# The effect of hydrothermal spring weathering processes and primary productivity on lithium isotopes: Lake Myvatn, Iceland

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Lithium isotopes are rapidly becoming one of the most useful tracers of silicate weathering processes, but little is known on their behaviour in groundwaters and hydrothermal springs, and how these sources might influence the weathering signal in surface waters. This study presents lithium isotope compositions ($\delta^7$Li) for cold groundwaters (3–7°C) and hydrothermal springs that were at geothermal temperatures (200–300°C) but have cooled during transport (17–44°C). Both represent an important source of water and nutrients for Lake Myvatn, Iceland. We also present a time-series from the Laxa River, which is the single outflow from the lake. The $\delta^7$Li values in the input springs to Lake Myvatn are highly variable (5–27‰), and correlate inversely with temperature and total dissolved solids. These co-variations imply that even in such waters, the processes controlling $\delta^7$Li variations during weathering still operate: that is, the ratio of primary rock dissolution to secondary mineral formation, where the latter preferentially incorporates $^6$Li with a temperature-dependent fractionation factor. In high-temperature geothermal waters (>300°C) secondary mineral formation is inhibited, and has a low fractionation factor, leading to little $\delta^7$Li fractionation. Even in waters that have cooled considerably over several months from their geothermal temperatures, fractionation is still low, and $\delta^7$Li values are similar to those reported from waters measured at >350°C. In contrast, cooler groundwaters promote relatively high proportions of clay formation, which scavenge dissolved solids (including $^6$Li). The time series on the Laxa River, the single outflow from Lake Myvatn, shows little $\delta^7$Li variation with time over the 12 month sampling period (17-21‰), demonstrating that in contrast to tracers such as Si isotopes, Li isotopes are unaffected by the significant seasonal phytoplankton blooms that occur in the lake. Thus, these results clearly illustrate that Li isotopes are ideally suited to constrain silicate weathering processes, because fractionation by secondary mineral formation operates even when groundwater and hydrothermal inputs are significant, and because Li isotopes are demonstrably unaffected by phytoplankton or plant growth.

## 1.0 Introduction

The chemical weathering of continental Ca-Mg silicates is one of the primary processes that remove atmospheric $CO_2$, causing it to eventually be sequestered in the oceans and carbonate rocks (Berner, 2003; Walker et al., 1981). Chemical weathering also affects the carbonate saturation state of the oceans on shorter, millennial, timescales, affecting its pH and ability to store $CO_2$ (Archer et al., 2000). Therefore, silicate weathering is a critical part of the carbon cycle, and is a process that urgently requires accurate quantification, both in the present, and in the past. Without these data, our knowledge regarding the mechanisms and rates of climate stabilisation is lacking. The weathering of basalts, in particular, exerts a greater effect on global $CO_2$ budgets than would be anticipated from the extent of global basaltic terrains (Dessert et al., 2003; Gaillardet et al., 1999; Gislason, 2005; Gislason et al., 2009), and therefore is a fruitful area to examine global weathering processes.

Traditionally, radiogenic isotopes (e.g. $^{87}Sr/^{86}Sr$) have been used to understand weathering processes, and quantify palaeo-weathering (Allegre et al., 2010; Blum and Erel, 1997; Jones and Jenkyns, 2001; Raymo et al., 1988). However, such systems tend to be strongly influenced by the isotope ratio of the rock undergoing weathering, and, importantly, often cannot distinguish between weathering of silicates over carbonates (where the latter does not sequester atmospheric $CO_2$ over geologic time) (Oliver et al., 2003; Palmer and Edmond, 1992). Hence, novel isotopic tracers of weathering have been sought that are independent of lithology and other non-weathering processes, such as biology. Lithium isotopes ($^6$Li and $^7$Li, where the ratio is reported as $\delta^7$Li) have proved to be one of the most useful of these tracers, and are currently the only known tracer that solely responds to silicate weathering processes (Pogge von Strandmann and Henderson, 2015). This is because the Li isotope ratio is thought to be unaffected by uptake into plants (Lemarchand et al., 2010), and because Li, even in carbonate catchments, is demonstrably dominantly sourced from silicates (Kisakürek et al., 2005; Millot et al., 2010b). The Li isotope ratio of silicate rocks describes a very narrow range ($\delta^7\mathrm{Li}_{\mathrm{continental\ crust}} \sim 0.6 \pm 0.6$‰ (Sauzeat et al., 2015; Teng et al., 2004); $\delta^7\mathrm{Li}_{\mathrm{basalt}} = \sim 3–5$‰ (Elliott et al., 2006; Tomascak et al., 2008)), relative to that reported in river waters ($\delta^7$Li = 2–44‰; global mean 23‰ (Dellinger et al., 2015; Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Lemarchand et al., 2010; Liu et al., 2015; Millot et al., 2010b; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2014b; Rad et al., 2013; Vigier et al., 2009; Wang et al., 2015; Wimpenny et al., 2010b; Witherow et al., 2010)). This high variability in rivers is caused by weathering processes: dissolution of silicates causes no isotope fractionation, but secondary minerals formed during weathering preferentially take up $^6$Li, driving residual waters isotopically heavy (Huh et al., 2001; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2010; Vigier et al., 2008; Wimpenny et al., 2010a). Therefore, surface water $\delta^7$Li is controlled by the ratio of primary mineral dissolution (low $\delta^7$Li, high [Li]) relative to secondary mineral formation (driving waters to high $\delta^7$Li, and low [Li]). This ratio has also been described as the weathering congruency (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013), weathering efficiency (Pogge von Strandmann and Henderson, 2015) or weathering intensity (Dellinger et al., 2015): when riverine $\delta^7$Li = rock $\delta^7$Li, then weathering is congruent (water chemistry = rock chemistry), efficient (cations are not retained in clays, but are delivered to the oceans) and low intensity (little clay formation, and a low weathering to denudation ratio – bearing in mind that "weathering intensity" has been used in different ways by different authors).

