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

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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 ^6Li ($\delta^7\text{Li} = +4.9$ to $+10.5\text{‰}$) compared to the fresh basaltic glass ($\delta^7\text{Li} = +10.3 \pm$
 30 0.4‰). 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 ± 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°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.

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1. INTRODUCTION

Silicate weathering has a major impact on the carbon cycle over long timescales, because Ca and Mg are released during dissolution of silicate minerals which in turn leads to consumption of atmospheric carbon dioxide via formation of carbonate in the oceans (e.g. Ludwig et al., 1999; Dupré et al., 2003; Lerman et al., 2007; Franck et al., 2008; Hartmann et al., 2009). Basalt are among the most easily weathered silicate rocks, therefore basalt weathering potentially represents a significant atmospheric CO₂ sink and a major source of oceanic Ca and Mg (Louvat and Allègre, 1997, 1998; Gaillardet et al., 1999; Dessert et al., 2003). Assessing the contribution of basaltic weathering to rivers is therefore of primary importance. A significant portion of basalt weathering is likely due to alteration of basaltic glass: the glassy phase and hyaloclastites have been shown to play a key role in determining the chemical and isotope compositions of river waters in volcanic regions (e.g. Gislason and Oelkers, 2003, and references therein; Wolff-Boenisch et al., 2004; Vigier et al., 2006). This is consistent with their more rapid dissolution relative to basalt minerals (e.g. Wolff-Boenisch et al., 2006).

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

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

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

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

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

2. EXPERIMENTAL METHODS AND ANALYTICAL PROCEDURES

2.1. Experimental setup

2.1.1. Materials

A synthetic basaltic glass was doped with 1% Li₂O using the procedure described in Techer et al. (2001), i.e. by melting a mixture of powdered oxides, carbonates, nitrates and phosphates in alumina crucibles for 3 h at 1500°C. The resulting melt was then poured into graphite crucibles preheated at 700°C. The glass was heat treated at 670°C for 1 h, then cooled to room temperature in 10 h. Concentrations of major cations (Si, Al, Fe, Mn, Mg, Ca, Na K, Ti, and P) were determined by ICP-AES (IRIS Thermo Elemental) at the SARM (French national facilities, Nancy). Li concentrations were analyzed using atomic absorption spectrometry (AAS) (VARIAN220 FS) at the SARM. Uncertainties range between 5 and 20% depending on the element and its concentration.

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

2.1.2. Reactive surface area determination

The synthetic basaltic glass was ground and sieved in order to recover the 40-100 μm particle size fraction which was then washed and ultrasonicated in acetone in order to remove any finer particles remaining. The glass powder was stirred in a beaker containing 12 cm depth of acetone. According to Stokes' law, >40 μm particles reach the bottom of the beaker in 15 s; after this time, the supernatant solution is removed from the beaker. This procedure was repeated until the supernatant was clear. The specific surface area was measured by krypton adsorption using the BET method and is 842 ± 5 cm² g⁻¹. To assess the consistency of

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

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

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

2.1.3. Experiments

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

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

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

The pH was measured at the in situ temperature. However, the temperature of the sampled aliquot can rapidly decrease during pH measurements. Consequently, the temperature was also monitored during the pH measurement for calculations. The samples were filtered at 0.45 μm , and then acidified with concentrated HNO_3 to obtain 0.3 N HNO_3 for ICP-AES and AAS analyses.

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

2.2. Li isotope analyses

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

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

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

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

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

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

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

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

2.3. Calculation of solution saturation states

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

3. RESULTS

3.1. Composition of the fresh synthetic basaltic glass

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

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

3.2. pH and chemical composition of the leachates

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

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

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

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

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

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

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

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

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

3.3. Alteration kinetics of the basaltic glass

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

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

3.3.1. Glass dissolution rate

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

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

The 'initial' dissolution rate r_0 is thus estimated to be 0.927 g/m²/d, i.e. 3.8×10^{-7} mol Si/m²/s at 90°C and pH 8.6, and 0.0062 g/m²/d, i.e. 2.6×10^{-9} mol Si/m²/s at 50°C and pH 6.6 (Fig. 3a). These values are consistent with published data obtained at similar pH and temperatures although it should be noted that there are large differences among basaltic glass dissolution rate estimates reported in the literature (mainly caused by difficulties assessing the reactive surface area). Initial dissolution rates for basaltic glass at pH between 8.2 and 8.6, and at temperatures between 90°C and 100°C, range between 1.1×10^{-8} and 9.8×10^{-7} mol Si/m²/s (Guy and Schott, 1989; Daux et al., 1997; Techer et al., 2000; Gislason and Oelkers, 2003). At 50°C, the initial rate at neutral pH ranges between 2.1×10^{-10} and 1.9×10^{-8} mol Si/m²/s (Guy and Schott, 1989; Gislason and Oelkers, 2003).

