Experimental determination of Li isotope behaviour during basalt weathering

Philip A.E. Pogge von Strandmann1, Wesley T. Fraser2, Samantha J. Hammond3,
Gary Tarbuck1, Ian G. Wood1, Eric H. Oelkers1, Melissa J. Murphy1

1 London Geochemistry and Isotope Centre (LOGIC), University College London and Birkbeck, University of London, Gower Place, London, WC1E 6BT.
2 Geography, Oxford Brookes University, Oxford, OX3 0BP
3 School of Environment, Earth and Ecosystems Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA

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

Abstract

Silicate weathering is the primary control of atmospheric CO₂ concentrations on multiple timescales. However, tracing this process has proven difficult. Lithium isotopes are a promising tracer of silicate weathering. This study has reacted basalt sand with natural river water for ~9 months in closed experiments, in order to examine the behaviour of Li isotopes during weathering. Aqueous Li concentrations decrease by a factor of ~10 with time, and δ⁷Li increases by ~19‰, implying that Li is being taken up into secondary phases that prefer ⁶Li. Mass balance using various selective leaches of the exchangeable and secondary mineral fractions suggest that ~12–16% of Li is adsorbed, and the remainder is removed into neoformed secondary minerals. The exchangeable fractionation
factors have a $\Delta^7\text{Li}_{\text{exch-soln}} = -11.6$ to $-11.9\%$, while the secondary minerals impose $\Delta^7\text{Li}_{\text{secmin-soln}} = -22.5$ to $-23.9\%$. Overall the experiment can be modelled with a Rayleigh fractionation factor of $\alpha = 0.991$, similar to that found for natural basaltic rivers. The mobility of Li relative to the carbon-cycle-critical cations of Ca and Mg changes with time, but rapidly evolves within one month to remarkably similar mobilities amongst these three elements. The evolution shows a linear relationship with $\delta^7\text{Li}$ (largely due to a co-variation between aqueous [Li] and $\delta^7\text{Li}$), suggesting that Li isotopes have the potential to be used as a tracer of Ca and Mg mobility during basaltic weathering, and ultimately CO$_2$ drawdown.

1.0 Introduction

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

Significant effort has gone into understanding and quantifying silicate weathering, both in the present (e.g. Maher, 2011; West et al., 2005), and in the geological past (e.g. Foster and Vance, 2006; Pogge von Strandmann et al., 2017a; Vance et al., 2009). Traditionally, marine radiogenic strontium isotopes have been used to determine past weathering changes (McArthur et al., 2001), but
their interpretation is far from unambiguous, because seawater isotope ratios are impacted by hydrothermal inputs and riverine isotope ratios are strongly dependent on the lithology undergoing weathering. This is further complicated by the inability to distinguish between carbonate and silicate weathering, where only the latter draws down CO$_2$ on the long-term (Allegre et al., 2010; Oliver et al., 2003). Hence, other tracers have been sought – ideally ones that are relatively unaffected by lithology, by carbonate weathering (which does not affect pCO$_2$ on $>10^4$ year timescales) or by biology and plant growth. So far, the only tracer that meets all these criteria is lithium isotopes.

