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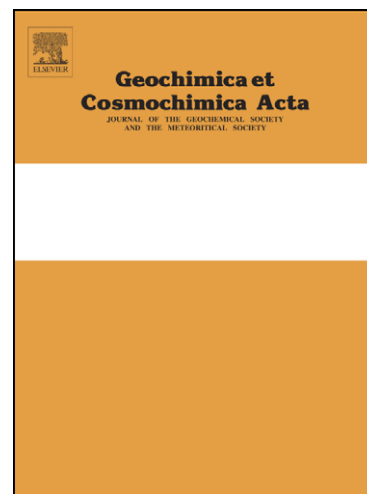
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1 Experimental determination of the role of diffusion on Li isotope fractionation  
2 during basaltic glass weathering

3

4

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17 Keywords: Li isotopes, isotope fractionation, diffusion, basaltic glass

18 **Abstract**

19

20 In order to use lithium isotopes as tracers of silicate weathering, it is of primary  
21 importance to determine the processes responsible for Li isotope fractionation and to  
22 constrain the isotope fractionation factors caused by each process as a function of  
23 environmental parameters (e.g. temperature, pH). The aim of this study is to assess Li isotope  
24 fractionation during the dissolution of basalt and particularly during leaching of Li into  
25 solution by diffusion or ion exchange. To this end, we performed dissolution experiments on a  
26 Li-enriched synthetic basaltic glass at low ratios of mineral surface area/volume of solution  
27 (S/V), over short timescales, at various temperatures (50 and 90°C) and pH (3, 7, and 10).  
28 Analyses of the Li isotope composition of the resulting solutions show that the leachates are  
29 enriched in  ${}^6\text{Li}$  ( $\delta^7\text{Li} = +4.9$  to  $+10.5\text{‰}$ ) compared to the fresh basaltic glass ( $\delta^7\text{Li} = +10.3 \pm$   
30  $0.4\text{‰}$ ). The  $\delta^7\text{Li}$  value of the leachate is lower during the early stages of the leaching process,  
31 increasing to values close to the fresh basaltic glass as leaching progresses. These low  $\delta^7\text{Li}$   
32 values can be explained in terms of diffusion-driven isotope fractionation. In order to quantify  
33 the fractionation caused by diffusion, we have developed a model that couples Li diffusion  
34 with dissolution of the glassy silicate network. This model calculates the ratio of the diffusion  
35 coefficients of both isotopes ( $a=D_7/D_6$ ), as well as its dependence on temperature, pH, and  
36 S/V.  $a$  is mainly dependent on temperature, which can be explained by a small difference in  
37 activation energy ( $0.10 \pm 0.02$  kJ/mol) between  ${}^6\text{Li}^+$  and  ${}^7\text{Li}^+$ . This temperature dependence  
38 reveals that Li isotope fractionation during diffusion is low at low temperatures ( $T < 20^\circ\text{C}$ ),  
39 but can be significant at high temperatures. However, concerning hydrothermal fluids ( $T >$   
40  $120^\circ\text{C}$ ), the dissolution rate of basaltic glass is also high and masks the effects of diffusion.  
41 These results indicate that the high  $\delta^7\text{Li}$  values of river waters, in particular in basaltic

42 catchments, and the fractionated values of hydrothermal fluids are mainly controlled by  
43 precipitation of secondary phases.

ACCEPTED MANUSCRIPT

44

**1. INTRODUCTION**

45

46 Silicate weathering has a major impact on the carbon cycle over long timescales,  
47 because Ca and Mg are released during dissolution of silicate minerals which in turn leads to  
48 consumption of atmospheric carbon dioxide via formation of carbonate in the oceans (e.g.  
49 Ludwig et al., 1999; Dupré et al., 2003; Lerman et al., 2007; Franck et al., 2008; Hartmann et  
50 al., 2009). Basalt are among the most easily weathered silicate rocks, therefore basalt  
51 weathering potentially represents a significant atmospheric CO<sub>2</sub> sink and a major source of  
52 oceanic Ca and Mg (Louvat and Allègre, 1997, 1998; Gaillardet et al., 1999; Dessert et al.,  
53 2003). Assessing the contribution of basaltic weathering to rivers is therefore of primary  
54 importance. A significant portion of basalt weathering is likely due to alteration of basaltic  
55 glass: the glassy phase and hyaloclastites have been shown to play a key role in determining  
56 the chemical and isotope compositions of river waters in volcanic regions (e.g. Gislason and  
57 Oelkers, 2003, and references therein; Wolff-Boenisch et al., 2004; Vigier et al., 2006). This  
58 is consistent with their more rapid dissolution relative to basalt minerals (e.g. Wolff-Boenisch  
59 et al., 2006).

60 In this context, lithium isotopes could represent a powerful tracer of basalt weathering  
61 as river Li isotope compositions appear to be correlated with weathering rates of silicate  
62 lithologies present within the basin (Kisakürek et al., 2005; Vigier et al., 2009; Pogge von  
63 Strandmann et al., 2010; Millot et al., 2010b). Lithium has two stable isotopes, <sup>6</sup>Li and <sup>7</sup>Li,  
64 whose large relative mass difference is responsible for significant isotopic fractionation  
65 during physico-chemical processes. Lithium is comparatively enriched in silicates (5 to 33  
66 ppm for the continental crust, Teng et al, 2008) but is present at low concentrations in  
67 carbonates (< 2 ppm, Hoefs and Sywall, 1997). Moreover, this element does not play a  
68 significant role in biological or atmospheric cycles (Lemarchand et al., 2010; Millot et al.,

69 2010c). The Li isotope compositions of catchment rocks and river waters are significantly  
70 different with rivers systematically enriched in  $^7\text{Li}$ . To date, this has been interpreted as the  
71 result of Li isotopic fractionation during silicate weathering (Huh et al., 1998, 2001; Pogge  
72 von Strandmann et al., 2008, 2010; Vigier et al., 2009; Millot et al., 2010a). In more detail,  
73 the  $^7\text{Li}$  enrichment of dissolved loads of river waters has been explained by (1) the formation  
74 of secondary phases, especially clay minerals, and their preferential uptake of  $^6\text{Li}$  (e.g. Chan  
75 and Edmond, 1988; Chan et al., 1992; Vigier et al., 2008) and (2) a preferential release of  $^7\text{Li}$   
76 from the mineral into solution (Huh et al., 2004; Kısakürek et al., 2004; Rudnick et al., 2004;  
77 Teng et al., 2004). This second assumption was supported by the particularly high  $\delta^7\text{Li}$  values  
78 ( $\delta^7\text{Li} = ((^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{LSVEC}} - 1) \times 1000$ ) measured in river waters draining areas  
79 with little or no soils, such as the Canadian shield (Millot et al., 2010b) or high altitude zones  
80 in the Andes and the Himalayas (Huh et al., 2001; Kısakürek et al., 2005).

81 Preferential uptake of  $^6\text{Li}$  during the formation of clay minerals was initially suggested  
82 by field studies (e.g. Chan and Edmond, 1988; Chan et al., 1992, 1994, 2002; Zhang et al.,  
83 1998) and then confirmed by experimental work (e.g. Williams and Hervig, 2005; Vigier et  
84 al., 2008; Pistiner and Henderson, 2003). In contrast, preferential release of  $^7\text{Li}$  during  
85 weathering of minerals has not been verified in the laboratory. Leaching experiments have  
86 been performed with basalt, weathered basalt and sediments at high temperatures (up to  
87  $350^\circ\text{C}$ ) and pressures (400-800 bars) with the aim of assessing the contributions of basalt  
88 and/or sediment leaching to the Li budget during alteration in hydrothermal systems (Chan et  
89 al., 1994; Seyfried et al., 1998, James et al., 2003). These authors reported fluid  $\delta^7\text{Li}$  values  
90 initially heavier than those of the mineral but then progressively becoming lighter  
91 (approaching that of the starting mineral). All these experiments were conducted under rock-  
92 dominated conditions (i.e. high reactive surface area/volume of solution, S/V, or low  
93 water/rock ratio, W/R). These conditions greatly favour the formation of secondary mineral

94 phases which could also influence the Li isotopic compositions measured in solution.  
95 Experiments conducted by Millot et al. (2010a) were carried out at lower temperatures (25 to  
96 250°C), but also at relatively low W/R ratio, with the intention of precipitating secondary  
97 phases even at the onset of the experiment. Pistiner and Henderson (2003) performed basalt  
98 alteration experiments at low pH (~ 1) and low S/V (to avoid precipitation of secondary  
99 minerals), and did not observe any significant isotope fractionation after 1 week of  
100 dissolution. Finally, recent forsterite and basalt glass dissolution experiments were conducted  
101 by Wimpenny et al. (2010) at far from equilibrium conditions and at low pH and temperature.  
102 The results revealed no isotope fractionation during leaching of forsterite. For the basalt glass  
103 the  $\delta^7\text{Li}$  values of the leachates produced by weathering are equal or slightly lower than the  
104 fresh glass  $\delta^7\text{Li}$  value.

105 In this study, we performed leaching experiments on basaltic glass at far from  
106 equilibrium conditions in order to favour leaching/dissolution processes, and to minimise any  
107 potential secondary mineral precipitation. The objective is to quantify Li isotopic  
108 fractionation during the leaching/dissolution process. To this end, the experiments were  
109 conducted at very low S/V ratios (i.e. very high water/rock ratio). The basaltic glass was  
110 highly enriched in lithium in order to permit precise measurements of Li isotope in the  
111 leachates during the early stages of the alteration process. By combining major element and  
112 Li isotope data, we have developed a coupled diffusion-dissolution model which quantifies Li  
113 isotope fractionation.

114

## 115 **2. EXPERIMENTAL METHODS AND ANALYTICAL PROCEDURES**

116

### 117 **2.1. Experimental setup**

118



119 *2.1.1. Materials*

120 A synthetic basaltic glass was doped with 1% Li<sub>2</sub>O using the procedure described in  
121 Techer et al. (2001), i.e. by melting a mixture of powdered oxides, carbonates, nitrates and  
122 phosphates in alumina crucibles for 3 h at 1500°C. The resulting melt was then poured into  
123 graphite crucibles preheated at 700°C. The glass was heat treated at 670°C for 1 h, then  
124 cooled to room temperature in 10 h. Concentrations of major cations (Si, Al, Fe, Mn, Mg, Ca,  
125 Na K, Ti, and P) were determined by ICP-AES (IRIS Thermo Elemental) at the SARM  
126 (French national facilities, Nancy). Li concentrations were analyzed using atomic absorption  
127 spectrometry (AAS) (VARIAN220 FS) at the SARM. Uncertainties range between 5 and 20%  
128 depending on the element and its concentration.

129 The homogeneity of Li isotopic composition of the glass was determined by ion  
130 microprobe (CAMECA ims3f), using classical energy filtering techniques (Chaussidon and  
131 Robert, 1998). The samples were sputtered with a 3nA primary O<sup>-</sup> beam then secondary  
132 positive ions including <sup>6</sup>Li<sup>+</sup> and <sup>7</sup>Li<sup>+</sup> were accelerated at 4.5 kV and were analysed at a mass  
133 resolution M/ΔM of 1200 (to remove the interfering <sup>6</sup>LiH<sup>+</sup> at mass 7) and with the energy slit  
134 centred and fully opened. Counting times were 9s for <sup>6</sup>Li and 3s for <sup>7</sup>Li over 40 cycles.

