

1 **Experimental determination of Li isotope behaviour during basalt**  
2 **weathering**

3

4 Philip A.E. Pogge von Strandmann<sup>1\*</sup>, Wesley T. Fraser<sup>2</sup>, Samantha J. Hammond<sup>3</sup>,  
5 Gary Tarbuck<sup>1</sup>, Ian G. Wood<sup>1</sup>, Eric H. Oelkers<sup>1</sup>, Melissa J. Murphy<sup>1</sup>

6

7 <sup>1</sup>London Geochemistry and Isotope Centre (LOGIC), University College London  
8 and Birkbeck, University of London, Gower Place, London, WC1E 6BT.

9 <sup>2</sup>Geography, Oxford Brookes University, Oxford, OX3 0BP

10 <sup>3</sup>School of Environment, Earth and Ecosystems Sciences, The Open University,  
11 Walton Hall, Milton Keynes, MK7 6AA

12 \*Corresponding author: p.strandmann@ucl.ac.uk

13

14

15 Abstract

16 Silicate weathering is the primary control of atmospheric CO<sub>2</sub> concentrations on  
17 multiple timescales. However, tracing this process has proven difficult. Lithium  
18 isotopes are a promising tracer of silicate weathering. This study has reacted  
19 basalt sand with natural river water for ~9 months in closed experiments, in  
20 order to examine the behaviour of Li isotopes during weathering. Aqueous Li  
21 concentrations decrease by a factor of ~10 with time, and  $\delta^7\text{Li}$  increases by  
22 ~19‰, implying that Li is being taken up into secondary phases that prefer <sup>6</sup>Li.  
23 Mass balance using various selective leaches of the exchangeable and secondary  
24 mineral fractions suggest that ~12–16% of Li is adsorbed, and the remainder is  
25 removed into neoformed secondary minerals. The exchangeable fractionation

26 factors have a  $\Delta^7\text{Li}_{\text{exch-soln}} = -11.6$  to  $-11.9\text{‰}$ , while the secondary minerals  
27 impose  $\Delta^7\text{Li}_{\text{secmin-soln}} = -22.5$  to  $-23.9\text{‰}$ . Overall the experiment can be modelled  
28 with a Rayleigh fractionation factor of  $\alpha = 0.991$ , similar to that found for natural  
29 basaltic rivers. The mobility of Li relative to the carbon-cycle-critical cations of  
30 Ca and Mg changes with time, but rapidly evolves within one month to  
31 remarkably similar mobilities amongst these three elements. The evolution shows  
32 a linear relationship with  $\delta^7\text{Li}$  (largely due to a co-variation between aqueous  
33 [Li] and  $\delta^7\text{Li}$ ), suggesting that Li isotopes have the potential to be used as a tracer  
34 of Ca and Mg mobility during basaltic weathering, and ultimately  $\text{CO}_2$  drawdown.

35

36

### 37 1.0 Introduction

38 Chemical weathering of continental silicate rocks is one of the primary  
39 drivers of the long-term carbon cycle and climate (Chamberlin, 1899; Walker et  
40 al., 1981). Weathering provides nutrients to the ocean to fertilise primary  
41 productivity, clay particles to help bury organic carbon (Hawley et al., 2017),  
42 and, critically, alkalinity and cations such as Ca and Mg for the precipitation of  
43 marine carbonate (Berner et al., 1983). All of these processes sequester  
44 atmospheric  $\text{CO}_2$  on various timescales, making chemical weathering a  
45 fundamental Earth climate system process.

46 Significant effort has gone into understanding and quantifying silicate  
47 weathering, both in the present (e.g. Maher, 2011; West et al., 2005), and in the  
48 geological past (e.g. Foster and Vance, 2006; Pogge von Strandmann et al., 2017a;  
49 Vance et al., 2009). Traditionally, marine radiogenic strontium isotopes have  
50 been used to determine past weathering changes (McArthur et al., 2001), but

51 their interpretation is far from unambiguous, because seawater isotope ratios  
52 are impacted by hydrothermal inputs and riverine isotope ratios are strongly  
53 dependent on the lithology undergoing weathering. This is further complicated  
54 by the inability to distinguish between carbonate and silicate weathering, where  
55 only the latter draws down CO<sub>2</sub> on the long-term (Allegre et al., 2010; Oliver et  
56 al., 2003). Hence, other tracers have been sought – ideally ones that are relatively  
57 unaffected by lithology, by carbonate weathering (which does not affect pCO<sub>2</sub> on  
58 >10<sup>4</sup> year timescales) or by biology and plant growth. So far, the only tracer that  
59 meets all these criteria is lithium isotopes.

60 Lithium isotopes (reported as δ<sup>7</sup>Li, the ‰ deviation from a normalising  
61 standard) are unaffected by carbonate weathering, because silicates are orders  
62 of magnitude more concentrated in Li than carbonates (Kisakürek et al., 2005;  
63 Millot et al., 2010; Pogge von Strandmann et al., 2017b), or by plant growth or  
64 primary productivity (Lemarchand et al., 2010; Pogge von Strandmann et al.,  
65 2016). The δ<sup>7</sup>Li range in primary silicate rocks (continental crust ~0‰; basalt  
66 3–5‰ (Elliott et al., 2006; Sauzeat et al., 2015)) is narrow compared to that  
67 observed in rivers draining those rocks (δ<sup>7</sup>Li = 2–44‰, mean 23‰ (Dellinger et  
68 al., 2015; Huh et al., 1998; Pogge von Strandmann et al., 2006)). This range is due  
69 to the formation of secondary minerals (clays, zeolites and Fe-Mn-Al  
70 oxyhydroxides) during weathering, where these minerals preferentially take up  
71 the light isotope, <sup>6</sup>Li, driving residual river and soil waters isotopically heavy  
72 (Vigier et al., 2008; Wimpenny et al., 2010). These secondary minerals also  
73 adsorb Li onto their exchangeable sites, imposing the same isotopic fractionation  
74 direction (Hindshaw et al., 2019; Pistiner and Henderson, 2003). Hence, Li  
75 isotopes in natural waters are controlled by the ratio of primary mineral

76 dissolution (low  $\delta^7\text{Li}$ ) relative to secondary mineral formation (driving solution  
77  $\delta^7\text{Li}$  high). This ratio is known as the “weathering congruency” (Misra and  
78 Froelich, 2012; Pogge von Strandmann and Henderson, 2015), which may be  
79 used as a tracer of chemical weathering intensity (Dellinger et al., 2015). Overall,  
80 this ratio also informs on the efficiency of weathering in removing  $\text{CO}_2$ , because if  
81 cations are being trapped by secondary minerals on the continents within clays  
82 and soils, they will not enter the ocean to form carbonate and sequester  $\text{CO}_2$ .

83         However, while the general mechanics of Li isotope fractionation during  
84 weathering are fairly well understood, there is less information available on the  
85 precise processes that  $\delta^7\text{Li}$  traces, such as whether the primary fractionation  
86 mechanism is adsorption onto secondary mineral surfaces, uptake into interlayer  
87 sites, or via structural or lattice-bound incorporation into neoformed minerals  
88 (Hindshaw et al., 2019; Pistiner and Henderson, 2003; Pogge von Strandmann et  
89 al., 2010; Wimpenny et al., 2015). Further, fractionation factors and reaction  
90 kinetics are also poorly known.

91         In this study, we react basalt with river water for around nine months in  
92 closed system experiments, following the methods of previous experiments  
93 (Jones et al., 2012). The primary goal is to examine Li isotope behaviour during  
94 these weathering experiments, to determine which phases affect Li isotopes  
95 during weathering, and to quantify their response.

96

## 97 2.0 Methods

### 98 *2.1 Experimental methods*

99         Following the methods of Jones et al. (2012), approximately 250g of the  
100 natural basaltic sand used in the Jones et al. experiments was placed in 1L pre-

101 leached PTFE beakers containing 900ml of water. This sand was collected from  
102 the bottom of the Borgarfjörður estuary in Iceland, and was characterised by  
103 Jones et al. (2012). These data are repeated in Supplemental Table 1 for  
104 completeness' sake. The sand consists of fairly fresh basalt (for example it  
105 contains significant basaltic glass), but also contains small amounts of  
106 phyllosilicates only just detectable by X-Ray Diffraction, as described below. For  
107 the water to be naturally charge-balanced and have a natural amount of  
108 alkalinity, the water used in the experiments was collected from the local Great  
109 Ouse River in eastern England. While the composition of this water is not  
110 identical to that in Iceland where the sand was sampled, the similarities in  
111 temporal fluid concentration behaviour (described below) between this study  
112 and Jones et al. (2012), which used Icelandic water, suggest that the differences  
113 in these water compositions only has a minor effect on experimental results.

114 Two identical experiments were run at 20°C in a shaking bath reactor, in  
115 order to determine that the Li isotope behaviour was not anomalous. Closed  
116 systems were used (rather than through-flow reactors) in order to be able to  
117 mass balance the reactants, and to facilitate retrieval of isotopic fractionation  
118 factors. Trace element concentrations were only determined from one of the  
119 experiments. At periodic intervals, the water pH was measured, and 50 ml of  
120 water was removed and filtered through 0.2µm cellulose acetate syringe filters,  
121 and stored in pre-cleaned PTFE bottles. Sampling frequency was initially daily,  
122 but decreased throughout the experiment (Table 1).

123 Post-experiment, the reacted basalt was dried and stored. The pre- and  
124 post-experimental basalts were also leached, to examine their exchangeable  
125 fraction. This leach followed the Tessier method, by leaching the basalt in 1M

126 sodium acetate for 1 hour at room temperature (Hindshaw et al., 2019; Pogge  
127 von Strandmann et al., 2013; Tessier et al., 1979). Following this, the residue was  
128 leached for 1 hour with 0.6M HCl, which attacks the secondary mineral fraction,  
129 i.e. clays as well as oxyhydroxides and zeolites (Pogge von Strandmann et al.,  
130 2014; Tessier et al., 1979). Bulk basalt was dissolved in a standard method of  
131 concentrated HF-HNO<sub>3</sub>-HClO<sub>4</sub>, followed by HNO<sub>3</sub> and 6M HCl.