Lithium isotopes (reported as $\delta^7$Li, the ‰ deviation from a normalising standard) are unaffected by carbonate weathering, because silicates are orders of magnitude more concentrated in Li than carbonates (Kisakürek et al., 2005; Millot et al., 2010; Pogge von Strandmann et al., 2017b), or by plant growth or primary productivity (Lemarchand et al., 2010; Pogge von Strandmann et al., 2016). The $\delta^7$Li range in primary silicate rocks (continental crust ~0‰; basalt 3–5‰ (Elliott et al., 2006; Sauzeat et al., 2015)) is narrow compared to that observed in rivers draining those rocks ($\delta^7$Li = 2–44‰, mean 23‰ (Dellinger et al., 2015; Huh et al., 1998; Pogge von Strandmann et al., 2006)). This range is due to the formation of secondary minerals (clays, zeolites and Fe-Mn-Al oxyhydroxides) during weathering, where these minerals preferentially take up the light isotope, $^6$Li, driving residual river and soil waters isotopically heavy (Vigier et al., 2008; Wimpenny et al., 2010). These secondary minerals also adsorb Li onto their exchangeable sites, imposing the same isotopic fractionation direction (Hindshaw et al., 2019; Pistiner and Henderson, 2003). Hence, Li isotopes in natural waters are controlled by the ratio of primary mineral
dissolution (low $\delta^7$Li) relative to secondary mineral formation (driving solution $\delta^7$Li high). This ratio is known as the “weathering congruency” (Misra and Froelich, 2012; Pogge von Strandmann and Henderson, 2015), which may be used as a tracer of chemical weathering intensity (Dellinger et al., 2015). Overall, this ratio also informs on the efficiency of weathering in removing CO$_2$, because if cations are being trapped by secondary minerals on the continents within clays and soils, they will not enter the ocean to form carbonate and sequester CO$_2$.

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

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

2.0 Methods

2.1 Experimental methods

Following the methods of Jones et al. (2012), approximately 250g of the natural basaltic sand used in the Jones et al. experiments was placed in 1L pre-
leached PTFE beakers containing 900ml of water. This sand was collected from the bottom of the Borgarfjörður estuary in Iceland, and was characterised by Jones et al. (2012). These data are repeated in Supplemental Table 1 for completeness’ sake. The sand consists of fairly fresh basalt (for example it contains significant basaltic glass), but also contains small amounts of phyllosilicates only just detectable by X-Ray Diffraction, as described below. For the water to be naturally charge-balanced and have a natural amount of alkalinity, the water used in the experiments was collected from the local Great Ouse River in eastern England. While the composition of this water is not identical to that in Iceland where the sand was sampled, the similarities in temporal fluid concentration behaviour (described below) between this study and Jones et al. (2012), which used Icelandic water, suggest that the differences in these water compositions only has a minor effect on experimental results.

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

Post-experiment, the reacted basalt was dried and stored. The pre- and post-experimental basalts were also leached, to examine their exchangeable fraction. This leach followed the Tessier method, by leaching the basalt in 1M
sodium acetate for 1 hour at room temperature (Hindshaw et al., 2019; Pogge von Strandmann et al., 2013; Tessier et al., 1979). Following this, the residue was leached for 1 hour with 0.6M HCl, which attacks the secondary mineral fraction, i.e., clays as well as oxyhydroxides and zeolites (Pogge von Strandmann et al., 2014; Tessier et al., 1979). Bulk basalt was dissolved in a standard method of concentrated HF-HNO₃-HClO₄, followed by HNO₃ and 6M HCl.

2.2 XRD and FTIR methods

X-ray powder diffraction analysis was carried out on a “whole sample” basis. Samples were prepared by grinding the material under ethanol using an agate pestle and mortar and the dried powder was side-filled against a ground-glass surface into a rectangular sample holder 20 x 20 mm in area and 1.5 mm deep. Diffraction patterns were collected with Co radiation, using a PANalytical X’Pert Pro diffractometer with Bragg-Brentano para focusing reflection geometry. This instrument is equipped with a Ge(1 1 1) Johansson-type focusing monochromator, producing a CoKα₁ incident beam. The X-ray tube was operated at 40 kV and 30 mA. Variable-width divergence and anti-scatter slits were used, together with a 15 mm wide beam mask in the incident beam, so as to illuminate a constant 15mm x 15mm area of the sample; 0.04 radian Soller slits were present in both the incident and diffracted beams to reduce the axial divergences. The X-ray detector was an “X’Celerator” position-sensitive detector; this device covers an angular range in 2θ of ±1.061°, with an effective fixed step size of 0.0167°. Data were collected over the 2θ range from 5° to 70° (20.5 Å < d < 1.56 Å), with data collection times of 15 hours.
Fourier-transform infrared (FTIR) analyses were conducted on dried samples using a Perkin-Elmer Spectrum 2 (Seer Green, Buckinghamshire, UK) attenuated total reflectance-FTIR (ATR-FTIR) spectrometer, fitted with a single-bounce diamond ATR cell. A total of 8 scans were used to generate an average spectrum for each sample at a resolution of 4 cm$^{-1}$. Spectra spanned the range 4000-600 cm$^{-1}$. All samples were analysed in triplicate.