135

136 *2.1.2. Reactive surface area determination*

137 The synthetic basaltic glass was ground and sieved in order to recover the 40-100 μm  
138 particle size fraction which was then washed and ultrasonicated in acetone in order to remove  
139 any finer particles remaining. The glass powder was stirred in a beaker containing 12 cm  
140 depth of acetone. According to Stokes' law, >40 μm particles reach the bottom of the beaker  
141 in 15 s; after this time, the supernatant solution is removed from the beaker. This procedure  
142 was repeated until the supernatant was clear. The specific surface area was measured by  
143 krypton adsorption using the BET method and is 842 ± 5 cm<sup>2</sup> g<sup>-1</sup>. To assess the consistency of

144 this result, the BET value was compared with the geometric surface area (in  $\text{cm}^2 \text{g}^{-1}$ ) which  
 145 can be expressed as the product of the surface area of a sphere ( $S_{\text{sphere}}$ ) by the number of  
 146 spheres ( $n$ ) divided by the mass ( $m$ ) of the  $n$  spheres:

147

$$148 \quad S_{\text{geo}} = \frac{n \times S_{\text{sphere}}}{m} = \frac{n \times 4\pi r^2}{n \times \frac{4}{3}\pi r^3 \times \rho} = \frac{3}{\rho \times r} \quad (1)$$

149

150 where  $\rho$  is the density of the glass ( $2.7 \pm 0.1 \text{ g cm}^{-3}$ , measured by pycnometry) and  $r$  is the  
 151 grain average radius (in cm). While Eq. (1) yields a geometric surface area of  $350 \text{ cm}^2 \text{g}^{-1}$  that  
 152 is 2.4 times lower than the measured surface area these results are nevertheless consistent  
 153 because surface roughness and the non-spherical nature of the grains will increase true surface  
 154 area compared to that calculated by Eq. (1).

155

### 156 2.1.3. Experiments

157 The objective of the experiments (PW-90, PH3-90, PH10-90, and PW-50; Table 1)  
 158 was to determine the evolution of Li concentration and isotopic composition of the leachate at  
 159 'far from equilibrium' conditions. For this, these experiments were carried out in Savillex®  
 160 PTFE reactors under static conditions, at a low S/V ratio ( $0.7 \text{ cm}^{-1}$ ) and over short timescales  
 161 ( $< 4$  days). The batch solution was not stirred in order to prevent grinding of the glass and  
 162 progressive increase of the reactive surface area. However, the mass of glass introduced in the  
 163 reactor is sufficiently low ( $\sim 50$  mg for the majority of experiments) so that transport processes  
 164 are never rate-limiting.

165 For the experiments performed in pure water (Milli-Q water) (PW) at 90 and 50°C  
 166 (PW-90 and PW-50), a separate reactor was used for each run. Typically, 50 mg of glass  
 167 powder was placed in the Savillex® PTFE reactors with 50 mL of solution. For the other

168 experiments, one single larger reactor (120 or 250 mL) was used. Each time the solution was  
169 sampled, the reactor was manually agitated and opened for a maximum of a few minutes.

170 The pH was measured at the in situ temperature. However, the temperature of the  
171 sampled aliquot can rapidly decrease during pH measurements. Consequently, the  
172 temperature was also monitored during the pH measurement for calculations. The samples  
173 were filtered at 0.45  $\mu\text{m}$ , and then acidified with concentrated  $\text{HNO}_3$  to obtain 0.3 N  $\text{HNO}_3$   
174 for ICP-AES and AAS analyses.

175 Both the influence of pH (pure water, pH 3 and pH 8.4 at 90°C) and temperature (50  
176 and 90°C) were tested. An initial pH of 3 was obtained by addition of 0.001 M HCl, and an  
177 initial pH of 8.4 at 90°C was obtained by addition of 0.0001 M NaOH. In order to determine  
178 the influence of the S/V ratio, two leaching experiments were carried out with pure water at  
179 90°C, with a S/V ratio of 0.7 and 7  $\text{cm}^{-1}$  respectively, simply by changing the amount of glass  
180 powder initially introduced into the beaker (experiments SV1 and SV2, respectively, see  
181 Table 1).

182

## 183 2.2. Li isotope analyses

184

185 In order to analyse the Li isotopic composition of the synthetic basaltic glass, the  
186 complete dissolution of ~ 10 mg of glass was performed using a mixture of concentrated  
187 hydrofluoric and nitric acids heated on a hotplate at 100°C, in a closed Teflon beaker for 1  
188 day. The solutions were then evaporated, re-dissolved in 1M HCl, and ultrasonicated.

189 For analysis of the leachate samples, an aliquot containing 30 - 60 ng of Li was  
190 evaporated and re-dissolved in 1 M HCl.

191 Li was separated from the sample matrix by cation exchange chromatography, as  
192 described in Vigier et al. (2008) and Lemarchand et al. (2010). Li isotopes were measured on

193 pure Li fractions with a Thermo-Fisher Neptune Multi Collector-ICP-MS at the BRGM  
194 (Orléans, France) (Millot et al., 2004 ), and with a Nu Instruments Multi Collector-ICP-MS at  
195 the ENS (Lyon, France). Li isotope ratios were measured relative to the L-SVEC standard  
196 solution (NIST SRM 8545, Flesch et al., 1973) using a standard-sample bracketing technique  
197 in order to correct for instrumental mass bias. Li isotope ratios are expressed in  $\delta$  notation as  
198 the part per thousand (‰) deviation from L-SVEC composition.

199 For MC-ICP-MS measurements with the Neptune (BRGM), the analytical protocol  
200 involved acquisition of 15 ratios with 16 s integration time per ratio, and yielded in-run  
201 precision better than 0.2‰ ( $2\sigma$ ). Blank values were low (i.e. 0.2‰ of the Li signal) and 5  
202 minutes wash time was sufficient to reach a stable background value. The Li concentration in  
203 solution required for analysis was 30 ppb. The accuracy and reproducibility of the whole  
204 method (separation + MC-ICP-MS analysis) was tested by repeated measurements of a  
205 seawater standard solution (IRMM BCR-403, Millot et al., 2004) and the Li7-N reference  
206 solution (Carignan et al., 2007) (Table 2).

207 The Li isotopic compositions we determined for Li7-N and seawater BCR-403 were  
208  $+30.8 \pm 0.5$  ‰ ( $n = 10$ ) and  $+31.3 \pm 0.4$  ‰ ( $n = 10$ ), respectively, which are in agreement  
209 with published values (Millot et al., 2004; Carignan et al., 2007 and references therein). The  
210 accuracy and reproducibility of the MC-ICP-MS analysis (without separation chemistry) was  
211 also assessed during the session with two standards, Li7-N and Li-6N (Carignan et al., 2007).  
212 The average values are  $\delta^7\text{Li} = +30.3 \pm 0.2$  ‰ ( $n = 10$ ) for Li7-N and  $\delta^7\text{Li} = -8.1 \pm 0.3$  ‰ ( $n =$   
213  $10$ ) for Li6-N, and are similar to values reported in the literature (Carignan et al., 2007).

214 For both sessions of MC-ICP-MS measurements with the Nu Instruments (ENS-  
215 Lyon), the typical Li concentration of the analysed solutions was 60 ppb. The accuracy and  
216 reproducibility of the method was tested with the JB-2 basalt standard (Table 2). The  $\delta^7\text{Li}$   
217 value of JB-2 is  $+4.0 \pm 0.3$  ‰ ( $n = 1$ ) which is consistent with published values (e.g. Carignan

218 et al., 2007). The values of the three standards, SW BCR403, Li7-N, and Li6-N, are also in  
219 agreement with previously reported values (Table 2). Reference solutions were also analysed  
220 at reduced concentrations in order to assess the reproducibility and the confidence in  
221 measuring lower concentration solutions (Table 2). The  $\delta^7\text{Li}$  of SW BCR403 at 15 ppb is  
222  $+30.5 \pm 0.7 \text{ ‰}$  ( $n = 2$ ). The  $\delta^7\text{Li}$  of Li7-N (10 to 40 ppb) does not change significantly as a  
223 function of Li content. However, the corresponding internal errors are higher when the Li  
224 concentrations are lower (see Table 2).

225

### 226 **2.3. Calculation of solution saturation states**

227

228 Analyses of the chemical composition and temperature measurements of the leachate  
229 solutions can be used to calculate mineral saturation indices using the JCHESS speciation  
230 code (van der Lee and De Windt, 2002). JCHESS uses a thermodynamic database which is  
231 based on the EQ3/6 database (Wolery, 1992). Because of the rapid cooling (around 75°C) of  
232 the solution during the pH measurements, the solution pH was recalculated from the major  
233 cation concentrations, by assuming electroneutrality at the measurement temperature. If the  
234 agreement between the measured pH and the calculated value is good, then both the solution  
235 analyses and the pH measurements are valid. The solution pH at the temperature of the  
236 experiment (90 or 50°C) was recalculated by changing the temperature in JCHESS.

237

238

## 3. RESULTS

239

### 240 **3.1. Composition of the fresh synthetic basaltic glass**

241

242 The composition of the synthetic basaltic glass is given in Table 3. Its composition is  
243 consistent with published analyses for the same glass (Techer et al., 2001). Except for the  
244 enrichment in Li, the composition is typical of basalt from mid-ocean ridges (MORB) (e.g.  
245 Schiano et al., 1997).

246 The bulk Li isotopic composition of the fresh synthetic basaltic glass was determined  
247 for 3 different powder aliquots by MC-ICP-MS and is  $+10.3 \pm 0.4 \text{ ‰}$  ( $2\sigma$ ). The homogeneity  
248 of the glass Li isotopic composition was also determined by ion microprobe. The standard  
249 deviation of 34 measurements in 2 different grains is  $0.7\text{‰}$ . The standard deviation of the  
250 GB4 glass standard (Chaussidon and Robert, 1998) analysed during the same session is  $0.4\text{‰}$   
251 ( $n=7$ ). The synthetic basaltic glass used for the alteration experiments is therefore considered  
252 to be isotopically homogeneous, relative to the overall uncertainty of the Li isotope  
253 measurements.

254

### 255 **3.2. pH and chemical composition of the leachates**

256

257 At  $90^\circ\text{C}$ , the agreement between measured and calculated pH (from major elements)  
258 was good. For example, the pH measured at  $75^\circ\text{C}$  for the PH10-90 experiment after 1 day was  
259 8.5. The pH calculated from elemental concentrations in solution is also 8.5 at  $75^\circ\text{C}$ . Thus the  
260 pH recalculated at the temperature of the experiment, i.e.  $90^\circ\text{C}$ , is 8.3 (see Table 4). For this  
261 experiment the difference between experimental and calculated pH at the measurement  
262 temperature is never higher than 0.1 pH unit. For the other experiments, the difference is  
263 always less than 0.3 pH unit, except for the fluid sampled towards the end of the experiments  
264 (34 d for pH3-90, 63 d for experiments SV1 and SV2) where the discrepancy reaches 0.7 pH  
265 unit, probably because of carbonation effects that decrease the measured pH.

266 For experiments performed in pure water at 90°C (PW-90, SV1, SV2), the pH rapidly  
267 increases to 8.5-9. For the experiment PH10-90, the initial pH of 8.4 remains more or less  
268 constant. In the experiments with dilute nitric acid, the pH starts at a value of 3 and then does  
269 not evolve significantly, except at 34 days. In the experiment performed at 50°C, pH increases  
270 from 6.6 to 7.7 (Table 4).

271 The evolution of the silicon concentration in solution (Table 4, Fig. 1a) is quite similar  
272 for all of the experiments performed at 90°C. The Si content increases linearly as a function  
273 of time, as expected by a pure and constant dissolution process, and then reaches a plateau at  
274 around 15-18 mg L<sup>-1</sup> after a few days. It is noteworthy that lithium concentration is not a  
275 linear function of time, and the pattern is different for different experiments (Table 4, Fig 1b).  
276 Solution lithium contents are lower for experiments at S/V=0.7 cm<sup>-1</sup> than they are for  
277 experiments with S/V = 7 cm<sup>-1</sup>.

278 In order to compare the behaviour of all the analysed elements in more detail,  
279 concentrations can be converted to the normalized mass loss ( $NL(i)$ ).  $NL(i)$  corresponds to the  
280 concentration  $C_i$  in solution (where  $i$  is the element analyzed) in g L<sup>-1</sup> corrected for the S/V  
281 ratio and the initial glass mass fraction.  $NL(i)$  is expressed in g m<sup>-2</sup> and is given by:

282

$$283 \quad NL(i) = \frac{C_i \times V}{S \times x_i} \quad (2)$$

284

285 where  $x_i$  is the initial fraction of the element  $i$  in the bulk glass.