A considerable body of literature has built up over the past decades on riverine Li behaviour (Bagard et al., 2015; Dellinger et al., 2014; Huh et al., 2001; Huh et al., 1998; Kisakürek et al., 2005; Lemarchand et al., 2010; Liu et al., 2015; Millot et al., 2010b; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2014b; Rad et al., 2013; Teng et al., 2010; Vigier et al., 2009; Wang et al., 2015; Wimpenny et al., 2010b; Witherow et al., 2010), and more recently, forays into palaeo-weathering have emerged (Hall et al., 2005; Hathorne and James, 2006; Hoefs and Sywall, 1997; Lechler et al., 2015; Misra and Froelich, 2012; Pogge von Strandmann et al., 2013; Ullmann et al., 2013). However, groundwaters, and their influence on weathering and the continental Li isotope signal, remain poorly characterised (Bagard et al., 2015; Hogan and Blum, 2003; Meredith et al., 2013; Negrel et al., 2010; Negrel et al., 2012; Pogge von Strandmann et al., 2014b; Tomascak et al., 2003), as does the potential influence of land-based hydrothermal groundwaters and springs (Henchiri et al., 2014; Millot et al., 2010a; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006). It is clear, however, that continental hydrothermal systems (including island arcs and ocean islands) can have very high Li concentrations (up to ~37 mmol/l (Chan et al., 1993; Chan et al., 1994; Millot et al., 2010a)), and therefore may influence the global riverine isotope composition, given the high significance of basaltic weathering to the global mean (Dessert et al., 2003; Gaillardet et al., 1999). Changes in this input over time may also have led to changes in the global mean riverine and groundwater composition, and therefore groundwater and riverine fluxes to the oceans, as has also been proposed for the Sr isotope system (Allegre et al., 2010).

This study presents Li isotope data for hydrothermal groundwaters that comprise the dominant source of Lake Myvatn, in northern Iceland. These waters have experienced water-rock interactions at a range of temperatures, from ~300°C (cooled during transport to 17–44°C) hydrothermal springs to cold groundwaters (3–7°C). This approach allows the comparison of "hot" and "cold" groundwaters from the same region, and their individual impact on Li isotope behaviour. Both groundwater types may, in many global regions, have significant impact on river water chemistry. We also report Li isotope data for a time series from the Laxa River, the single outflow from the lake, to constrain how seasonal variations in biological productivity potentially affect Li isotopes. The latter is important, as it provides a natural laboratory to study the effects of significant variation in primary productivity and biocycling on Li isotopes. These data will be compared with previously published silicon isotope data for the same samples which show large variations in both isotope composition and elemental abundances due to seasonal diatom blooms within the lake (Opfergelt et al., 2011). It has been shown that some plants do not fractionate Li isotopes (Lemarchand et al., 2010), but that study remains the only assertion that Li isotopes are not fractionated during biological uptake. It is therefore important to test this assumption, to determine whether Li isotopes are really such a useful tracer of silicate weathering processes in isolation from any biological effects.

## 2.0 Field area and samples

Lake Myvatn is a shallow eutrophic lake in NE Iceland (65°35'N, 17°00'W), located just beneath the Arctic Circle (Fig. 1). The lake is at 278 m above sea level, and has a maximum depth of 4.2 m, and an area of 37 km$^2$. During the ice-free season (mid May to late September), the entire water column is well-mixed. The lake is almost entirely groundwater fed, with cold springs feeding the southern basin (Sydrifloi), and warm springs feeding the northern basin (Ytrifloi). The latter springs gain their heat from the Namafjall and Krafla geothermal fields (Kristmannsdottir and Armannsson, 2004). The main outflow from the lake is via the Laxa River, yielding a residence time for water in the lake of about 27 days (Olafsson, 1979) (Fig. 1).

The lake was formed ~2300 years ago by a major basaltic volcanic eruption (Hauptfleisch and Einarsson, 2012; Thordarson and Hoskuldsson, 2002). This underlying geology has been modified during more recent eruptions, such as the 1725–1729 and 1975–1984 eruptions in the Krafla Volcano, 10km to the north (Thordarson and Hoskuldsson, 2002).

The lake is one of the most productive in the northern hemisphere, despite winter ice cover. This is related largely to nutrient-rich groundwater inflow, reflected by very high seasonal diatom, green algae and cyanobacteria productivity (Gislason et al., 2004). The concentrations of many dissolved metals in the lake are largely controlled by biological activity. In the ice-covered winter, the top sediment pore waters are enriched in nutrients by several orders of magnitude relative to the lake waters. These nutrients are released in the ice-free summer by bioturbation, sediment resuspension and diffusion, leading to high nutrient fluxes (Gislason et al., 2004).

Samples were taken from both the “cold” and “hot” springs sourcing the lake, and a monthly time series spanning March 2000 to March 2001 was taken from the Laxa River draining the lake following sampling protocols outlined in Opfergelt et al., 2011.

## 3.0 Methods

Major and trace element concentrations are from Opfergelt et al., 2011, and were determined by ICP-MS and ion chromatography. For Li isotope analysis, 15 ml of sample was dried down, and passed through a two-step cation exchange chromatography (AG50W X-12), using dilute HCl as an eluent. Isotopic analyses were conducted on a Nu Instruments multi-collector ICP-MS, relative to the standard L-SVEC (Flesch et al., 1973). The exact methods for chemistry and analysis are detailed elsewhere (Pogge von Strandmann et al., 2011; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2013). Seawater was run as an “unknown” standard, yielding $\delta^7$Li = 31.3 ± 0.6‰ (n=48, chemistry=48) over a three-year period. The total procedural blank of this method was effectively undetectable (<0.005ng Li), which is insignificant relative to the 10–20 ng of Li analysed in each sample.