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

2.3 Concentration analyses

The solution concentrations were analysed at The Open University, using an Agilent 8800 triple quadrupole inductively coupled plasma mass spectrometer (ICP-QQQ-MS). The instrument has two quadrupole mass filters, which are separated by a collision / reaction cell (allowing targeted interference removal in the cell). We ran in two modes of analysis, no gas for Li (as no interference ions are present on mass) and in He collision mode for all other analytes. In no gas mode, oxide levels (measured as CeO$^+$/Ce$^+$) were at 0.96% and doubly charged species (Ce$_2^+$/Ce$^+$) at 1.80%. In He mode, these were at 0.44% and 1.30% respectively.

Prior to analysis, samples were diluted 10 fold from the original solution in 2% HNO$_3$ to allow analysis of all masses in the same analytical session. Analyses were calibrated against a suite of synthetic multi-element solutions, which were made up to cover the range of concentrations in the experimental
solutions. An on-line internal standard (Rh and In) was added to each sample and standard also, to monitor and correct for instrument drift. In addition, drift was further monitored by running a measurement block consisting of the original water used in the experiments, one of the calibration standards and a 2% HNO₃ blank every 5 – 6 unknowns (5 times during the analytical session). Where concentrations are above the detection limit in the initial water, reproducibility is better than 2.5% (relative standard deviation from the mean of the five measurements). Accuracy was also determined using the international river water reference standard SLRS-5, and was within uncertainty of certified values. Lithium and silicon are not certified in SLRS-5, so in this case we compared to published concentrations and were also within uncertainty (Heimburger et al., 2013).

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

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

2.4 Li isotope analyses
Approximately 15ml of water was evaporated, and passed through a two-stage cation exchange column procedure, using AG50W-X-12 resin, and eluting with dilute HCl (Pogge von Strandmann et al., 2011). Column splits were collected before and after the main elute, and analysed for Li content, to determine how much Li was in the sample. Using this method, it was determined that >99.9% of sample was collected in the main column elution.

Purified samples were analysed using a new Nu Plasma 3 multi-collector ICP-MS at the LOGIC laboratories. A sample-standard bracketing procedure was used relative to the IRMM-016 standard. Each sample was measured three separate times during an analytical procedure, repeat measurements being separated by several hours, but during the same analysis session. Each individual measurement consisted of 10 ratios (50 s total integration time), giving a total integration time of 150 s/sample for the three repeat measurements that constitute a single analysis (n=1). We use the 2sd (standard deviation) of these three measurements as an assessment of our individual uncertainty, although values reported in Table 1 have also been compounded for the difference in normalising standards described below.

This mass spectrometer has new cones (compared to previous Nu MC-ICP-MSs), and, using the specific “super-lithium cones”, and a Cetac Aridus 2 desolvation system, a 5 µg/L solution gives a signal intensity of 100–140 pA (10–14V) of $^7$Li$^+$ at an uptake rate of ~100 µl/min. Background, instrumental Li intensities, typically ~0.07 pA (7mV), were subtracted from the sample and standard intensities. Total procedural blanks were generally indistinguishable from background, and contain <0.003 ng Li.
Lithium isotope ratios are commonly reported relative to the LSVEC standard (Flesch et al., 1973). LSVEC analysed relative to IRMM-016 yields δ⁷Li = -0.003 ± 0.054 (2se, n=19), which is in close agreement with past corresponding measurements (Jeffcoate et al., 2004; Phan et al., 2016). All reported δ⁷Li values have been re-normalised to LSVEC, and the reported uncertainty has been propagated to encompass analytical uncertainty on both samples, normalising standards and LSVEC.