286  $NL(i)$  therefore represents the equivalent quantity of leached glass per unit area.  
287 Consequently, the NL notation allows a direct comparison of each element ( $i$ ) released into  
288 solution for all the experiments. Indeed, if the NL values are equal for all elements, then  
289 dissolution can be considered to be congruent. In contrast, if the NL value of a particular  
290 element is higher or lower than the NL values for silicon, then the element is probably

291 affected by processes in addition to dissolution, such as diffusion or secondary phase  
292 formation.

293 The NL values based on all the elements analysed in this study are reported in Table 5.  
294 For the experiment PW-90, Al, Ca, and Mg releases are congruent with Si release, as they all  
295 display similar NL values (Fig. 2). Ca and Mg are modifier cations in silicate network,  
296 whereas Al and Si are network-forming cations. However, under the experimental conditions  
297 used in this study, their behaviour is similar, indicating negligible formation of secondary  
298 minerals. The alkalis (Na and Li) are mobile elements and their rates of release are greater  
299 than Si, as NL values for Na and Li are systematically higher (Table 5). Their behaviour is  
300 clearly non-stoichiometric. All the experiments display this discrepancy ( $NL(Li,Na) >$   
301  $NL(Si)$ ), except for the experiment at pH 3, where the dissolution is nearly congruent for  
302 alkalis as well.

303

### 304 **3.3. Alteration kinetics of the basaltic glass**

305

306 The release of Si into solution is caused by hydrolysis of the glass network (Bunker,  
307 1994; Oelkers, 2001). The dissolution rate intrinsically depends on the properties of the glass  
308 (composition, structure, etc.), but also on the chemistry of the solution. Two kinetic regimes  
309 can be distinguished: (1) The 'initial' or 'forward' dissolution rate is measured if the solution is  
310 sufficiently renewed or diluted. Under these conditions, the evolution of Si concentrations in  
311 solution (and therefore  $NL(Si)$ ) is linear as a function of time, as observed in the first few  
312 hours of the experiments (Fig. 2). (2) The dissolution rate drops as the solution chemical  
313 composition approaches equilibrium (e.g. Aagard and Helgeson, 1982), and a gel layer forms  
314 at the surface of the glass (e.g. Frugier et al., 2008). The accumulation of elements in solution,  
315 especially silicon, decreases the dissolution rate, as it reduces the chemical affinity between



316 the solution and the glass. This chemical affinity term is a parameter often used in kinetic  
317 laws describing glass alteration (Grambow, 1985; Berger et al., 1994; Daux et al., 1997;  
318 Frugier et al., 2009; Verney-Carron et al., 2010). The release of dissolved elements in solution  
319 may also lead to the formation of secondary minerals. If this is the case, the dissolution  
320 becomes incongruent.

321

### 322 3.3.1. Glass dissolution rate

323 For the experiment in pure water at 90°C (PW-90), the evolution of NL(Si) as a  
324 function of time is constant between 0 and 0.6 days (Fig. 2). For the experiment in pure water  
325 at 50°C (PW-50), the Si release rate is constant for the whole duration of the experiment (2  
326 days). In both cases, the corresponding initial dissolution rate ( $r_0$ ) normalized to the Si content  
327 can be determined by linear regression of the data (Fig. 3a):

328

$$329 \quad r_0 = \frac{dNL(Si)}{dt} \quad (3)$$

330

331 The 'initial' dissolution rate  $r_0$  is thus estimated to be 0.927 g/m<sup>2</sup>/d, i.e.  $3.8 \times 10^{-7}$  mol Si/m<sup>2</sup>/s  
332 at 90°C and pH 8.6, and 0.0062 g/m<sup>2</sup>/d, i.e.  $2.6 \times 10^{-9}$  mol Si/m<sup>2</sup>/s at 50°C and pH 6.6 (Fig.  
333 3a). These values are consistent with published data obtained at similar pH and temperatures  
334 although it should be noted that there are large differences among basaltic glass dissolution  
335 rate estimates reported in the literature (mainly caused by difficulties assessing the reactive  
336 surface area). Initial dissolution rates for basaltic glass at pH between 8.2 and 8.6, and at  
337 temperatures between 90°C and 100°C, range between  $1.1 \times 10^{-8}$  and  $9.8 \times 10^{-7}$  mol Si/m<sup>2</sup>/s  
338 (Guy and Schott, 1989; Daux et al., 1997; Techer et al., 2000; Gislason and Oelkers, 2003).  
339 At 50°C, the initial rate at neutral pH ranges between  $2.1 \times 10^{-10}$  and  $1.9 \times 10^{-8}$  mol Si/m<sup>2</sup>/s  
340 (Guy and Schott, 1989; Gislason and Oelkers, 2003).

341 For the experiment in pure water at 90°C (PW-90), the Si release rate slows down after  
342 0.6 days (Fig. 2). The corresponding dissolution rate calculated by linear regression is 0.08  
343  $\text{g m}^{-2} \text{d}^{-1}$  between 0.6 and 4 days, i.e. one order of magnitude lower than the initial dissolution  
344 rate ( $r_0$ ). A similar feature is observed for the other experiments after a few hours (Table 4).  
345 This highlights the feedback effect of the solution chemistry, especially dissolved silicon, on  
346 glass dissolution kinetics (Aagard and Helgeson, 1982). For longer times ( $> 15$  days), in  
347 experiments SV1, SV2, pH3-90, and pH10-90, Si concentrations reach a plateau, which is  
348 around 15-18  $\text{mg L}^{-1}$  for experiments performed at 90°C. This plateau was also observed by  
349 Techer et al. (2001) under similar conditions (pure water, 90°C,  $S/V = 0.5 \text{ cm}^{-1}$ ) and likely  
350 corresponds to a saturation state of the solution, i.e. to a decrease of the chemical affinity  
351 term, and to secondary phase precipitation. The solution is still thermodynamically  
352 undersaturated relative to silica phases, but is close to the solubility product of quartz (i.e. 19  
353  $\text{mg L}^{-1}$  at 90°C and  $\text{pH} < 9.2$ ).

354 As discussed previously, the formation of secondary phases can be assessed by  
355 comparing the normalized mass losses (NL). Iron forms oxides or hydroxides, whose  
356 solubilities are very low, and  $\text{NL}(\text{Fe})$  is much lower than  $\text{NL}(\text{Si})$ . Generally, Si, Al, Mg, and  
357 Ca are able to be incorporated into secondary minerals, especially smectites, which are  
358 frequently associated with basaltic glass alteration at these temperatures (Stroncik and  
359 Schmincke, 2001; Crovisier et al., 2003). However, the relative difference between NL for  
360 Ca, Al, Mg, and Si in all the experiments performed in this study is never more than 25%,  
361 which is close to analytical uncertainties. Solution saturation indices have been calculated  
362 using JCHESS in order to assess the potential formation of secondary minerals. In solutions  
363 where Al concentrations were below detection limits, the leachates are undersaturated relative  
364 to all the minerals of the database. The leachates where Al concentrations could be measured  
365 are over-saturated relative to Al (oxi-)hydroxides (boehmite, diaspore, gibbsite), kaolinite

366 (rarely observed as an alteration product of the basaltic glass), and smectites for the  
 367 experiments at alkaline pH (pH10-90). It is therefore possible that smectites formed during  
 368 our experiments but in insufficient quantity to significantly affect the congruency of the  
 369 dissolution, or to be observed by SEM.

370

### 371 3.3.2. *Li apparent diffusion coefficients*

372 The behaviour of the alkalis is non-stoichiometric for the first leaching steps of most  
 373 experiments: the release rate of these elements is higher than that of Si, as witnessed by their  
 374 greater normalized mass losses. This strongly suggests that the alkalis are controlled by a  
 375 diffusion process, while Si is mainly controlled by dissolution at this stage of the experiment  
 376 (as demonstrated by its initial linear evolution through time). Moreover, the Li normalized  
 377 mass losses follows a square root time evolution, (Fig. 3b), as predicted by Fick's second law  
 378 which predicts how diffusion causes concentration changes with time:

379

$$380 \left( \frac{\partial C}{\partial t} \right) = D \left( \frac{\partial^2 C}{\partial x^2} \right) \quad (4)$$

381

382 where the coordinate  $x$  is zero at the original glass surface, and where  $C = 0$  at  $x = 0$ .

383 The resolution of this law can therefore be used to determine the apparent diffusion  
 384 coefficient  $D_{app}$  of glass alkalis into solution from their concentrations in solution (e.g. Chave  
 385 et al., 2007). For lithium, resolution of Eq. (4) leads to:

386

$$387 E_{HG} = \frac{NL(Li)}{\rho} = 2\sqrt{\frac{D_{app}t}{\pi}} \quad (5)$$

388

389 where  $E_{HG}$  is the equivalent hydrated glass thickness over which diffusion occurs,  $NL(Li)$  the  
390 normalized mass loss for lithium,  $\rho$  the glass density ( $\rho = 2.7 \text{ g cm}^{-3}$ ). The  $D_{app}$  values can be  
391 calculated by linear regressions ( $NL(Li) = f(\sqrt{t})$ ). The slope corresponds to  $2\rho\sqrt{(D_{app}/\pi)}$ . The  
392 calculated apparent diffusion coefficients for Li are  $6.0 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  at  $90^\circ\text{C}$  and pH 9, and  
393  $3.5 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$  at  $50^\circ\text{C}$  and pH 6.6 (Fig. 3b).

394

### 395 **3.4. Respective contribution of the diffusion and dissolution processes**

396

397 In the early stages of the alteration process, Si is a tracer of dissolution while Li is  
398 affected by diffusion and by dissolution. Consequently, the solution Si/Li ratio gives an  
399 indication of the respective contribution of both processes (Table 4). Si/Li (%wt ratio) of the  
400 fresh basaltic glass is 51. For all the experiments, the Si/Li ratios of the leachates are much  
401 lower in the early stages of alteration (between 5 and 40, Table 4). This highlights Li  
402 diffusion through the leached layer. The lowest Si/Li ratios (between 5 and 10) are found for  
403 the experiment performed at  $50^\circ\text{C}$ , suggesting that the relative role of diffusion (compared to  
404 dissolution) is greater at low temperature. This implies that the activation energy of the  
405 diffusion process is lower than the activation energy of the dissolution process. For  
406 experiments SV1 and SV2, characterized by different initial S/V, Si/Li ratios measured in the  
407 leachates are significantly different, with Si/Li being 1.5 times lower for the high S/V ratio  
408 experiment (SV2). With a greater reactive surface area, the silicon concentration of the  
409 solution remains the same at saturation, but Li contents are significantly higher. This, again,  
410 suggests that diffusion, which is a surface dependent process, partly controls the release of Li.

411

### 412 **3.5. Li isotopic composition of the leachates**

413

414 All the  $\delta^7\text{Li}$  values of the leachates are equal to or lower than the  $\delta^7\text{Li}$  of the fresh  
415 basaltic glass (Fig. 4, Table 4), ranging between  $+4.9 \pm 0.2 \text{ ‰}$  and  $+10.5 \pm 0.2 \text{ ‰}$ . The  
416 amount of Li released in solution is always low compared to the amount of the Li available in  
417 the glass: generally less than 10%, and less than 5% in the early stages of alteration. The  
418 lowest solution  $\delta^7\text{Li}$  values are found during the early stages of alteration. Then for  
419 experiments PW-90, PH10-90 and SV1,  $\delta^7\text{Li}$  increases with time to a plateau which is close to  
420 the  $\delta^7\text{Li}$  value of the fresh basaltic glass (Fig. 4). However, at a given temperature ( $90^\circ\text{C}$ ), the  
421  $\delta^7\text{Li}$  value of the plateau is "lower" at high S/V ( $+9.6 \pm 0.2 \text{ ‰}$  for experiment SV2) (Fig. 4c).