The groundwater and river elemental concentrations were used to calculate mineral saturation states using PHREEQC (Parkhurst and Appelo, 1999). These are reported as SI, the saturation index, which is a logarithmic scale, with positive numbers indicating oversaturation, and negative numbers undersaturation. The uncertainty depends on the individual mineral, but is typically around 1–2 log units (Stefansson and Gislason, 2001).

## 4.0 Results

### 4.1 Mineral saturation

Groundwater pH, generally the dominant control on mineral saturation in Iceland (Gíslason et al., 1996; Stefansson and Gislason, 2001; Stefansson et al., 2001), varies between 8.1 and 10.0 (Table 1 – groundwater pH was measured at spring temperature, while outflow pH was measured at room temperature (Opfergelt et al., 2011)). Consequently, primary minerals, such as forsterite, are significantly undersaturated (Stefansson et al., 2001). Clay minerals such as kaolinite and smectites are oversaturated between pH 8–9.5, and undersaturated at pH >9.5, as are zeolites (common zeolites like laumontite or phillipsite are at or below saturation at pH>9 in these waters). In contrast, minerals such as chlorite tend to dominate at high pH. This is similar to the trends observed in Icelandic rivers (Gíslason et al., 1996; Pogge von Strandmann et al., 2008a; Pogge von Strandmann et al., 2006; Stefansson and Gislason, 2001; Stefansson et al., 2001).

Mineral saturation in the Laxa time series varies strongly with time. Primary minerals, such as forsterite, are highly undersaturated in the winter, and approach saturation in the summer. In contrast, secondary minerals such as kaolinite and smectite are undersaturated only in the summer. Calcite becomes oversaturated at highest pH during the summer.

### 4.2 Lithium

Lithium concentrations in the groundwater samples vary between 130 and 10,000 nmol/l, and between 116 and 237 nmol/l in the Laxa River outflow (Table 1). These concentrations are up to two orders of magnitude higher than those in most Icelandic rivers, although similar to other hydrothermal springs, and rivers affected by them (Louvat et al., 2008; Pogge von Strandmann et al., 2006; Vigier et al., 2009). Equally, the concentrations in Icelandic soil pore waters are also generally similar to these springs (Pogge von Strandmann et al., 2012).

Lithium isotope ratios ($\delta^7$Li) vary between 5.1 and 27.2‰ in the springs, showing a negative correlation with Li concentration (shown as the reciprocal in

Fig. 2), as well as with temperature, and total dissolved solids concentration. Similar correlations with concentration have been observed in many rivers, groundwaters and pore waters, reflecting the controlling factors on Li, namely primary mineral dissolution to secondary mineral formation (Kisakürek et al., 2005; Millot et al., 2010b; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2014b). Relatively low $\delta^7$Li (1–11‰) have been observed in other high-temperature hydrothermal springs, both from Iceland (Pogge von Strandmann et al., 2006), and other basaltic terrains (Millot et al., 2010a; Pogge von Strandmann et al., 2010). Equally, the global mean hydrothermal input to the oceans at mid-ocean ridges is thought to be ∼8‰ (Chan et al., 1993; Chan et al., 1994; Hathorne and James, 2006; Misra and Froelich, 2012).

In contrast, $\delta^7$Li in the Laxa varies much less (17.2–20.8‰), with no obvious time-dependent trends. This is a narrow range, compared to other Icelandic rivers (15–44‰), where values of ∼10‰ have been reported in rivers with high hydrothermal influence (Pogge von Strandmann et al., 2006; Vigier et al., 2009).

## 5.0 Discussion

### *5.1 Hydrothermal springs*

As with most aqueous systems, and particularly relatively simple systems sourced solely by basalt (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann et al., 2012), the springs sourcing Myvatn exhibit a negative co-variation between $\delta^7$Li and Li concentrations (Fig. 2). This co-variation confirms that Li isotopes in these springs are being controlled by the same processes that dominate Li isotopes in other weathering environments, namely the ratio of primary mineral dissolution to secondary mineral formation. Because secondary minerals preferentially take up $^6$Li, when their formation rate is relatively high, they will deplete waters in Li, and drive them to higher $\delta^7$Li. This process has been observed in most global river catchments, and also likely operates for the global mean riverine flux to the oceans. At hydrothermal temperatures, however, different secondary minerals form compared to low temperature environments. At up to ~200°C, smectites, zeolites and mixed-layer clays dominate, while chlorites dominate at 250°C, and by ~300°C secondary minerals that fractionate Li do not form at all, and alteration minerals such as epidote or actinolite are common (Henley and Ellis, 1983). At the same time, higher temperatures result in lower isotopic fractionation factors, and experimental evidence suggests that smectite causes <2‰ fractionation at 250°C (Vigier et al., 2008). Analyses of altered basalt suggests that at these temperatures, chlorite causes similar fractionation (Verney-Carron et al., 2015). Experiments and data that approach Li isotope fractionation from the high-temperature end, however, suggest that fluids should be around 6.5‰ higher than corresponding solids at 250°C, and 5.5‰ higher at 300°C (Chan et al., 1993; Marschall et al., 2007; Wunder et al., 2006). Hence, there is some ambiguity on the exact fractionation caused by secondary minerals at these temperatures, and hence whether a lack of fractionation is caused by a low fractionation factor, and/or whether fractionating minerals are sparsely present.

