett, 2012). The high-resolution FPA FTIR images and profiles of host quartz from the
403 flow pumice sample (Fig. 5A–B) confirm a strong, systematically decreasing H₂O towards the
404 crystal rims (i.e., over the outermost 450–600 μm of the crystal). Notably, this does not appear to
405 follow a simple error function shape, indicating that the decrease may not be related to simple H
406 diffusion. An additional feature revealed by the FPA images is a 10 to 50 μm -thick halo of higher
407 OH-related absorbance around the crystallised MIs (Fig. 5A; Supplementary Table S4 and S6)
408 compared to the absorbance in the core.

409

410 ----INSERT FIGURE 5 - H₂O concentration in host quartz and glassy melt inclusions ----

411

412 **4.5. Lithium isotope compositions**

413 The four investigated brown glassy MIs hosted in two quartz grains have $\delta^7\text{Li}$ values from
414 $-7.1 \pm 1.2\text{‰}$ to $+2.8 \pm 1.3\text{‰}$ ($n = 7$, n including multiple analyses per inclusion). The single
415 analysed bubble-bearing glassy MI falls in the same range ($-7.1 \pm 1.5\text{‰}$). The 38 studied
416 colourless glassy MIs hosted in 19 quartz crystals display a larger, yet overlapping spread of Li
417 isotopic compositions ($\delta^7\text{Li}$ from $-8.0 \pm 1.6\text{‰}$ to $+12.3 \pm 1.2\text{‰}$; $n = 58$, n including multiple
418 analyses per inclusion). For 13 out of 43 glassy MIs, at least two measurements were obtained and
419 show that the Li isotopic composition may vary within a single inclusion. In eight inclusions, $\delta^7\text{Li}$
420 values of the rims are between 2.1‰ and 7.2‰ lower compared to the cores. Two inclusions show

421 no significant internal $\delta^7\text{Li}$ variations within the analytical uncertainties. Three inclusions have
422 isotopically heavier rims compared to their cores, with the $\delta^7\text{Li}$ difference from 2.1‰ to 3.5‰.
423 Despite these differences, the range of $\delta^7\text{Li}$ values obtained in all rims, on one hand, and all cores
424 on the other hand, overlap. The $\delta^7\text{Li}$ values for rims range from $-7.4 \pm 1.3\text{‰}$ to $+12.3 \pm 1.2\text{‰}$
425 whereas the $\delta^7\text{Li}$ values for all cores range from $-8.0 \pm 1.6\text{‰}$ to $+12.0 \pm 1.3\text{‰}$. No $\delta^7\text{Li}$ data for
426 crystallised MIs are presented as there is no SIMS reference material that can reliably be applied
427 to a multi-phase matrix.

428 The $\delta^7\text{Li}$ of the groundmass glass from the flow pumice sample varies from $+9.4 \pm 0.7\text{‰}$
429 to $+20.5 \pm 0.7\text{‰}$ (average: 15.6‰; $n = 42$). In the basal pumice sample, the Li isotopic variation
430 of the groundmass glass is smaller ($+9.0 \pm 1.6\text{‰}$ to $+14.9 \pm 1.4\text{‰}$; average: 12.0‰; $n = 14$), but
431 overlapping that of the flow pumice sample. Therefore, the total difference in Li isotopic
432 composition between glassy MIs and groundmass glass ($\Delta^7\text{Li}_{\text{MI-glass}}$) is up to -29‰ for the flow
433 pumice sample and up to -23‰ for the basal pumice sample (Fig. 6). No correlation was found
434 between Li isotopic composition and textural position of the analytical spot within the groundmass
435 glass (i.e., relative distance to, and size of, the nearest vesicles or crystals).

436 The average $\delta^7\text{Li}$ values of the groundmass glass that were measured using SIMS ($+14.9\text{‰}$
437 to $+15.6\text{‰}$; this study) are in apparent disagreement with the published $\delta^7\text{Li}$ values measured in
438 bulk samples using MC-ICPMS ($+6.5\text{‰}$ to $+7.5\text{‰}$; Neukampf et al. 2019). This discrepancy might
439 result from the bulk glass fraction dissolved for MC-ICPMS analysis containing minor amounts
440 of other mineral phases (e.g., feldspar). This could lower the average $\delta^7\text{Li}$ value, as these phases
441 are all isotopically lighter than the groundmass glass (Neukampf et al., 2019). This also explains
442 the differences in the Li concentrations of the glass between MC-ICPMS and LA-ICPMS analyses
443 noted by Neukampf et al. (2019).

444

445 ----INSERT FIGURE 6 Li isotopic composition ----

446

447 **5. Discussion**

448 A key finding of this work is the extreme range of $\delta^7\text{Li}$ between individual quartz-hosted glassy
449 MIs (about 20‰), and between MIs and groundmass glass ($\Delta^7\text{Li}_{\text{MI-glass}}$ from -23 to -29‰), in the
450 two investigated pumice samples from MFT. Similar Li isotopic heterogeneity has been found in
451 previous studies, which focused on arc magmas. Gurenko et al. (2005) investigated the Li
452 systematics of MIs (Li = 20–60 ppm, $\delta^7\text{Li}$ from +4‰ to +15‰) in plagioclase and orthopyroxene
453 from a dacitic pumice (Plat Pays Volcanic Complex, Dominica, Lesser Antilles). Bouvier et al.
454 (2010) reported on an even larger range in Li elemental and isotopic composition (Li = 1.1–12
455 ppm, $\delta^7\text{Li}$ from -24‰ to +8.2‰) for mafic olivine-hosted MIs from basaltic lavas (Grenada
456 Island, Lesser Antilles). Likewise, Kobayashi et al. (2004) analysed olivine-hosted MIs from
457 Hawaiian lavas and revealed $\delta^7\text{Li}$ variations from -10.2‰ to +8.4‰. In contrast, Schiavi et al.
458 (2012) described a significantly reduced range in Li isotopic composition ($\delta^7\text{Li}$ from -1.7‰ to
459 +2.3‰) for mafic olivine-hosted MIs from a basaltic lava (San Bartolo, Stromboli, Italy).

460 These studies mostly suggested the observed $\delta^7\text{Li}$ range by variable contribution of distinct
461 sources, namely slab-derived fluids, sediments, and pristine or metasomatised mantle (Kobayashi
462 et al., 2004; Schiavi et al., 2012). Previous isotopic work on the Yellowstone eruptive rocks also
463 highlighted multiple source components in the mantle and lower to upper crust (Doe et al., 1982;
464 Hildreth et al., 1991; Jean et al., 2014; Wotzlaw et al., 2015), as well as the potential influence of
465 the Farallon slab (Swallow et al., 2018). The largest isotopic contrasts have been observed between
466 the different igneous units of the Snake River Province, while the Yellowstone rhyolites have

467 relatively homogeneous isotopic compositions (Hildreth et al., 1991; Jean et al., 2014). Moreover,
468 the MFT pumices show very homogeneous major and trace element compositions of groundmass
469 glass and crystals (Neukampf et al., 2019). These observations imply that even if multiple sources
470 are involved, thorough mixing during magma genesis may lead to a Li-homogeneous parental
471 magma for the MFT. In this context, preserving source-related $\delta^7\text{Li}$ variations in excess of 20‰ is
472 unlikely, especially considering how rapidly Li diffuses in silicic melts (Richter et al., 2009;
473 Holycross et al., 2018).

474 In the following, we discuss five alternative explanations to source heterogeneity in light of the
475 other observations, notably the variations of Li and H₂O contents in host quartz and MIs.