422 For a given S/V,  $\delta^7\text{Li}$  evolves towards the fresh basaltic glass value more slowly at  
423  $50^\circ\text{C}$  (PW-50) than at  $90^\circ\text{C}$  (PW-90) (Fig. 4a). After two days of leaching,  $\delta^7\text{Li}$  is around  
424  $+7.5 \pm 0.4 \text{ ‰}$  for the experiment performed at  $50^\circ\text{C}$ , whereas the fresh basaltic glass  $\delta^7\text{Li}$   
425 value is reached after less than 1 day for the  $90^\circ\text{C}$  experiments.

426 Comparison between the  $90^\circ\text{C}$  experiments performed at variable pH shows that at pH  
427 3, the leachate  $\delta^7\text{Li}$  remains lower than the fresh glass value for a longer time (up to 34 days).  
428 In contrast, at high pH,  $\delta^7\text{Li}$  rapidly reaches the fresh basaltic glass value (after a few hours)  
429 and then remains constant, within uncertainties (Fig. 4b).

430 Wimpenny et al. (2010) performed experimental leaching of a natural basaltic glass at  
431 far-from-equilibrium conditions in mixed through-flow reactors (open system). The  $\delta^7\text{Li}$   
432 values of the leachates in their experiments are also generally slightly lower than the mean  
433  $\delta^7\text{Li}$  value of the pristine basaltic glass. Si/Li of the solutions, when analyzed, are also lower  
434 than the mean basaltic glass value, at temperatures ranging between 25 and  $45^\circ\text{C}$  (the  
435 temperature was varied during the experiment), suggesting a role of diffusion on the release  
436 of Li into solution at these conditions.

437

438

## 4. DISCUSSION

439

440 **4.1. A coupled diffusion-dissolution model**

441

442 The low  $\delta^7\text{Li}$  values relative to the fresh basaltic glass measured in the solutions  
443 collected in the early stages of alteration strongly suggest that diffusion affects the Li isotope  
444 signature of these solutions. Indeed, diffusion is expected to result in light isotope ( $^6\text{Li}$ )  
445 enrichment in the solution relative to the solid phase. The role of diffusion on the Li isotope  
446 signature at the beginning of the experiments is also supported by the fact that the lowest  $\delta^7\text{Li}$   
447 values also correspond to the lowest Si/Li (Table 4, section 3.4).

448 In order to quantify diffusion coefficients for  $^6\text{Li}$  and  $^7\text{Li}$ , we have developed a model  
449 that takes into account both processes: release of Li by diffusion and release of Li by  
450 dissolution of the glass network (Fig. 5). During alteration, glass network modifier cations,  
451 such as alkali metals ( $\text{Na}^+$ ,  $\text{Li}^+$ ), are replaced by hydrogen species ( $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}$ ) present in  
452 solution. This leads to a selective leaching of these metals, and to the formation of a "leached  
453 layer" at the glass surface (Rana and Douglas, 1961a,b; Hamilton et al., 2000; White and  
454 Claasen, 1980; Luo and Ebert, 1998). This diffusion process can lead to kinetic isotopic  
455 fractionation as the diffusivity of an isotope is a function of its mass (Eq. (5)): light isotopes  
456 diffuse more rapidly than heavy ones. It has been shown that Li isotope fractionation can  
457 occur during diffusion through silicate melts (Richter et al., 2003; Lundstrom et al., 2005),  
458 and in water (Richter et al., 2006). The ratio of  $^6\text{Li}$  and  $^7\text{Li}$  diffusion coefficients ( $a$ ) is  
459 expressed as:

460

$$461 \quad a = \frac{D_{^7\text{Li}}}{D_{^6\text{Li}}} = \left( \frac{m_{^6\text{Li}}}{m_{^7\text{Li}}} \right)^\beta \quad (6)$$

462

463 The value of the exponent '  $\beta$  ' is not equal to 0.5, as it would be for a theoretical ideal gas.

464 The value of  $a$  (or in other words the  $\beta$  value) must be determined experimentally.

465 The model for determining the  $a$  coefficients must take into account not only diffusion  
 466 but also dissolution of the hydrated layer. Dissolution occurs either by hydrolysis of ionic–  
 467 covalent bonds (Si–O–Si, Si–O–Al) (Bunker, 1994) and/or by metal (Al, Si)-proton exchange  
 468 reactions (Oelkers, 2001; Oelkers and Gislason, 2001; Gislason and Oelkers, 2003). The  
 469 dissolution process itself does not lead to isotope fractionation, because all of the network  
 470 bonds are broken (as supported by the congruent behaviour of elements such as Si, Al, Ca and  
 471 Mg (section 3.2)). Consequently, all the Li present in the leached layer is assumed to be  
 472 released into solution. Thus, while diffusion results in low  $\delta^7\text{Li}$  in solution (relative to the  
 473 basaltic glass value), dissolution of the hydrated layer - which is enriched in  $^7\text{Li}$  due to  
 474 diffusion - tends to increase the  $\delta^7\text{Li}$  value of the solution. Since all of our experiments are  
 475 performed in closed systems, the maximum  $\delta^7\text{Li}$  value for the solution is the fresh basaltic  
 476 glass  $\delta^7\text{Li}$  value ( $+10.3 \pm 0.4\%$ ) (unless secondary phases are formed).

477 The diffusion coefficient deduced from Eq. (4) is only apparent because Li is also  
 478 released by dissolution of the hydrated glass. Dissolution of the glass surface displaces the  
 479 surface towards the interior of the glass at a rate  $r$  (Boksay et al., 1968). The coordinate  $x$   
 480 becomes  $x = y - rt$  with  $C = 0$  at  $x = 0$ ,  $x$  moving at a rate  $r$ , and  $y$  corresponding to  $E_{HG}$ , the  
 481 equivalent hydrated glass thickness over which diffusion occurs (Eq. (5)). By differentiation,  
 482  $x = y - rt$  becomes:

483

$$484 \left( \frac{\partial x}{\partial t} \right) = \left( \frac{\partial y}{\partial t} \right) - r \quad (7)$$

485

486 Eq. (4) can be expressed as:

487

$$488 \quad \left(\frac{\partial C}{\partial t}\right) = \left(\frac{\partial C}{\partial x}\right)\left(\frac{\partial x}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial x^2}\right) \quad (8)$$

489

490 It is considered that:

491

$$492 \quad \left(\frac{\partial C}{\partial x}\right) = \left(\frac{\partial C}{\partial y}\right) \quad (9)$$

493

494 By combining Eq. (7), (8) and (9), Eq. (4) becomes:

495

$$496 \quad \left(\frac{\partial C}{\partial y}\right)\left(\frac{\partial y}{\partial t} - r\right) = D\left(\frac{\partial^2 C}{\partial y^2}\right) \quad (10)$$

497

498 and:

499

$$500 \quad \left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial y^2}\right) + r\left(\frac{\partial C}{\partial y}\right) \quad (11)$$

501

502 Following the resolution of this equation by Boksay et al. (1968), the solution of Eq. (11) for

503 lithium is:

504

$$505 \quad \frac{dQ_{Li}}{dt} = c \cdot r \cdot (1 - 0.5 \cdot \operatorname{erf}(s)) + c \cdot \sqrt{\frac{D_{Li}}{\pi \cdot t}} \cdot \exp(-s^2) \quad (12)$$

506



507 where  $dQ_{Li}/dt$  is the release rate of Li into solution (in  $\text{g m}^{-2} \text{d}^{-1}$ ),  $r$  the glass dissolution rate  
 508 (in  $\text{m d}^{-1}$ ),  $c$  the Li concentration in the bulk glass (in  $\text{g m}^{-3}$ ),  $D_{Li}$  the Li diffusion coefficient  
 509 (in  $\text{m}^2 \text{d}^{-1}$ ).  $s$  is dimensionless and is expressed as:

510

$$511 \quad s = \frac{y - r \cdot t}{\sqrt{4 \cdot D \cdot t}} \quad (13)$$

512

513 Eq. (12) can be numerically integrated in order to determine  $Q_{Li}$ . All the parameters  
 514 are known except  $D_{Li}$  which can be adjusted in order to best fit the data set (by the least  
 515 squares method). The total altered glass thickness ( $y$  or  $E_{HG}$ ) is deduced from Eq. (5). The  
 516 dissolution rate ( $r$ ) is determined for each experiment from  $NL(\text{Si})$  (Table 5):

517

$$518 \quad r = \frac{dNL(\text{Si})}{dt} = r_0 \cdot \exp\left(-\frac{t}{\tau}\right) \quad (14)$$

519

520 with  $\tau$  a characteristic time of decrease.

521

522 Therefore:

523

$$524 \quad NL(\text{Si}) = r_0 \cdot \tau \cdot \left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \quad (15)$$

525

526 Note that only the onset of the experiments is considered here (see Table 6). All the calculated  
 527 Li diffusion coefficients are detailed in Table 6.

528 Eq. (12) and its numerical integration can also be used to calculate the Li isotopic  
 529 composition of the solution. The second step of the modelling consists therefore of fitting the

530 solution  $\delta^7\text{Li}$  values (as a function of time) and determining the best value for  $a$  (Eq. (6)). This  
531 was performed using a least squares method (Fig. 6). The range of uncertainties obtained for  
532 the  $a$  coefficients was determined so as to cover the whole range of  $\delta^7\text{Li}$  values.

533 The best fit for the experiment at 50°C corresponds to a  $a$  value of  $0.991 \pm 0.003$  (Fig.  
534 6a). At 90°C and pH 3,  $a$  is  $0.994 \pm 0.004$  (Fig. 6b). For the experiments at various S/V, the  $a$   
535 values are  $1.000 \pm 0.002$  and  $0.997 \pm 0.002$  (Fig. 6c) for S/V = 0.7 and 7  $\text{cm}^{-1}$ , respectively.  
536 The best fit for the experiment at 90°C is  $a = 0.990$  considering all the data, and  $a = 0.997 \pm$   
537  $0.003$  without considering the first point (Fig. 6a), which has a much lower pH (as shown in  
538 Table 4).

539

#### 540 4.2. Influence of temperature

541

542 It is difficult to assess the role of temperature based on this study alone, since only two  
543 temperatures were tested, and since the value obtained for  $a$  at 90°C in pure water is  
544 associated with a large uncertainty ( $0.9935 \pm 0.005$ ). The  $\delta^7\text{Li}$  values of the leachates in the  
545 experiment performed at 50°C are lower than in the experiment at 90°C (Fig. 4a). This could  
546 be explained by a greater relative contribution of Li from diffusion at 50°C, as highlighted by  
547 the particularly low Si/Li in solution (see section 3.4.). In fact, the solution  $\delta^7\text{Li}$  depends on  
548 the  $a$  coefficient (responsible for Li isotope fractionation during diffusion), but also on the  
549 relative rate of diffusion and dissolution (see section 4.4). As shown in Fig. 7a, for a given  $a$   
550 value of  $a$ , various glass dissolution rates can lead to a wide range of  $\delta^7\text{Li}$  values.

551 In order to better determine the role of temperature on the  $a$  coefficients, we have  
552 compiled data available from the literature (Fig. 8). The published data mainly correspond to  
553 high-temperature fractionation among silicate minerals, determined experimentally or by field  
554 studies. Richter et al. (2003) performed experiments of Li diffusion between rhyolite and

555 basalt at 1350-1450°C and determined a value for the  $a$  coefficient of 0.9674. Teng et al.  
556 (2006) studied amphibolites and schists of the Tin Mountain pegmatite and determined  $a =$   
557 0.982 and 0.977 for temperatures ranging between 340 and 600°C. Parkinson et al. (2007)  
558 modelled profiles of Li concentrations and isotope compositions measured *in situ* in zoned  
559 clinopyroxene and olivine phenocrysts from primitive arc lavas of the New Georgia Group  
560 (Solomon Islands) and estimated  $a$  values between 0.971 and 0.959 (1050-1100°C).