The $\delta^7$Li of the springs co-varies negatively with both temperature (3–44°C) and conductivity. The $\delta^7$Li values of the higher temperature waters (~5–10‰) are similar those reported from significantly hotter hydrothermal waters, both at mid-ocean ridges (6–11‰, temp = 270–350°C (Chan et al., 1993; Chan et al., 1994)), and in continental volcanic settings (1.0–10.9‰, temp = 33–250°C) (Millot et al., 2010a; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Pogge von Strandmann and Henderson, 2015). In a series of hydrothermal experiments, both Chan et al. (1994) and Millot et al. (2010a) showed that the $\delta^7$Li of hydrothermal fluids decreases with higher temperatures. The $\delta^7$Li of the fluids reached ~5‰ (basaltic values) at ~350°C, due to more efficient leaching of basalt at higher temperatures promoting isotopic equilibration with the host rock, and particularly, a lack of secondary mineral formation at higher temperatures (Henley and Ellis, 1983) and lower isotopic fractionation factors in those minerals that still form at those temperatures. In the Myvatn spring samples, a similar trend is observed, but values of ~5‰ are achieved at temperatures ~20°C. This suggests that the “hot” Myvatn springs were at significantly higher temperatures in the Krafla geothermal fields, and cooled during their at least two month's travel (Kristmannsdottir and Armannsson, 2004) to Myvatn, preserving their original isotopic signature. Hence, despite the 200–250°C cooling the "hot" springs have undergone (Bodvarsson et al., 1984), relatively little effect by secondary mineral formation has occurred, causing a maximum $\delta^7$Li fractionation of around 6‰ from basalt.

In contrast, the "cold" groundwater springs are highly fractionated from basalt, with $\delta^7$Li values up to 27‰ (23‰ higher than basalt), likely due to the formation of secondary minerals such as smectites or zeolites. This therefore agrees with the hypothesis of Millot et al., (2010a), that temperature is a direct control on hydrothermal fluid $\delta^7$Li, via inhibition of secondary mineral formation and depression of fractionation factors.

Overall, several different reaction-flow models (Bouchez et al., 2013; Liu et al., 2015; Pogge von Strandmann et al., 2014b; Wanner et al., 2014) have proposed that it is the water-rock interaction time that controls riverine Li isotope ratios. For rivers with significant hydrothermal input, this effect may be diluted, because of the input of waters that have had high water-rock interaction time at high temperatures will still have unfractionated Li isotope ratios. Hence, Li isotopes will likely not function as a tracer of water-rock interaction in rivers with a hydrothermal input.

### 5.1.1 Elemental mobility and weathering tracers

Warmer spring waters generally have more Na, K, Ca and Si than the colder waters, as well as low $\delta^7$Li values (see above). Low dissolved $\delta^7$Li values suggest a high ratio of primary rock dissolution relative to secondary mineral formation. In other words, the lower and more rock-like the dissolved $\delta^7$Li is, the more nominally congruent silicate weathering is (relatively less secondary mineral formation). As discussed above, it is also possible that rock-like $\delta^7$Li values are due to a lack of isotope fractionation at higher temperatures (Verney-Carron et al., 2015; Vigier et al., 2008), although compilations suggest there should still be significant Li isotope fractionation at 300–350°C (Marschall et al., 2007). Therefore, in these hydrothermal springs, higher temperatures appear to promote more congruent weathering (corresponding to higher dissolution rates (Stefansson et al., 2001)), accounting for the higher elemental concentrations in warmer waters. This applies to elements such as the alkali metals (Li, Na, K), but not for elements such as Mg or Fe, which are trace elements in geothermal waters (Albarede and Michard, 1986; Elderfield and Schultz, 1996; Holland, 2005), as also shown by a positive co-variation of Mg/Na and Li isotopes (not shown), where low Mg/Na ratios coincide with low $\delta^7$Li and high temperatures.

A general weathering (primary mineral dissolution vs. secondary mineral formation) control on Li is confirmed by a negative co-variation between $\delta^7$Li and conductivity (Fig. 3). Effectively, the more minerals that are dissolving and/or the less cations that are being retained in secondary minerals (relative to those provided by dissolution), the higher the conductivity (and individual elemental concentrations). In turn, the higher conductivity is, the more cations will eventually be washed into the oceans. Thus, a higher conductivity (itself caused by greater total dissolved solids) is a function of more efficient silicate weathering, in that relatively less material is being sequestered into secondary minerals (i.e. greater primary mineral dissolution or less secondary mineral formation). The relationship between Li isotopes and secondary minerals formation has therefore led to the suggestion that $\delta^7$Li is a tracer for the silicate weathering efficiency (Pogge von Strandmann and Henderson, 2015). The relatively less cations (mainly Ca and Mg) that are retained in secondary minerals, the more efficient chemical weathering will be at transporting cations to the oceans, where they will allow carbonate precipitation, and therefore, eventually, $CO_2$ sequestration (Pogge von Strandmann and Henderson, 2015).