Given that this is the first Li isotope study published at the new LOGIC isotope mass spectroscopy facilities, we have gone to some effort to determine the accuracy and precision of our analyses. We have therefore analysed seawater (both IAPSO and North Atlantic seawater) and the USGS rock standards BCR-2 (basalt), G-2 (granite), PCC-1 (peridotite) and SGR-1b (shale). Relative to LSVEC, seawater δ⁷Li = 31.11 ± 0.38‰ (2sd; n=12) (identical to other published values, e.g. Dellinger et al., 2015; James and Palmer, 2000; Jeffcoate et al., 2004; Pogge von Strandmann and Henderson, 2015). Our other values also compared well to published values: BCR-2: δ⁷Li = 2.64 ± 0.31‰ (n=5) (e.g. 2.6±0.3‰ (Pogge von Strandmann et al., 2011); 2.7±1.3‰ (Liu et al., 2013); 2.9 ± 0.3‰ (John et al., 2012)); G-2: δ⁷Li = 0.14 ± 0.16‰ (n=3) (e.g. 0.1 ± 0.8‰ (Phan et al., 2016); 0.6 ± 1.8‰ (Sauzeat et al., 2015)); PCC-1: δ⁷Li = 8.72 ± 0.13‰ (n=3) (e.g. 8.9 ± 0.4‰ (Magna et al., 2006)); SGR-1b: δ⁷Li = 4.00 ± 0.24‰ (e.g. 4.7 ± 0.7‰ (Phan et al., 2016); 3.6 ± 0.4‰ (Pogge von Strandmann et al., 2017b); 4.9 ± 1.9‰ (Hindshaw et al., 2018)). Hence, our standard results show that our Li isotope analyses are accurate, and have a long-term external precision (for the twelve months the new laboratory has been operational) of better than ±0.4‰ (2sd).
3.0 Results

3.1 Concentrations

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

Compared to the bulk basalt composition, the sodium acetate leach (exchangeable fraction) of the unreacted basalt has considerably higher Mg/Si ratios (mass ratio \( \frac{\text{Mg}}{\text{Si}}_{\text{bulk basalt}} = 0.27 \), while \( \frac{\text{Mg}}{\text{Si}}_{\text{exch}} = 25.3 \) (Table 2). Silicon (as a neutral species) should not be present in the exchangeable leach, and its presence (albeit at very low concentrations) implies that the leach is not fully efficient due to a small contribution of Si from the dissolution of silicate minerals (Hindshaw et al., 2019). Lower Mg/K ratios in the exchangeable fractions (\( \frac{\text{Mg}}{\text{K}}_{\text{bulk basalt}} = 13.7 \), while \( \frac{\text{Mg}}{\text{K}}_{\text{exch}} = 0.75 \)), and undetectable Al and Fe demonstrate that the exchangeable fraction of the initial basalt is enriched in the elements that would be expected to partition into this fraction (Renforth et al., 2015; Sigfusson et al., 2008; Tessier et al., 1979). The exchangeable fractions of the reacted basalts have somewhat lower Mg/Si (8.2–9.5). Li/Si is also several orders of magnitude higher in the unreacted exchangeable fraction than the initial bulk basalt (0.04 compared to \( 3 \times 10^{-5} \)), and decreases slightly in the reacted basalts (0.015–0.03), showing that Li is considerably more affiliated with sorption than Si.
In contrast, the HCl leach (that should attack the secondary mineral phases) of the unreacted basalt has similar Mg/Si to the bulk basalt (0.29 compared to 0.27). However, elements that would be expected to be enriched in clays and oxyhydroxides are enriched: Al/Si is 0.63 in the leach, compared to 0.36 in the bulk basalt, while Fe/Si is 0.92 compared to 0.53. Li/Si is also over an order of magnitude higher in the leaches. The reacted basalts’ leached Li/Si ratios are slightly lower than the unreacted basalt (Table 2). Overall, the leaches appear to have targeted the expected phases: the adsorbed fraction is enriched in exchangeable cations, and the secondary mineral plus Fe and Al oxyhydroxides fraction is enriched in elements such as Fe, Al and Li, as demonstrated before for basalts (Chapela Lara et al., 2017; Hindshaw et al., 2019; Opfergelt et al., 2014; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2014; Sigfusson et al., 2008; Tessier et al., 1979).