561 Combining our data with the published values for  $a$  as a function of temperature, a  
562 relatively good correlation is obtained for diffusion in molten solids ( $R^2=0.95$ ) (Fig. 8) over a  
563 large range of temperatures (50-1450°C). A single law can be determined from these data:

564

$$565 \ln(a) = 0.092 \cdot \frac{1000}{RT} - 0.041 \quad (16)$$

566

567 T is the temperature in K and R the ideal gas constant (in  $\text{J mol}^{-1} \text{K}^{-1}$ ).

568 Experiments carried out by Richter et al. (2006) at 75°C ( $a = 0.9977$ ) and Kunze and  
569 Fuoss (1962) at 25°C ( $a = 0.9965$ ) also plot on the same trend, although diffusion of lithium  
570 occurs in water in both studies (Fig. 8, in grey). The results of Fritz (1992) (reported in  
571 Richter et al., 2006) were not used in our compilation as Richter et al. (2006) mentioned that  
572 the experimental design uses a dialysis membrane which might induce isotopic fractionation.

573 We suggest that the correlation between temperature and  $a$  coefficients is due to a  
574 difference in the activation energies ( $Ea$ ) for  ${}^6\text{Li}^+$  and  ${}^7\text{Li}^+$  diffusivity (corresponding to an  
575 exchange between  $\text{Li}^+$  and  $\text{H}^+$  for example). The dependency of the diffusion coefficient on  
576 temperature would therefore follow an Arrhenius law (McGrail et al., 1984, Chave et al.,  
577 2007; Verney-Carron et al., 2010), such that:

578

$$579 \quad a = \frac{D_7}{D_6} = \frac{D_{07} \cdot \exp(-E_{a7} / RT)}{D_{06} \cdot \exp(-E_{a6} / RT)} = a_0 \cdot \exp((E_{a6} - E_{a7}) / RT) \quad (17)$$

580

581 The linear regression of the data (Eq. (16)) shows that the difference between  
582 activation energies for  $^6\text{Li}$  and  $^7\text{Li}$  diffusivity ( $E_{a6} - E_{a7}$ ) is  $0.10 \pm 0.02$  kJ/mol. Although this  
583 difference is small, it leads to significant isotope fractionation during diffusion.

584 Overall, the positive correlation highlighted between temperature and  $a$  shows that  
585 isotopic fractionation caused by diffusion will increase with temperature.

586

### 587 4.3. Influence of other parameters

588

589 The  $a$  values are relatively similar at pH 3-4 ( $0.994 \pm 0.004$ , experiment PH3-90) and  
590 at pH 8-9 ( $0.997 \pm 0.002$ , experiment PH10-90) (Table 6). Therefore, based on our data, pH  
591 has no obvious effect on diffusion induced Li isotope fractionation. In contrast, the rate of Li  
592 diffusion and the rate of glass dissolution are expected to vary with pH. Basaltic glass  
593 dissolution rates increase as pH decreases, but are also elevated toward alkaline pH. The  
594 evolution of the dissolution rate as a function of pH displays a U-shape with a minimum at  
595 around pH 4-6 (Guy and Schott, 1989; Gislason and Oelkers, 2003). Guy and Schott (1989)  
596 have shown that in the acidic pH region, dissolution is promoted by adsorption of  $\text{H}^+$  on Al  
597 and Fe surface sites, whereas in the alkaline pH region, dissolution is promoted by the  
598 adsorption of  $\text{OH}^-$  on Si sites. According to Guy and Schott, (1989), the dissolution rate at  
599  $100^\circ\text{C}$  is  $1.6 \times 10^{-7}$  molSi/m<sup>2</sup>/s at pH 3, and  $9.8 \times 10^{-7}$  molSi/m<sup>2</sup>/s at pH 8.6 whereas Gislason  
600 and Oelkers (2003) measured different values at  $100^\circ\text{C}$ :  $2.5 \times 10^{-8}$  molSi/m<sup>2</sup>/s at pH 3, and  $5.2$   
601  $\times 10^{-8}$  molSi/m<sup>2</sup>/s at pH 8.6. However, both studies show that the dissolution rate is lower at  
602 pH 3 than at pH 8.6, in agreement with our data (see  $r_0$  in Table 6).

603 In contrast to silicate dissolution rates, the Li diffusion coefficient is expected to  
604 increase as pH decreases (White and Claasen, 1980; Bunker, 1994; Chave et al., 2007;  
605 Verney-Carron et al., 2010), because ion exchange (assumed to be responsible for the  
606 diffusion of alkalis during alteration) depends on the  $H^+$  concentration in solution. However,  
607 in the experiments performed at pH 3, the estimated Li diffusion is surprisingly low.

608 The S/V ratio appears to have an effect on the  $a$  ratio (Fig. 6c), since SV1 and SV2  
609 experiments lead to contrasting  $a$  values (1 and 0.997, respectively). However, these  
610 experiments were longer than the low S/V experiments and may be affected by secondary  
611 phase formation. For both SV1 and SV2 experiments, saturation (Si  $\sim$  15 mg/L) was reached  
612 quickly, after 20 days. Nevertheless, in order to obtain the same Si concentration in solution,  
613 10 times more glass had to be altered in the experiment with  $S/V = 0.7 \text{ cm}^{-1}$  (SV1) compared  
614 with SV2 which contained 10 times less glass in the beaker. This suggests that more  
615 secondary minerals, potentially incorporating Li, could have precipitated during experiment  
616 SV1. Since at  $90^\circ\text{C}$  the isotope fractionation using Li incorporation into clays can be  
617 significant (e.g. -10‰ for smectites, Vigier et al., 2008), this effect could also explain the  
618 higher  $\delta^7\text{Li}$  in the leachates of experiment SV1.

619 In summary, we show that the  $a$  parameter for Li isotope fractionation during diffusion  
620 seems to be primarily influenced by temperature. Also, we show that, at a given temperature,  
621 the relative diffusion and dissolution contributions can significantly affect the Li isotope  
622 composition of the solution.

623

#### 624 **4.4. Implications for natural systems**

625

626 The results of this study have shown that weathering of basaltic glass cannot lead to an  
627 enrichment in  $^7\text{Li}$  of the solution, which suggests that high  $\delta^7\text{Li}$  values in river waters draining  
628 basalts must be due to the preferential uptake of  $^6\text{Li}$  by secondary phases.

629 The data also reveal the importance of diffusion-driven Li isotope fractionation under  
630 conditions that inhibit secondary phase precipitation. The temperature dependency of this  
631 isotope fractionation ( $\alpha$  ratio) (Fig. 8) indicates a greater potential effect at high temperatures,  
632 such as those that have been measured in hydrothermal fluids ( $\alpha$  ranges between 0.985 and  
633 0.979 for 150-350°C). However, this effect is not directly demonstrated by  $\delta^7\text{Li}$  measured in  
634 hydrothermal fluids, which are systematically higher than  $\delta^7\text{Li}$  determined for fresh MORB  
635 (the average  $\delta^7\text{Li}$  for hydrothermal fluids is  $\sim +8.1 \pm 1.8$  ‰, Chan and Edmond, 1988; Chan  
636 et al., 1993, 1994; Foustoukos et al., 2004; Millot et al., 2010).

637 In fact, the Li isotope compositions of solutions also depend on the relative  
638 contribution of diffusion and dissolution. At high temperatures, the release rate of Li from  
639 solid phases is high, resulting in the high Li contents of hydrothermal fluids (Seyfried et al.,  
640 1984; Berger et al., 1988). The initial dissolution rate ( $r_0$ ) and Li diffusion coefficients ( $D$ )  
641 calculated from the experiments performed at 50 and 90°C (PW-50 and PW-90) can be  
642 extrapolated to lower and higher temperatures by using an Arrhenius law. Thus, the activation  
643 energies of diffusion and dissolution are found to be 102 and 110 kJ mol $^{-1}$ , respectively.  
644 These values are slightly higher than published data for basaltic glass (e.g. Techer et al.,  
645 2000) and show that the relative contribution of diffusion compared to dissolution decreases  
646 as temperature increases. In other words,  $r_0/D$  increases as a function of temperature. Fig. 7b  
647 displays the initial stages of the  $\delta^7\text{Li}$  temporal evolution in solution at various temperatures  
648 (from 50 to 120°C) (following the model developed in section 4.1) At temperatures higher  
649 than 120°C, the contribution of dissolution is high and masks the effect of isotope  
650 fractionation occurring during diffusion of Li through the leached layer. The model also

651 predicts that at temperatures between 50 and 90°C, the role of diffusion dominates over  
652 dissolution, resulting in solution  $\delta^7\text{Li}$  which are lower than the fresh glass value. At lower  
653 temperatures (< 50°C), the solution  $\delta^7\text{Li}$  goes back towards the fresh basaltic glass value,  
654 since the isotope fractionation occurring during diffusion becomes negligible ( $\alpha$  close to 1).  
655 Overall, these simulations highlight that the solution  $\delta^7\text{Li}$ , in absence of secondary mineral  
656 formation, strongly depends on temperature since this parameter influences the dissolution  
657 rate, the diffusion coefficients, and the Li isotope fractionation factor. Also, the S/V ratio  
658 which can be related to parameters such as water/rock ratio, porosity and specific surface area  
659 plays a key role, as it can drastically change the relative contribution of diffusion and  
660 dissolution. In the field, these parameters should therefore influence the Li isotope  
661 composition of the fluids before formation of any secondary minerals starts. In models, the  
662 initial composition of the fluid may therefore not be strictly equal to the isotope composition  
663 of the fresh rock or minerals that it drains.

664 In summary, diffusion should not play a significant role in low-temperature natural  
665 systems as the isotope fractionation factor is close to 1. In high temperature hydrothermal  
666 systems, the dissolution rates are significant and may entirely mask the effect of diffusion.  
667 However, the role of diffusion should be taken into account for modelling alteration processes  
668 occurring at moderate temperatures.

669

670

## 5. SUMMARY AND CONCLUSIONS

671

672 The results of basaltic glass alteration experiments performed at various temperatures  
673 (50 and 90°C), various pH (3 and around 9) and various S/V ratio (0.7 and 7 cm<sup>-1</sup>) have  
674 shown that the alteration of basaltic glass at far from equilibrium conditions produces a  
675 solution with a lighter Li isotopic composition than the starting material. This challenges the

676 idea that the weathering of silicate glasses could preferentially release  $^7\text{Li}$  into rivers. The Li  
677 isotopic composition of the solution can be modeled in terms of mass-dependent isotope  
678 fractionation of Li, as Li diffuses through the hydrated glass into solution. This fractionation  
679 can be explained by a difference in the diffusion coefficients of  $^6\text{Li}$  and  $^7\text{Li}$ . The ratio  $a$ ,  
680 defined as the ratio of these diffusion coefficients ( $a = D_7/D_6$ ), decreases as a function of  
681 temperature. The relationship between  $a$  and temperature appears to follow an Arrhenius' law,  
682 and may be related to a difference in the activation energies of the  $^6\text{Li}^+$  and  $^7\text{Li}^+$  diffusivity.  
683 These results can help to interpret the Li isotope signatures of natural systems. Without  
684 considering the role of secondary mineral formation it seems that the effect of diffusion on the  
685 Li isotopic composition is not negligible for systems where water rock interactions occur at  
686 moderate temperatures (50-100°C).

687



688

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Figure captions

Figure 1. Evolution of Si (a) and Li (b) concentrations in solution with time for all the experiments performed at 90°C (see Table 4).

Figure 2. Normalized mass losses (Eq. (2)) of Ca, Al, Si, Mg, Na, and Li during alteration for the experiment in pure water at 90°C (PW-90). The solid line represents a fit of the normalized mass losses for alkalis (see Eq. (5)) using a square root function and the dashed line corresponds to a fit of the normalized mass losses for the other elements using two linear functions.

