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1 Time scales of syneruptive volatile loss in silicic magmas
2 quantified by Li isotopes

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13 **ABSTRACT**

14 Most explosive, silicic volcanoes spend thousands of years in repose between
15 eruptive events. The timing of the switch from repose to eruption is key to interpreting
16 monitoring signals and improving the safety of people living close to active volcanoes.
17 We addressed this question using a novel technique based on lithium isotopic ($\delta^7\text{Li}$) and
18 elemental concentration profiles within plagioclase crystals from the Mesa Falls Tuff of
19 the Yellowstone volcanic system (California, USA), constraining volatile degassing to
20 occur on minimum time scales of tens of minutes prior to eruption. During this ephemeral
21 time, Li abundances drop by a factor of four to 10 from crystal cores to rims,
22 accompanied by an increase in $\delta^7\text{Li}$ of as much as 10‰, reflecting diffusion-driven

23 equilibration between plagioclase cores and outgassed, Li-poor melt. New times scales
24 obtained in this study show the potential for rapid syneruptive changes in the volatile
25 inventory of magmas.

26 INTRODUCTION

27 A key aim of volcanology is to improve the forecasting of volcanic eruptions in
28 order to safeguard millions of people who live in volcanically prolific regions.
29 Understanding magma dynamics, particularly the time scales of bubble nucleation and
30 magma degassing, which control eruptive explosivity (e.g., Sparks et al., 1994; Mangan
31 and Sisson, 2000), can help minimize this hazard. The study of volcanic deposits remains
32 fundamental to understanding and quantifying the processes occurring immediately prior
33 to eruption (Humphreys et al., 2006; Cashman et al., 2017). This requires the ability to
34 define and characterize the factors that lead to changes in chemical (major and trace
35 elements, volatile contents) (Shea et al., 2015) and isotopic compositions in melt and
36 associated crystals (Oeser et al., 2015). In particular, crystals in rapidly quenched,
37 nonwelded deposits can record magmatic histories from storage in the magma chamber to
38 eruption and provide information about changes in volatile concentration, magma
39 composition, temperature, and pressure before and during eruptions (e.g., Sparks, 1978;
40 Ellis et al., 2018).

41 The Yellowstone volcanic system (California, USA) represents the archetypal
42 supervolcano. Silicic volcanism at Yellowstone has predominantly produced rhyolitic
43 lavas punctuated by three voluminous caldera-forming eruptions (Huckleberry Ridge
44 Tuff, Mesa Falls Tuff, and Lava Creek Tuff) (Christiansen, 2001). The 1.3 Ma Mesa
45 Falls Tuff (MFT; Fig. 1) represents a large-volume explosive event that produced a

46 variably welded ignimbrite sheet overlying fallout deposits (Rivera et al., 2016). While
47 the MFT is well characterized in many respects, the final processes that tipped the system
48 from stability to eruption remain unknown.

49 The groundmass glass from the MFT is depleted in lithium (Li) (36–52 ppm)
50 relative to quartz-hosted melt inclusions (70–397 ppm) (Neukampf et al., 2019). We
51 propose that Li was lost with a H₂O-rich fluid upon syneruptive degassing. Although the
52 fluid-melt partitioning behavior of Li is debated, natural fluid-melt inclusion pairs
53 consistently show that Li tends to partition in favor of a H₂O- and Cl-rich fluid phase,
54 thereby depleting the melt in Li (Zajacz et al., 2008; Fiedrich et al., 2020), as supported
55 by some experimental results (Webster et al., 1989).

56 ~~During bubble formation,~~ K Kinetic isotopic fractionation has been proposed to
57 occur between the faster-diffusing ⁶Li and the slower-diffusing ⁷Li during bubble
58 formation, enriching the vapor in ⁶Li and, conversely, the melt in ⁷Li (Vlastélic et al.,
59 2011). These processes, as shown experimentally (Holycross et al., 2018) and
60 theoretically (Watson, 2017), can produce significant Li elemental and isotopic variations
61 between groundmass glass and mineral phases as the system strives to reestablish
62 equilibrium. The extent to which diffusion can homogenize these records reflects the time
63 between onset and termination of diffusion upon quenching. Here, we use a novel
64 technique combining Li concentration and Li stable-isotope ratios (Steinmann et al.,
65 2020) in plagioclase phenocrysts from the MFT and applying diffusion modeling to
66 constrain time scales of Li loss from the melt.