The possibility of using $\delta^7$Li to trace overall weathering and $CO_2$ drawdown efficiency depends on whether the behaviour of Li in the weathering environment is similar to the elements implicated in carbonate formation, primarily Ca and Mg. In basaltic rivers, the mobility relative to the most mobile cation, Na (where relative mobility = $[X_{dissolved}/Na_{dissolved}]/[X_{rock}/Na_{rock}]$ (Gíslason et al., 1996)), can be calculated. It must be stressed that there are some secondary minerals in Iceland (principally zeolites) that can take up Na, although these are generally observed to only form at hundreds of metres basalt depth (Alfredsson et al., 2013)). In Icelandic rivers, Ca is on average $3.6^{+3.8}_{-1.7}$ times more mobile than Li (Pogge von Strandmann et al., 2006). Catchments with a high degree of glaciation (i.e. significant supply of fine-grained, fresh, primary material) exhibit close-to-identical Ca and Li mobility, whereas in older catchments, Ca is more mobile than Li. In the Azores, Ca is on average 4.2 times more mobile than Li (Pogge von Strandmann et al., 2010), while in Reunion, this value is 3.1 (Louvat and Allegre, 1997). Overall, this suggests that in basaltic rivers, Li is 3–4 times less mobile than Ca. This relative similarity is also demonstrated by correlations between Li and Ca isotopes in Icelandic rivers (Hindshaw et al., 2013). Similarly, in Icelandic rivers, Mg is $1.6^{+2.3}_{-0.8}$ times more mobile than Li, and Si is $1.2^{+2.4}_{-0.5}$ times more mobile (Pogge von Strandmann et al., 2006). Overall, therefore, this means that Li is one of the trace elements with the closest relative mobility to these three key elements (trace elements such as Fe, Al or Mn are orders of magnitude less mobile (Gíslason et al., 1996)), and therefore this suggests that in some rivers Li isotopes are a useful tracer of silicate weathering efficiency, and hence $CO_2$ drawdown efficiency (supported by a correlation between $\delta^7$Li and Ca isotopes (Hindshaw et al., 2013)). However, in hydrothermal springs, which can be a major source of cations to rivers in many basaltic catchments, especially in ocean islands or arc settings, elemental mobility is different. In the Myvatn springs, Ca is on average 0.4 times as mobile as Li in low temperature springs, and 0.1 times as mobile in high temperature springs. Similarly, Mg is 0.3 times as mobile in low temperature, and 0.04 times as mobile in high temperature springs as Li. Hence, the apparent mobility of Li will increase in rivers with hydrothermal sources, meaning that such rivers must be corrected for before Li isotopes can be used as meaningful weathering tracers.

This utility of Li isotopes as a tracer of secondary mineral formation processes is also highlighted by co-variations between $\delta^7$Li and several different elemental ratio tracers of weathering processes. A recent study of weathering of the Columbia River Basalts has proposed Li/Na ratios as another tracer that, like $\delta^7$Li, is sensitive to the degree of water-rock interaction over time (Liu et al., 2015). Reactive transport models suggest that Li/Na increases with decreasing residence time, while $\delta^7$Li decreases (Liu et al., 2015). This model is supported both by published basaltic terrain data (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009) and this study

(Fig. 4), and can be explained as reflecting incorporation of Li into secondary minerals (assisted by less isotopic fractionation at high temperatures), while Na is highly mobile and present in greater proportion, and is not affected to the same degree by secondary mineral formation.

Equally, Myvatn spring $\delta^7$Li co-varies with another proposed tracer of weathering intensity, K/(Na+K), where high values reflect supply-limited weathering, and low values reflect kinetic-limited reactions (Edmond et al., 1995; Pogge von Strandmann et al., 2010; Stallard and Edmond, 1983; Stallard and Edmond, 1987). As in the basaltic Azores (Pogge von Strandmann et al., 2010), these samples exhibit a negative relationship between K/(Na+K) and $\delta^7$Li (Fig. 4). Although several studies have demonstrated that the overall relationship between Li isotopes and weathering regime is more complex than a linear relationship, especially in lithologically complex terrains, and likely reflects an inverse bell-shaped curve, due to leaching of light secondary clays (Bouchez et al., 2013; Dellinger et al., 2015), it is not surprising that in a simple weathering regime like Iceland or the Azores such a relationship is linear, because dissolution of previously formed secondary minerals is unlikely to have a significant influence on Li isotopes. Hence, in a kinetic-limited regime, as defined by low K/(Na+K), with short residence times, $\delta^7$Li values are low, and vice versa in supply-limited regimes (Bouchez et al., 2013; Dellinger et al., 2015; Pogge von Strandmann et al., 2010).

Finally, the effect of clay mineral formation on Li isotopes can be tested by comparing solution $\delta^7$Li with the ratio of a mobile to an immobile element, such as Na/Ti or Na/Al (Fig 4a). Such a ratio should in principle behave in the same manner as Li isotopes in a monolithologic environment, because it should respond to mineral dissolution relative to clay formation. This is demonstrated by a negative relationship between Na/Ti and $\delta^7$Li (Fig. 4 – a similar relationship for Na/Al is not shown). Combined, these elemental relationships confirm that even in hydrothermal groundwaters, Li isotopes are controlled by the same processes that are thought to control their behaviour in river systems: the ratio of primary mineral dissolution to secondary mineral formation, which has variously been termed weathering intensity, weathering congruency or weathering efficiency (Dellinger et al., 2015; Misra and Froelich, 2012; Pogge von

Strandmann et al., 2010; Pogge von Strandmann and Henderson, 2015; Pogge von Strandmann et al., 2013). However, in contrast to rivers, the key controlling process of weathering intensity is temperature rather than interaction time, and its effect on inhibiting secondary mineral formation, promoting fully congruent weathering at high temperatures. Isotopic fractionation factors are also less at these higher temperatures, although it is likely that around 5–6‰ $\delta^7$Li would still occur if secondary minerals were abundantly present (Marschall et al., 2007).

