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

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

INTRODUCTION

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

The Yellowstone volcanic system (California, USA) represents the archetypal supervolcano. Silicic volcanism at Yellowstone has predominantly produced rhyolitic lavas punctuated by three voluminous caldera-forming eruptions (Huckleberry Ridge Tuff, Mesa Falls Tuff, and Lava Creek Tuff) (Christiansen, 2001). The 1.3 Ma Mesa 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 (An_{17–31}) 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

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

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

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

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

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

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

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

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

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

scales are ~~between~~ 1–13 min at 789 °C and 0.3–4.5 min at 856 °C for concentration 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 for the diffusion modeling of concentration and isotopic profiles are thus mutually consistent.

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

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

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

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

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FIGURE CAPTIONS

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

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

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

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

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

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

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

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