132

### 133 *2.2 XRD and FTIR methods*

134 X-ray powder diffraction analysis was carried out on a “whole sample”  
135 basis. Samples were prepared by grinding the material under ethanol using an  
136 agate pestle and mortar and the dried powder was side-filled against a ground-  
137 glass surface into a rectangular sample holder 20 x 20 mm in area and 1.5 mm  
138 deep. Diffraction patterns were collected with Co radiation, using a PANalytical  
139 X’Pert Pro diffractometer with Bragg-Brentano parafocusing reflection geometry.  
140 This instrument is equipped with a Ge(1 1 1) Johansson-type focusing  
141 monochromator, producing a CoK $\alpha_1$  incident beam. The X-ray tube was operated  
142 at 40 kV and 30 mA. Variable-width divergence and anti-scatter slits were used,  
143 together with a 15 mm wide beam mask in the incident beam, so as to illuminate  
144 a constant 15mm  $\times$  15mm area of the sample; 0.04 radian Soller slits were  
145 present in both the incident and diffracted beams to reduce the axial  
146 divergences. The X-ray detector was an “X’Celerator” position-sensitive detector;  
147 this device covers an angular range in  $2\theta$  of  $\pm 1.061^\circ$ , with an effective fixed step  
148 size of  $0.0167^\circ$ . Data were collected over the  $2\theta$  range from  $5^\circ$  to  $70^\circ$  ( $20.5 \text{ \AA} < d$   
149  $< 1.56 \text{ \AA}$ ), with data collection times of 15 hours.

150 Fourier-transform infrared (FTIR) analyses were conducted on dried  
151 samples using a Perkin-Elmer Spectrum2 (Seer Green, Buckinghamshire, UK)  
152 attenuated total reflectance-FTIR (ATR-FTIR) spectrometer, fitted with a single-  
153 bounce diamond ATR cell. A total of 8 scans were used to generate an average  
154 spectrum for each sample at a resolution of  $4\text{cm}^{-1}$ . Spectra spanned the range  
155  $4000\text{-}600\text{ cm}^{-1}$ . All samples were analysed in triplicate.

156 Clay minerals typically show a pronounced broad absorption band  
157 centred at  $c.3300\text{cm}^{-1}$  associated with hydroxyl (OH) groups interacting via  
158 hydrogen bonding within the clay structure, thus an increase in OH spectral  
159 response indicates an increase in clay mineral content of a sample.

160

### 161 *2.3 Concentration analyses*

162 The solution concentrations were analysed at The Open University, using  
163 an Agilent 8800 triple quadrupole inductively coupled plasma mass  
164 spectrometer (ICP-QQQ-MS). The instrument has two quadrupole mass filters,  
165 which are separated by a collision / reaction cell (allowing targeted interference  
166 removal in the cell). We ran in two modes of analysis, no gas for Li (as no  
167 interference ions are present on mass) and in He collision mode for all other  
168 analytes. In no gas mode, oxide levels (measured as  $\text{CeO}^+/\text{Ce}^+$ ) were at 0.96%  
169 and doubly charged species ( $\text{Ce}^{2+}/\text{Ce}^+$ ) at 1.80%. In He mode, these were at  
170 0.44% and 1.30% respectively.

171 Prior to analysis, samples were diluted 10 fold from the original solution  
172 in 2%  $\text{HNO}_3$  to allow analysis of all masses in the same analytical session.

173 Analyses were calibrated against a suite of synthetic multi-element solutions,  
174 which were made up to cover the range of concentrations in the experimental

175 solutions. An on-line internal standard (Rh and In) was added to each sample  
176 and standard also, to monitor and correct for instrument drift. In addition, drift  
177 was further monitored by running a measurement block consisting of the  
178 original water used in the experiments, one of the calibration standards and a  
179 2% HNO<sub>3</sub> blank every 5 – 6 unknowns (5 times during the analytical session).  
180 Where concentrations are above the detection limit in the initial water,  
181 reproducibility is better than 2.5% (relative standard deviation from the mean of  
182 the five measurements). Accuracy was also determined using the international  
183 river water reference standard SLRS-5, and was within uncertainty of certified  
184 values. Lithium and silicon are not certified in SLRS-5, so in this case we  
185 compared to published concentrations and were also within uncertainty  
186 (Heimbürger et al., 2013).

187 Major elemental concentrations of the starting basalt are taken from  
188 Jones et al. (2012), except for Li concentrations, which were determined by ICP-  
189 MS analyses in a similar manner to the dissolved concentrations, while running  
190 BCR-2 as an external standard, whose values were within uncertainty ( $\pm 6\%$ ) of  
191 isotope-dilution determined Li concentrations in BCR-2 (Pogge von Strandmann  
192 et al., 2011). All concentrations are reported in the Supplement.

193 The elemental ratios of the leachates were determined using a Varian  
194 720ES ICP-OES. Samples were calibrated using matrix-matched synthetic  
195 standards (i.e. in Na acetate and dilute HCl).

196

197

198 *2.4 Li isotope analyses*



199            Approximately 15ml of water was evaporated, and passed through a two-  
200 stage cation exchange column procedure, using AG50W X-12 resin, and eluting  
201 with dilute HCl (Pogge von Strandmann et al., 2011). Column splits were  
202 collected before and after the main elute, and analysed for Li content, to  
203 determine how much Li was in the sample. Using this method, it was determined  
204 that >99.9% of sample was collected in the main column elution.  
205 Purified samples were analysed using a new Nu Plasma 3 multi-collector ICP-MS  
206 at the LOGIC laboratories. A sample-standard bracketing procedure was used  
207 relative to the IRMM-016 standard. Each sample was measured three separate  
208 times during an analytical procedure, repeat measurements being separated by  
209 several hours, but during the same analysis session. Each individual  
210 measurement consisted of 10 ratios (50 s total integration time), giving a total  
211 integration time of 150 s/sample for the three repeat measurements that  
212 constitute a single analysis (n=1). We use the 2sd (standard deviation) of these  
213 three measurements as an assessment of our individual uncertainty, although  
214 values reported in Table 1 have also been compounded for the difference in  
215 normalising standards described below.

216            This mass spectrometer has new cones (compared to previous Nu MC-  
217 ICP-MSs), and, using the specific “super-lithium cones”, and a Cetac Aridus 2  
218 desolvation system, a 5 µg/L solution gives a signal intensity of 100–140 pA (10–  
219 14V) of <sup>7</sup>Li<sup>+</sup> at an uptake rate of ~100 µl/min. Background, instrumental Li  
220 intensities, typically ~0.07 pA (7mV), were subtracted from the sample and  
221 standard intensities. Total procedural blanks were generally indistinguishable  
222 from background, and contain <0.003 ng Li.

223 Lithium isotope ratios are commonly reported relative to the LSVEC  
224 standard (Flesch et al., 1973). LSVEC analysed relative to IRMM-016 yields  $\delta^7\text{Li} =$   
225  $-0.003 \pm 0.054$  (2se, n=19), which is in close agreement with past corresponding  
226 measurements (Jeffcoate et al., 2004; Phan et al., 2016). All reported  $\delta^7\text{Li}$  values  
227 have been re-normalised to LSVEC, and the reported uncertainty has been  
228 propagated to encompass analytical uncertainty on both samples, normalising  
229 standards and LSVEC.

230 Given that this is the first Li isotope study published at the new LOGIC isotope  
231 mass spectroscopy facilities, we have gone to some effort to determine the  
232 accuracy and precision of our analyses. We have therefore analysed seawater  
233 (both IAPSO and North Atlantic seawater) and the USGS rock standards BCR-2  
234 (basalt), G-2 (granite), PCC-1 (peridotite) and SGR-1b (shale). Relative to LSVEC,  
235 seawater  $\delta^7\text{Li} = 31.11 \pm 0.38\text{‰}$  (2sd; n=12) (identical to other published values,  
236 e.g. Dellinger et al., 2015; James and Palmer, 2000; Jeffcoate et al., 2004; Pogge  
237 von Strandmann and Henderson, 2015). Our other values also compared well to  
238 published values: BCR-2:  $\delta^7\text{Li} = 2.64 \pm 0.31\text{‰}$  (n=5) (e.g.  $2.6 \pm 0.3\text{‰}$  (Pogge von  
239 Strandmann et al., 2011);  $2.7 \pm 1.3\text{‰}$  (Liu et al., 2013);  $2.9 \pm 0.3\text{‰}$  (John et al.,  
240 2012)); G-2:  $\delta^7\text{Li} = 0.14 \pm 0.16\text{‰}$  (n=3) (e.g.  $0.1 \pm 0.8\text{‰}$  (Phan et al., 2016);  $0.6 \pm$   
241  $1.8\text{‰}$  (Sauzeat et al., 2015)); PCC-1:  $\delta^7\text{Li} = 8.72 \pm 0.13\text{‰}$  (n=3) (e.g.  $8.9 \pm 0.4\text{‰}$   
242 (Magna et al., 2006)); SGR-1b:  $\delta^7\text{Li} = 4.00 \pm 0.24\text{‰}$  (e.g.  $4.7 \pm 0.7\text{‰}$  (Phan et al.,  
243 2016);  $3.6 \pm 0.4\text{‰}$  (Pogge von Strandmann et al., 2017b);  $4.9 \pm 1.9\text{‰}$  (Hindshaw  
244 et al., 2018)). Hence, our standard results show that our Li isotope analyses are  
245 accurate, and have a long-term external precision (for the twelve months the  
246 new laboratory has been operational) of better than  $\pm 0.4\text{‰}$  (2sd).

247

## 248 3.0 Results

### 249 *3.1 Concentrations*

250           The same basalt sand as used by Jones et al. (2012) was also used for this  
251 experiment, and details are given in Supplementary Table 1. The Li  
252 concentration of the unreacted basalt is 5.53  $\mu\text{g/g}$ , similar to MORB and other  
253 Icelandic basalts (Elliott et al., 2006; Pistiner and Henderson, 2003). The post-  
254 reaction basalts have indistinguishable bulk Li concentrations of 5.3–5.6  $\mu\text{g/g}$ .

255           Compared to the bulk basalt composition, the sodium acetate leach  
256 (exchangeable fraction) of the unreacted basalt has considerably higher Mg/Si  
257 ratios (mass ratio  $\text{Mg}/\text{Si}_{\text{bulk basalt}} = 0.27$ , while  $\text{Mg}/\text{Si}_{\text{exch}} = 25.3$ ) (Table 2). Silicon  
258 (as a neutral species) should not be present in the exchangeable leach, and its  
259 presence (albeit at very low concentrations) implies that the leach is not fully  
260 efficient due to a small contribution of Si from the dissolution of silicate minerals  
261 (Hindshaw et al., 2019). Lower Mg/K ratios in the exchangeable fractions  
262 ( $\text{Mg}/\text{K}_{\text{bulk basalt}} = 13.7$ , while  $\text{Mg}/\text{K}_{\text{exch}} = 0.75$ ), and undetectable Al and Fe  
263 demonstrate that the exchangeable fraction of the initial basalt is enriched in the  
264 elements that would be expected to partition into this fraction (Renforth et al.,  
265 2015; Sigfusson et al., 2008; Tessier et al., 1979). The exchangeable fractions of  
266 the reacted basalts have somewhat lower Mg/Si (8.2–9.5). Li/Si is also several  
267 orders of magnitude higher in the unreacted exchangeable fraction than the  
268 initial bulk basalt (0.04 compared to  $3 \times 10^{-5}$ ), and decreases slightly in the  
269 reacted basalts (0.015–0.03), showing that Li is considerably more affiliated with  
270 sorption than Si.

