

1           Time scales of syn-eruptive volatile loss in silicic magmas  
2                           quantified by Li-isotopes

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## 13 **METHODS**

### 14 **Major element measurements**

15 *Backscattered electron imaging by scanning electron microscope (SEM) and electron*  
16 *probe (EPMA) analyses* (Si, Na, Mg, Al, Ca, K, Sr, Ti, Fe, Ba) of plagioclase grains were obtained  
17 at the Institute of Geochemistry and Petrology, ETH Zürich. Profiles were measured from core to  
18 rim with 5 to 10 µm steps with standards every 30 to 40 measurements. All analyses were measured  
19 with 15 kV acceleration voltage, a beam diameter of 10 µm and a beam current of 20 nA with  
20 counting times of 20 s on peak and 10 s on background. All analyses were performed so that the  
21 mobile elements (Na, K) were measured first. To ensure measurement accuracy, in-house  
22 reference minerals (albite, anorthite and microcline) from the ETH collection were used as  
23 secondary standards and reproducibility was better than 5 %.

### 24 **Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) mapping**

25 *Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) mapping* was  
26 undertaken at The University of Queensland Centre for Geoanalytical Mass Spectrometry,  
27 Radiogenic Isotope Facility (UQ RIF-lab). Plagioclase crystals embedded in 1-inch polished resin  
28 mounts were analyzed following a published mapping method (Ubide et al., 2015; Ubide et al.,  
29 2019). The analytical set up comprised an ASI RESolution 193 nm excimer UV ArF laser ablation  
30 system with a dual-volume Laurin Technic ablation cell, coupled to a Thermo iCap RQ quadrupole  
31 mass spectrometer. Ablation was performed in ultra-pure He to which Ar make-up gas with a trace  
32 amount of N<sub>2</sub> was added for efficient transport and to aid ionization. The mapping area was built  
33 by overlapping ablation lines to form a rectangular grid, using a 20x20 µm square-shaped laser  
34 aperture, 20 µm/s translation speed, 10 Hz repetition rate, 3 J/cm<sup>2</sup> fluence, and 1 µm overlap  
35 between lines. A baseline measurement of 20-30 s was programmed between lines. Pre-ablation of

36 the crystals using large, quick rasters (100  $\mu\text{m}$  spot, 200  $\mu\text{m/s}$  speed and 20 Hz repetition rate) was  
37 found to improve the subsequent mapping. The total dwell cycle was 115 ms, including maximized  
38 dwell time for  $^7\text{Li}$  (50 ms). The instrument was tuned with scans on NIST SRM 612 silicate wafer  
39 reference material. NIST SRM 612 silicate wafer was employed as calibration standard and silicon  
40 concentrations (homogenous throughout single crystals) obtained by EPMA for each of the  
41 plagioclase crystals as internal standard. Spatially registered, quantitative multi-elemental maps  
42 were built with Iolite (Paton et al., 2011) v2.5, using CellSpace (Paul et al., 2012). Accuracy and  
43 precision were monitored via analysis of BHVO-2G, BCR-2G and GSD-1G glasses as secondary  
44 standards, using the same parameters as for the unknowns. Accuracy was better than 5 % for Li  
45 and better than 10 % for all other analyzed elements. Limits of detection (Longerich et al., 1996)  
46 were at the sub-ppm level for Li as well as all other trace elements.

#### 47 ***In situ* Lithium isotope analysis of plagioclase crystals by femtosecond laser ablation-MC-** 48 **ICPMS**

49 For the *in situ* determination of Li isotope composition in plagioclase phenocrysts a  
50 femtosecond laser based ablation system (Spectra-Physics Solstice) coupled to a multi-collector-  
51 ICP-MS (Thermo-Finnigan Neptune Plus) at the Leibniz Universität Hannover, Germany, was  
52 used. The ablation beam had a pulse duration of  $\sim 100$  fs and wavelength of 194 nm which was  
53 generated via frequency conversion from an infrared beam with 775 nm wavelength in an in-house  
54 built mirror and lens system and focused on the sample surface via a modified New Wave (ESI)  
55 stage combined with an optical microscope (Horn et al., 2006). The laser spot size of  $\sim 26$   $\mu\text{m}$  on  
56 the komatiite reference glass wafer GOR132-G (MPI DING) allowed for sufficient spatial  
57 resolution. Isotope measurements were performed according to the published method of

58 Steinmann et al., (2019), by employing standard-sample-bracketing with the GOR132-G glass as  
59 a bracketing standard according to Equation 1 and recalculation to IRMM-16.

$$60 \quad \delta \text{ } ^7\text{Li} = \left[ \frac{\left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{sample}}}{\left( \frac{^7\text{Li}}{^6\text{Li}} \right)_{\text{GOR132-G}}} - 1 \right] \times 1000 \quad (1)$$