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

Aqueous solution concentration behaviour is generally similar to that reported by Jones et al. (2012). Most major elemental concentrations increase with reaction time (Fig. 1), with an overall 3% increase in Na, 24% in Mg, 93% in Si, while at the same time K and Ca concentrations decrease slightly (on the
order of 10%). This behaviour for the individual elements is similar to that observed by Jones et al. (2012), although the enrichment amounts vary. This is likely due to the different composition of the waters used in these experiments (Jones et al., 2012). Minor elements like Al and Mn also increase. Almost all of these elements reach apparent steady-state (stable concentrations) after ~50–100 days after the beginning of the experiments. Importantly for these experiments, as also shown by Jones et al. (2012), Li concentrations decrease, from 13.5 µg/L in pre-experimental water to 1.3 µg/L by the end of the experiment. By comparison, the flow-weighted mean global river concentration is 1.5 µg/L (Huh et al., 1998). This behaviour results in a rapid increase in some elemental ratios including Mg/Na, which attains a near steady value after ~12 days. The Li/Na ratios evolve to a constant value more slowly, due to the more gradual decline in Li concentrations.

3.2 Li isotopes

The δ7Li of the pre-experimental bulk basalt is 4.4‰, similar to other Icelandic and MORB basalts (Elliott et al., 2006; Pogge von Strandmann et al., 2006; Pogge von Strandmann et al., 2012; Vigier et al., 2009). The post-experimental bulk basalts from the two experiments have a δ7Li of 4.1–4.5‰, within analytical uncertainty of the pre-experimental basalt (Table 2).

The exchangeable fraction (sodium acetate leach) of the pre-experimental basalt has a δ7Li of 17.8‰, with a Li concentration of 0.7 µg/L (compared to a total procedural blank of 0.03 µg/L). Given the presence of minor quantities of Si in these leaches from the dissolution of silicate minerals (see Section 3.1), the leachate δ7Li is likely slightly lower value than if the leach were fully efficient.
The secondary mineral fraction (HCl leach) has a $\delta^7\text{Li}$ of 5.3‰ with a Li concentration in the leach of 11.6 ng/g. As for the exchangeable leach, the secondary mineral leach is unlikely to have been totally efficient (Hindshaw et al., 2019), although elemental ratios in this leach (Table 2) are close to stoichiometry for some examples of smectite.

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

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

4.0 Discussion
4.1 Lithium mass balance

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

We also assume that Li added to solution by primary basalt dissolution can be calculated by assuming that the increase in fluid of Mg or Si represents stoichiometric dissolution (Jones et al., 2012), such that the Li/Mg or Li/Si concentration ratios remain constant during dissolution. Stoichiometric weathering is unlikely to be a perfect assumption, given that both Mg and Si are also known to partition into secondary minerals as well (e.g. (Opfergelt et al., 2014; Pogge von Strandmann et al., 2012)). However, constant elemental ratios during dissolution is likely a robust assumption, as Li is a moderately incompatible element, and does not partition preferentially into any primary basaltic minerals (Penniston-Dorland et al., 2017). In any case, the amount of Li added from basalt dissolution is minor compared to that lost from solution. According to the Mg and Si concentration increase, between 0.015 and 0.07 g of the ~250 g basalt samples dissolved during the experiments, which is around 4% of the total Li mass balance (~0.4µg Li, assuming constant Li/Mg ratios).
In the experiments, when normalised to the amount of material used, the exchangeable fraction gained ~1.4–1.8 µg Li, while the secondary minerals gained ~9.4–9.9 µg Li. The solution (when corrected for fluid loss due to sampling) lost ~11.4 µg Li by the end of the experiment.