Figure 3. (a) Determination of the 'initial' dissolution rate ( $r_0$ ) for the experiments in pure water at 90°C (PW-90) and 50°C (PW-50) using Eq. (3). The initial dissolution rate is deduced from the slope of the linear regression on  $dNL(Si)/dt$ . (b) Determination of the Li diffusion coefficient ( $D$ ) for the experiments in pure water at 90°C (PW-90) and 50°C (PW-50) using Fick's second law (Eq. (5)). The slope of the linear regression on  $dNL(Li)/dt$  corresponds to  $2\rho\sqrt{Dt}$ .

Figure 4. Evolution of the Li isotopic composition of the leachate solutions ( $\delta^7Li$ ) with time: (a) for the experiments at 90°C and 50°C (in pure water and  $S/V = 0.7 \text{ cm}^{-1}$ ), (b) at pH 3 and 9 (at 90°C and  $S/V = 0.7 \text{ cm}^{-1}$ ), (c) at  $S/V$  of 0.7 and  $7 \text{ cm}^{-1}$  (in pure water and 90°C). The thick black line corresponds to the fresh synthetic basaltic glass value with its uncertainties in grey.

Figure 5. Schematic view of the diffusion - dissolution model described in the text. The alteration process is considered as two processes: formation of a leached layer by interdiffusion between alkalis and protons and dissolution of the leached layer.

Figure 6. Modeling the experiments: (a) at 90 and 50°C (in pure water and  $S/V = 0.7 \text{ cm}^{-1}$ ), (b) at pH 3 (90°C and  $S/V = 0.7 \text{ cm}^{-1}$ ), (c) at  $S/V$  of 0.7 and  $7 \text{ cm}^{-1}$  (in pure water and 90°C). The thick black horizontal line corresponds to the fresh synthetic basaltic glass value with uncertainties in grey. The curves correspond to the fit of the data with the  $a$  value determined from the least square method.

Figure 7. Simulation of  $\delta^7Li$  values of the leaching solution of the synthetic basaltic glass as a function of time: (a) at 90°C by considering the measured values of  $D$  and  $r_0$ ,  $r_0/10$ ,  $r_0/100$ ; (b) at various temperatures (between 20 and 120°C). The results are obtained from Eq. (12) and (13) and by considering  $r_0$  and  $D$  extrapolated from our measured data to 50 and 90°C. The  $a$  ratio is calculated from Eq. (16).

Figure 8. Logarithm of the  $a$  ratio as a function of the inverse of the temperature.  $R$  is the ideal gas constant. According to Arrhenius' law and Eq. (17), the slope corresponds to the difference of activation energies for diffusion of  $^6Li$  and  $^7Li$ , respectively.

Figure 1

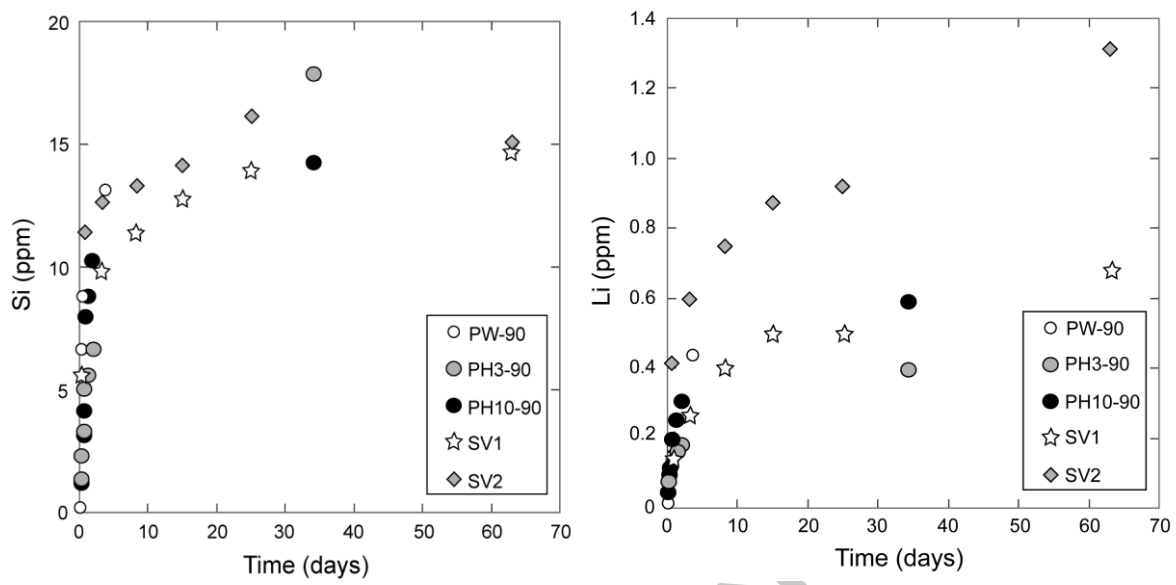


Figure 2

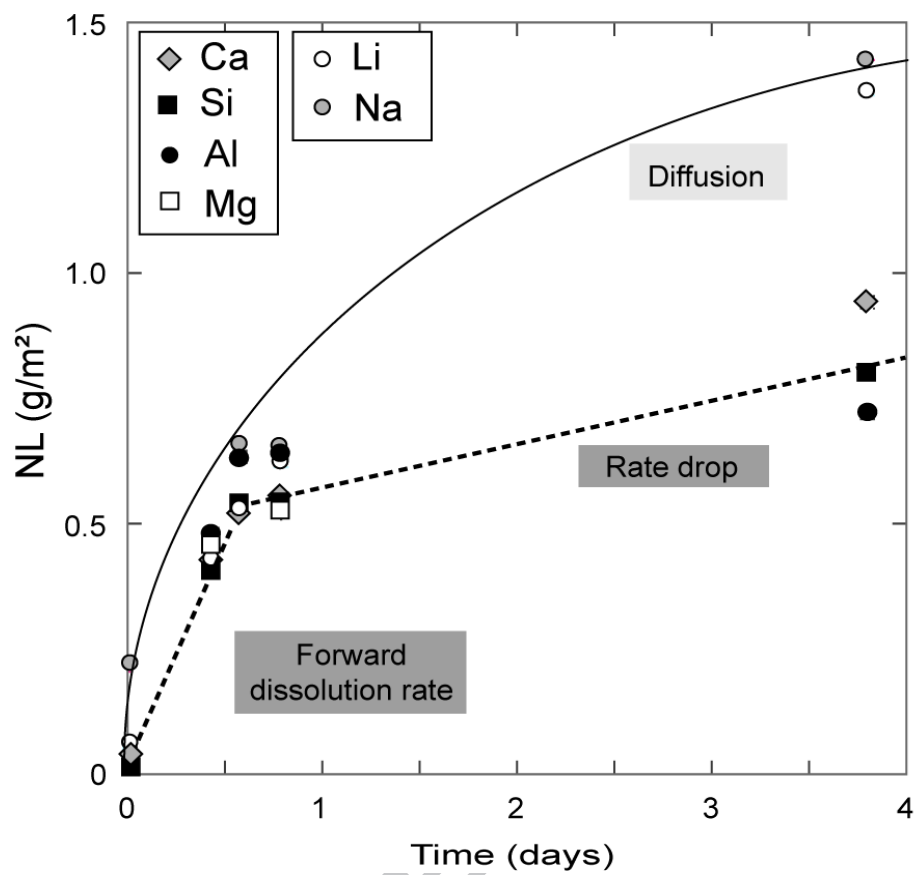


Figure 3

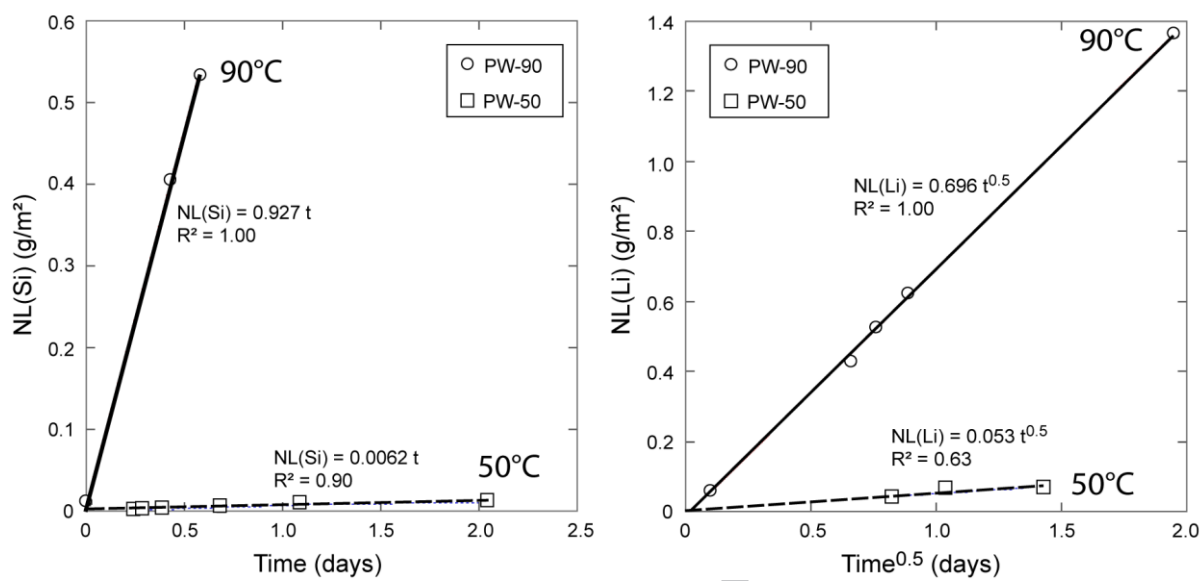
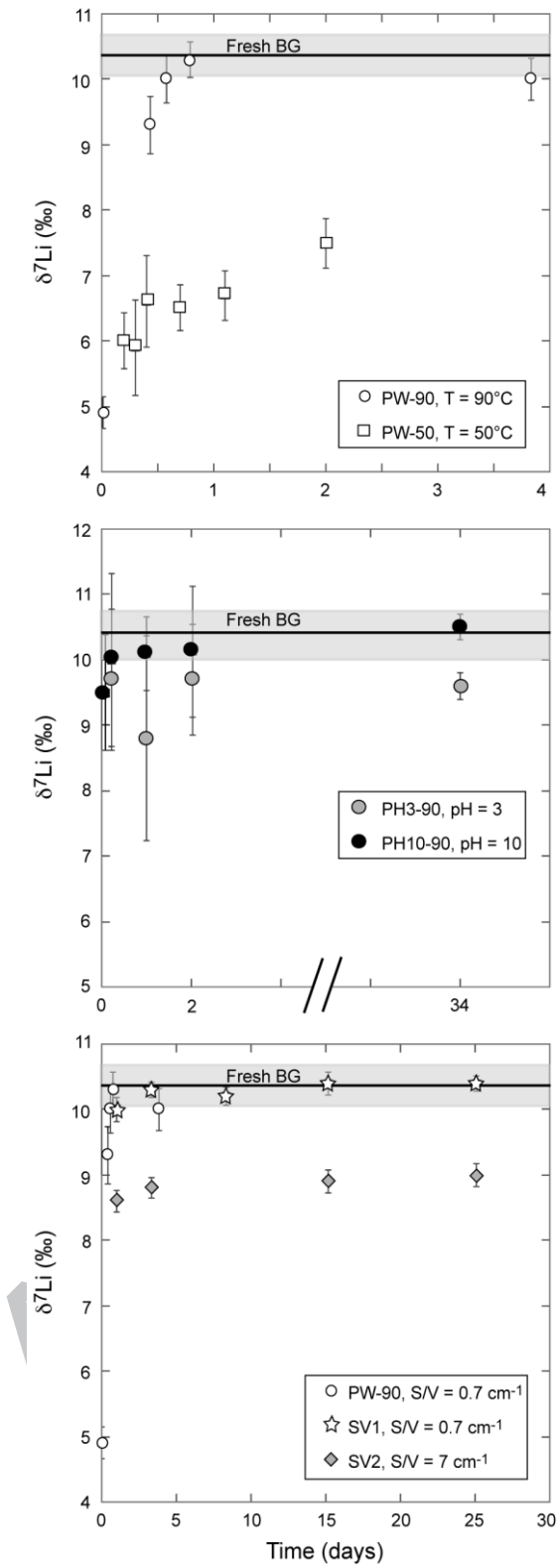