271 In contrast, the HCl leach (that should attack the secondary mineral  
272 phases) of the unreacted basalt has similar Mg/Si to the bulk basalt (0.29  
273 compared to 0.27). However, elements that would be expected to be enriched in  
274 clays and oxyhydroxides are enriched: Al/Si is 0.63 in the leach, compared to  
275 0.36 in the bulk basalt, while Fe/Si is 0.92 compared to 0.53. Li/Si is also over an  
276 order of magnitude higher in the leaches. The reacted basalts' leached Li/Si  
277 ratios are slightly lower than the unreacted basalt (Table 2). Overall, the leaches  
278 appear to have targeted the expected phases: the adsorbed fraction is enriched  
279 in exchangeable cations, and the secondary mineral plus Fe and Al  
280 oxyhydroxides fraction is enriched in elements such as Fe, Al and Li, as  
281 demonstrated before for basalts (Chapela Lara et al., 2017; Hindshaw et al.,  
282 2019; Opfergelt et al., 2014; Pogge von Strandmann et al., 2012; Pogge von  
283 Strandmann et al., 2014; Sigfusson et al., 2008; Tessier et al., 1979).

284 The concentrations of the initial unreacted water, and the experimental  
285 aqueous solutions are given in Table 1. A sample of the initial water was kept at  
286 the same conditions as the experiments (without any contact with basalt, and  
287 with atmospheric contact) to examine how the pH evolved. The initial pH of this  
288 aqueous solution started at 7.1, increased to 7.6 after a month, and then  
289 decreased to 7.3 by the end of the experiment (Table 1). Both basalt-water  
290 experiments showed the same pattern, but were consistently about 0.2 pH units  
291 lower.

292 Aqueous solution concentration behaviour is generally similar to that  
293 reported by Jones et al. (2012). Most major elemental concentrations increase  
294 with reaction time (Fig. 1), with an overall 3% increase in Na, 24% in Mg, 93% in  
295 Si, while at the same time K and Ca concentrations decrease slightly (on the

296 order of 10%). This behaviour for the individual elements is similar to that  
297 observed by Jones et al. (2012), although the enrichment amounts vary. This is  
298 likely due to the different composition of the waters used in these experiments  
299 (Jones et al., 2012). Minor elements like Al and Mn also increase. Almost all of  
300 these elements reach apparent steady-state (stable concentrations) after ~50–  
301 100 days after the beginning of the experiments. Importantly for these  
302 experiments, as also shown by Jones et al. (2012), Li concentrations decrease,  
303 from 13.5  $\mu\text{g/L}$  in pre-experimental water to 1.3  $\mu\text{g/L}$  by the end of the  
304 experiment. By comparison, the flow-weighted mean global river concentration  
305 is 1.5  $\mu\text{g/L}$  (Huh et al., 1998). This behaviour results in a rapid increase in some  
306 elemental ratios including Mg/Na, which attains a near steady value after ~12  
307 days. The Li/Na ratios evolve to a constant value more slowly, due to the more  
308 gradual decline in Li concentrations.

309

### 310 *3.2 Li isotopes*

311 The  $\delta^7\text{Li}$  of the pre-experimental bulk basalt is 4.4‰, similar to other  
312 Icelandic and MORB basalts (Elliott et al., 2006; Pogge von Strandmann et al.,  
313 2006; Pogge von Strandmann et al., 2012; Vigier et al., 2009). The post-  
314 experimental bulk basalts from the two experiments have a  $\delta^7\text{Li}$  of 4.1–4.5‰,  
315 within analytical uncertainty of the pre-experimental basalt (Table 2).

316 The exchangeable fraction (sodium acetate leach) of the pre-experimental  
317 basalt has a  $\delta^7\text{Li}$  of 17.8‰, with a Li concentration of 0.7  $\mu\text{g/L}$  (compared to a  
318 total procedural blank of 0.03  $\mu\text{g/L}$  Given the presence of minor quantities of Si  
319 in these leaches from the dissolution of silicate minerals (see Section 3.1), the  
320 leachate  $\delta^7\text{Li}$  is likely slightly lower value than if the leach were fully efficient.

321 The secondary mineral fraction (HCl leach) has a  $\delta^7\text{Li}$  of 5.3‰ with a Li  
322 concentration in the leach of 11.6 ng/g. As for the exchangeable leach, the  
323 secondary mineral leach is unlikely to have been totally efficient (Hindshaw et  
324 al., 2019), although elemental ratios in this leach (Table 2) are close to  
325 stoichiometry for some examples of smectite.

326 The post-experiment exchangeable fractions have  $\delta^7\text{Li}$  values of 21.3 and 21.8‰,  
327 while the HCl leach has  $\delta^7\text{Li}$  values of 9.3–10.8‰ (i.e. 4.0–5.5‰ higher than that  
328 of the unreacted pre-experimental basalt leach). Concentrations must be  
329 normalised to the amount of material in the experiment to be meaningful. Thus,  
330 exchangeable Li increases from 1.1  $\mu\text{g}$  in the total (250g) pre-experiment basalt  
331 to 2.5–2.9  $\mu\text{g}$  post-experiment. Similarly, the HCl leach increases from 17.6  $\mu\text{g}$  to  
332 27–27.5  $\mu\text{g}$ .

333 The  $\delta^7\text{Li}$  of the initial reactive aqueous fluid is 14‰, and these fluids then  
334 exhibit an increase with time to a final value of 33.3‰ in both experiments (Fig.  
335 2). The simultaneous decrease in Li concentrations of these fluids results in a  
336 negative correlation between  $\delta^7\text{Li}$  and [Li], which is frequently observed in  
337 basaltic rivers (Pogge von Strandmann et al., 2010; Pogge von Strandmann et al.,  
338 2006; Vigier et al., 2009), although natural rivers tend to have slightly lower  
339 concentrations (Fig. 3), likely due to the relatively higher [Li] in the starting  
340 solution of these experiments. In both experiments, an approximate steady-state  
341 appears to have been reached, with both Li concentrations and isotopes  
342 approximately stable for the last 125 days of the experiment.

343

344 4.0 Discussion

345 *4.1 Lithium mass balance*

346           The mass balance of lithium in the experiments can be used to determine  
347 the destination of Li lost from the fluid. In principle there are two phases that  
348 could be taking up Li from the fluid: the exchangeable fraction (i.e. sorbed Li) and  
349 the secondary mineral fraction (i.e. Li substituting into the crystal structures of  
350 neoforming minerals)(Chan and Hein, 2007; Millot and Girard, 2007; Pistiner  
351 and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2015; Wimpenny et  
352 al., 2010). For this mass balance, we assume that the Na acetate leach represents  
353 the exchangeable fraction, while the subsequent HCl leach represents Li  
354 recovered from secondary minerals (including oxyhydroxides and clays or  
355 zeolites).

356           We also assume that Li added to solution by primary basalt dissolution  
357 can be calculated by assuming that the increase in fluid of Mg or Si represents  
358 stoichiometric dissolution (Jones et al., 2012), such that the Li/Mg or Li/Si  
359 concentration ratios remain constant during dissolution. Stoichiometric  
360 weathering is unlikely to be a perfect assumption, given that both Mg and Si are  
361 also known to partition into secondary minerals as well (e.g. (Opfergelt et al.,  
362 2014; Pogge von Strandmann et al., 2012)). However, constant elemental ratios  
363 during dissolution is likely a robust assumption, as Li is a moderately  
364 incompatible element, and does not partition preferentially into any primary  
365 basaltic minerals (Penniston-Dorland et al., 2017). In any case, the amount of Li  
366 added from basalt dissolution is minor compared to that lost from solution.  
367 According to the Mg and Si concentration increase, between 0.015 and 0.07 g of  
368 the ~250 g basalt samples dissolved during the experiments, which is around  
369 4% of the total Li mass balance (~0.4µg Li, assuming constant Li/Mg ratios).

370 In the experiments, when normalised to the amount of material used, the  
371 exchangeable fraction gained  $\sim 1.4\text{--}1.8\mu\text{g}$  Li, while the secondary minerals  
372 gained  $\sim 9.4\text{--}9.9\mu\text{g}$  Li. The solution (when corrected for fluid loss due to  
373 sampling) lost  $\sim 11.4\mu\text{g}$  Li by the end of the experiment.

374 Given weighing errors and propagated analytical uncertainty, the  
375 experiments therefore can be mass balanced, with around  $\sim 82\text{--}87\%$  of the Li  
376 lost from the fluid substituting into secondary phases, and  $\sim 12\text{--}16\%$  being taken  
377 into the exchangeable fraction (Fig. 4). This result demonstrates that the sorbed  
378 fraction is of sufficient importance to be an integral consideration of future  
379 lithium weathering studies.

380

#### 381 *4.2 Mineral saturation states*

382 Mineral saturation states in the fluids were calculated using the PHREEQC  
383 programme (Parkhurst and Appelo, 1999). Basaltic primary minerals (olivine,  
384 plagioclase, pyroxene) are undersaturated in all the experimental fluids, and  
385 hence are likely to dissolve. The undersaturation of these minerals is maintained  
386 by supersaturation (and hence likelihood of precipitation) of secondary minerals  
387 (Gíslason et al., 1996). For example, both kaolinite and smectite are consistently  
388 supersaturated in all the experimental solutions. However, while kaolinite's  
389 saturation is broadly constant, that of smectite increases with time. Iron  
390 oxyhydroxides (e.g. amorphous  $\text{Fe}(\text{OH})_3$ , another common basaltic secondary  
391 mineral) starts out undersaturated, but becomes supersaturated after about 4  
392 days of reaction.