67 **LITHIUM CONCENTRATION MAPS AND PROFILES**

68 Seven plagioclase crystals from the nonwelded portion of the MFT were
69 geochemically characterized by electron microprobe and laser ablation inductively
70 coupled plasma mass spectrometry (LA-ICPMS). Only plagioclase crystals rimmed by
71 groundmass glass were used, to ensure that crystal rim measurements truly reflect
72 plagioclase in contact with the surrounding melt. Lithium concentration maps obtained by
73 LA-ICPMS (Figs. 2A and 2B) reveal homogeneous crystal interiors with high Li
74 concentrations mantled by a narrow zone ($\leq 200 \mu\text{m}$) where Li contents continuously
75 decrease toward crystal edges (Figs. 2C and 2D).

76 Concentration profiles through crystals confirm high-Li cores, from 12 to 33 ppm
77 depending on the crystal (mean 22 ppm; $n = 1440$), decreasing to 19 to ~ 5 ppm at the
78 very edge of the crystals (mean 12 ppm; $n = 208$). The anorthite content (An) varies
79 between crystals (An₁₇₋₃₁) but is homogenous within grains, and all other major and trace
80 elements lack any strong, systematic core-to-rim variation (Fig. 2C and 2D).

81 Some crystals exhibit ~~similar~~-Li depletion-~~as in rims~~ along cracks within the
82 crystal interior **similar to that in rims**. These cracks likely formed due to depressurization
83 during eruptive ascent allowing melt inclusions to expand and fracture their host
84 plagioclase (Fig. 2B). Interestingly, concentration profiles perpendicular to magmatic
85 cracks return steeper depletion profiles (Fig. 2D) compared to measurements at crystal
86 rims. This supports the interpretation that the cracks developed at a later stage during
87 ascent, leading to shorter Li diffusion times.

88 ***IN SITU* $\delta^7\text{Li}$ MEASUREMENTS**

89 Lithium isotopic composition ($\delta^7\text{Li}$) was measured *in situ* using a femtosecond
90 laser ablation system coupled to a multicollector ICPMS (fs-LA-MC-ICPMS) along

91 transects following crystal zoning patterns. The $\delta^7\text{Li}$ profiles exhibit large but systematic
92 differences (of as much as 10‰; Fig. 2E), with Li-poor plagioclase rims isotopically
93 heavier (−3.8‰ to +5.9‰; mean +1.0‰ ± 2.5‰; two standard errors [2 SE], $n = 19$) than
94 the Li-rich cores (−11‰ to +2‰; mean −4.2‰ ± 2‰; 2 SE, $n = 85$). Measurements
95 associated with magmatic cracks mimic those from crystal rims (−4.9‰ to +5.4‰; mean
96 +1.2‰ ± 2.6‰; [[2 SE? Alternatively, state at the definition of “2 SE” above that all
97 error values throughout the paper represent 2 SE]] $n = 13$), resulting in a broad
98 negative correlation between Li concentrations and $\delta^7\text{Li}$ across all crystals (Fig. 2F).

99 The observed Li loss toward crystal edges and magmatic cracks requires charge
100 balancing by other elements. Hydrogen is unsuitable, as it would behave similarly to Li.
101 The charge balance can occur by an exchange reaction of $\text{Li}^+ + \text{Al}^{3+} \rightarrow \text{Si}^{4+}$ and/or
102 oxidation of Fe^{2+} to Fe^{3+} during eruption. Although none of these elements correlates
103 with the observed edgeward decrease in Li, their higher abundance relative to the small
104 concentration change (~20 ppm) observed in Li challenges the identification of the
105 charge-balance mechanism. We favor the oxidation of Fe^{2+} to Fe^{3+} because it is
106 independent from elemental diffusion.

107 The variation in Li abundance cannot result from simple crystal-liquid
108 equilibrium partitioning during crystal growth because Li is moderately incompatible in
109 plagioclase (K_d [[Define]] = 0.1–0.7; Neukampf et al., 2019) and other mineral phases
110 present in the MFT (Tomascak et al., 2016; Neukampf et al., 2019). Hence, continued
111 crystal growth would enrich Li in the melt, thereby increasing the Li concentration
112 toward the plagioclase rim assuming that Li is not lost into the volatile phase. This
113 process would result in isotopically lighter rims because the resulting concentration

114 gradient would foster ${}^6\text{Li}$ diffusion into the crystal as observed for magmatic olivine and
115 clinopyroxene (Jeffcoate et al., 2007). Magma recharge with a Li-poor, ${}^7\text{Li}$ -enriched melt
116 can be excluded because no other element correlates with the decrease in Li toward
117 plagioclase rims.