476

477 **5.1 Evidence for degassing-driven Li and H₂O diffusion in MFT quartz**

478 Quartz from the two studied samples shows significant intra- and inter-crystal variations
479 in Li contents (Fig. 7), whereas the concentrations of other elements are more homogeneous (Figs.
480 4 and 7). In particular, the Al concentrations of the quartz crystals from basal pumice (Al = 88–
481 117 ppm) and flow pumice (Al = 93–147 ppm) from the MFT are mostly overlapping. The main
482 mechanism of Li incorporation in quartz is assessed through coupled substitution with Al
483 ($\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^+$; Denen, 1966; Perny et al., 1992). However, as previously shown (e.g., Audétat
484 and Günther, 1999; Peterková and Dolejš, 2019; Jollands et al. 2020) this substitution may involve
485 other monovalent cations that can compete with Li in this reaction. One of these other cations is
486 possibly H⁺, as supported by the different H₂O concentrations of quartz from the two samples: the
487 Li-poorer quartz from the basal pumice shows indeed higher H₂O contents (17 ± 6 ppm; Tollan et
488 al., 2019) than the Li-richer quartz from the flow pumice (5 ± 1 ppm as obtained here). This
489 potentially competing role of H is supported by comparing Li and Al concentrations with the

490 isoatomic Li:Al 1:1 line (Fig. 7A). All MFT quartz plot in the Al-excess region, indicating that
491 solely Li is insufficient to charge balance Al. Including H reduces the charge deficit substantially
492 (Fig. 7B): the atomic sum of monovalent cations between the two samples is much more similar
493 once H is included (<10% difference) compared to considering Li only (80–90% difference). This
494 indicates that H and Li are indeed both charge-compensating Al and explains the differences in Li
495 concentration between quartz from both samples.

496 However, even considering H in addition to Li does not entirely charge balance Al (Fig.
497 7B). This has previously been observed by Jollands et al. (2020), who proposed four possible
498 explanations: (1) inaccurate H₂O analyses using FTIR due to a wrong H absorption coefficient
499 and/or a baseline subtraction routine; (2) inaccurate Li and/or Al concentrations obtained using
500 LA-ICPMS; (3) the presence of other charge-compensators that are not considered (e.g.,
501 phosphorus); and (4) incomplete charge balancing of Al. Assuming that our analyses are accurate
502 (which for LA-ICPMS is ensured by the results of the quartz secondary reference material;
503 Supplementary Table S8), the Al excess thus most likely results from other charge-compensating
504 elements that are not considered here, pointing to more complex substitution reactions in quartz
505 (e.g., Peterková and Dolejš, 2019). Nevertheless, this effect has a minor influence compared to the
506 charge balancing effect from H, which clearly has an important effect on the capacity of quartz to
507 incorporate Li (and vice versa).

508

509 ----INSERT FIGURE 7- Li concentration in host quartz ----

510

511 The reason for different relative concentrations of Li and H between the two samples can
512 be further investigated through the study of intra-grains variations. Tollan et al. (2019) imaged the

513 distribution of H₂O in quartz grains from the basal pumice sample. They described a steeper
514 inwards increase in H in the outermost rim (in the first 200 µm) of the crystals. In comparison, two
515 quartz crystals from the flow pumice sample analysed during the present study show a larger
516 increase in the H₂O content from 450 to 600 µm inwards until reaching a plateau in the core. The
517 intra-grain variations in H₂O contents are not systematically correlated to variations in Al
518 concentrations, which happen at different length scales and/or in opposite directions as expected
519 from substitution laws (Fig. 4C–D). However, they are well correlated to Li concentration profiles.
520 Indeed, quartz from the basal pumice sample, only shows a small inwards decrease in Li content
521 within the outermost rim (Fig. 4F), whereas Li in quartz from the flow pumice sample shows more
522 pronounced zoning, extending over a larger distance from the rim (Fig. 4E).

523 One possible hypothesis to explain the observed Li and H₂O concentration profiles involves
524 variations in melt composition during quartz crystallisation, as a result of differentiation or magma
525 mixing. A rim-ward increase of Li concentrations could reflect Li enrichment in the melt due to
526 the incompatible character of Li in mineral phases present in MFT (Neukampf et al., 2019).
527 However, this would also be recorded in co-crystallised plagioclase and sanidine (cf. Neukampf
528 et al., 2019; Ellis et al., 2022), whilst their Li systematics rather hint at a rim-ward decrease of Li
529 content (Neukampf et al., 2021). As discussed earlier, this would almost certainly require an
530 unreasonable extent of melt differentiation. Moreover, the crystallisation of the anhydrous mineral
531 assemblage of the MFT would lead to an increase of H₂O in the melt during differentiation, with
532 a rim-ward increase of H₂O content in quartz, exactly opposite to the observed decrease. Magma
533 mixing with a compositionally different melt resulting from magma recharge or cumulate melting
534 can also be excluded. The groundmass glass, MIs and mineral phases from both samples show
535 very similar and homogeneous major–trace element compositions.

536 Alternatively, changes in the physical–chemical parameters of a volatile phase coexisting with
537 quartz and melt may explain the Li–H systematics in MFT quartz. Charlier et al. (2012) reported
538 on a rim-to-core decrease of Li contents in feldspar and quartz from the rhyolitic Oruanui super
539 eruption (Taupo, New Zealand) and explained this feature by Li re-partitioning from fluid into the
540 melt due to the extraction of chloride into a co-existing vapour phase. Fluxing of an Li-rich volatile
541 phase described for Mount St. Helens (Berlo et al., 2004; Kent et al., 2007; Rowe et al., 2008), or
542 Li-rich gas accumulation as described for the Stromboli volcano (Viccaro et al., 2021), can also
543 lead to an increase of Li concentration in the rims of co-existing minerals. However, all of these
544 processes can be excluded, because they would again lead to Li-enriched rims not only in quartz
545 but also in the co-crystallised feldspar, in contrast to the observations (Neukampf et al., 2021).

546 Neukampf et al. (2021) proposed that the Li concentration profiles in MFT plagioclase
547 result from diffusive re-equilibration with Li-depleted melt as a result of pre-eruptive degassing.
548 This process would also impoverish the melt in H₂O and by inference, trigger diffusive H⁺ loss
549 from crystal rims. In plagioclase, Li and H loss can be readily compensated by limited Na and K
550 diffusion or, to a lesser extent, by the oxidation of multivalent cations such as Fe (Tollan et al.,
551 2018). All of these elements occur in quartz in much lower concentrations than Li and H.
552 Therefore, when H⁺ is lost from the host quartz, the most plausible charge balancing substitution
553 is the incorporation of Li⁺, especially given that both elements have very similar diffusivities
554 (Jollands et al., 2020). Diffusive loss of H⁺ due to melt degassing not only explains the
555 complementary Li–H concentration profiles in MFT quartz, but also the fact that these profiles
556 have different shapes between the two samples. The early erupted basal pumice sample would
557 have indeed experienced a lower degree of degassing relative to the late erupted flow pumice

558 sample, resulting in H^+ - Li^+ exchange affecting only the outermost rim ($<200\ \mu m$) of quartz
559 crystals vs. a thicker rim zone ($450\text{--}600\ \mu m$), respectively.

560 It must be noted, however, that post-eruptive cooling of the ignimbrite deposits could also account
561 for H_2O loss from quartz crystals (Biró et al., 2017) and related Li enrichment via substitution
562 (Ellis et al., 2018). However, no microlite growth in the groundmass glass was observed in any of
563 the two samples which would be indicative of a protracted cooling. Biró et al. (2017) investigated
564 the stratigraphic variations of hydroxyl defects in quartz crystals in thick ignimbrite deposits from
565 N Hungary and showed that the corresponding H_2O concentration decreases from ~ 12 ppm at the
566 base to ~ 3 ppm at $6.5\text{--}10$ m above the base, with a more abrupt decrease in the case of welded
567 deposits. However, both of our samples were collected ca. 2 m apart from the non-welded part of
568 the deposit, respectively from the fallout below the base for the basal pumice; and the basal part
569 of the MFT for the flow pumice. Therefore, our samples correlate to the lowermost parts of the
570 deposits investigated by Biró et al. (2017), which experienced the lowest amount of post-
571 depositional H diffusion. In addition, Biró et al. (2017) modelled post-depositional dehydration
572 across the deposit via diffusional loss over a range of temperatures ($300\text{--}700^\circ C$) and found that
573 contrasting cooling rates and different crystal sizes do not account for the observed H_2O
574 concentration profiles. They concluded that other factors like magma chamber zoning and the pre-
575 depositional thermal history also influence the distribution of H_2O concentrations in quartz crystals
576 from ignimbrite deposits, as argued here.