393 Mineral saturation states provide insight into whether neoformation or  
394 sorption is dominantly controlling Li isotope fractionation. There is a clear co-



395 variation between the saturation state of smectite (Aberdeen-montmorillonite)  
396 and  $\delta^7\text{Li}$  that does not exist for any other modelled secondary minerals. As the  
397 smectite saturation state increases, so as the likelihood of precipitation  
398 increases, the  $\delta^7\text{Li}$  also increases, because more  $^6\text{Li}$  is being incorporated into  
399 precipitating smectites. It is also noticeable that extrapolation of the trend line  
400 ( $r^2 = 0.94$ ) back into undersaturated conditions ( $\text{SI} < 0$ ) leads to the initial  $\delta^7\text{Li}$   
401 values of the basalts used (Fig. 5). In other words, when no smectite is forming, it  
402 appears that the solutions would have an identical  $\delta^7\text{Li}$  value to primary basalt  
403 (i.e. congruent weathering). As smectite precipitation increases,  $^6\text{Li}$  is  
404 preferentially removed from the fluid, increasing solution  $\delta^7\text{Li}$  values. In  
405 contrast, were Fe oxyhydroxide the dominant secondary mineral controlling Li,  
406 its undersaturated conditions at the start of the experiment should result in  
407 unfractionated Li isotopes, which is not observed.

408         Therefore, this confirms that clay formation strongly affects Li isotope  
409 fractionation (Bouchez et al., 2013; Wimpenny et al., 2015; Wimpenny et al.,  
410 2010), but also adds to the mass balance argument made above, that it is  
411 secondary mineral formation, rather than sorption, that is largely controlling Li  
412 isotope fractionation in this experiment (84–88% of Li by mass balance)  
413 (Hindshaw et al., 2019; Pistiner and Henderson, 2003; Vigier et al., 2008;  
414 Wimpenny et al., 2015).

415

#### 416 *4.3 Li isotope fractionation*

417         Assuming that the Li concentrations and isotope ratios measured in the  
418 exchangeable and secondary mineral fractions represent fractionation from the

419 youngest (most recent) experimental fluids in the dissolved fraction, it is  
420 possible to calculate fractionation factors into both solid fractions.

421 The  $\Delta^7\text{Li}_{\text{exch-soln}}$  of the experiments is -11.6 to -11.9‰, while the  $\Delta^7\text{Li}_{\text{secmin-}}$   
422  $\text{soln}$  is -22.5 to -23.9‰. The weighted fractionation factor of total Li taken into  
423 both fractions combined is on average  $\sim$ -22‰. Iceland basaltic rivers exhibit  
424  $\Delta^7\text{Li}$  values between unleached suspended loads and complementary dissolved  
425 loads of up to  $\sim$ -36‰, although with an average of -22‰, similar to the results  
426 here (Pogge von Strandmann et al., 2006; Vigier et al., 2009). Rivers from the  
427 basaltic Azores exhibit an average  $\Delta^7\text{Li}_{\text{susp-soln}} \sim -17 \pm 7\text{‰}$  (Pogge von  
428 Strandmann et al., 2010), while rivers draining the Columbia River Basalts show  
429 an average  $\Delta^7\text{Li}_{\text{susp-soln}} \sim -17 \pm 4\text{‰}$  (Liu et al., 2015). Comparatively, alteration of  
430 the fresh oceanic basalts (one of the primary sinks of Li from seawater) cause -  
431  $26 \pm 1\text{‰}$  fractionation from solution (in this case seawater), while weathered  
432 oceanic basalts exhibit  $-22 \pm 4\text{‰}$  (Chan et al., 1992), and dredged ophiolite is  
433 fractionated by  $\sim$ -17‰ (Coogan et al., 2017). Even subaerial basalts, when  
434 weathered by seawater, show -21‰ fractionation (Pogge von Strandmann et al.,  
435 2008). Thus, while there are apparently subtle differences in fractionation  
436 between different terrains (bearing in mind that riverine suspended loads do not  
437 necessarily only consist of secondary minerals), observed fractionations appears  
438 to be broadly similar, around  $\sim$ 20‰. The observed fractionation in these  
439 experiments is also similar to the overall variability observed in a global  
440 compilation of published riverine values (Murphy et al., 2019), and the mean  
441 discharge-weighted  $\delta^7\text{Li}$  of  $\sim$ 23‰ observed in rivers (Huh et al., 1998).

442 In several different river studies, including in basaltic terrains, Li/Na  
443 ratios have been reported to have a similar behaviour as Li isotope ratios,

444 because Na is considered to be highly mobile (and hence remains in the fluid  
445 phase) (Dellinger et al., 2015; Liu et al., 2015; Millot et al., 2010; Pogge von  
446 Strandmann et al., 2017b). Hence, Li/Na ratios are likely also be controlled by  
447 the ratio of dissolution to precipitation, and might be a good proxy for the extent  
448 of water-rock interaction time.

449         The relationship between  $\delta^7\text{Li}$  and Li/Na has been possible to simulate  
450 with isotopic fractionation models, which yield the fractionation factors that  
451 might be mineral-specific (Pogge von Strandmann et al., 2017b). Hence, overall,  
452 as Li/Na decreases (because Li is removed from solution relative to Na),  $\delta^7\text{Li}$   
453 increases. Generally it seems that most large global rivers can be simulated  
454 assuming an equilibrium fractionation relationship, although global basaltic  
455 rivers appear to be following more of a Rayleigh fractionation relationship  
456 (Pogge von Strandmann et al., 2017b).

457         In the case of this study, the data show a logarithmic relationship between  
458 Li/Na and  $\delta^7\text{Li}$  as it evolves from the starting point of the initial water (Fig. 6).  
459 This relationship can be modelled with a Rayleigh fractionation equation, given  
460 that the experiments in this study behaved as a closed system. Hence, ~90% of  
461 the initial Li was taken up into various secondary phases. All the data form a  
462 single fractionation relationship stemming from the initial fluid composition,  
463 with a best-fit Rayleigh  $\alpha$  value of 0.991 ( $r^2 = 0.96$ ). This is generally similar to  
464 fractionation factors reported during natural basalt weathering: MORB-seawater  
465 and basalt particle-seawater interaction have  $\alpha \sim 0.985$  (Chan et al., 1992; Pogge  
466 von Strandmann et al., 2008), and the best-fit to a global compilation of basaltic  
467 rivers is to a Rayleigh relationship with  $\alpha \sim 0.992$  (Pogge von Strandmann et al.,  
468 2017b). This factor is likely related both to the experimental fluid composition

469 (and hence the starting fluid composition and the composition of the basalt)  
470 because it is likely to control the precise secondary mineralogy.

471

#### 472 *4.4 Mobility and $\delta^7\text{Li}$*

473 One of the prevailing questions about the use of Li isotopes as a palaeo-  
474 weathering proxy is what process precisely these isotopes are tracing. Generally  
475 Li isotopes are considered to be able to trace weathering congruency (Pogge von  
476 Strandmann and Henderson, 2015) or weathering intensity (Dellinger et al.,  
477 2015), but not directly weathering rates (Pogge von Strandmann et al., 2017b).  
478 Often in models of palaeo-records, Li isotopes are considered likely to be able to  
479 act as a tracer for the riverine Li concentration and/or flux (Lechler et al., 2015;  
480 Li and West, 2014; Pogge von Strandmann et al., 2017a; Pogge von Strandmann  
481 et al., 2013). However, even if  $\delta^7\text{Li}$  were a perfect tracer for the Li flux, there is  
482 little knowledge of how these fluxes might relate to those of elements critical to  
483 the precipitation of marine carbonate and hence to the carbon cycle, such as Ca  
484 or Mg. Hence, it has become important to determine the relationship between  
485 the behaviour of Li in relation to that of Ca and Mg.

486 Elemental mobility during weathering is the tendency of a particular  
487 element to go into the fluid phase versus being taken up by secondary minerals  
488 during weathering. During basaltic weathering, Na is the most mobile major  
489 cation (Gíslason et al., 1996), and hence the mobility of other cations is  
490 commonly reported as the relative mobility to Na, where the formula is  
491  $(x/\text{Na})_{\text{solution}}/(x/\text{Na})_{\text{rock}}$ . In Icelandic basalts relatively mobile elements such as  
492 Ca and Mg are approximately  $\sim 10\times$  less mobile than Na, while immobile  
493 elements such as Al or Fe are about three orders of magnitude less mobile than

494 Na (Gíslason et al., 1996). Natural studies have rarely measured Li  
495 concentrations, and hence the relative difference between the weathering  
496 mobility of Li and Ca or Mg remains poorly understood.

497         In the case of our experiments, the final equilibrium mobilities are similar  
498 to the natural values reported by Gíslason et al. (1996), but show a clear trend of  
499 evolution with time. Magnesium starts at around 13× less mobile than Na, but  
500 within 4 days has evolved slightly to its final value of ~11× less mobile (Fig. 7).  
501 Cations such as Ca behave similarly, albeit in the case of Ca the relative mobility  
502 decreases slightly with time. The relative mobility of lithium, on the other hand,  
503 changes more dramatically, starting out at almost 75% of the mobility of Na, and  
504 decreasing, and stabilising at, about 10% after ~100 days reaction. Over 80% of  
505 this change in mobility occurs within the first month of the experiment. This  
506 observation supports the hypothesis that secondary mineral formation, rather  
507 than solely the more rapidly reacting exchangeable fraction, is largely affecting  
508 the Li isotope composition. Exchangeable reactions take a few hours to occur  
509 (Pistiner and Henderson, 2003), while the kinetics of secondary mineral  
510 formation are thought to be relatively slow (on the order of  $10^{-19}$  mol/cm<sup>2</sup>/s  
511 (Yokoyama and Banfield, 2002)). However, those observations on secondary  
512 mineral kinetics were largely made using major elements, not more sensitive  
513 trace elements such as Li, and our data suggest that at least amorphous  
514 secondary phases begin to form within a few days.

515         From the point of using Li as a tracer of overall chemical weathering  
516 processes, especially the transport of Ca and Mg to the oceans to form carbonate  
517 thereby drawing down CO<sub>2</sub>, the relative mobility difference between Li and Ca or  
518 Mg is more revealing: Li starts the experiment as ~15× more mobile than Ca

519 (and  $\sim 9\times$  more mobile than Mg), but these values decrease with time during the  
520 experiment to Li being only  $2.2\times$  more mobile than Ca (and  $1.0\times$  as mobile as  
521 Mg)(Fig. 8). This temporal evolution is almost entirely driven by the significant  
522 changes in Li concentration, although there is also a relatively small decrease in  
523 Ca mobility as well. Most of these change occurs within the first month of the  
524 experiments, while for the subsequent  $>7$  months significantly less changes  
525 occur. The relatively slower evolution of Li mobility (compared to major  
526 elements) suggests that Li may be a very sensitive element for tracing very early  
527 and small amounts of incipient secondary mineral formation. Certainly  
528 measurements using X-Ray Diffraction (XRD) of the pre- and post-experiment  
529 basalts cannot distinguish the amounts of phyllosilicates or Fe oxides in the two  
530 basalts. Hence the partitioning of Li is clearly more sensitive to the inception of  
531 secondary mineral formation than XRD.