Figure 4



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Figure 5

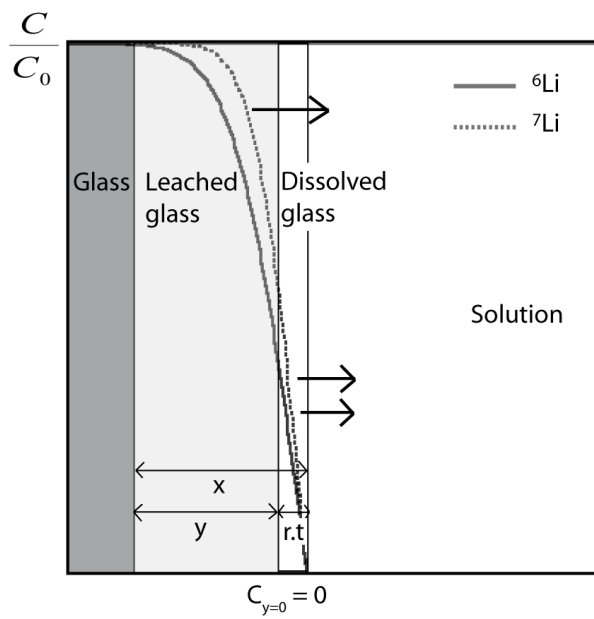




Figure 6

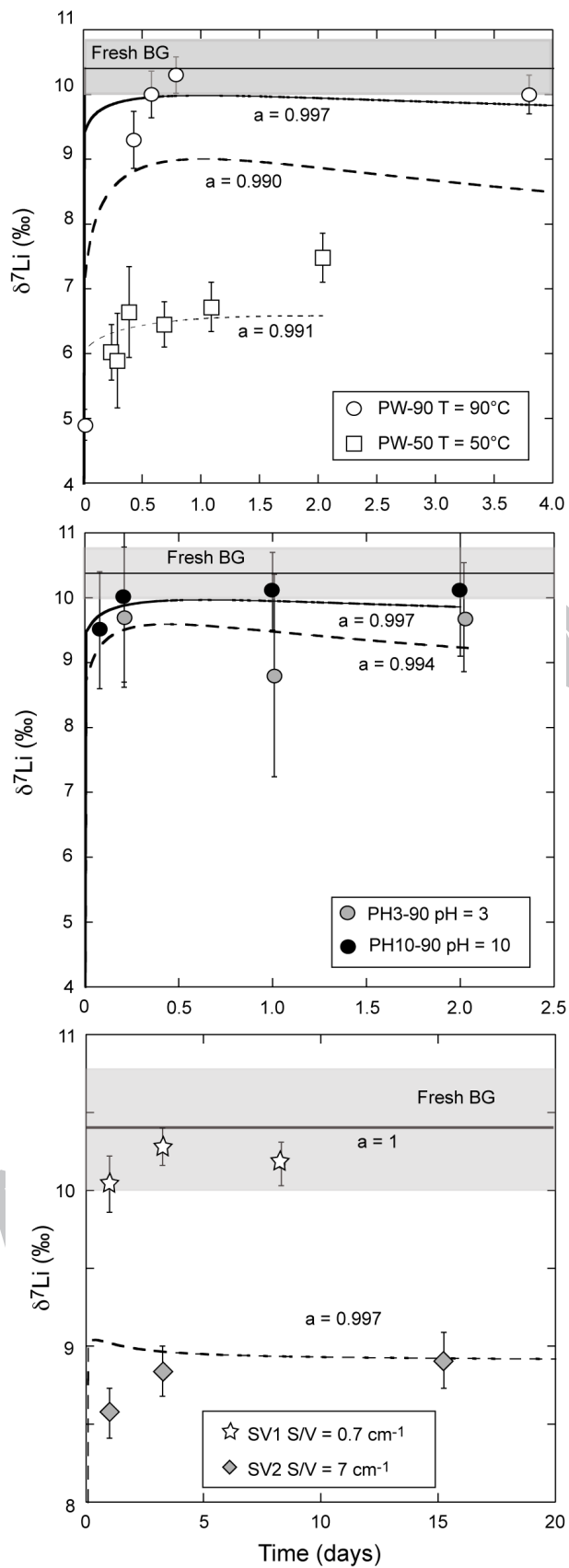


Figure 7.

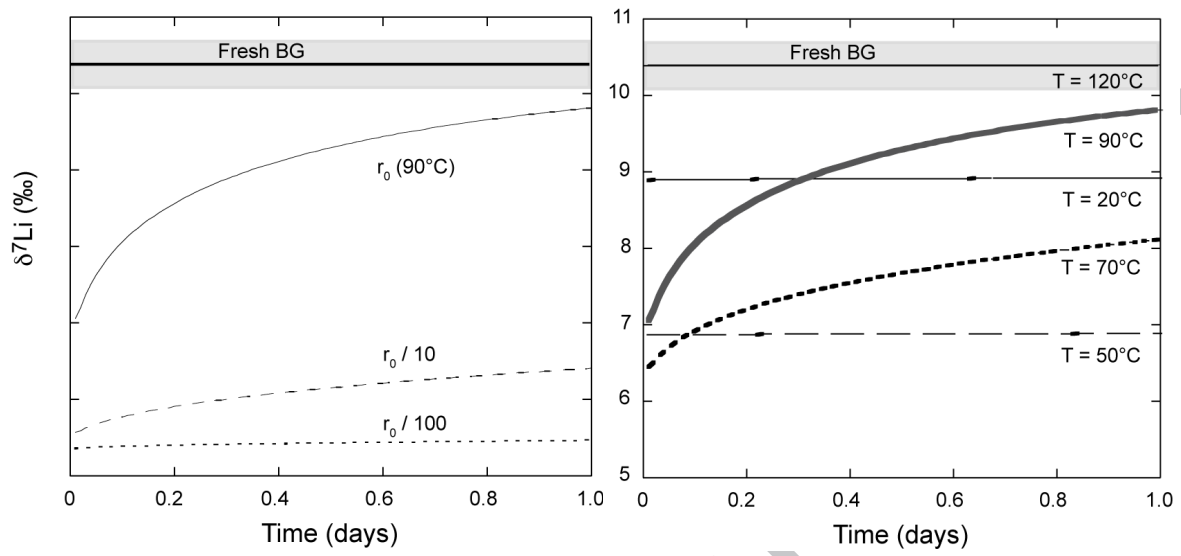


Figure 8.

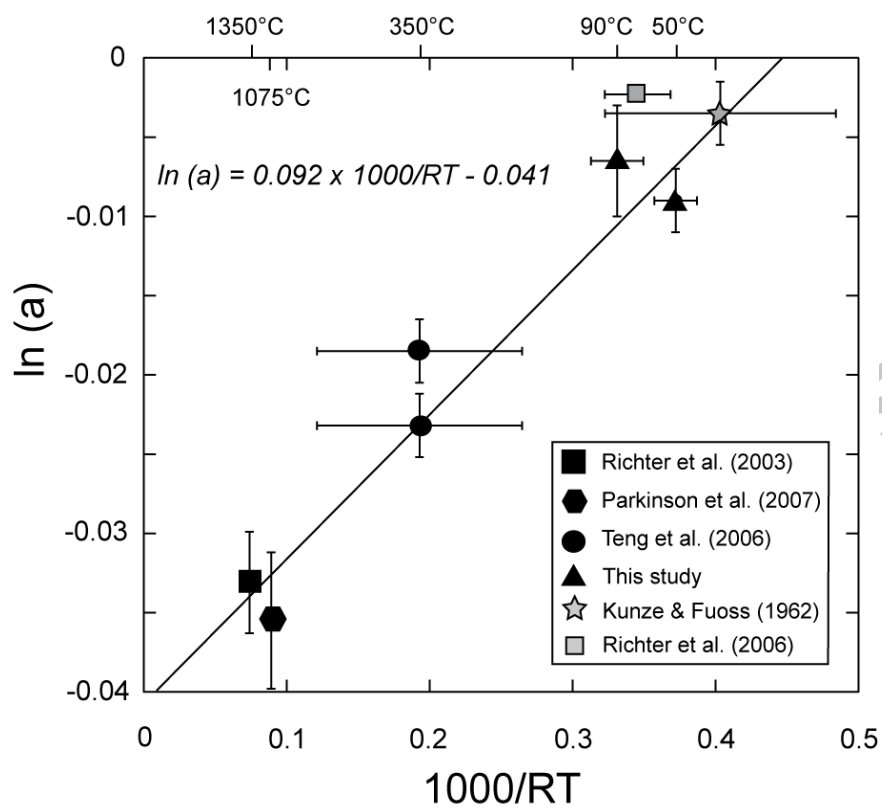


Table 1. Summary of experimental conditions.

Exp. name	Temp. °C	Solution	BG* mass g	Sol. volume mL	S/V** cm <sup>-1</sup>	Time days
PW-90-t1	90	Pure water	0.042	50.4	0.70	0.02
PW-90-t2	90	Pure water	0.042	50.1	0.71	0.42
PW-90-t3	90	Pure water	0.043	50.1	0.72	0.58
PW-90-t4	90	Pure water	0.042	50.0	0.71	0.79
PW-90-t5	90	Pure water	0.042	50.0	0.71	4
PH3-90	90	0.001M HCl (pH 3 at 25°C)	0.168	200.2	0.71	0.08, 0.21, 0.33, 1, 1.3, 2, 34
PH10-90	90	0.0001M NaOH (pH 10 at 25°C)	0.168	199.8	0.71	0.08, 0.21, 0.33, 1, 1.3, 2, 34
SV1	90	Pure water	0.167	199.9	0.70	1, 3, 8, 15, 25, 63
SV2	90	Pure water	0.884	100.2	7.4	1, 3, 8, 15, 25, 63
PW-50-t1	50	Pure water	0.047	50.9	0.78	0.25
PW-50-t2	50	Pure water	0.041	50.2	0.69	0.29
PW-50-t3	50	Pure water	0.042	50.4	0.70	0.38
PW-50-t4	50	Pure water	0.043	51.6	0.70	0.67
PW-50-t5	50	Pure water	0.042	50.0	0.71	1.1
PW-50-t6	50	Pure water	0.042	51.7	0.68	2.0

\* BG is basaltic glass

\*\* S/V is the ratio of the basaltic glass reactive surface area (measured by BET) to the volume of solution used in the experiment

Table 2.  $\delta^7\text{Li}$  (‰) obtained for several reference materials during sessions (1) and (2) using the Neptune MC-ICP-MS and the Nu Instruments MC-ICP-MS

Standard name		$\delta^7\text{Li}$ (‰)	$\delta^7\text{Li}$ (‰) published values
<i>Neptune (BRGM)</i>			
SW BCR-403 30 ppb		$+31.3 \pm 0.4$ (n=10)	$+31.0 \pm 0.1$ Millot et al. (2004)
Li7-N 30 ppb		$+30.8 \pm 0.5$ ‰ (n = 10)	$+30.2 \pm 0.3$ Carignan et al. (2007)
Li7-N* 30 ppb		$+30.3 \pm 0.2$ ‰ (n = 10)	
Li6-N* 30 ppb		$-8.1 \pm 0.2$ ‰ (n = 10)	$-8.0 \pm 0.3$ Carignan et al. (2007)
<i>Nu Instruments (ENS)</i>			
Basalt JB-2	(1)	$+4.0 \pm 0.3$ (n = 1)	$+4.6 \pm 0.9$ Carignan et al. (2007)
SW BCR-403	(1)	$+30.9 \pm 0.2$ (n = 1)	$+31.3 \pm 0.6$ Millot et al. (2004)
SW BCR-403 30-60 ppb	(2)	$+30.8 \pm 0.6$ (n = 3)	
SW BCR-403 15 ppb	(2)	$+30.5 \pm 0.7$ (n = 2)	
Li7-N (50-100 ppb)*	(1)	$+30.2 \pm 0.3$ ‰ (n = 4)	$+30.2 \pm 0.3$ Carignan et al. (2007)
Li7-N (25 ppb)*	(1)	$+30.0 \pm 0.4$ ‰ (n = 2)	
Li7-N (50-75 ppb)*	(2)	$+30.0 \pm 0.4$ ‰ (n = 14)	
Li7-N (10 to 40 ppb)*	(2)	$+29.9 \pm 0.6$ ‰ (n = 11)	
Li6-N (25-50 ppb)*	(1)	$-8.1 \pm 0.4$ ‰ (n = 3)	$-8.0 \pm 0.3$ Carignan et al. (2007)
Li6-N (50 ppb)*	(2)	$-8.1 \pm 0.4$ ‰ (n = 7)	

Uncertainties are given at the  $2\sigma$  level. See text for more details.