577 Collectively, we interpret the Li and H_2O zoning of quartz from the two samples, and the
578 different shapes of the resulting concentration profiles between them, as a result of different
579 timescales and/or extents of pre-eruptive degassing.

580

581 **5.2. Effects of degassing on Li and H₂O in melt inclusions**

582 Having established that degassing controls the Li and H₂O systematics of the host quartz
583 from the two samples, we now address how MIs may reveal more details on the pre- and syn-
584 eruptive volatile behaviour of the MFT magma system.

585 Strikingly, the two samples show different MI types: mostly glassy in the basal pumice vs.
586 mostly partly crystallised in the flow pumice. In addition, crystallised MIs show higher average Li
587 contents relative to the glassy ones (Fig. 3A). We postulate that in the flow pumice sample,
588 diffusive H₂O loss from the MI would have potentially triggered the crystallisation of the MIs. In
589 mafic melts and minerals (e.g., olivine-hosted MIs), this process is generally associated with Fe
590 oxidation (Danyushevsky et al., 2002; Gaetani et al., 2012), but due to the low Fe contents of both
591 quartz and high-silica rhyolitic MIs in the case of the MFT, this is likely compensated by inward
592 Li diffusion to ensure charge balance. Moreover, outward diffusion of H₂O from the MI would
593 explain the “halo” of increased H₂O concentration surrounding crystallised MIs in the host quartz
594 (Fig. 5A).

595 This explanation is supported by the experimental results of Zajacz et al. (2009), who determined
596 that MIs can suffer post-entrapment modification of trace element contents due to the in- and
597 outward migration of molecular H₂ and H₂O resulting from a concentration gradient at
598 temperatures and pressures typical for upper crustal felsic magma storage. This gradient can result
599 in a rapid diffusion of H⁺, Li⁺ and Na⁺ parallel to the *c*-axis in quartz that needs to be charge
600 balanced (e.g., Audétat and Günther, 1999, Rottier et al., 2017). Other experiments showed that
601 H-bearing species (OH⁻, H₂O) can diffuse through the host quartz as a result of the pressure
602 gradient that the MIs experience (Qin et al., 1992; Severs et al., 2007), i.e., during the ascent of
603 the magma. In the case of Yellowstone, this process has been proposed as an explanation for the

604 spread in H₂O concentrations of MIs from the Huckleberry Ridge Tuff (HRT; 0.5–4.5 wt.%; Fig.
605 5C and D) (Myers et al., 2016), suggesting in turn that some MIs potentially lost up to ~80% of
606 their original H₂O concentration (Myers et al., 2019).

607 In the case of the MFT samples, loss of H₂O from crystallised MI is apparently in contradiction
608 with their similar H₂O and CO₂ concentrations (2.2–3.8 wt.% and 120–470 ppm respectively, as
609 estimated here) to those of the glassy MIs (2.8–3.7 wt.% and 68–416 ppm, respectively; Tollan et
610 al., 2019). However, loss of up to a few thousand ppm H₂O from MIs, which is well within the
611 error of the FTIR measurements (about ± 0.4 wt.%), would be sufficient to explain the “halo” of
612 increased H₂O concentration surrounding crystallised MIs in the host quartz. Therefore, compared
613 to the quartz-hosted MIs from the HRT, those of the MFT have lost a smaller fraction of their H₂O
614 budget, i.e., a maximum of 30% (~1 wt.%, corresponding to the observed concentration range).

615 This presumably results from the less complex magmatic history of the MFT compared to that of
616 the HRT. Considering the experimental results (e.g., Qin et al., 1992; Severs et al., 2007), we
617 advocate for equilibration of the host quartz with its surrounding melt during ascent, which then
618 also affects the MIs. As proposed to explain the Li–H₂O concentration profiles in the host quartz,
619 pre-eruptive degassing would deplete the surrounding melt in H₂O, thereby producing the chemical
620 gradient required for the diffusive loss of H species from MIs. In accord with the differences in
621 quartz concentration profiles, longer and/or more pronounced degassing in the case of the later
622 erupted flow pumice explains that this sample contains mostly crystallised MIs, whereas the early
623 erupted basal pumice contains mostly glassy MIs. This process can further explain the zonation in
624 Li concentration and $\delta^7\text{Li}$ in the glassy MIs in the basal pumice sample. Lithium concentrations
625 and $\delta^7\text{Li}$ values generally are independent of MI size and the location of the melt inclusion in the
626 crystal. When the glassy MIs experienced diffusive loss of H-bearing species, charge balancing by

627 Li likely also happened through diffusion insofar both species have similar diffusivities (Jollands
628 et al., 2020). As ${}^6\text{Li}$ diffuses $\sim 3.5\%$ faster compared to ${}^7\text{Li}$ (Parkinson et al., 2007; Richter et al.,
629 2009; Holycross et al., 2018) the rims of the MIs become enriched in ${}^6\text{Li}$ (i.e., isotopically lighter)
630 compared to the cores. From this perspective, cores of glassy MIs potentially represent the least
631 modified sections in terms of Li concentrations and $\delta^7\text{Li}$ values of the melt.

632

633 **5.3. Kinetic fractionation of lithium isotopes in melt during ascent (open-system** 634 **degassing)**

635 The groundmass glass from both samples shows a broad negative correlation between $\delta^7\text{Li}$ and Li
636 contents (Fig. 6). During degassing of felsic melts, Li partitions into the immediately formed
637 vapour phase (Webster et al., 1989), so that the melt would become progressively depleted in Li
638 (e.g., Neukampf et al., 2021). If degassing is an open-system disequilibrium process, then this
639 should be accompanied by kinetic Li isotopic fractionation between melt and vapour phase because
640 ${}^6\text{Li}$ moves $\sim 3.5\%$ faster than ${}^7\text{Li}$ (Parkinson et al., 2007; Richter et al., 2009; Holycross et al.,
641 2018). During degassing, the melt will thus acquire a heavier Li isotopic signature. This process
642 would adequately explain the observed co-variation between $\delta^7\text{Li}$ and Li content in groundmass
643 glass, with Li-richer (ca. 45 ppm) and the isotopically lightest ($\delta^7\text{Li}$ of ca. $+10\text{‰}$) glass
644 representing the closest composition to an undegassed melt.

645 In addition, the Li isotopic composition of the groundmass glass between the two samples varies
646 on average by 3.4‰ , with glass from the basal pumice sample ($\delta^7\text{Li} = +9\text{‰}$ to $+14.9\text{‰}$) being
647 isotopically lighter and on average more homogeneous than that of the flow pumice sample ($\delta^7\text{Li}$
648 $= +9.4\text{‰}$ to $+20.5\text{‰}$) (Fig. 6). This may be explained by the variability in decompression and
649 cooling rates during the eruption, and thus by variability in the efficiency of degassing. We propose

650 that rapid decompression and cooling minimises Li loss by degassing and associated Li isotope
651 fractionation between the formed vapour phase and melt (Ionov and Seitz, 2008), explaining the
652 elemental and isotopic composition of groundmass glass from the basal pumice sample. In
653 contrast, protracted degassing entails more Li moving into the vapour phase, resulting in an
654 isotopically progressively heavier melt with time as recorded by groundmass glass in the flow
655 pumice sample. This would be consistent with the relative timing of eruption between the two
656 samples and the interpretation of the quartz Li–H₂O data discussed above.