532 Equally, no discernible difference in clay-associated OH abundance could  
533 be detected between the starting samples and the experimental samples using  
534 Fourier-transform infrared (FTIR). This therefore also suggests that the  
535 difference between pre- and post-experiment samples are small.

536 These results therefore suggest two points: 1) the changes in the phases  
537 controlling the Li isotope ratios are very small, showing that  $\delta^7\text{Li}$  is considerably  
538 more sensitive to these changes than the more standard methods of XRD and  
539 FTIR; 2) once a steady-state is reached, Li has a similar mobility to both Ca and  
540 Mg, meaning that Li is a useful tracer for the behaviour during weathering of  
541 these two critical elements (Pogge von Strandmann et al., 2016).

542 Notably, given that only Li isotope ratios are useful in the marine  
543 geological record, and not absolute Li concentrations, there is a correlation

544 between solution  $\delta^7\text{Li}$  and the relative mobility of Li to Ca and Li to Mg (Fig. 8). In  
545 the case of Ca, the negative relationship has an  $r^2$  of 0.99. After four days of  
546 reaction, the Li to Ca mobility begins to decrease and  $\delta^7\text{Li}$  to further increase  
547 (Fig. 8), again largely driven by the change in Li concentration correlating with  
548  $\delta^7\text{Li}$ . In other words, during the experiment, the Li/Ca and Li/Mg ratios of the  
549 secondary minerals must be increasing as Li is increasingly removed from  
550 solution. After a month (34 days) of reaction, the rates of change of Li to Ca  
551 mobility and of  $\delta^7\text{Li}$  dramatically decline, as the reaction reaches apparent  
552 steady-state.

553 Thus, not only does Li rapidly (from a natural weathering perspective)  
554 reach a similar mobility to Ca and Mg, but also  $\delta^7\text{Li}$  is therefore an excellent  
555 tracer of Li mobility. This is useful from the point of palaeo-reconstructions. For  
556 example, speleothem reconstructions using Li isotopes have determined the Li  
557 mobility over time (Pogge von Strandmann et al., 2017c). The same calculations  
558 can be performed for seawater archives, assuming that both hydrothermal input  
559 rates (possibly via reconstructed spreading rates), and the starting rock  
560 composition of rivers are “known”. Using the equilibrium Li to Ca mobility  
561 (based on  $\delta^7\text{Li}$ ) for the riverine input, it would then be possible to determine the  
562 past behaviour of riverine Ca or Mg fluxes from Li isotopes. Before this can be  
563 properly adopted, similar experiments are required on different primary  
564 lithologies (e.g. granites, shales, etc.), but it raises the possibility of  $\delta^7\text{Li}$  being a  
565 direct quantitative proxy for the behaviour of Ca and Mg, and hence  $\text{CO}_2$   
566 drawdown over geologic time.

567

568 5.0 Conclusions

569 Basalts were experimentally reacted with water in closed reactors for  
570 over nine months. During this time, while solution major elements such as Mg or  
571 Si increased in concentration in the fluid phase (implying basalt dissolution),  
572 dissolved Li concentrations decreased, and  $\delta^7\text{Li}$  increased, implying removal of Li  
573 into or sorption onto secondary phases.

574 Mass balance calculations using selective leaches of the pre- and post-  
575 experiment basalts, shows that, of the Li removed from solution, ~12–16% was  
576 taken up by the exchangeable fraction (imparting a ~12‰ fractionation to  $\delta^7\text{Li}$ ),  
577 and the remainder by neoformed secondary minerals (imparting ~23‰  
578 fractionation). For at least the final 6 months of the experiment, Li fractionation  
579 appears to have reached steady-state conditions, and isotope ratios remain  
580 approximately constant. The  $\delta^7\text{Li}$  vs. Li/Na trends of the experiment follow an  
581 overall closed-system Rayleigh relationship with an  $\alpha = 0.991$ , similar to other  
582 basaltic rivers.

583 The solution Li isotope ratio also correlates with the modelled saturation  
584 index of smectite, where an extrapolation of the trend to saturated conditions (SI  
585 = 0) converges towards basaltic  $\delta^7\text{Li}$  compositions, further implying that  
586 neoformation of secondary minerals may be largely controlling solution  $\delta^7\text{Li}$ .  
587 This suggests that Li isotopes are more susceptible to this early mineral  
588 formation than major element ratios, or to standard methods of clay detection  
589 such as X-Ray diffraction and Fourier-transform infrared. Equally, this implies  
590 that the onset of clay formation (or even amorphous clays) is much more rapid  
591 than initially thought (on the order of a few days to months).



592 Finally, the relatively mobility of Li to those cations critical in the carbon  
593 cycle (Ca and Mg) evolves with time, but rapidly (within one month) reaches a  
594 point where the behaviour of Li is broadly similarly mobile to both elements.  
595 There is also a direct correlation between  $\delta^7\text{Li}$  and this mobility, implying that Li  
596 isotopes can be used to trace Li mobility, and therefore can be used to trace Ca  
597 and Mg mobility (at least during basalt weathering), and ultimately  $\text{CO}_2$   
598 drawdown.

599

#### 600 Acknowledgements

601 The experiments and experimental equipment were funded by Royal Society  
602 Research Grant 537708. PPvS and MJM were funded by ERC Consolidator grant  
603 682760 CONTROLPASTCO<sub>2</sub>. We thank Ed Tipper, Josh Wimpenny and an  
604 anonymous reviewer for their comments.

605

606

607 Allegre, C.J. et al., 2010. The fundamental role of island arc weathering in the  
608 oceanic Sr isotope budget. *Earth and Planetary Science Letters*, 292(1-2):  
609 51-56.  
610 Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The Carbonate-Silicate  
611 Geochemical Cycle and Its Effect on Atmospheric Carbon-Dioxide over the  
612 Past 100 Million Years. *American Journal of Science*, 283(7): 641-683.  
613 Bouchez, J., von Blanckenburg, F., Schuessler, J.A., 2013. Modeling novel stable  
614 isotope ratios in the weathering zone. *American Journal of Science*, 313.  
615 Chamberlin, T.C., 1899. An attempt to frame a working hypothesis of the cause of  
616 glacial periods on an atmospheric basis. *Journal of Geology*, 7(6): 545-  
617 584.  
618 Chan, L.H., Edmond, J.M., Thompson, G., Gillis, K., 1992. Lithium isotopic  
619 composition of submarine basalts: implications for the lithium cycle in the  
620 oceans. *Earth and Planetary Science Letters*, 108(1-3): 151-160.  
621 Chan, L.H., Hein, J.R., 2007. Lithium contents and isotopic compositions of  
622 ferromanganese deposits from the global ocean. *Deep-Sea Research*, 54:  
623 1147-1162.  
624 Chapela Lara, M., Buss, H.L., Pogge von Strandmann, P.A.E., Schuessler, J.A.,  
625 Moore, O.W., 2017. The influence of critical zone processes on the Mg

626 isotope budget in a tropical, highly weathered andesitic catchment.  
627 *Geochimica Et Cosmochimica Acta*, 202: 77–100.

628 Coogan, L.A., Gillis, K.M., Pope, M., Spence, J., 2017. The role of low-temperature  
629 (off-axis) alteration of the oceanic crust in the global Li-cycle: Insights  
630 from the Troodos ophiolite. *Geochimica Et Cosmochimica Acta*, 203: 201–  
631 215.

632 Dellinger, M. et al., 2015. Riverine Li isotope fractionation in the Amazon River  
633 basin controlled by the weathering regimes. *Geochimica Et Cosmochimica*  
634 *Acta*, 164: 71–93.

635 Elliott, T., Thomas, A., Jeffcoate, A., Niu, Y.L., 2006. Lithium isotope evidence for  
636 subduction-enriched mantle in the source of mid-ocean-ridge basalts.  
637 *Nature*, 443(7111): 565–568.

638 Flesch, G.D., Anderson, A.R., Svec, H.J., 1973. A secondary isotopic standard for  
639  $6\text{Li}/7\text{Li}$  determinations. *Int. J. Mass Spectrom. Ion Process.*, 12: 265–272.

640 Foster, G.L., Vance, D., 2006. Negligible glacial-interglacial variation in  
641 continental chemical weathering rates. *Nature*, 444(7121): 918–921.

642 Gíslason, S.R., Arnorsson, S., Armannsson, H., 1996. Chemical weathering of  
643 basalt in southwest Iceland: Effects of runoff, age of rocks and  
644 vegetative/glacial cover. *American Journal of Science*, 296(8): 837–907.

645 Hawley, S.M., Pogge von Strandmann, P.A.E., Burton, K.W., Williams, H.M.,  
646 Gíslason, S.R., 2017. Continental weathering and terrestrial  
647 (oxyhydr)oxide export: Comparing glacial and non-glacial catchments in  
648 Iceland. *Chemical Geology*, 462: 55–66.

649 Heimbürger, A. et al., 2013. SLRS-5 Elemental Concentrations of Thirty-Three  
650 Uncertified Elements Deduced from SLRS-5/SLRS-4 Ratios. *Geostandards*  
651 *and Geoanalytical Research*, 37(1): 77–85.

652 Hindshaw, R.S., Aciego, S.M., Tipper, E.T., 2018. Li and U Isotopes as a Potential  
653 Tool for Monitoring Active Layer Deepening in Permafrost Dominated  
654 Catchments. *Frontiers in Earth Science*, 6.

655 Hindshaw, R.S. et al., 2019. Experimental constraints on Li isotope fractionation  
656 during clay formation. *Geochimica Et Cosmochimica Acta*, 250: 219–237.

657 Huh, Y., Chan, L.H., Zhang, L., Edmond, J.M., 1998. Lithium and its isotopes in  
658 major world rivers: Implications for weathering and the oceanic budget.  
659 *Geochimica Et Cosmochimica Acta*, 62(12): 2039–2051.

660 James, R.H., Palmer, M.R., 2000. The lithium isotope composition of international  
661 rock standards. *Chemical Geology*, 166(3-4): 319–326.