118 The decreased Li concentration and elevated $\delta^7\text{Li}$ toward crystal edges can be
119 explained by scavenging of Li from the melt into the vapor phase during magma ascent
120 and degassing (e.g., Genareau et al., 2009; Giuffrida et al., 2018; Steinmann et al., 2020).
121 ${}^6\text{Li}$ preferentially moves into the vapor phase during vesiculation (Watson, 2017),
122 resulting in the depletion of ${}^6\text{Li}$ along with Li concentrations in the melt, inducing a
123 disequilibrium between plagioclase and melt (Fig. 3). This disequilibrium causes
124 diffusion of Li—preferentially ${}^6\text{Li}$ because it diffuses faster than ${}^7\text{Li}$ —from the rim of the
125 plagioclase into the melt. This in turn leads to a disequilibrium within the plagioclase
126 between the Li-depleted rim and its interior, driving Li diffusion toward the rims. Such a
127 scenario results in the observed depletion of Li and enrichment of ${}^7\text{Li}$ in the plagioclase
128 rims.

129 **DIFFUSION MODELING OF LITHIUM CONCENTRATIONS AND $\delta^7\text{Li}$**

130 Lithium diffusion profiles in plagioclase can be used to determine time spans of
131 this disequilibrium process (Fig. 4). Estimating such time scales depends on the applied
132 diffusion coefficient (D), requiring an accurate temperature determination. Here, we
133 investigated a temperature range based on different mineral thermometers for the MFT
134 (Tollan et al., 2019). Diffusion coefficients are calculated using the Arrhenius parameters
135 for Li that were experimentally determined for an anorthitic plagioclase (Giletti and
136 Shanahan, 1997). The published ${}^6\text{Li}$ diffusion coefficient can be applied because Li

137 diffusivity in feldspar is compositionally independent (Giletti and Shanahan, 1997). The
138 minimum applied temperature is 789 °C based on a sanidine-melt thermometer (Putirka,
139 2008) with a corresponding $D^{6\text{Li}} = 1.05 \times 10^{-11} \text{ m}^2/\text{s}$. Lower temperatures are implausible
140 because the melt was rapidly quenched upon eruption as supported by the absence of
141 microlites. Moreover, the pre-eruptive water content of the MFT melt was ~3 wt%
142 (Tollan et al., 2019). At the pre-eruptive storage pressure of the MFT (<1.5 kbar; Befus
143 and Gardner, 2016), this implies minimum temperatures of 770–780 °C (Holtz et al.,
144 2001). The maximum temperature is 856 °C, which is determined by a magnetite-
145 ilmenite thermometer (Sauerzapf et al., 2008), with a corresponding $D^{6\text{Li}} = 2.79 \times 10^{-11}$
146 m^2/s . Both calculated diffusion coefficients are applied to the concentration profiles.

147 To calculate time scales for the isotope profiles, ^6Li and ^7Li are considered as two
148 independent species with different diffusion coefficients. Because no published diffusion
149 coefficient is available for ^7Li in plagioclase (Giletti and Shanahan, 1997), we
150 recalculated them[[the diffusion coefficients? Or the time scales?]] based on those used
151 for ^6Li and considering that ^6Li moves 3.5% faster than ^7Li in melt (Holycross et al.,
152 2018). This calculation yields $D^{7\text{Li}} = 1.01 \times 10^{-11} \text{ m}^2/\text{s}$ for 789 °C and $D^{7\text{Li}} = 2.69 \times 10^{-11}$
153 m^2/s for 856 °C. We recognize that the relative diffusivity of the two isotopes in
154 plagioclase could differ from that in melt and may furthermore be composition
155 dependent, as observed for olivine (in which ^6Li moves 3% faster; Dohmen et al., 2010)
156 and clinopyroxene (in which ^6Li moves 4% faster; Richter et al., 2014). However, these
157 differences in relative isotope diffusivities between phases are much smaller than that
158 resulting from our inferred temperature range. The $\delta^7\text{Li}$ fit is calculated as the ratio of
159 individual Li isotope paths (Equation S1 in the Supplemental Material¹). Estimated time

160 scales are ~~between~~ 1–13 min at 789 °C and 0.3–4.5 min at 856 °C for concentration
161 profiles, and 0.5–15 min at 789 °C and 0.2–6 min at 856 °C for $\delta^7\text{Li}$ profiles. The results
162 for the diffusion modeling of concentration and isotopic profiles are thus mutually
163 consistent.