657 Alternatively, the Li isotopic variation within the groundmass glass within samples could be
658 explained by different bubble sizes during degassing. Large-sized bubbles would lead to more ⁶Li
659 diffusing from the melt into the vapour phase, resulting in heavier $\delta^7\text{Li}$ in the melt, whereas smaller
660 bubbles would lead to a lesser extent of depletion of ⁶Li in the melt. This has only been
661 theoretically addressed by Watson (2017) and still needs to be assessed experimentally. In any
662 case, we did not observe any correlation between Li isotopic composition of the groundmass glass
663 and the size of the nearest vesicle that would be indicative of this process.

664 Collectively, we propose that Li isotopic variations in the groundmass glass of both samples
665 require disequilibrium (kinetic) open-system degassing occurring over a short period of time and
666 thereby controlled by diffusive kinetic fractionation between ⁶Li and ⁷Li. Geospeedometry based
667 on Li elemental and isotopic diffusion profiles in plagioclase indicates that the timescales of such
668 degassing were on the order of tens of minutes (Neukampf et al., 2021), similar to experimental
669 results of Coogan (2011). In turn, preserving the signature of such an open-system, fast
670 fractionation process implies that it is not related to processes taking place in the magma reservoir
671 and, instead, it must have taken place during ascent in the conduit immediately prior to eruption.

672 It is possible to model the kinetic Li isotopic fractionation during open-system degassing
673 in the conduit using the following equation:

674

$$675 \quad (\delta^7\text{Li})_{melt} = [(\delta^7\text{Li})_0 + [(\alpha_{vapour-melt} - 1) \times 1000] \times (\ln(F))],$$

676

677 where $(\delta^7\text{Li})_{melt}$ represents Li isotope composition of the degassed melt, $(\delta^7\text{Li})_0$ is the $\delta^7\text{Li}$
678 value of the initial magma, $\alpha_{vapour-melt}$ is the bulk Li isotopic fractionation factor between vapour
679 and melt, and F represents the fraction of Li remaining in the melt. The Li concentration in the
680 degassed magma can be calculated following Schiavi et al. (2010):

681

$$682 \quad Li_{melt} = Li_0(F^{D-1}),$$

683

684 where Li_0 is the initial Li concentration, Li_{melt} is the Li concentration after degassing, and
685 D is the bulk distribution coefficient of Li between melt and vapour. To calculate $(\delta^7\text{Li})_{melt}$ and
686 Li_{melt} the parameter $\alpha_{vapour-melt}$ and D need to be determined. In the case of kinetic fractionation,
687 the parameter $\alpha_{vapour-melt}$ can be calculated as $\alpha_{vapour-melt} = \left(m_{6\text{Li}}/m_{7\text{Li}}\right)^\beta$ with $\beta = 0.228$ as the
688 empirical constant of the kinetic fractionation of Li isotopes obtained from experiments close to
689 the composition of the MFT melt (Holycross et al., 2018). This results in a value of 0.965 for
690 $\alpha_{vapour-melt}$, consistent with ^6Li preferentially fractionating in the vapour phase. This is in good
691 agreement with $\alpha_{vapour-melt}$ established by Beck et al (2004) for Li_2O $\alpha_{vapour-melt} = 0.966$ and Li_2S
692 $\alpha_{vapour-melt} = 0.978$. Koga et al. (2008) showed, based on experiments using mass balance, that
693 $D_{vapour-melt}$ should be between 1 and 30. Here, all values $D > 3$ fail to explain our data and are,
694 therefore, not displayed. To estimate the best fitting $D_{vapour-melt}$ a range from 1 to 3 with different

695 $\alpha_{\text{vapour-melt}}$ (0.965 and 0.978) were tested. We used $(\delta^7\text{Li})_0 = 9.4\text{‰}$ and $[\text{Li}] = 46.3$ ppm as a
696 plausible starting composition, reflecting a melt present in the MFT reservoir, and not yet affected
697 by conduit degassing (Fig. 8A). Both $\alpha_{\text{vapour-melt}}$ values (0.965 and 0.978) can explain the kinetic
698 fractionation observed within the samples (Fig. 8A). Best fits are obtained for a $D_{\text{vapour-melt}} = 1.5$
699 when considering an $\alpha_{\text{vapour-melt}} = 0.965$, and for a $D_{\text{vapour-melt}} = 2$ when considering an $\alpha_{\text{vapour-melt}} =$
700 0.978. Only 30% ($F = 0.7$) degassing is required to fractionate Li to obtain the high $\delta^7\text{Li}$ values
701 that were measured in the groundmass glass. Therefore, the model of open-system degassing with
702 disequilibrium kinetic fractionation of the Li isotopes appears to successfully explain the data
703 distribution. As both samples have a wide range in $\delta^7\text{Li}$ values and Li concentrations it is possible
704 that Li is degassing as Li_2O and Li_2S ; LiCl is not considered because no experimental data is yet
705 available for $\alpha_{\text{vapour-melt}}$ and $D_{\text{vapour-melt}}$ although we posit that LiCl may be an important species
706 during degassing.

707

708 ----INSERT FIGURE 8 Li isotopic composition model----

709

710 **5.4. Fractionation of lithium isotopes in the magma reservoir as recorded in melt** 711 **inclusions**

712 The kinetic fractionation that takes place during degassing in the conduit explains the
713 variations in Li and H_2O concentrations in the host quartz between the two samples; the zoning in
714 Li in MIs; and the differences in Li contents and isotopic compositions between groundmass glass
715 of the two samples. However, it cannot explain the large variation in $\delta^7\text{Li}$ and Li contents in MIs
716 between different grains of the same sample. Different MIs measured within one grain show
717 limited variations in $\delta^7\text{Li}$ and Li contents compared to the overall variation of the entire population,

718 indicating that they sample a compositionally uniform melt and possibly were trapped within a
719 short period of time. As there is no relationship between $\delta^7\text{Li}$, the size of MIs and their position
720 relative to the rim of the quartz crystals (Fig. 6), post-entrapment diffusive loss of Li has to be
721 excluded. Furthermore, contrary to what is observed for the groundmass glass, there is a broad
722 positive correlation between Li and $\delta^7\text{Li}$ (Fig. 6). Therefore, we must consider that the groundmass
723 glass and the MIs represent melts that were sampled from different parts and/or evolutionary stages
724 of the magmatic system. Likewise, a distinct process occurring within the magma reservoir, i.e.,
725 taking place together with quartz crystallisation and related entrapment of MIs, must be
726 responsible for the $\delta^7\text{Li}$ and Li content variations of MIs.

727 The pre-eruptive evolution of the magma reservoir parental to the MFT involved several
728 successive magma injections as well as the co-existence of crystal-poor vs. crystal-rich domains,
729 as demonstrated by the relationships between high-precision zircon U–Pb ages and trace element
730 concentrations (Rivera et al., 2016). Like zircons, the MFT quartz phenocrysts containing the MIs
731 likely derived from these different regions of the magmatic reservoir. In particular, we postulate
732 that the mushy domains, such as marginal granophyric rinds, were disaggregated during the
733 eruption and sampled by crystal-poor rhyolitic magma representing a deeper and hotter part of the
734 reservoir, as proposed for phenocryst-rich pumice clasts in other silicic volcanic units such as the
735 Kos Plateau Tuff (Allen, 2001; Fiedrich et al., 2020). Therefore, it is likely that the MFT quartz
736 phenocrysts grew from a melt, now represented by MIs, that underwent different extents of Li loss
737 through passive degassing within the magma reservoir; whereas the groundmass glass represents
738 “primitive” Li-rich melt that degassed only in the conduit during the eruption. This hypothesis is
739 in good agreement with the fact that the trends defined by the groundmass glass and the MIs

740 converge at their high-Li end (Fig. 6, Fig. 8), which is likely close to the original composition of
741 the less degassed melt prior to the MFT eruption.

742 In the following we discuss possible explanations for the observed variations in $\delta^7\text{Li}$ and
743 Li between the different MIs of MFT.