### 5.1.2 Comparison to Si isotopes as a weathering tracer

Silicon isotope ratios have also been determined in these samples (Opfergelt et al., 2011). In theory, $\delta^{30}$Si behaves similarly to $\delta^7$Li, in that both systems are used as silicate weathering tracers, where secondary minerals preferentially take up light isotopes, driving river waters and seawater to isotopically heavy values (De la Rocha et al., 2000; Georg et al., 2006; Georg et al., 2007; Opfergelt et al., 2013; Opfergelt et al., 2009; Ziegler et al., 2005). In addition, for Si isotopes, biology and plant growth exerts an influence, and preferentially take up light isotopes (Opfergelt et al., 2006). The mobility of Si in Icelandic river waters is $1.2^{+2.4}_{-0.5}$ times as mobile as Li (Pogge von Strandmann et al., 2006), again suggesting the two systems might have similar weathering behaviour in rivers. In contrast, in the Myvatn springs, Si is approximately 0.2 ± 0.1 times as mobile as Li. Silicon isotope ratios in these groundwaters are heavier than the host basalt or basaltic soils, but are within the range exhibited by Icelandic soil pore waters (Pogge von Strandmann et al., 2012), suggesting that weathering processes also dominate the Si budget here (Fig. 5). However, $\delta^{30}$Si in these groundwaters is fairly uniform (0.35–0.62‰), and shows no co-variation with $\delta^7$Li or any of the factors that appear to influence the Li isotope ratio of these waters. A lack of co-variation between Li and Si isotopes has been observed before in the weathering environment (Georg et al., 2007; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2014b; Vigier et al., 2009), and generally implies that the behaviour of Si, an element that is a major component of rocks and secondary minerals, is quite different from that of a minor element, such as Li, that adsorbs to mineral surfaces and substitutes into mineral lattices. Thus, the $\delta^{30}$Si variation in these springs is considerably less than that observed in Icelandic rivers or soil pore waters, while the $\delta^{7}$Li variability in all three phases is similar.

Given that it is unlikely that biology plays a significant role in these springs, it is possible that the increased $\delta^{30}$Si variability in rivers and pore waters relative to these springs is due to Si utilisation by plants or diatoms in the river/pore waters. However, it has been demonstrated that $\delta^{30}$Si in Icelandic soil pore waters in a relatively plant-rich area is controlled by silicate weathering processes, rather than biology (Pogge von Strandmann et al., 2012), which suggests overall plants do not control Si isotopes in Icelandic environments.

There are no co-variations between Si isotope ratios and secondary mineral saturation states, and virtually no correlations for Li isotope ratios, which suggests that the effects of a series of different precipitating minerals are entangled. Both isotope systems are also affected by adsorption onto minerals with no Si component, such as Fe oxyhydroxides (Delstanche et al., 2009). However, the fractionation factors for both systems are known (Delstanche et al., 2009; Millot and Girard, 2007; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2012), and would not account for large $\delta^{7}$Li variability with little $\delta^{30}$Si fractionation. This therefore suggests that the reaction kinetics of the two isotope systems are distinctly different. Lithium has been shown to diffuse on the cm scale extremely quickly (on the order of minutes) at temperatures of 75°C in aqueous solutions up to magmatic temperatures in silicates (Richter et al., 2003; Richter et al., 2006; Teng et al., 2010). Hence, it seems likely that the water-rock interaction time of these springs provides sufficient time for significant Li isotope fractionation, but not for Si isotope fractionation, if the reaction remains kinetic. In contrast, soil pore waters provide sufficient water-rock interaction time for Si isotope fractionation to occur as well as Li, and these fractionations are inherited by river waters.

### *5.2 Outflow (Laxa River) time series*

The key aspect of Myvatn is that it is a very productive lake, which is also lined with high Si, low Al diatomaceous sediments, which inhibit Al-silicate clay formation in the lake. Given Iceland's latitude, the lake's productivity is strongly seasonal. The Laxa River is the only outflow from the lake, and therefore a time series taken from this river shows that the concentration of most elements is also strongly seasonal. Nutrients such as $NO_3$ are more concentrated in the winter, and less in the summer, when they are being utilised in primary productivity by diatoms, algae and cyanobacteria. Other bio-utilised elements (Na, K, Fe, etc.) are similarly affected. In particular, Si concentrations are around eight times higher in the winter than the summer, due to diatom growth (Opfergelt et al., 2011). This also has a strong affect on Si isotopes, which characterise two diatom blooms that drive lake water $\delta^{30}$Si ~0.7‰ higher in the summer.

The effect of the change in productivity on elemental concentrations is also reflected in calculations of mineral stability, although it is difficult to ascertain whether the saturation of both primary and secondary mineral is truly affected, or whether biology dominates elemental concentrations. In any case, lithium is the only element of those measured that is completely unaffected by the changes in productivity during the year. Lithium concentrations show no trend with time whatsoever (Fig. 6), although they do exhibit some non-systematic variation, which is likely due to relative variations in the groundwater spring input into Myvatn. Equally, Li isotope ratios are unaffected by changes in primary productivity. There is no trend of $\delta^7$Li with time (slightly higher $\delta^7$Li values in spring 2001 did not occur in spring 2000), and the ~3.7‰ variation within the Laxa River time series is very small, especially when compared to almost 40‰ variation observed in all rivers draining basaltic terrains (Liu et al., 2015; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006; Vigier et al., 2009).

This lack of $\delta^7$Li change provides a very strong indication that Li does not behave as a nutrient used in primary productivity. It has been suggested that Li isotopes are not affected by plant growth (Lemarchand et al., 2010), but this is the first test that demonstrates that primary phytoplankton productivity is also not a factor in affecting Li isotope ratios. As a consequence Li has a significant advantage over other weathering tracers, especially the major elements (e.g. Mg, Si, Ca isotopes), which are demonstrably affected by biological processes (Black et al., 2006; Bolou-Bi et al., 2010; Bolou-Bi et al., 2012; Fantle and Tipper, 2014; Opfergelt et al., 2010; Opfergelt et al., 2011; Pogge von Strandmann, 2008; Pogge von Strandmann et al., 2014a). This, therefore, enhances the potential role of Li isotopes as the only tracer that solely responds to silicate weathering processes, and is unaffected by biological processes or carbonate weathering.

## 6.0 Conclusions

This study has analysed Li isotopes in the hydrothermal springs that are the dominant source of cations to Lake Myvatn, as well as a time series for the Laxa River, the only point of outflow from the lake.