164 Figure 4C shows that for some profiles, a slight mismatch exists between time
165 scales derived from concentration profiles and isotope profiles. This can be a result of
166 different errors that are introduced into the model, e.g., different spatial resolution and
167 analytical errors on the measurements and/or inaccurate diffusion coefficients. To better
168 estimate errors on the time scales, the model boundary conditions (Tables S1–S3 in the
169 Supplemental Material) were set to match the highest and the lowest $^7\text{Li}/^6\text{Li}$ ratio within
170 analytical uncertainty (Fig. 4B) and modeled for the best fit. The time difference between
171 the best fit and the model using the highest and the lowest $^7\text{Li}/^6\text{Li}$ ratio is used as a more
172 realistic uncertainty (Fig. 4C) on the time scales derived from the diffusion models.

173 Crystal size has no influence on the estimated time scales, but crystal geometry
174 and magmatic cracks can have a non-negligible impact. There might be a diffusional
175 anisotropy of Li isotopes along different crystallographic directions, as reported for
176 olivine (Dohmen et al., 2010). Audétat et al. (2018) recognized that Li has two, slow-
177 versus fast-diffusing pathways in plagioclase. If the used diffusion coefficients represent
178 the latter, the resulting time scales are minima. However, even considering that Li
179 diffusion could be two orders of magnitude slower, the maximum time scales would
180 increase to only a few hours. Our results agree well with decompression time scales from
181 a study of the Huckleberry Ridge Tuff (Myers et al., 2016), which yields durations of <12
182 h to 5 days. A recent study of Li concentration profiles in plagioclase from Mount Etna

183 (Italy; Giuffrida et al., 2018) predicts time scales of ascent and degassing within minutes.
184 Other studies have also recognized Li gradients in plagioclase (e.g., Kent et al., 2007;
185 Charlier et al., 2012), but these investigations have suggested magmatic processes other
186 than degassing to be responsible for formation of Li gradients.

187 With particular attention to the suitability of individual crystals, e.g., identifying
188 the rims that were in contact with melt, crystal geometry, and three-dimensional effects,
189 the new combination of Li concentrations and *in situ* $\delta^7\text{Li}$ measurements in phenocrysts
190 represents a powerful tool and affords new opportunities for understanding time scales of
191 late magmatic processes. Our results show that at minimum a few tens of minutes elapse
192 between the onset of the eruptive volatile degassing of the magma and quenching. The
193 possibility of such rapid shifts from quiescence to explosivity underscores the need for
194 the improved understanding of the dynamics of magmatic systems and the causes for the
195 formation of a magmatic volatile phase. This study strengthens the role of petrology in
196 assisting in the key observations in monitoring potentially explosive volcanoes in real
197 time.

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331 **FIGURE CAPTIONS**

332 Figure 1. Map showing sample location (44°7'8.49"N, 111°26'39.49"W; Ellis et al.,
333 2017) of Mesa Falls Tuff (in blue), indicated with a red star. Inferred Henry's Folk
334 caldera (Christiansen, 2001) is in light gray, and state borders are in red.

335 **[[In the figure, change apostrophes to prime symbols in lat/lon labels; capitalize**
336 **“IS” in “ArcGIS”; insert a space in “20 km”]]**

337

338 Figure 2. Lithium elemental and isotopic zoning in Mesa Falls Tuff plagioclase
339 (Yellowstone volcanic system, California, USA). (A,B) Backscatter electron images
340 combined with Li concentration maps (by laser ablation–inductively coupled plasma–