744 In our models we assume that Li partitions solely into the formed vapour phase. Lithium
745 partitioning into a non-vapour (i.e., supercritical) fluid phase, though possible (e.g., Iveson et al.,
746 2019), is not considered because the partitioning parameters related to such a process are not yet
747 constrained. For the variations between the MIs, we infer that the magma prior to eruption is
748 degassing in the upper part of the magma reservoir over a longer period of time (days to years),
749 and we therefore consider equilibrium, either open- or closed-system degassing. This means that
750 fractionation between ^7Li and ^6Li between melt and vapour phase is controlled by equilibrium
751 partitioning rather than diffusive fractionation.

752 In the case of closed-system degassing the vapour-hosted Li can still exchange with the
753 melt. This can be calculated using the following equations:

754

$$755 \quad (\delta^7\text{Li})_{\text{magma}} = \delta^7\text{Li}_0 - [(1-F) \times 10^3 \times \ln \alpha_{\text{vapour-melt}}],$$

756

757 and

758

$$759 \quad Li_{\text{magma}} = Li_0 / [(1 - D_{\text{vapour-melt}}) \times F + D_{\text{vapour-melt}}],$$

760

761 where $(\delta^7\text{Li})_{\text{magma}}$ represents Li isotope composition of the degassed magma, and $(\delta^7\text{Li})_0$ is
762 the $\delta^7\text{Li}$ value of the initial magma. The parameter $\alpha_{\text{vapour-melt}}$ has not yet been determined

763 experimentally in the case of Rayleigh distillation for this melt composition and the relevant
 764 temperature and pressure conditions. Previous studies have used $\alpha_{\text{vapour-melt}} = 1.0100$ or 1.0099
 765 (Vlastélic et al., 2011) and $\alpha_{\text{vapour-melt}} = 1.005$ to 1.015 (Schiavi et al., 2010). As they are the best
 766 estimates available so far, we have explored this range of $\alpha_{\text{vapour-melt}}$ in the model. Concerning
 767 $D_{\text{vapour-melt}}$, we used the range determined in section 5.3 ($D_{\text{vapour-melt}} = 1-3$) as the best proxy for
 768 the considered rhyolite compositions. For $(\delta^7\text{Li})_0$ and Li_0 we assumed that the highest $\delta^7\text{Li}$ values
 769 with the highest Li concentration measured in the cores of the MIs represent the least modified
 770 pre-eruptive composition of the melt. Accordingly, two starting points for the model were chosen:
 771 (1) the highest Li concentration in a MI ($[\delta^7\text{Li}]_0 = 9.9\text{‰}$; $\text{Li}_0 = 59.9$ ppm), and (2) the heaviest Li
 772 isotopic composition ($[\delta^7\text{Li}]_0 = 12\text{‰}$; $\text{Li}_0 = 51.4$ ppm). Figure 8D shows the results for $\alpha_{\text{vapour-melt}}$
 773 $= 1.005$, 1.010 and 1.015 and with $D_{\text{vapour-melt}} = 2$. When assuming up to 100% ($F = 0$) degassing
 774 and using $\alpha_{\text{vapour-melt}}$ equal to 1.005 , $\delta^7\text{Li}$ values are fractionated by 5‰, for $\alpha_{\text{vapour-melt}}$ equal to
 775 1.010 , $\delta^7\text{Li}$ is fractionated by up to 9‰, and for $\alpha_{\text{vapour-melt}}$ equal to 1.015 up to 14‰ change is
 776 modelled for $^7\text{Li}/^6\text{Li}$. All modelled fractionation curves fail to explain the isotope data as they
 777 cannot explain the lightest $\delta^7\text{Li}$ values ($< -2.5\text{‰}$) and only lead to a small change in Li
 778 concentration. Therefore, closed-system degassing is excluded as a possible explanation for the
 779 MI data.

780 Another possibility is open-system degassing taking place in the magma reservoir (Fig. 9),
 781 assuming equilibrium fractionation. Therefore, the simple Rayleigh distillation law can be applied:

782

$$783 \quad (\delta^7\text{Li})_{\text{magma}} = [(\delta^7\text{Li})_0 + 1000]F^{\alpha-1} - 1000,$$

784

785 and residual Li concentration in the magma can be calculated following Schiavi et al.
786 (2010):

787

$$788 \quad Li_{residual} = Li_0(F^{(D-1)}),$$

789

790 where Li_0 is the initial Li concentration, and $Li_{residual}$ is the Li concentration after degassing.

791 We applied the same values for δ^7Li_0 , F , D and $\alpha_{vapour-melt}$ as for the closed-system degassing model

792 above. In figure 8B only one starting point is used to estimate the best fitting $D_{vapour-melt}$ ($D_{vapour-$

793 $melt = 1.5$ to 3) whereby $D_{vapour-melt} = 2$ yields the best fit to the data set; other D values resulted in

794 a strong misfit. Figure 8C highlights that the best fit is achieved when using $\alpha_{vapour-melt} = 1.010$

795 (with $D_{vapour-melt} = 2$). Our results show that up to 85% ($F = 0.15$) of Li degassing is required to

796 account for the lightest δ^7Li . Thus, our model for open-system degassing in the magma reservoir

797 successfully explains the data distribution observed for δ^7Li between different MIs.

798 Although open-system Rayleigh fractionation explains most of the data, there is residual

799 scatter that cannot be accounted for by this model. It is therefore possible that other processes are

800 superimposed on those resulting from degassing, e.g., fractional crystallisation that simultaneously

801 takes place during MI entrapment. An alternative explanation is a multistage ascent within a

802 magma reservoir, whereby the isotopically lightest melt inclusions were trapped first, and during

803 continuous loss of 6Li via degassing, the melt and trapped MIs became isotopically heavier.

804 However, this is not supported by the Li concentration of the MIs as the concomitant increase

805 would require more than 50% of crystal fractionation (unsupported by other geochemical

806 evidence) to reach the Li concentration of the groundmass glass and the highest Li concentrations

807 in the MIs.

808

809 **6. Conclusion**

810 The main conclusions reached in this study are:

- 811 (1) Quartz-hosted MIs in pyroclastic deposits from the MFT are heterogeneous in $\delta^7\text{Li}$
812 composition (from -8.0‰ to $+12.3\text{‰}$) and Li concentration (10–61 ppm), as a result
813 of variable extents of equilibrium open-system degassing of rhyolitic melt at depth in
814 the magma reservoir, over long timescales (days to years) prior to eruption (Fig. 9A).
- 815 (2) During melt ascent within tens of minutes (Neukampf et al., 2021) prior to eruption,
816 the Li and H_2O composition of host quartz is modified by diffusive exchange between
817 degassing melt and quartz, with Li charge balancing the outward diffusion of the
818 different H species from the quartz (Fig. 9B-D).
- 819 (3) Some rims of the MIs are modified post entrapment by diffusional exchange between
820 host quartz and MIs during the ascent. Therefore, only the cores of some MIs preserve
821 the least modified pre-eruptive Li concentration and $\delta^7\text{Li}$ values of the MFT magma
822 reservoir.
- 823 (4) Degassing in the conduit occurred as an open-system disequilibrium process, which led
824 to kinetic fractionation of Li isotopes between melt and vapour phase with ^6Li
825 preferentially fractionating into the vapour phase (Fig. 9B–D), resulting in higher $\delta^7\text{Li}$
826 values and lower Li concentrations of groundmass glass.
- 827 (5) Different timescales and/or extents of degassing resulted in more pronounced chemical
828 and isotopic exchange between quartz, MIs, melt and vapour (Fig. 9C–D), as recorded
829 by the later erupted flow pumice sample. Further kinetic fractionation between melt
830 and vapour resulted in the negative correlation between $\delta^7\text{Li}$ and Li contents of

831 groundmass glass. The diffusive Li–H₂O exchange in quartz affected larger distances
832 from the crystal rims; simultaneously, H₂O is lost from the MIs leading to their
833 crystallisation and Li enrichment due to charge balance.