662 Jeffcoate, A.B., Elliott, T., Thomas, A., Bouman, C., 2004. Precise, small sample size  
663 determinations of lithium isotopic compositions of geological reference  
664 materials and modern seawater by MC-ICP-MS. *Geostandards and*  
665 *Geoanalytical Research*, 28(1): 161–172.

666 John, T. et al., 2012. Volcanic arcs fed by rapid pulsed fluid flow through  
667 subducting slabs *Nature Geoscience*, 5: 489–492.

668 Jones, M.T., Pearce, C.R., Oelkers, E.H., 2012. An experimental study of the  
669 interaction of basaltic riverine particulate material and seawater.  
670 *Geochimica Et Cosmochimica Acta*, 77: 108–120.

671 Kisakürek, B., James, R.H., Harris, N.B.W., 2005. Li and  $\delta^7\text{Li}$  in Himalayan rivers:  
672 Proxies for silicate weathering? *Earth and Planetary Science Letters*,  
673 237(3-4): 387–401.

674 Lechler, M., Pogge von Strandmann, P.A.E., Jenkyns, H.C., Prosser, G., Parente, M.,  
675 2015. Lithium-isotope evidence for enhanced silicate weathering during  
676 OAE 1a (Early Aptian Selli event). *Earth and Planetary Science Letters*,  
677 432: 210–222.

678 Lemarchand, E., Chabaux, F., Vigier, N., Millot, R., Pierret, M.C., 2010. Lithium  
679 isotope systematics in a forested granitic catchment (Strengbach, Vosges  
680 Mountains, France). *Geochimica Et Cosmochimica Acta*, 74: 4612-4628.

681 Li, G., West, A.J., 2014. Evolution of Cenozoic seawater lithium isotopes: Coupling  
682 of global denudation regime and shifting seawater sinks. *Earth and  
683 Planetary Science Letters*, 401: 284–293.

684 Liu, X.-L., Rudnick, R.L., McDonough, W.F., Cummings, M.L., 2013. Influence of  
685 chemical weathering on the composition of the continental crust: Insights  
686 from Li and Nd isotopes in bauxite profiles developed on Columbia River  
687 Basalts. *Geochimica Et Cosmochimica Acta*, 115: 73–91.

688 Liu, X.-M., Wanner, C., Rudnick, R.L., McDonough, W.F., 2015. Processes  
689 controlling  $\delta^{7}\text{Li}$  in rivers illuminated by study of streams and  
690 groundwaters draining basalts. *Earth and Planetary Science Letters*, 409:  
691 212–224.

692 Magna, T., Wiechert, U., Halliday, A.N., 2006. New constraints on the lithium  
693 isotope compositions of the Moon and terrestrial planets. *Earth and  
694 Planetary Science Letters*, 243(3-4): 336-353.

695 Maher, K., 2011. The role of fluid residence time and topographic scales in  
696 determining chemical fluxes from landscapes. *Earth and Planetary  
697 Science Letters*, 312: 48–58.

698 McArthur, J.M., Howarth, R.J., Bailey, T.R., 2001. Strontium isotope stratigraphy:  
699 LOWESS version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma  
700 and accompanying look-up table for deriving numerical age. *Journal of  
701 Geology*, 109(2): 155-170.

702 Millot, R., Girard, J.P., 2007. Lithium Isotope Fractionation during adsorption  
703 onto mineral surfaces, International meeting, Clays in natural &  
704 engineered barriers for radioactive waste confinement, Lille, France.

705 Millot, R., Vigier, N., Gaillardet, J., 2010. Behaviour of lithium and its isotopes  
706 during weathering in the Mackenzie Basin, Canada. *Geochimica Et  
707 Cosmochimica Acta*, 74: 3897–3912.

708 Misra, S., Froelich, P.N., 2012. Lithium Isotope History of Cenozoic Seawater:  
709 Changes in Silicate Weathering and Reverse Weathering. *Science*, 335:  
710 818–823.

711 Murphy, M.J. et al., 2019. Tracing silicate weathering processes in the  
712 permafrost-dominated Lena River watershed using lithium isotopes.  
713 *Geochimica Et Cosmochimica Acta*, 245: 154–171.

714 Oliver, L. et al., 2003. Silicate weathering rates decoupled from the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
715 of the dissolved load during Himalayan erosion. *Chemical Geology*, 201(1-  
716 2): 119–139.

717 Opfergelt, S. et al., 2014. Magnesium retention on the soil exchange complex  
718 controlling Mg isotope variations in soils, soil solutions and vegetation in  
719 volcanic soils, Iceland. *Geochimica Et Cosmochimica Acta*, 125: 110–130.

720 Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (version 2) - a  
721 computer program for speciation, batch-reaction, one-dimensional  
722 transport, and inverse geochemical calculations.

723 Penniston-Dorland, S., Liu, X.-M., Rudnick, R.L., 2017. Lithium Isotope  
724 Geochemistry, *Rev. Min. Geochem.*, pp. 165–217.

725 Phan, T.T. et al., 2016. Factors controlling Li concentration and isotopic  
726 composition in formation waters and host rocks of Marcellus Shale,  
727 Appalachian Basin. *Chemical Geology*, 420: 162–179.

728 Pistiner, J.S., Henderson, G.M., 2003. Lithium-isotope fractionation during  
729 continental weathering processes. *Earth and Planetary Science Letters*,  
730 214(1-2): 327-339.

731 Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P.,  
732 Gislason, S.R., 2010. Assessing the role of climate on uranium and lithium  
733 isotope behaviour in rivers draining a basaltic terrain. *Chemical Geology*,  
734 270: 227–239.

735 Pogge von Strandmann, P.A.E. et al., 2006. Riverine behaviour of uranium and  
736 lithium isotopes in an actively glaciated basaltic terrain. *Earth and*  
737 *Planetary Science Letters*, 251: 134–147.

738 Pogge von Strandmann, P.A.E. et al., 2016. The effect of hydrothermal spring  
739 weathering processes and primary productivity on lithium isotopes: Lake  
740 Myvatn, Iceland. *Chemical Geology*, 445: 4–13.

741 Pogge von Strandmann, P.A.E. et al., 2017a. Global climate stabilisation by  
742 chemical weathering during the Hirnantian glaciation. *Geochemical*  
743 *Perspective Letters*, 3: 230–237.

744 Pogge von Strandmann, P.A.E. et al., 2011. Variations of Li and Mg isotope ratios  
745 in bulk chondrites and mantle xenoliths. *Geochimica Et Cosmochimica*  
746 *Acta*, 75: 5247–5268.

747 Pogge von Strandmann, P.A.E., Frings, P.J., Murphy, M.J., 2017b. Lithium isotope  
748 behaviour during weathering in the Ganges Alluvial Plain. *Geochimica Et*  
749 *Cosmochimica Acta*, 198: 17–31.

750 Pogge von Strandmann, P.A.E., Henderson, G.M., 2015. The Li isotope response to  
751 mountain uplift. *Geology*, 43(1): 67–70.

752 Pogge von Strandmann, P.A.E., James, R.H., van Calsteren, P., Gíslason, S.R.,  
753 Burton, K.W., 2008. Lithium, magnesium and uranium isotope behaviour  
754 in the estuarine environment of basaltic islands. *Earth and Planetary*  
755 *Science Letters*, 274(3-4): 462-471.

756 Pogge von Strandmann, P.A.E., Jenkyns, H.C., Woodfine, R.G., 2013. Lithium  
757 isotope evidence for enhanced weathering during Oceanic Anoxic Event 2.  
758 *Nature Geoscience*, 6: 668–672.

759 Pogge von Strandmann, P.A.E. et al., 2012. Lithium, magnesium and silicon  
760 isotope behaviour accompanying weathering in a basaltic soil and pore  
761 water profile in Iceland. *Earth and Planetary Science Letters*, 339–340:  
762 11–23.

763 Pogge von Strandmann, P.A.E. et al., 2014. Chemical weathering processes in the  
764 Great Artesian Basin: Evidence from lithium and silicon isotopes. *Earth*  
765 *and Planetary Science Letters*, 406: 24–36.

766 Pogge von Strandmann, P.A.E. et al., 2017c. Lithium isotopes in speleothems:  
767 Temperature-controlled variation in silicate weathering during glacial  
768 cycles. *Earth and Planetary Science Letters*, 469: 64–74.

769 Renforth, P., Pogge von Strandmann, P.A.E., Henderson, G.M., 2015. The  
770 dissolution of olivine added to soil: Implications for enhanced weathering.  
771 *Applied Geochemistry*, 61: 109–118.

772 Sauzeat, L., Rudnick, R.L., Chauvel, C., Garcon, M., Tang, M., 2015. New  
773 perspectives on the Li isotopic composition of the upper continental crust  
774 and its weathering signature. *Earth and Planetary Science Letters*, 428:  
775 181–192.

776 Sigfusson, B., Gislason, S.R., Paton, G.I., 2008. Pedogenesis and weathering rates  
777 of a Histic Andosol in Iceland: Field and experimental soil solution study.  
778 *Geoderma*, 144(3-4): 572-592.

779 Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure  
780 for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7):  
781 844-851.

782 Vance, D., Teagle, D.A.H., Foster, G.L., 2009. Variable Quaternary chemical  
783 weathering fluxes and imbalances in marine geochemical budgets. *Nature*,  
784 458: 493–496.

785 Vigier, N. et al., 2008. Quantifying Li isotope fractionation during smectite  
786 formation and implications for the Li cycle. *Geochimica Et Cosmochimica*  
787 *Acta*, 72: 780–792.

788 Vigier, N., Gislason, S.R., Burton, K.W., Millot, R., Mokadem, F., 2009. The  
789 relationship between riverine lithium isotope composition and silicate  
790 weathering rates in Iceland. *Earth and Planetary Science Letters*, 287(3-  
791 4): 434–441.

792 Walker, J.C.G., Hays, P.B., Kasting, J.F., 1981. A Negative Feedback Mechanism for  
793 the Long-Term Stabilization of Earths Surface-Temperature. *Journal of*  
794 *Geophysical Research-Oceans and Atmospheres*, 86(NC10): 9776-9782.

795 West, A.J., Galy, A., Bickle, M., 2005. Tectonic and climatic controls on silicate  
796 weathering. *Earth and Planetary Science Letters*, 235(1-2): 211–228.

797 Wimpenny, J. et al., 2015. Lithium isotope fractionation during uptake by  
798 gibbsite. *Geochimica Et Cosmochimica Acta*, 168: 133–150.