Given weighing errors and propagated analytical uncertainty, the experiments therefore can be mass balanced, with around ~82–87% of the Li lost from the fluid substituting into secondary phases, and ~12–16% being taken into the exchangeable fraction (Fig. 4). This result demonstrates that the sorbed fraction is of sufficient importance to be an integral consideration of future lithium weathering studies.

4.2 Mineral saturation states

Mineral saturation states in the fluids were calculated using the PHREEQC programme (Parkhurst and Appelo, 1999). Basaltic primary minerals (olivine, plagioclase, pyroxene) are undersaturated in all the experimental fluids, and hence are likely to dissolve. The undersaturation of these minerals is maintained by supersaturation (and hence likelihood of precipitation) of secondary minerals (Gíslason et al., 1996). For example, both kaolinite and smectite are consistently supersaturated in all the experimental solutions. However, while kaolinite’s saturation is broadly constant, that of smectite increases with time. Iron oxyhydroxides (e.g. amorphous Fe(OH)₃, another common basaltic secondary mineral) starts out undersaturated, but becomes supersaturated after about 4 days of reaction.

Mineral saturation states provide insight into whether neoformation or sorption is dominantly controlling Li isotope fractionation. There is a clear co-
variation between the saturation state of smectite (Aberdeen-montmorillonite) and $\delta^7$Li that does not exist for any other modelled secondary minerals. As the smectite saturation state increases, so as the likelihood of precipitation increases, the $\delta^7$Li also increases, because more $^6$Li is being incorporated into precipitating smectites. It is also noticeable that extrapolation of the trend line ($r^2 = 0.94$) back into undersaturated conditions (SI < 0) leads to the initial $\delta^7$Li values of the basalts used (Fig. 5). In other words, when no smectite is forming, it appears that the solutions would have an identical $\delta^7$Li value to primary basalt (i.e. congruent weathering). As smectite precipitation increases, $^6$Li is preferentially removed from the fluid, increasing solution $\delta^7$Li values. In contrast, were Fe oxyhydroxide the dominant secondary mineral controlling Li, its undersaturated conditions at the start of the experiment should result in unfractionated Li isotopes, which is not observed. Therefore, this confirms that clay formation strongly affects Li isotope fractionation (Bouchez et al., 2013; Wimpenny et al., 2015; Wimpenny et al., 2010), but also adds to the mass balance argument made above, that it is secondary mineral formation, rather than sorption, that is largely controlling Li isotope fractionation in this experiment (84–88% of Li by mass balance) (Hindshaw et al., 2019; Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2015).

4.3 Li isotope fractionation

Assuming that the Li concentrations and isotope ratios measured in the exchangeable and secondary mineral fractions represent fractionation from the
youngest (most recent) experimental fluids in the dissolved fraction, it is possible to calculate fractionation factors into both solid fractions.

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

In several different river studies, including in basaltic terrains, Li/Na ratios have been reported to have a similar behaviour as Li isotope ratios,
because Na is considered to be highly mobile (and hence remains in the fluid phase) (Dellinger et al., 2015; Liu et al., 2015; Millot et al., 2010; Pogge von Strandmann et al., 2017b). Hence, Li/Na ratios are likely also be controlled by the ratio of dissolution to precipitation, and might be a good proxy for the extent of water-rock interaction time.

The relationship between δ⁷Li and Li/Na has been possible to simulate with isotopic fractionation models, which yield the fractionation factors that might be mineral-specific (Pogge von Strandmann et al., 2017b). Hence, overall, as Li/Na decreases (because Li is removed from solution relative to Na), δ⁷Li increases. Generally it seems that most large global rivers can be simulated assuming an equilibrium fractionation relationship, although global basaltic rivers appear to be following more of a Rayleigh fractionation relationship (Pogge von Strandmann et al., 2017b).