834

835 ----INSERT FIGURE 9 Comic----

836

837 This study shows that particular attention should be exercised with regard to the selection
838 of MIs for geochemical analyses, especially when Li is considered. Our data shows that degassing
839 processes alone, both at depth prior to eruption and happening rapidly in the conduit during
840 eruption, can result in a substantial variability of $\delta^7\text{Li}$ (up to nearly 30‰) in melts and resulting
841 MIs/groundmass glass. Therefore, Li isotopic compositions of MIs should be used with great
842 caution when applied directly as a proxy to track changes in the melt. To discuss source
843 characteristics, it is therefore important to conduct a comprehensive study of MIs and apply Li
844 isotopes in tandem with other isotope systems that are unaffected by degassing at depth and in the
845 conduit. However, we posit that Li can provide important information regarding pre- and syn-
846 eruptive degassing in silicic volcanic systems. The combination of Li concentration, *in situ* $\delta^7\text{Li}$
847 measurements in quartz-hosted MIs and groundmass glass and diffusion modelling of Li
848 concentration gradients in quartz potentially represents a powerful tool to understand late-stage
849 magmatic processes.

850

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860 Appendix A. Supplementary Material

861 The supplementary data file includes the major- and trace element composition as well as
862 the $\delta^7\text{Li}$ composition of groundmass glass and quartz-hosted melt inclusions from the two samples
863 (basal and flow pumice sample) used in this study. In the supplement file the basal pumice sample
864 is referred to as 11022 and the flow pumice samples as 13005. Additionally, the trace element
865 composition of the quartz crystals that hosted the melt inclusions are given as well as their H_2O
866 concentration and FTIR maps. The secondary standards used during major- and trace element as
867 well as lithium isotope measurements are provided.

868

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Figure Captions

1139
1140 **Figure 1** – Aerial photograph centred on the Yellowstone National Park in NW United States
1141 (general location indicated in the inset) showing the geographic extent of Mesa Falls Tuff (dark
1142 brown). The sampling location ($44^{\circ}7'8.49''\text{N}$, $111^{\circ}26'39.49''\text{W}$; Ellis et al., 2017) is indicated
1143 with a red star. Inferred Henry's Folk caldera (Christiansen, 2001) in light brown and state lines
1144 in green. Modified after Neukampf et al. (2021).

1145 **Figure 2** – Representative images of double-polished quartz crystals and their melt inclusion
1146 populations (A) Transmitted light image of a quartz with glassy melt inclusions (MI1 and MI3
1147 = brown MI; MI2 = colourless MI, basal pumice sample). (B) Back-Scattered Electron (BSE)
1148 image of MI2 with SIMS spots and corresponding $\delta^7\text{Li}$ values (larger spots correspond to the
1149 analysis of $\delta^{11}\text{B}$, whose results are not presented here). The uncertainty on the $\delta^7\text{Li}$
1150 measurements is up to 2%. (C) BSE image of MI1 with gold (Au) coating filling a crack. The
1151 arrows indicate SIMS spots and corresponding $\delta^7\text{Li}$ values. (D) Transmitted light image of a
1152 quartz with crystallised MIs (flow pumice sample). (E) and (F) BSE images of MI1 and MI2
1153 from (D), showing that the crystallised fraction mainly consists of tiny ($<1\ \mu\text{m}$) quartz crystals
1154 and a thin quartz layer formed at the inner rim of the MI.

1155 **Figure 3** – (A) Plot of Sm (considered immobile during degassing) vs. Li concentrations in the
1156 analysed MIs (colourless, brown or with a bubble; MIs in the figures are displayed with the
1157 same symbol) and groundmass glass (gg). Literature data by Neukampf et al. (2019) are plotted
1158 for comparison. Crystallised MIs are enriched in Li and glassy MIs have a lower Li
1159 concentration than corresponding groundmass glass. Pale yellow (basal pumice) and purple
1160 (flow pumice) bands indicate the ranges of Li concentration in the host quartz. (B) Plot of Rb

1161 (proxy for contamination from host quartz, as concentrations would strongly decrease
1162 whenever the laser spot used for measurement includes host-quartz) vs. Li concentrations of
1163 glassy MIs (multiple points per MI), distinguishing measurements occurring in the rim vs. the
1164 core of the MIs. Rim and Core pairs are connected by grey tie lines.

1165 **Figure 4** – CL images of quartz in the flow pumice (**A**) and basal pumice sample (**B**) (MI =
1166 melt inclusion) with measured LA-ICP-MS trace element profiles in light blue (red indicates
1167 failed measurement), and diagrams showing concentrations of several elements (Li, Al, P and
1168 Ti in ppm) along the corresponding profiles (**C** and **D**). Figure 4A and 4B show one example
1169 of representative quartz crystals from each sample. (**E**) Additional Li concentration profile
1170 from a quartz from the flow pumice sample with an increase of Li content towards the rim and
1171 a decrease towards the MI. (**F**) Additional Li concentration profile from a quartz crystal from
1172 the basal pumice sample with an increase of Li content towards the MI. Grey bar shows area
1173 with no meaningful data.

1174 **Figure 5** – (**A**) Focal plane array FTIR image of a quartz crystal from the flow pumice sample
1175 from MFT, colour-coded for IR absorbance. Red line represents an extracted profile shown in
1176 (**B**). Inset shows transmitted light image of the quartz crystal. (**B**) A representative rim-to-rim
1177 IR absorption profile in the crystal shown in (**A**). As the orientation of the crystal is unknown
1178 the H₂O concentration is reported as an overtone. (**C**) CO₂ versus H₂O concentrations of glassy
1179 MIs from the basal pumice sample compared to literature data (Tollan et al. 2019 for Mesa
1180 Falls Tuff and Myers et al. 2016 for Huckleberry Ridge Tuff). Blue lines are volatile saturation
1181 isobars calculated at 800 °C, using VolatileCalc (Newman and Lowenstern 2002). (**D**) Lithium

1182 versus H₂O concentrations in glassy MIs from the basal pumice sample of MFT and literature
1183 data (Myers et al. 2016, Tollan et al. 2019).

1184 **Figure 6** – Plot of Li isotopic composition (as $\delta^7\text{Li}$ relative to L-SVEC reference material)
1185 versus Li concentration of glassy MIs and groundmass glass (gg). Symbols for MIs have an
1186 additional green (core), purple (intermediate zone) or yellow (rim) frame representing the
1187 position of the MI in the quartz crystal based on CL images. Rim and Core pairs are connected
1188 by grey tie lines. Red stars indicate MIs where the Li concentration was not obtained by LA-
1189 ICP-MS but recalculated from Li concentration determined by SIMS.

1190 **Figure 7** – Plot of Li versus Al concentrations in quartz from the MFT samples. The black
1191 thick line represents the isoatomic Li:Al 1:1 line (ideal substitution of $\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^+$),
1192 whereas the two coloured lines consider that Al incorporation is charge balanced by both Li^+
1193 + H^+ , with two different corresponding H₂O concentrations.

1194 **Figure 8** – Plot of Li isotopic composition (as $\delta^7\text{Li}$ relative to L-SVEC reference material)
1195 versus Li concentration showing the results of models of Li elemental and isotopic evolution
1196 during the two inferred degassing stages (stage 1 in the magma reservoir, stages 2/3 in the
1197 conduit immediately before eruption) and the data from MIs and groundmass glass in MFT
1198 samples. Data is displayed in grey when not relevant for the degassing stage considered in the
1199 modelling scenario. Tick marks indicate the fraction of degassed Li (in %) based on the model.
1200 (A) An open-system degassing model driven by kinetic fractionation, considering two different
1201 $\alpha_{\text{vapour-melt}}$ values (0.965 and 0.978) with four different values of $D_{\text{vapour-melt}}$ (1, 1.5, 2, 3). (B)
1202 A model of open-system equilibrium degassing model considering four different $D_{\text{vapour-melt}}$
1203 values. (C) A model of open-system equilibrium degassing scenarios using different $\alpha_{\text{vapour-}}$

1204 *melt* with two different starting points ($\delta^7\text{Li} = 12.0\text{‰}$ and $\text{Li} = 51.4$ ppm; $\delta^7\text{Li} = 9.9\text{‰}$ and $\text{Li} =$
1205 59.9 ppm, respectively). **(D)** A model of closed-system degassing (Rayleigh fractionation)
1206 using three different $\alpha_{\text{vapour-melt}}$ values (1.005, 1.010, 1.015).