799 Wimpenny, J. et al., 2010. The behaviour of Li and Mg isotopes during primary  
800 phase dissolution and secondary mineral formation in basalt. *Geochimica*  
801 *Et Cosmochimica Acta*, 74: 5259-5279.

802 Yokoyama, T., Banfield, J.F., 2002. Direct determinations of the rates of rhyolite  
803 dissolution and clay formation over 52,000 years and comparison with  
804 laboratory measurements. *Geochimica Et Cosmochimica Acta*, 66: 2665–  
805 2681.

806

807

808

809

810

811

Sample	Time days	pH	Na mg/L	Mg mg/L	Al μg/L	Si mg/L	K mg/L	Ca mg/L	Li μg/L	δ <sup>7</sup> Li ‰	2sd
Initial water	0	6.84	48.5	7.87	b.d.l.	2.59	11.1	11.8	13.5	14.7	0.4
15.1	1	6.91	47.8	9.28	8.50	3.19	9.63	11.9	9.9	15.8	0.1
15.2	2	6.86	48.4	9.92	5.58	3.41	9.32	11.5	9.9	16.8	0.5
15.3	4	6.89	48.4	10.6	8.65	3.61	8.95	11.0	8.2	19.6	0.2
15.4	12	7.17	48.6	10.9	11.7	4.22	8.67	10.8	4.7	26.2	0.3
15.5	34	7.60	48.8	11.2	10.7	4.83	8.56	10.6	2.9	31.0	0.2
15.6	68	7.33	48.9	11.2	10.7	5.20	8.46	10.6	2.2	32.7	0.4
15.7	126	7.08	48.7	11.4	12.3	5.71	8.35	10.8	1.6	34.4	0.3
15.8	252	7.04	49.4	11.5	11.7	6.18	8.35	10.8	1.3	33.3	0.3
16.1	1	7.26							9.5	15.4	0.3
16.2	2	7.05							9.5	16.0	0.5
16.3	4	7.13							8.0	19.6	0.6
16.4	12	7.43							4.8	24.1	0.4
16.5	34	7.49							2.8	31.5	0.1
16.6	68	7.29							2.3	33.2	0.1
16.7	126	7.16							1.4	34.9	0.4
16.8	252	7.31							1.4	33.3	0.4

Table 1. Concentration and isotope ratios from the experimental fluids.

812

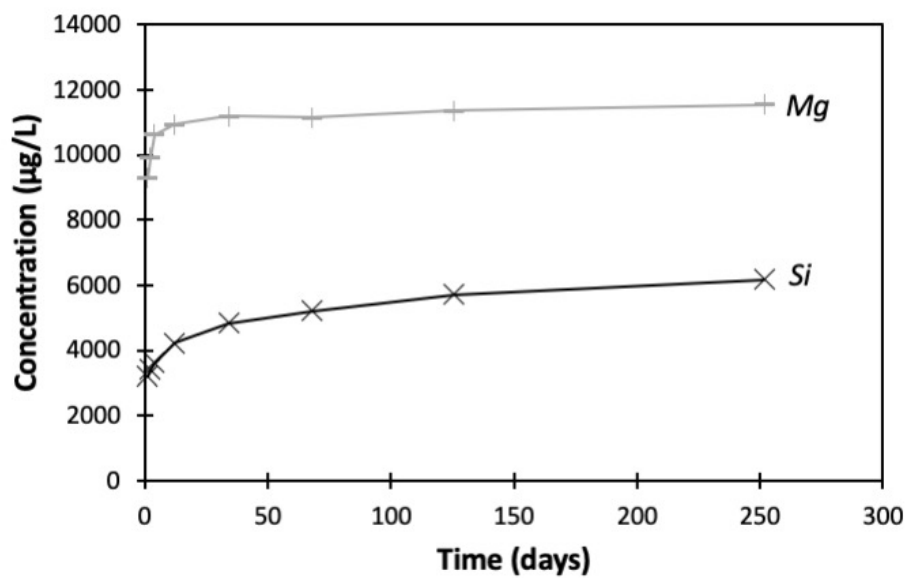
813

Sample	$\delta^{7}\text{Li}$ ‰	2sd	Li in experiment $\mu\text{g}$	Mg/Si	Ca/Si	K/Si	Li/Si	Al/Si	Fe,
Exp 15	21.3	0.4	2.47	9.47	113	12.6	0.030		
Exp 16	21.8	0.5	2.90	8.24	96.4	10.4	0.015		
Unreacted	17.8	0.1	1.10	25.3	104	9.3	0.038		
Exp 15	9.3	0.6	27.5	0.271	0.439	0.014	0.0003	0.567	0.8
Exp 16	10.8	0.1	27.0	0.292	0.426	0.013	0.0002	0.634	0.9
Unreacted	5.3	0.5	17.6	0.294	0.426	0.013	0.0005	0.635	0.9
Exp 15	4.5	0.2	1320						
Exp 16	4.1	0.3	1390						
Unreacted	4.4	0.2	1380	0.269	0.590	0.020	0.00003	0.358	0.5

Table 2. Li amounts and isotope ratios, as well as elemental ratios, from the different

leached and bulk phases. Sec. mins. stands for secondary minerals.

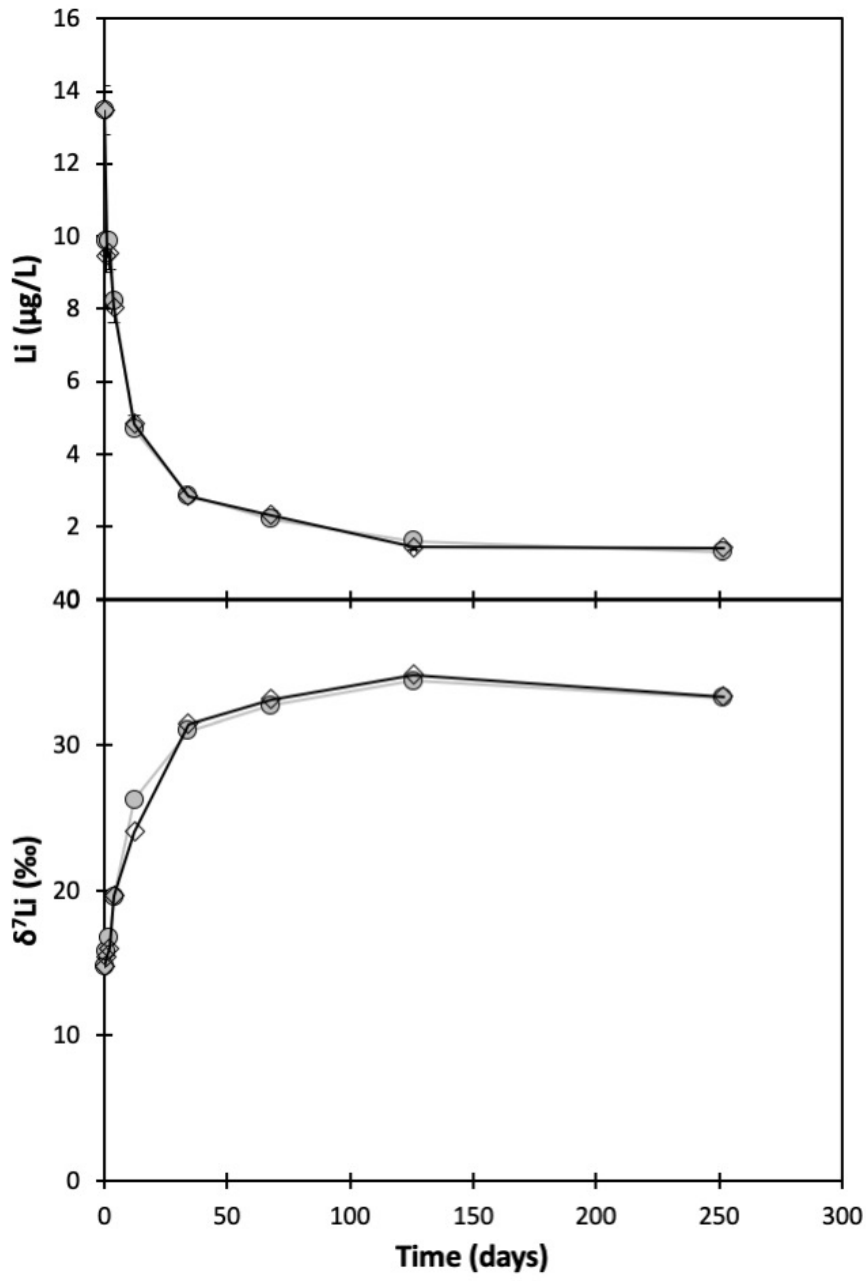
814



815

816 Figure 1. Measured aqueous Mg and Si concentrations during the experiment.

817 Analytical uncertainty is smaller than the symbol sizes.

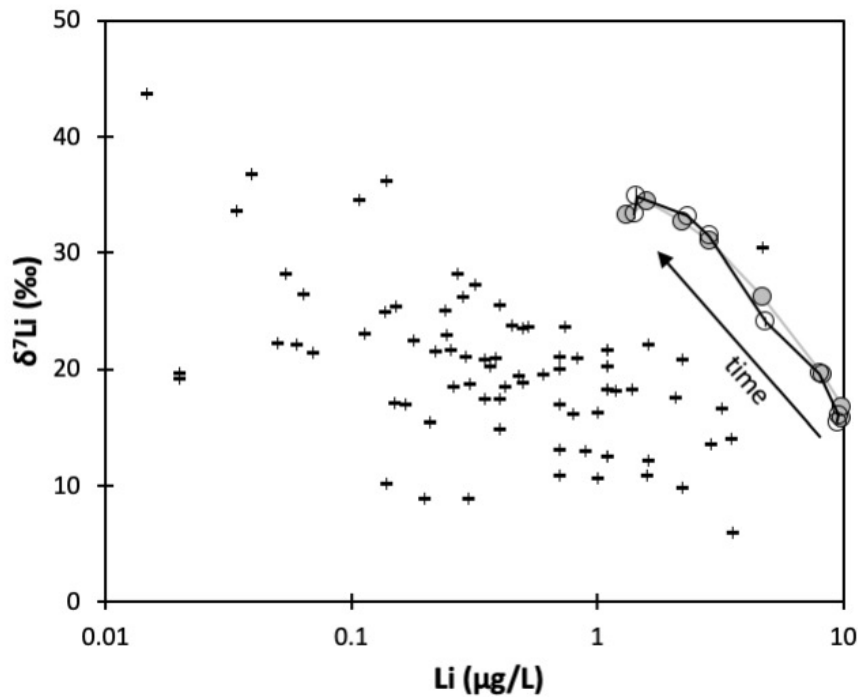


818

819 Figure 2. Solution Li concentrations and isotope ratios with time throughout the  
 820 experiment. The open diamonds and filled circles represent the two different  
 821 experiments. Analytical uncertainty is smaller than the symbol sizes.