In the case of this study, the data show a logarithmic relationship between Li/Na and δ⁷Li as it evolves from the starting point of the initial water (Fig. 6). This relationship can be modelled with a Rayleigh fractionation equation, given that the experiments in this study behaved as a closed system. Hence, ~90% of the initial Li was taken up into various secondary phases. All the data form a single fractionation relationship stemming from the initial fluid composition, with a best-fit Rayleigh α value of 0.991 (r² = 0.96). This is generally similar to fractionation factors reported during natural basalt weathering: MORB-seawater and basalt particle-seawater interaction have α~0.985 (Chan et al., 1992; Pogge von Strandmann et al., 2008), and the best-fit to a global compilation of basaltic rivers is to a Rayleigh relationship with α~0.992 (Pogge von Strandmann et al., 2017b). This factor is likely related both to the experimental fluid composition
(and hence the starting fluid composition and the composition of the basalt) because it is likely to control the precise secondary mineralogy.

4.4 Mobility and $\delta^7$Li

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

Elemental mobility during weathering is the tendency of a particular element to go into the fluid phase versus being taken up by secondary minerals during weathering. During basaltic weathering, Na is the most mobile major cation (Gíslason et al., 1996), and hence the mobility of other cations is commonly reported as the relative mobility to Na, where the formula is $(x/Na)_{solution}/(x/Na)_{rock}$. In Icelandic basalts relatively mobile elements such as Ca and Mg are approximately ~$10 \times$ less mobile than Na, while immobile elements such as Al or Fe are about three orders of magnitude less mobile than
Natural studies have rarely measured Li concentrations, and hence the relative difference between the weathering mobility of Li and Ca or Mg remains poorly understood. In the case of our experiments, the final equilibrium mobilities are similar to the natural values reported by Gislason et al. (1996), but show a clear trend of evolution with time. Magnesium starts at around 13× less mobile than Na, but within 4 days has evolved slightly to its final value of ~11× less mobile (Fig. 7). Cations such as Ca behave similarly, albeit in the case of Ca the relative mobility decreases slightly with time. The relative mobility of lithium, on the other hand, changes more dramatically, starting out at almost 75% of the mobility of Na, and decreasing, and stabilising at, about 10% after ~100 days reaction. Over 80% of this change in mobility occurs within the first month of the experiment. This observation supports the hypothesis that secondary mineral formation, rather than solely the more rapidly reacting exchangeable fraction, is largely affecting the Li isotope composition. Exchangeable reactions take a few hours to occur (Pistiner and Henderson, 2003), while the kinetics of secondary mineral formation are thought to be relatively slow (on the order of 10⁻¹⁹ mol/cm²/s (Yokoyama and Banfield, 2002)). However, those observations on secondary mineral kinetics were largely made using major elements, not more sensitive trace elements such as Li, and our data suggest that at least amorphous secondary phases begin to form within a few days. From the point of using Li as a tracer of overall chemical weathering processes, especially the transport of Ca and Mg to the oceans to form carbonate thereby drawing down CO₂, the relative mobility difference between Li and Ca or Mg is more revealing: Li starts the experiment as ~15× more mobile than Ca
(and ~9× more mobile than Mg), but these values decrease with time during the experiment to Li being only 2.2× more mobile than Ca (and 1.0× as mobile as Mg)(Fig. 8). This temporal evolution is almost entirely driven by the significant changes in Li concentration, although there is also a relatively small decrease in Ca mobility as well. Most of these change occurs within the first month of the experiments, while for the subsequent >7 months significantly less changes occur. The relatively slower evolution of Li mobility (compared to major elements) suggests that Li may be a very sensitive element for tracing very early and small amounts of incipient secondary mineral formation. Certainly measurements using X-Ray Diffraction (XRD) of the pre- and post-experiment basalts cannot distinguish the amounts of phyllosilicates or Fe oxides in the two basalts. Hence the partitioning of Li is clearly more sensitive to the inception of secondary mineral formation than XRD.