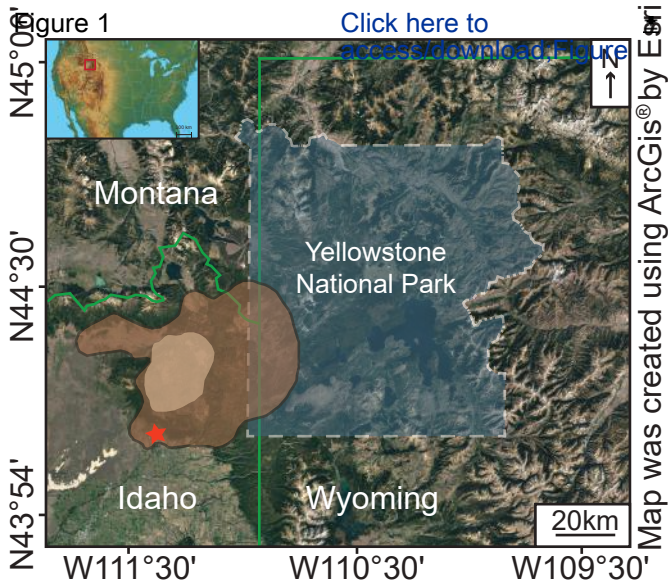
1207 **Figure 9** – Cartoon portraying a simplified model (not to scale) of the processes recorded in
1208 two investigated samples from the Mesa Falls Tuff. **(A)** Stage 1 represents Li isotopic
1209 composition of the melt in the magma reservoir prior to eruption with (1) equilibrium
1210 degassing in the magma reservoir leading to a progressively lighter Li isotopic composition of
1211 the melt. **(B)** Stage 2 shows open-system disequilibrium degassing in the conduit leading to
1212 the modification of Li isotopic composition and Li concentration of MIs, quartz crystals and
1213 groundmass glass in the basal pumice sample (2). **(C)** Stage 3 with prolonged open-system
1214 disequilibrium degassing and the influence on the flow pumice sample (6). **(D)** A detailed
1215 scheme of degassing of volatile phases (e.g., Li and H) with ^6Li moving faster into the volatile
1216 phase (4), ultimately leading to kinetic fractionation and the Li isotopic composition of glass
1217 becoming heavier. Small-scale diffusional exchange of H^+ and Li^+ causes H^+ diffusing out of
1218 the host quartz into the melt and Li^+ diffusing inwards (5); and Li^+ diffusing into an MI to
1219 charge balance H^+ loss (6). Below a theoretical profile of Li and H concentration of the host
1220 quartz in (D). **(E)** Continuing degassing influenced the Li isotopic composition of the
1221 groundmass glass (7) resulted in prolonged $\text{H}^+ \leftrightarrow \text{Li}^+$ diffusional exchange between quartz and
1222 melt (8): $\text{H}^+ \leftrightarrow \text{Li}^+$ and (9) shows. H^+/OH^- diffusing out of MI lead to crystallisation of the MI
1223 and Li^+ diffusing therein for charge balance (9). Below a theoretical profile of Li and H
1224 concentration in the host quartz shown in (E).

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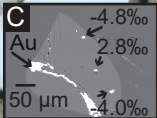
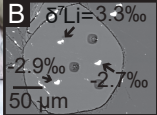
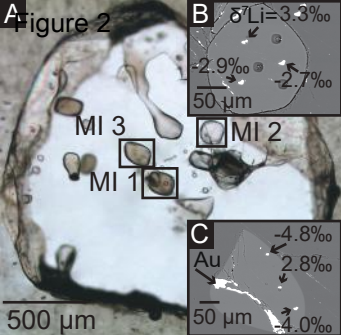
1226 **Table 1.** Trace element concentrations in glassy and crystallised MIs and groundmass glass
 1227 from both samples.

	glassy MI (basal pumice)		crystallised MI (flow pumice)		groundmass glass (basal pumice)		groundmass glass (flow pumice)	
	concentration (ppm)	avg. (ppm)	concentration (ppm)	avg. (ppm)	concentration (ppm)	avg. (ppm)	concentration (ppm)	avg. (ppm)
Zr	85–185	133	73–204	143	128–175	156	123–176	157
Ba	4–139	58	1–151	36	43–302	138	85–355	132
Rb	157–322	236	115–370	232	223–293	243	216–265	237
Sm	6–14	9	4–13	9	9–15	11	8–13	11
Li	10–61	34	9–190	76	32–46	41	32–51	41

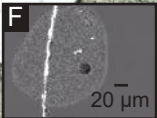
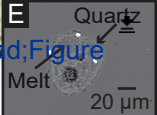
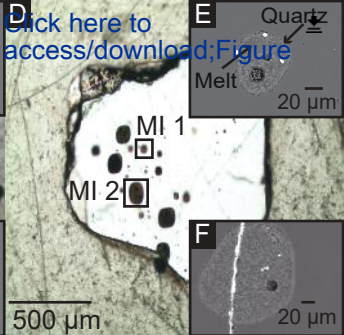
1228

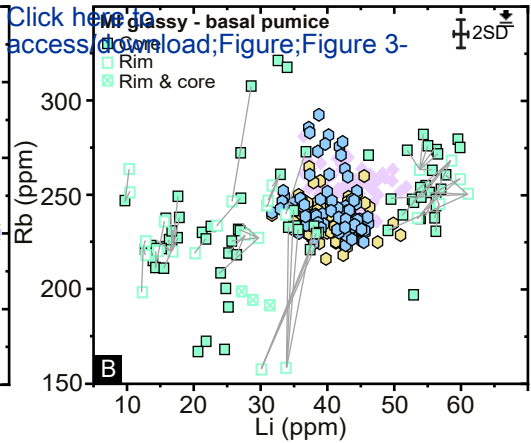
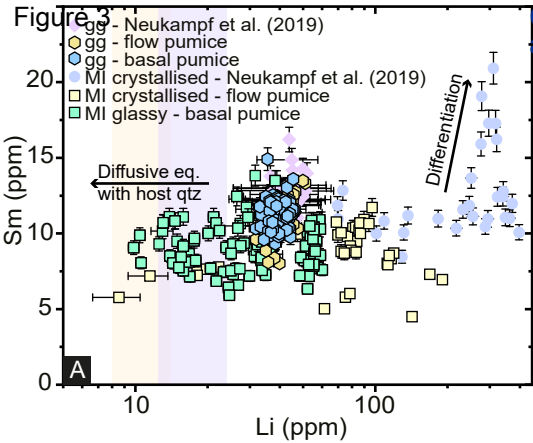