822





823

824 Figure 3. Measured Li isotopes ratios of the fluid phase from both experiments as

825 a function of the corresponding Li concentration. The grey and black lines

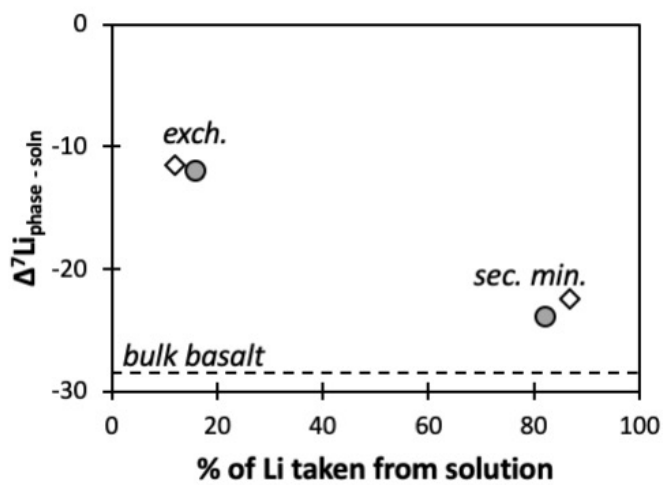
826 represent the two experiments. The black crosses are natural basaltic river

827 studies (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von

828 Strandmann et al., 2006; Vigier et al., 2009). Analytical uncertainty is smaller

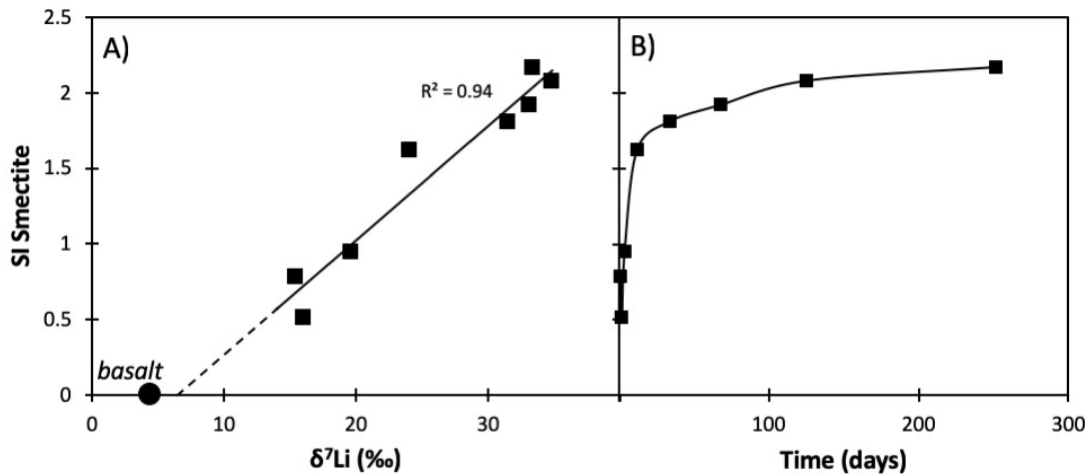
829 than the symbol sizes.

830



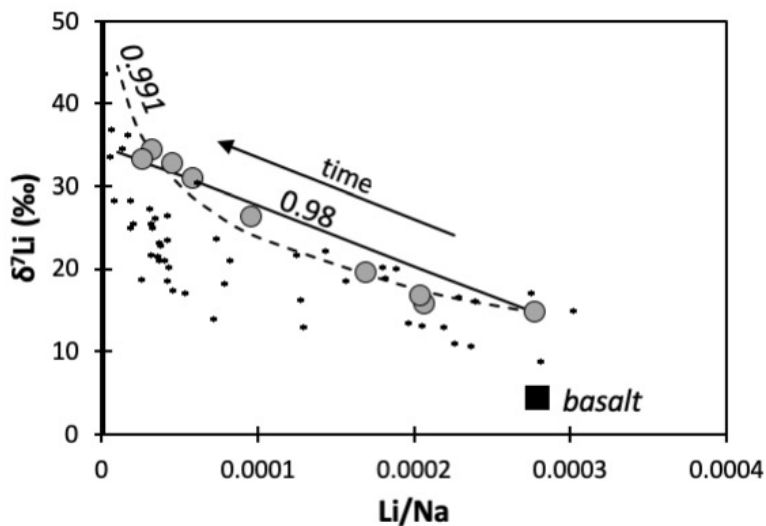
831

832 Figure 4. The mass balance of Li removed from solution by the different phases,  
 833 relative to the isotope fractionation from the experimental solution. The filled  
 834 circles represent Experiment 15, and the open diamonds Experiment 16.



835

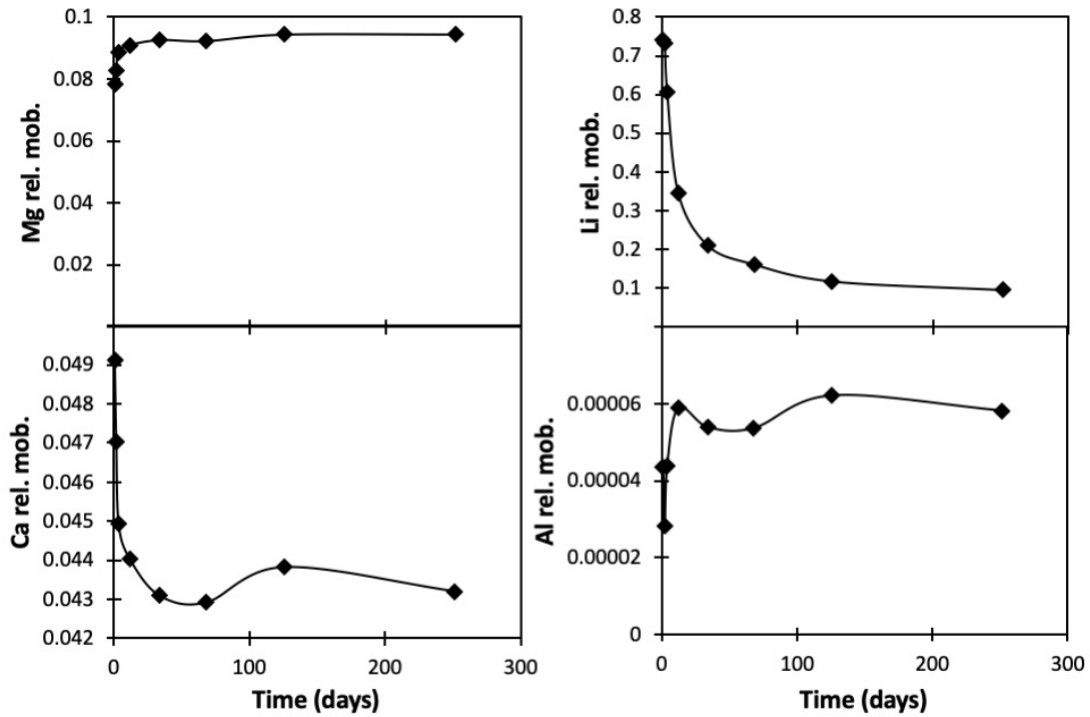
836 Figure 5. A) Li isotopes in solution as a function of PHREEQC-modelled smectite  
 837 saturation index. The dotted line is the extrapolated trend line to saturated  
 838 conditions. B) Trend of smectite saturation index with time during the  
 839 experiment.



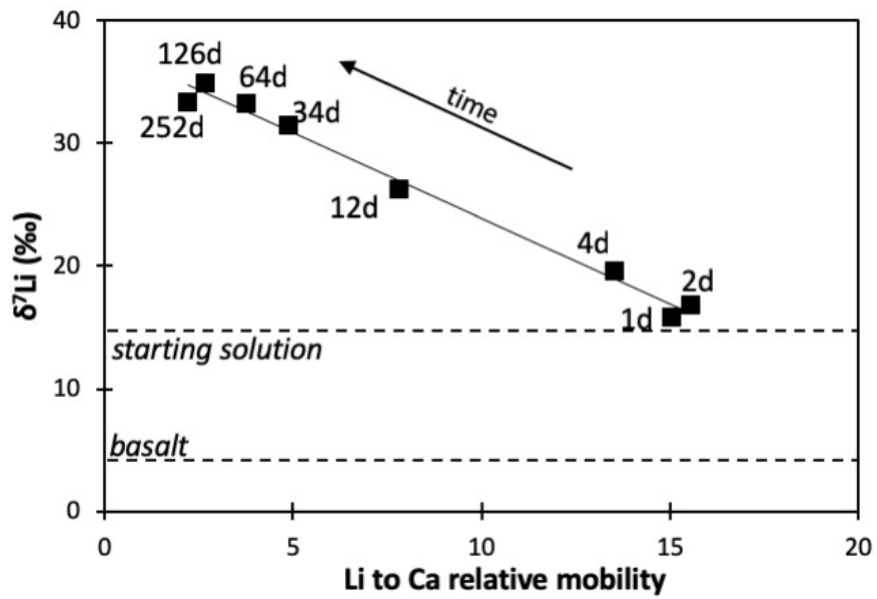
840

841 Figure 6. Experiment fluid δ⁷Li as a function of corresponding mass Li/Na ratio  
 842 (grey circles). The dotted illustrates a Rayleigh fractionation relationship, while  
 843 the solid line represents an equilibrium fractionation relationship. The numbers

844 next to the lines are the isotopic fractionation factors. The black crosses are  
845 natural basaltic river studies (Liu et al., 2015; Pogge von Strandmann et al., 2010;  
846 Pogge von Strandmann et al., 2006; Vigier et al., 2009). Analytical uncertainty is  
847 smaller than the symbol sizes.  
848



849  
850 Figure 7. Relative mobility (relative to Na) of Mg, Li, Ca and Al with time through  
851 the experiment. Note different scale on axes.  
852



853

854 Figure 8. The reactive fluid Li isotopes ratio compared to the relative mobility of

855 Li to Ca. The numbers next to each data point represent the experimental time

856 (in days). Analytical uncertainty is smaller than the symbol sizes.

857

858

859

860

861