Lithium isotope ratios in the high- and low-temperature springs co-vary with temperature. High-temperature springs (≤ 44°C) have similar $\delta^7$Li to continental and marine basaltic hydrothermal systems measured at ~350°C, implying that secondary mineral precipitation (inhibited at high temperatures) has not occurred during cooling as these waters migrated towards Myvatn from the Krafla geothermal field. Isotope fractionation during secondary mineral precipitation was also likely lower at these higher temperatures, although probably still substantial enough to have caused an observable effect if the minerals were present. In contrast, low-temperature groundwaters exhibit significant $\delta^7$Li fractionation due to secondary mineral formation.

Co-variations between $\delta^7$Li and a series of elemental tracers of weathering processes (Li/Na, K/(Na+K), etc.) show that $\delta^7$Li in these springs is controlled by the same processes that affect Li in rivers and groundwaters: the ratio of primary rock dissolution to secondary mineral formation (termed the weathering intensity, weathering congruency or weathering efficiency). Thus, weathering is highly congruent in the high-temperature springs (partly assisted by lower isotopic fractionation factors), and incongruent in low-temperature groundwaters. Hence, Li isotope signals in river waters can be strongly influenced by hydrothermal input, because waters that have had high water-rock interaction (which causes high Li isotope fractionation at low temperatures) at high temperatures will still have unfractionated Li isotope ratios. Interestingly, in the same springs, Si isotope ratios are relatively constant, highlighting the difference in reaction time and kinetic activity between these two purported silicate weathering tracers.

In contrast, while $\delta^{30}$Si exhibit strong seasonal variations, the time series outflow in the Laxa River exhibits little $\delta^{7}$Li variation. Myvatn has extremely high seasonal primary productivity, which strongly affects most elements, as well as Si isotopes. However, [Li] and $\delta^{7}$Li are unaffected by these productivity changes. This provides some of the strongest evidence yet reported that Li isotopes are not affected by plant growth or biology, meaning that Li isotopes remain the most useful tracer of solely silicate weathering processes available.

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| Sample | Sample month | Temperature °C | pH | Conductivity µS/cm | Li nM | Na mM | K mM | Mg mM | Ca mM | Al µM | Si mM | P µM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Input springs* | | | | | | | | | | | | |
| IC/MY/01.09 | | 3.4 | 9.27 | | 131 | 0.53 | 0.02 | 0.07 | 0.11 | 0.45 | 0.29 | 1.4 |
| IC/MY/02.09 | | 7.0 | 9.40 | 130 | 252 | 0.72 | 0.03 | 0.11 | 0.12 | 0.53 | 0.31 | 1.5 |
| IC/MY/03.09 | | 6.5 | 9.21 | 141 | 279 | 0.67 | 0.03 | 0.15 | 0.15 | 0.50 | 0.30 | 1.6 |
| IC/MY/04.09 | | 6.2 | 9.23 | 129 | 226 | 0.64 | 0.03 | 0.14 | 0.14 | 0.45 | 0.30 | 1.7 |
| IC/MY/05.09 | | 5.8 | 9.60 | 115 | 91 | 0.74 | 0.02 | 0.07 | 0.11 | 0.67 | 0.31 | 1.8 |
| IC/MY/06.09 | | 7.0 | 9.60 | 134 | 101 | 0.81 | 0.02 | 0.08 | 0.11 | 0.59 | 0.34 | 1.5 |
| IC/MY/07.09 | | 7.5 | 9.29 | 156 | 174 | 0.90 | 0.03 | 0.13 | 0.16 | 0.48 | 0.35 | 1.7 |
| IC/MY/08.09 | | 16.5 | 8.68 | 359 | 1100 | 2.02 | 0.10 | 0.16 | 0.30 | 0.62 | 1.38 | 0.9 |
| IC/MY/09.09 | | 37.3 | 8.29 | 505 | 1970 | 3.32 | 0.15 | 0.08 | 0.35 | 1.06 | 2.25 | 0.5 |
| IC/MY/10.09 | | 44.0 | 8.10 | 437 | 1920 | 2.64 | 0.15 | 0.09 | 0.28 | 0.20 | 2.23 | 0.5 |
| IC/MY/11.09 | | 24.3 | 8.29 | 396 | 917 | 1.73 | 0.10 | 0.16 | 0.51 | 0.32 | 1.20 | 0.8 |
| IC/MY/14.09 | | 20.0 | 3.50 | 620 | 10050 | 2.55 | 0.27 | 0.14 | 0.20 | | | 0.6 |
| IC/MY/12.09 - Mid-lake | | 10.2 | 9.82 | 157 | 227 | 0.77 | 0.03 | 0.11 | 0.15 | 0.39 | 0.15 | 1.0 |
| IC/MY/13.09 - lake outflow | | 10.7 | 10.00 | 162 | 236 | 0.79 | 0.03 | 0.12 | 0.15 | 0.31 | 0.13 | 0.8 |
| | | | | | | | | | | | | |
| *Laxa River* | | | | | | | | | | | | |
| 00A013 | Mar-00 | 1.2 | 8.37 | | 180 | 1.01 | 0.04 | 0.16 | 0.20 | 0.33 | 0.41 | |
| 00A023 | Apr-00 | 0.0 | 9.03 | | 137 | 0.78 | 0.03 | 0.15 | 0.16 | 0.03 | 0.30 | |
| 00A031 | May-00 | 6.0 | 8.52 | | 177 | 0.75 | 0.03 | 0.13 | 0.15 | 0.30 | 0.22 | |
| 00A044 | Jun-00 | 12.3 | 9.63 | | 146 | 0.88 | 0.03 | 0.15 | 0.18 | 0.40 | 0.10 | |
| 00A053 | Jul-00 | 15.7 | 9.93 | | 237 | 0.95 | 0.03 | 0.14 | 0.18 | 1.08 | 0.05 | |
| 00A062 | Aug-00 | 15.5 | 9.78 | | 167 | 1.04 | 0.04 | 0.17 | 0.20 | 0.49 | 0.09 | |
| 00A071 | Sep-00 | 8.3 | 9.35 | | 217 | 0.94 | 0.04 | 0.15 | 0.18 | 0.26 | 0.10 | |
| 00A080 | Oct-00 | 1.4 | 8.73 | | 155 | 0.95 | 0.04 | 0.16 | 0.18 | 0.15 | 0.16 | |
| 00A089 | Nov-00 | 0.6 | 8.32 | | 116 | 0.97 | 0.04 | 0.16 | 0.19 | 0.18 | 0.31 | |
| 01A006 | Jan-01 | 0.9 | 8.34 | | 153 | 0.97 | 0.04 | 0.16 | 0.19 | 0.47 | 0.41 | |
| 01A015 | Mar-01 | 0.5 | 8.43 | | 236 | 0.88 | 0.04 | 0.14 | 0.14 | 0.38 | 0.34 | |