341 mass spectrometry [LA-ICPMS]). White lines indicate measurement area of
342 concentration profiles, and white boxes represent areas used for $\delta^7\text{Li}$
343 measurements. **[[Explain the filled white boxes/bars shown at one end of each profile**
344 **line]]** Representative plagioclase crystal with magmatic cracks **is shown in B.** (C,D)
345 Concentration profiles measured from core to rim of crystals shown in A (grain 27 in the
346 Supplemental Material [see footnote 1]) and B (grain 21 in the Supplemental Material),
347 **respectively**, with Li (error within symbol size; **two standard deviations**) depletion toward
348 the rim and magmatic crack (D) while other trace **and** major elements, e.g., magnesium
349 (Mg) and titanium (Ti), and anorthite concentration (An), remain homogenous. **[[Explain**
350 **what the gray vertical error bars represent]]** (E) $\delta^7\text{Li}$ profile within the crystal shown
351 in A. $\delta^7\text{Li}$ value of bulk plagioclase separate (Neukampf et al., 2019) is illustrated **with a**
352 **brown bar**. Symbol width represents size of laser spot ($\sim 55 \mu\text{m}$). **[[Explain what the gray**
353 **vertical error bars represent]]** (F) All $\delta^7\text{Li}$ measurements (**two standard errors**) with
354 corresponding Li concentrations. **[[Explain what the circle-slash symbol means]]**
355 Larger symbols represent average values of rims, cracks, and cores.
356 **[[In the figure, panel B, make “inclusion” lowercase. In panels C and D, label the**
357 **vertical axes with a text description (e.g., “Concentration”). In panel F, italicize**
358 **instances of “n”, and insert a space on either side of each equals sign]]**

359

360 Figure 3. Schematic sketch of processes recorded in Mesa Falls Tuff plagioclase
361 **(Yellowstone volcanic system, California, USA).** Plagioclase color bar indicates low Li
362 concentration and high $\delta^7\text{Li}$ isotopic composition **in blue**, and red color represents higher
363 Li concentrations with low $\delta^7\text{Li}$ values. Melt Li contents are shown by light brown (low

364 Li) and dark brown (high Li). (A) Plagioclase in H₂O-undegassed melt with homogenous
365 Li concentration and isotopic composition. (B) Diffusion profile formed in plagioclase
366 due to the loss of Li during vesiculation of melt. (C) Theoretical concentration profile
367 across a crystal. (D) Theoretical $\delta^7\text{Li}$ profile.

368 **[[In the figure, capitalize “Melt” and “Plagioclase”; delete hyphens following “high”**
369 **and “low”. In panel A, change “&” to “and”, and add some space between the text**
370 **in A and the panel label “B”; change hyphen to en dash in “1–15”. In panel B,**
371 **capitalize “Magmatic”. In panels C and D, label the horizontal axes with a text**
372 **description]]**

373

374 Figure 4. Example of one-dimensional Li diffusion model for Mesa Falls Tuff plagioclase
375 (Yellowstone volcanic system, California, USA). (A) Representative diffusion profile
376 with measured (blue diamonds) concentration profile and its modeled best fit (blue
377 circles), *in situ* measured $\delta^7\text{Li}$ data (yellow hexagons), and best fit for $\delta^7\text{Li}$ profile
378 (orange circles). (B) Profiles shown in A with boundary conditions set to highest (red)
379 and lowest (pink) isotopic value within analytical error. (C) Comparison of time scales
380 obtained by diffusion modeling of Li concentration (Li abundance) and isotope ($\delta^7\text{Li}$)
381 profiles. Blue squares represent time scales at 789 °C, and red circles refer to time scales
382 at 856 °C. **[[Explain what the error bars represent; explain the lines labeled with**
383 **ratios, and the gray shading in between]]** (D) Time scales obtained from Li
384 concentration profiles ($n = 18$) shown as lines at 789 °C (blue) and 856 °C (red) for their
385 relative probability (Rel. prob.). Histogram (789 °C in blue, 856 °C in orange) shows
386 distribution of time scales. (E) Time scales obtained from all eight (two profiles in the

387 same crystal) analyzed $\delta^7\text{Li}$ profiles at 789 °C (pink) and at 856 °C (brown). Histogram
388 (789 °C in pink, 856 °C in brown) shows distribution of the time scales.

389 **[[In the figure, insert a space between “Li” and “(‰)” at the upper left corner;**
390 **replace hyphen with a space before each instance of “fit”. In panel B, insert a space**
391 **between “Li” and “(‰)”. In panel C, reword axis descriptions to place units of**
392 **measure (min) in parentheses—e.g., “Time from $\delta^7\text{Li}$ (min)”. In panels D and E,**
393 **italicize instances of “n”; make instances of “prob.” lowercase; insert a space**
394 **between each temperature value and “°C”]]**

395

396 ¹Supplemental Material. Supplemental material and analytical data. Please visit
397 <https://doi.org/10.1130/XXXXXX> to access the supplemental material, and contact
398 editing@geosociety.org with any questions.