61 Due to low Li concentrations (5-30 ppm) in the plagioclase a device was implemented for  
62 gas flow homogenization into the tubing system behind the ablation cell to homogenize the ablated  
63 aerosol with the transport Helium gas. Afterwards the make-up Ar gas was added and the gas-  
64 aerosol mixture was transported to the mass spectrometer. The homogenization of the gas flow  
65 was necessary to enhance signal stability and decrease the analytical error. In order to decrease  
66 matrix effects by avoiding the ionization of matrix elements in the plasma, relatively cool plasma  
67 conditions (RF power 900 W) were applied. *In situ* Li isotope ratio measurements were performed  
68 in static mode at low mass resolution which is sufficient to resolve atomic interferences. In order  
69 to keep background Li signals low, the measurements were performed under dry plasma  
70 conditions. For the detection of <sup>7</sup>Li, a Faraday cup equipped with a slow-response 10<sup>13</sup> Ω amplifier  
71 was deployed whereas a secondary ion multiplier was used for the detection of <sup>6</sup>Li. Due to the  
72 slower signal response of the 10<sup>13</sup> Ω amplifier a tau correction (Kimura et al., 2016) was applied  
73 for data evaluation.

74 Measurements of the bracketing standard were performed in raster ablation mode with a  
75 scan speed of 20 μm/s. The plagioclase profiles were measured in line ablation mode at the rims  
76 and raster ablation mode (26 μm by 56 μm) further into the grains, with lines and rasters arranged  
77 perpendicular to the crystal rim, each line/raster accounting for one measurement value. Individual  
78 measurements consisted of 180 cycles with an integration time of 1.049 s per cycle. The first ~35  
79 cycles were used for background correction using only the gas blank reading, followed by ~130

80 cycles of laser ablation. All analyses that represent one isotopic profile were measured during a  
81 single analytical session. As an internal control, the MPI DING reference glass T1-G was  
82 measured yielding a long-term reproducibility of 2.1 ‰ ( $\delta^7\text{Li} = 0.4 \text{ ‰}$ , 2 SD, n=64 in 16 sessions  
83 during 22 months) in agreement with Steinmann et al., (2019).

#### 84 **Trace element measurements**

85 Plagioclase trace element concentration profiles were obtained by LA-ICPMS using an  
86 Excimer 193 nm (ArF) Resolution (Australian Scientific Instruments) nanosecond laser ablation  
87 system coupled to a Nexion2000 (Perkin Elmer, Canada/USA) fast-scanning quadrupole ICPMS,  
88 at the Institute of Geochemistry and Petrology, ETH Zürich. The trace element concentration  
89 profiles in the plagioclase crystals were measured parallel to the previously analyzed chemical and  
90 Li isotopic profiles. The ablation was performed in a S-155 dual-volume ablation cell (Laurin  
91 Technic, Australia) under a carrier gas flow consisting of high-purity He (ca.  $0.5 \text{ l}\cdot\text{min}^{-1}$ ),  $\text{N}_2$  (cica  
92  $2 \text{ ml}\cdot\text{min}^{-1}$ ) and Ar make-up gas (ca.  $1.0 \text{ l}\cdot\text{min}^{-1}$ ) from the ICPMS. Line scans were ablated with a  
93 spot diameter of  $29 \mu\text{m}$ , a repetition rate of 10 Hz, a laser energy density of ca.  $3.5 \text{ J}\cdot\text{cm}^{-2}$  and a  
94 scan velocity of  $1 \mu\text{m}\cdot\text{s}^{-1}$ . All concentrations were quantified against the NIST SRM 612 silicate  
95 glass wafer as the primary standard (Jochum et al., 2011), using conventional standard-sample  
96 bracketing with one line between two standards. The USGS basaltic glass GSD-1G was used as  
97 the secondary standard to monitor for the accuracy and reproducibility of the analyses. Both  
98 reference materials were ablated with line scans under the same conditions as the unknown  
99 samples. The resulting raw intensities were processed using the Igor Pro-based Iolite v2.5 software  
100 (Hellstrom et al., 2008), using the implemented data reduction scheme for trace element  
101 quantification. The baseline-corrected intensities for each line scan were averaged over integration  
102 periods of 5 s (corresponding to 20 mass cycles with a sweep time of 0.25 s each), resulting in a

103 spatial resolution of 5  $\mu\text{m}$  for the final concentrations along the profiles. We used Si as an internal  
104 standard to correct for differences in relative sensitivities, based on the average  $\text{SiO}_2$  content of  
105 the analyzed plagioclase crystals ( $63\pm 0.5$  wt.%) measured by EPMA. The uncertainties on  
106 concentrations at each step of the profiles correspond to the scatter of the 20 measurement cycles  
107 integrated within the corresponding time step, quoted at 95% confidence level (2 S.D.).