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

These results therefore suggest two points: 1) the changes in the phases controlling the Li isotope ratios are very small, showing that δ7Li is considerably more sensitive to these changes than the more standard methods of XRD and FTIR; 2) once a steady-state is reached, Li has a similar mobility to both Ca and Mg, meaning that Li is a useful tracer for the behaviour during weathering of these two critical elements (Pogge von Strandmann et al., 2016).

Notably, given that only Li isotope ratios are useful in the marine geological record, and not absolute Li concentrations, there is a correlation
between solution $\delta^7\text{Li}$ and the relative mobility of Li to Ca and Li to Mg (Fig. 8). In the case of Ca, the negative relationship has an $r^2$ of 0.99. After four days of reaction, the Li to Ca mobility begins to decrease and $\delta^7\text{Li}$ to further increase (Fig. 8), again largely driven by the change in Li concentration correlating with $\delta^7\text{Li}$. In other words, during the experiment, the Li/Ca and Li/Mg ratios of the secondary minerals must be increasing as Li is increasingly removed from solution. After a month (34 days) of reaction, the rates of change of Li to Ca mobility and of $\delta^7\text{Li}$ dramatically decline, as the reaction reaches apparent steady-state.

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

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

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

The solution Li isotope ratio also correlates with the modelled saturation index of smectite, where an extrapolation of the trend to saturated conditions ($\text{SI} = 0$) converges towards basaltic $\delta^7$Li compositions, further implying that neoformation of secondary minerals may be largely controlling solution $\delta^7$Li. This suggests that Li isotopes are more susceptible to this early mineral formation than major element ratios, or to standard methods of clay detection such as X-Ray diffraction and Fourier-transform infrared. Equally, this implies that the onset of clay formation (or even amorphous clays) is much more rapid than initially thought (on the order of a few days to months).
Finally, the relatively mobility of Li to those cations critical in the carbon cycle (Ca and Mg) evolves with time, but rapidly (within one month) reaches a point where the behaviour of Li is broadly similarly mobile to both elements. There is also a direct correlation between $\delta^7$Li and this mobility, implying that Li isotopes can be used to trace Li mobility, and therefore can be used to trace Ca and Mg mobility (at least during basalt weathering), and ultimately CO$_2$ drawdown.

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Table 1. Concentration and isotope ratios from the experimental fluids.
Figure 1. Measured aqueous Mg and Si concentrations during the experiment. Analytical uncertainty is smaller than the symbol sizes.
Figure 2. Solution Li concentrations and isotope ratios with time throughout the experiment. The open diamonds and filled circles represent the two different experiments. Analytical uncertainty is smaller than the symbol sizes.
Figure 3. Measured Li isotopes ratios of the fluid phase from both experiments as a function of the corresponding Li concentration. The grey and black lines represent the two experiments. The black crosses are natural basaltic river studies (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009). Analytical uncertainty is smaller than the symbol sizes.
Figure 4. The mass balance of Li removed from solution by the different phases, relative to the isotope fractionation from the experimental solution. The filled circles represent Experiment 15, and the open diamonds Experiment 16.

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

Figure 6. Experiment fluid $\delta^7$Li as a function of corresponding mass Li/Na ratio (grey circles). The dotted illustrates a Rayleigh fractionation relationship, while the solid line represents an equilibrium fractionation relationship. The numbers
next to the lines are the isotopic fractionation factors. The black crosses are natural basaltic river studies (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009). Analytical uncertainty is smaller than the symbol sizes.

Figure 7. Relative mobility (relative to Na) of Mg, Li, Ca and Al with time through the experiment. Note different scale on axes.
Figure 8. The reactive fluid Li isotopes ratio compared to the relative mobility of Li to Ca. The numbers next to each data point represent the experimental time (in days). Analytical uncertainty is smaller than the symbol sizes.