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

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

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

3.3.2. *Li apparent diffusion coefficients*

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

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

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

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

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

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

3.4. Respective contribution of the diffusion and dissolution processes

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

3.5. Li isotopic composition of the leachates

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

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

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

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

4. DISCUSSION

4.1. A coupled diffusion-dissolution model

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

In order to quantify diffusion coefficients for ^6Li and ^7Li , we have developed a model that takes into account both processes: release of Li by diffusion and release of Li by dissolution of the glass network (Fig. 5). During alteration, glass network modifier cations, such as alkali metals (Na^+ , Li^+), are replaced by hydrogen species (H_3O^+ , H_2O) present in solution. This leads to a selective leaching of these metals, and to the formation of a "leached layer" at the glass surface (Rana and Douglas, 1961a,b; Hamilton et al., 2000; White and Claassen, 1980; Luo and Ebert, 1998). This diffusion process can lead to kinetic isotopic fractionation as the diffusivity of an isotope is a function of its mass (Eq. (5)): light isotopes diffuse more rapidly than heavy ones. It has been shown that Li isotope fractionation can occur during diffusion through silicate melts (Richter et al., 2003; Lundstrom et al., 2005), and in water (Richter et al., 2006). The ratio of ^6Li and ^7Li diffusion coefficients (a) is expressed as:

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

462

463 The value of the exponent ' β ' 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 β 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 ^7Li 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 ($+10.3 \pm 0.4\text{‰}$) (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

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

485

Eq. (4) can be expressed as:

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

It is considered that:

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

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

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

and:

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

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

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

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 (in m d^{-1}), c the Li concentration in the bulk glass (in g m^{-3}), D_{Li} the Li diffusion coefficient (in $\text{m}^2 \text{d}^{-1}$). s is dimensionless and is expressed as:

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

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

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

with τ a characteristic time of decrease.

Therefore:

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

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

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

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

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

4.2. Influence of temperature

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

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

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

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

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

T is the temperature in K and R the ideal gas constant (in J mol⁻¹ K⁻¹).

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

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

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

580

581 The linear regression of the data (Eq. (16)) shows that the difference between
582 activation energies for ^6Li and ^7Li diffusivity ($E_{a6} - E_{a7}$) is 0.10 ± 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 ± 0.004 , experiment PH3-90) and
590 at pH 8-9 (0.997 ± 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 H^+ on Al
597 and Fe surface sites, whereas in the alkaline pH region, dissolution is promoted by the
598 adsorption of OH^- on Si sites. According to Guy and Schott, (1989), the dissolution rate at
599 100°C is 1.6×10^{-7} molSi/m²/s at pH 3, and 9.8×10^{-7} molSi/m²/s at pH 8.6 whereas Gislason
600 and Oelkers (2003) measured different values at 100°C : 2.5×10^{-8} molSi/m²/s at pH 3, and 5.2
601 $\times 10^{-8}$ molSi/m²/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).

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

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

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

4.4. Implications for natural systems

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

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

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

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

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

5. SUMMARY AND CONCLUSIONS

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

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

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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 (δ^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 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 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 δ^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

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 ⁻¹	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 ± 0.2 ‰ (n = 10)	-8.0 ± 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 ± 0.4 ‰ (n = 3)	-8.0 ± 0.3	Carignan et al. (2007)
Li6-N (50 ppb)*	(2)	-8.1 ± 0.4 ‰ (n = 7)		

Uncertainties are given at the 2σ 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

Oxide Wt. %	VBS
SiO₂	49.08
Al₂O₃	14.78
Fe₂O₃	10.82
MnO	0.21
MgO	8.18
CaO	10.69
Na₂O	2.69
K₂O	0.18
TiO₂	1.73
P₂O₅	0.13
Li₂O	0.964
Total	99.46

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 σ level and correspond to the internal error.

Exp.	S/V cm ⁻¹	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	-	+6.0 ± 0.4
	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) $\text{g}\cdot\text{m}^{-2}$	NL(Al) $\text{g}\cdot\text{m}^{-2}$	NL(Fe) $\text{g}\cdot\text{m}^{-2}$	NL(Mg) $\text{g}\cdot\text{m}^{-2}$	NL(Ca) $\text{g}\cdot\text{m}^{-2}$	NL(Na) $\text{g}\cdot\text{m}^{-2}$	NL(Li) $\text{g}\cdot\text{m}^{-2}$
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 τ 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 β values (see Eq. (6)) are also shown.

Exp.	Time	τ (d)	r_0 (g/m ² /d)	D (m ² /d)	a	β
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 ± 0.004 (n=3)	0.039
PH10-90	$t \leq 2$ d	0.589	0.949	$1.9 \cdot 10^{-14}$	0.997 ± 0.002 (n=4)	0.019
SV1	$t \leq 15$ d	1.533	0.448	$1.7 \cdot 10^{-12}$	1.000 ± 0.002 (n=4)	0
SV2	$t \leq 15$ d	0.464	0.163	$6.0 \cdot 10^{-14}$	0.997 ± 0.002 (n=3)	0.019
PW50	$t \leq 2$ d	1.701	0.010	$4.0 \cdot 10^{-16}$	0.991 ± 0.003 (n=6)	0.059