A Figure 2



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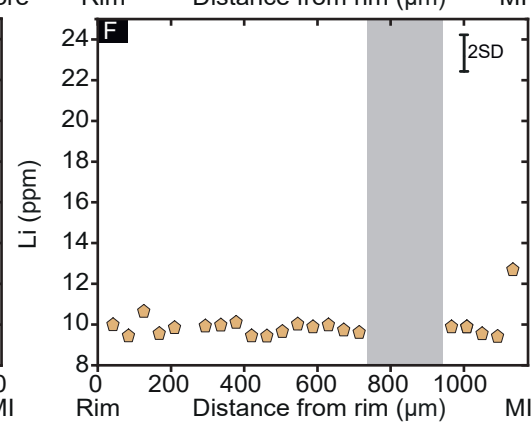
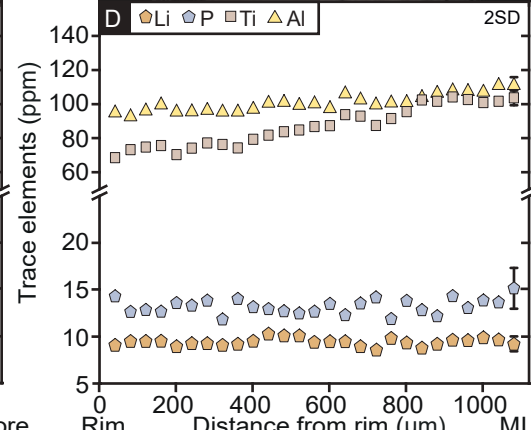
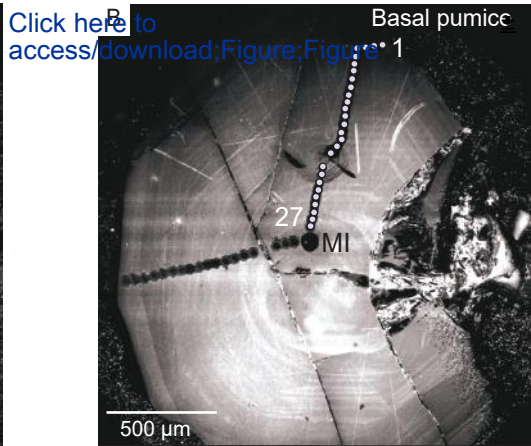
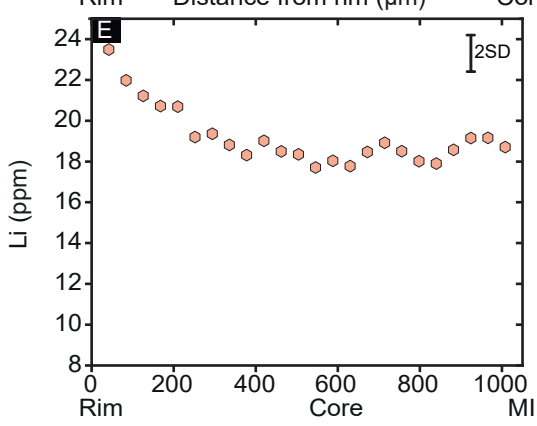
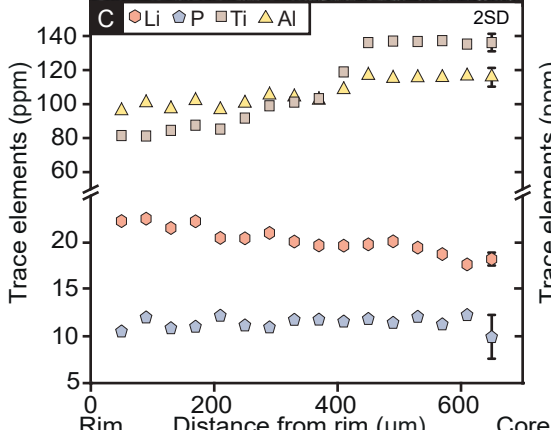
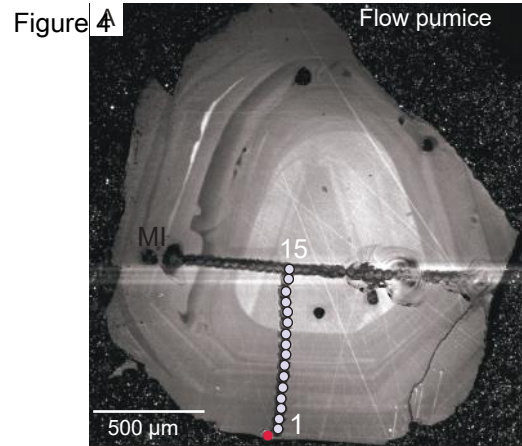
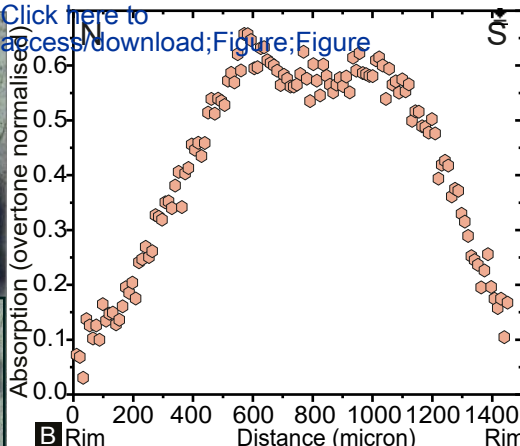
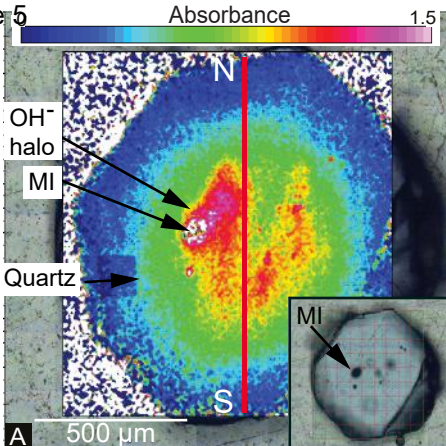


Figure 5



Literature data for MFT: ◆ Literature data for HRT: ○ This study: ■

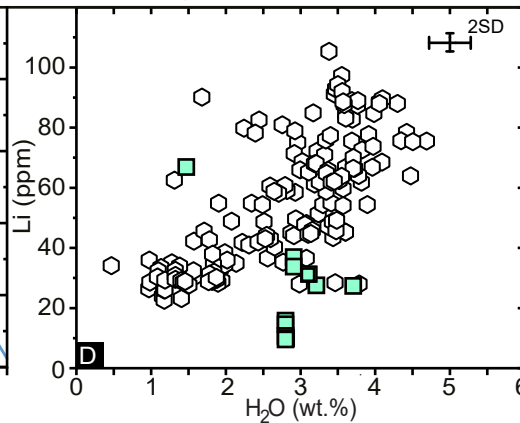
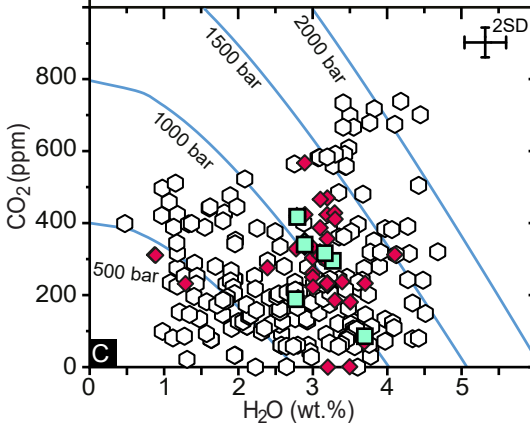


Figure 6

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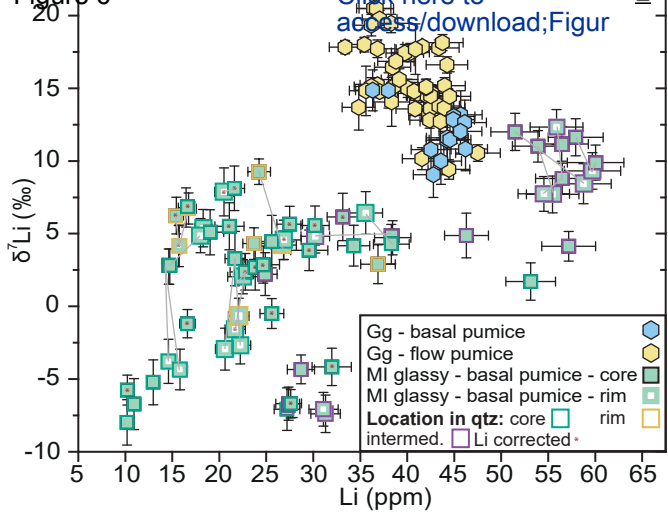


Figure 7 \pm 2SD

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