\* These standards were not passed through the chemical separation procedure

Table 3. Composition of the Li-enriched synthetic basaltic glass (VBS) used in all of the experiments

<b>Oxide</b> Wt. %	VBS
<b>SiO<sub>2</sub></b>	49.08
<b>Al<sub>2</sub>O<sub>3</sub></b>	14.78
<b>Fe<sub>2</sub>O<sub>3</sub></b>	10.82
<b>MnO</b>	0.21
<b>MgO</b>	8.18
<b>CaO</b>	10.69
<b>Na<sub>2</sub>O</b>	2.69
<b>K<sub>2</sub>O</b>	0.18
<b>TiO<sub>2</sub></b>	1.73
<b>P<sub>2</sub>O<sub>5</sub></b>	0.13
<b>Li<sub>2</sub>O</b>	0.964
<b>Total</b>	99.46

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Table 4. pH, elemental concentrations and  $\delta^7\text{Li}$  (‰) of the solutions recovered from alteration experiments. pH is given at the temperature of the experiment (90°C for all experiments, except PW-50 at 50°C). LD (limit of detection) are 1 ppm for Al, 0.02 ppm for Fe, 0.1 ppm for Mg. Leachates were diluted by a factor 2 in the experiments PH3-90 and PH10-90 and by a factor 5 for the experiments SV1 and SV2. Si/Li is in ppm/ppm. Uncertainties for  $\delta^7\text{Li}$  are given at the  $2\sigma$  level and correspond to the internal error.

Exp.	S/V cm <sup>-1</sup>	Time d	pH	Si ppm	Al ppm	Fe ppm	Mg ppm	Ca ppm	Na ppm	Li ppm	Si/Li	$\delta^7\text{Li}$ ‰
PW-90	0.70	0.02	7.9	0.19	< LD	< LD	< LD	0.28	0.30	0.020	9.5	+4.9 ± 0.2
	0.71	0.42	8.6	6.60	2.66	< LD	1.62	2.28	-	0.136	48.5	+9.3 ± 0.5
	0.72	0.58	8.6	8.80	3.57	< LD	< LD	2.94	0.95	0.170	51.8	+10.0 ± 0.4
	0.71	0.79	8.6	8.76	3.55	< LD	1.82	2.99	0.92	0.199	44.0	+10.3 ± 0.3
	0.71	3.8	8.6	13.1	4.01	< LD	< LD	5.11	2.02	0.434	30.2	+10.0 ± 0.3
PH3-90	0.71	0.08	3.0	1.28	< LD	0.570	< LD	0.870	0.256	0.065	19.7	nd
	0.72	0.21	3.1	2.30	< LD	0.661	< LD	1.15	0.336	0.095	24.2	+9.7 ± 1.1
	0.74	0.33	3.1	3.15	< LD	0.630	< LD	1.43	0.374	0.106	29.7	nd
	0.76	1.0	3.1	5.08	2.23	0.784	1.18	2.05	0.584	0.145	35.0	+8.8 ± 1.6
	0.78	1.3	3.3	5.56	2.38	0.798	1.24	2.05	0.587	0.163	34.1	nd
	0.80	2.0	3.4	6.63	2.79	0.884	1.51	2.42	0.677	0.175	37.9	+9.7 ± 0.8
	0.82	34.3	4.2	17.8	< LD	1.75	4.67	6.89	1.93	0.394	45.2	+9.6 ± 0.2
PH10-90	0.71	0.08	8.4	1.19	< LD	< LD	< LD	< LD	0.45	0.045	26.4	+9.5 ± 0.9
	0.73	0.21	8.4	3.06	< LD	< LD	< LD	0.784	0.64	0.092	33.3	+10.0 ± 1.3
	0.75	0.33	8.3	4.10	< LD	< LD	< LD	1.326	0.75	0.121	33.9	nd
	0.76	1.0	8.3	7.90	3.19	< LD	1.74	2.78	1.25	0.207	38.2	+10.1 ± 0.6
	0.79	1.3	8.2	8.74	3.53	< LD	1.88	2.80	1.21	0.249	35.1	nd
	0.81	2.0	8.2	10.3	4.15	< LD	2.20	3.37	1.49	0.299	34.4	+10.1 ± 1.0
	0.84	34.3	8.2	14.2	< LD	< LD	< LD	5.58	3.11	0.591	24.0	+10.5 ± 0.2
SV1	0.70	1.0	8.1	5.59	< LD	< LD	< LD	< LD	0.91	0.138	40.5	+10.0 ± 0.2
	0.73	3.3	8.7	9.76	< LD	< LD	< LD	3.36	1.25	0.259	37.7	+10.3 ± 0.2
	0.75	8.3	8.8	11.4	< LD	< LD	< LD	4.16	1.80	0.395	28.9	+10.2 ± 0.2
	0.77	15.2	8.5	12.7	< LD	< LD	< LD	-	2.61	0.491	25.9	+10.4 ± 0.2
	0.80	25.1	8.8	13.9	< LD	< LD	< LD	4.05	2.08	0.494	28.1	+10.4 ± 0.2
	0.81	63.3	8.9	14.8	< LD	< LD	< LD	4.96	3.49	0.674	22.0	nd
SV2	7.4	1.0	8.8	11.4	< LD	< LD	< LD	4.88	1.78	0.413	27.6	+8.6 ± 0.2
	7.5	3.3	8.5	12.6	< LD	< LD	< LD	< LD	2.30	0.595	21.2	+8.8 ± 0.2
	7.7	8.3	8.9	13.2	< LD	< LD	< LD	4.92	3.00	0.746	17.7	nd
	7.8	15.2	9.0	14.1	< LD	< LD	< LD	5.08	3.75	0.872	16.2	+8.9 ± 0.2
	7.9	25.1	9.0	16.1	< LD	< LD	< LD	6.01	3.96	0.918	17.5	+9.0 ± 0.2
	8.0	63.3	9.1	15.1	< LD	< LD	< LD	6.40	4.76	1.309	11.5	+8.9 ± 0.6
	PW-50	0.78	0.25	6.6	0.031	< LD	< LD	< LD	< LD	< LD	< LD	-
0.69		0.29	6.6	0.034	< LD	< LD	< LD	< LD	< LD	< LD	-	+5.9 ± 0.7
0.70		0.39	6.6	0.064	< LD	< LD	< LD	< LD	< LD	< LD	-	+6.6 ± 0.7
0.70		0.71	7.6	0.065	< LD	< LD	< LD	< LD	< LD	0.013	5.0	+6.5 ± 0.4
0.71		1.1	7.7	0.139	< LD	< LD	< LD	< LD	< LD	0.021	6.6	+6.7 ± 0.4
0.68		2.0	7.7	0.177	< LD	< LD	< LD	< LD	< LD	0.021	8.4	+7.5 ± 0.4

Table 5. Normalized mass losses of elements from the glass (Eq. (2)). Relative uncertainties are 10%.

Exp.	Time days	NL(Si) g·m <sup>-2</sup>	NL(Al) g·m <sup>-2</sup>	NL(Fe) g·m <sup>-2</sup>	NL(Mg) g·m <sup>-2</sup>	NL(Ca) g·m <sup>-2</sup>	NL(Na) g·m <sup>-2</sup>	NL(Li) g·m <sup>-2</sup>
PW-90	0.01	0.012				0.052	0.215	0.064
	0.43	0.405	0.479		0.462	0.420		0.428
	0.58	0.533	0.634			0.534	0.661	0.527
	0.79	0.538	0.639		0.520	0.551	0.649	0.626
	3.8	0.804	0.722			0.942	1.426	1.365
PH3-90	0.08	0.079		0.106		0.160	0.181	0.204
	0.21	0.139		0.121		0.209	0.234	0.295
	0.33	0.186		0.112		0.253	0.253	0.320
	1.0	0.291	0.375	0.136	0.315	0.353	0.385	0.426
	1.3	0.311	0.390	0.135	0.322	0.344	0.377	0.467
	2.0	0.361	0.446	0.146	0.383	0.396	0.424	0.488
	34.3	0.946		0.282	1.154	1.100	1.179	1.073
PH10-90	0.08	0.073					0.318	0.141
	0.21	0.183				0.141	0.439	0.281
	0.33	0.238				0.231	0.501	0.360
	1.0	0.453	0.537		0.464	0.479	0.824	0.608
	1.3	0.482	0.571		0.482	0.464	0.768	0.704
	2.0	0.554	0.655		0.551	0.545	0.922	0.824
	34.3	0.737				0.869	1.855	1.571
SV1	1.0	0.348					0.651	0.440
	3.3	0.583				0.602	0.858	0.792
	8.3	0.663				0.726	1.203	1.176
	15.2	0.719					1.699	1.423
	25.1	0.757				0.663	1.303	1.378
	63.3	0.798				0.804	2.164	1.862
SV2	1.0	0.067				0.086	0.121	0.125
	3.3	0.073					0.154	0.177
	8.3	0.075				0.084	0.195	0.216
	15.2	0.079				0.085	0.241	0.250
	25.1	0.089				0.100	0.251	0.259
	63.3	0.082				0.105	0.298	0.378
PW-50	0.24	0.002						
	0.29	0.002						
	0.39	0.004						
	0.69	0.004						0.041
	1.09	0.009						0.066
	2.04	0.011						0.069



Table 6. Parameters and results of the model. The parameters  $\tau$  and  $r_0$  are used to fit the dissolution rate  $r$  (Eq. (10)).  $D$  is the 'true' Li diffusion coefficient used in the model. The ratio  $a$  is the  $D_7/D_6$  ratio, and  $n$  is the number of data points used for the modelling. The range of uncertainties for  $a$  considers all of the measured  $\delta^7\text{Li}$  values. The corresponding  $\beta$  values (see Eq. (6)) are also shown.

Exp.	Time	$\tau$ (d)	$r_0$ (g/m <sup>2</sup> /d)	$D$ (m <sup>2</sup> /d)	$a$	$\beta$
PW90	$t \leq 4$ d	0.919	0.930	$2.6 \cdot 10^{-14}$	0.990 (n=5) 0.997 (n=4)	0.078 0.019
PH3-90	$t \leq 2$ d	0.419	0.812	$0.9 \cdot 10^{-14}$	$0.994 \pm 0.004$ (n=3)	0.039
PH10-90	$t \leq 2$ d	0.589	0.949	$1.9 \cdot 10^{-14}$	$0.997 \pm 0.002$ (n=4)	0.019
SV1	$t \leq 15$ d	1.533	0.448	$1.7 \cdot 10^{-12}$	$1.000 \pm 0.002$ (n=4)	0
SV2	$t \leq 15$ d	0.464	0.163	$6.0 \cdot 10^{-14}$	$0.997 \pm 0.002$ (n=3)	0.019
PW50	$t \leq 2$ d	1.701	0.010	$4.0 \cdot 10^{-16}$	$0.991 \pm 0.003$ (n=6)	0.059

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