## 108 **Diffusion modelling**

109 Diffusion modelling as shown in Fig. 4 was conducted using the diffusion coefficient of Li  
110 in an anorthitic plagioclase (Giletti and Shanahan, 1997). Each profile was modelled using a one-  
111 dimensional model, and a diffusion exchange at a constant temperature with an infinite medium  
112 (core is unaffected by diffusion) is assumed. The shape of the Li concentration profiles as well as  
113 the  $\delta^7\text{Li}$  profiles can be described by an error function. Therefore, the following equation (2) can  
114 be applied:

$$115 \quad C_x = (C_0 - 1) \left( 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right) + 1 \quad (2)$$

116 where  $C_x$  represents the composition at a distance  $x$  (in  $\mu\text{m}$ ) from the crystal surface,  $D$  is  
117 the Li diffusion coefficient in plagioclase, and  $t$  is the time since the diffusion started.  $C_0$  represents  
118 the composition in the core (used values are given in Table S1, S2 and S3). To calculate the  
119 timescales for the isotope profiles, the  $^6\text{Li}$  and  $^7\text{Li}$  are considered as two independent species with  
120 different diffusion coefficients. The temperature range used in this study is between 789  $^\circ\text{C}$   
121 (sanidine–melt thermometer; Putirka, 2008) to 856  $^\circ\text{C}$  (ilmenite–magnetite thermometer;  
122 Sauerzapf et al., 2008). Only ilmenite-magnetite pairs passing the equilibrium criteria (Bacon and  
123 Hirschmann, 1988) were used for temperature estimations.

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**TABLE S1. Time scales of Li diffusion from Li concentration in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively.**

Grain	Line	C <sub>0</sub> . Core (ppm)*	Rim (ppm)*	789 °C		856 °C	
				Time (min)	S.D.	Time (min)	S.D.
7	L1	20.2	5.3	3.0	0.5	1.5	0.5
	L2	19.6	6.7	3	1	1.0	0.2
11	L1.1	27.7	6.2	5	1	2.0	0.6
	L1.2	28.3	5.9	2.5	1.0	1.0	0.3
13	L1.1	27.2	5.0	6.5	0.5	2.0	0.5
	L1.2	30.0	6.8	6.0	1.0	2.0	0.2
15	L2.1	27.8	5.1	7	2	2.5	1
	L2.2	28.6	6.4	6	2	2.0	0.5
	L3.1	25.6	4.9	3	1	1	0.2
	L3.2	21.1	6.5	3	1	1	0.2
21	L1.1	20.1	6.7	1	0	0.3	0.1
	L1.2	22.3	8.5	1	1	0.3	0.1
	L3.1	28.6	7.7	3	1	1	0.2
	L3.2	28.7	7.4	4	2	1.5	0.5
25	L1	23.6	8.8	2.5	0.5	0.8	0.3
	L2	23.6	7.0	7	1	2.5	0.5
27	L1	23.4	6.2	13	2	4.5	1
	L2	28.4	8.4	3	1	1	0.5

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

\*Measured using a LA-ICPMS.

**TABLE S2. Time scales of Li diffusion from  $\delta^7\text{Li}$  profiles in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively.**

Grain	Line	C <sub>0</sub> - Core ( $\delta^7\text{Li}$ )*	Rim ( $\delta^7\text{Li}$ )*	789 °C		856 °C	
				Time (min)	SD	Time (min)	SD
7	L1	-9.1	-0.8	7.5	1	2.8	0.2
11	L1.1	-2.6	3.2	2.5	1	0.7	0.2
13	L1.1	-9.2	-1.2	1.5	1	0.5	0.5
15	L2.1	-1.4	0.7	0.5	0.1	0.2	0.1
21	L1.1	-7.0	-3.8	1	0.5	0.5	0.1
21	L3.1	-9.0	-1.9	5	1	1.5	0.5
25	L1	-7.0	2.9	13	5	5	2
27	L1	-8.3	2.6	15	3	6	2

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

\*Measured using a fs-LA-MC-ICPMS

**TABLE S3. Time scales of Li diffusion from  $\delta^7\text{Li}$  profiles in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively. The highest and lowest Li isotopic value within the error are taken as boundary conditions for the diffusion modelling.**

Grain	Line	$C_0 - \delta^7\text{Li}$ Core (‰)*	$\delta^7\text{Li}$ Rim (‰)*	789 °C	856 °C
				Time (min)	time (min)
<b>upper values</b>					
7	L1	-10.9	1.5	12	6
11	L1.1	-4.4	5.7	4	1.5
13	L1.1	-11.2	1.2	3.5	1.1
15	L2.1	-3.6	3.0	0.75	0.3
21	L1.1	-7.4	-1.7	0.75	0.3
21	L3.1	-11.0	1.0	8.5	3.25
25	L1	-9.0	5.1	16	6
27	L1	-10.1	5.0	30	12
<b>lower value</b>					
7	L1	-7.3	-3.0	4.5	1.6
11	L1.1	-0.7	0.8	1	0.35
13	L1.1	-7.1	-3.6	0.9	0.4
15	L2.1	-1.6	0.8	0.3	0.1
21	L1.1	-2.7	-5.9	0.15	0.05
21	L3.1	-7.0	-4.7	2.75	1
25	L1	-5.1	0.6	5.5	2.2
27	L1	-6.5	0.1	10	4

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

\*Measured using a fs-LA-MC-ICPMS