Table 1. Physical measurements, trace element concentrations and Li isotopes ratios (‰) from the input springs to Myvatn, and the time series across the outflowing Laxa River. Trace element data aside from Li concentrations are from Opfergelt et al. (2011). Spring pH was measured at their inherent temperature, while river pH was measured at room temperature.

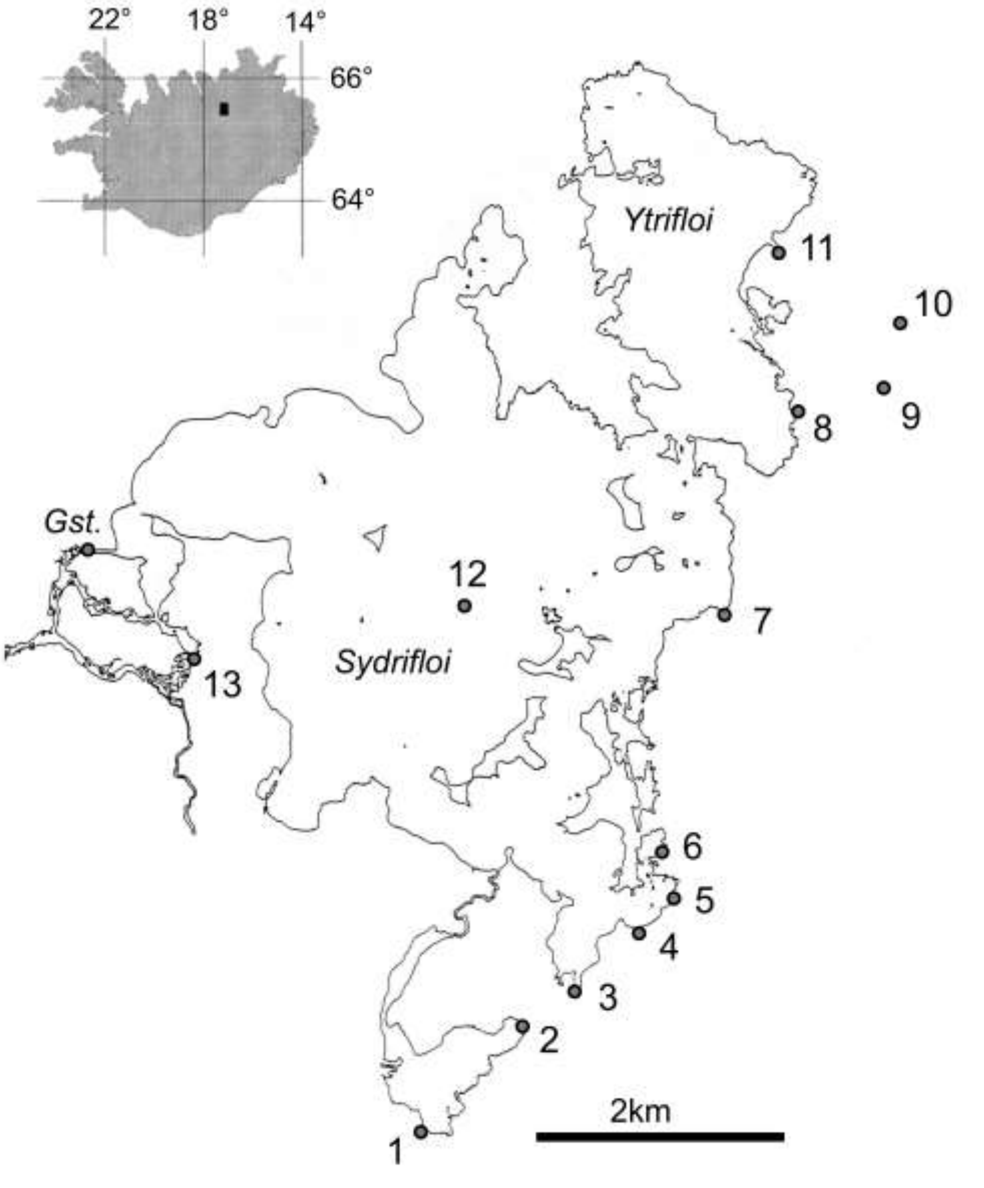

Figure 1. Sample location map of Lake Myvatn with the two main basins (Ytrifloi and Sydrifloi): "cold" springs (MY01 to 07), "hot" springs (MY08 to 11), middle lake water (MY12) and Laxa River outlet (MY13). The monitoring over 2000–2001 was made at the outlet Geirastadaskurdur (Gst.). From Opfergelt et al., 2011.

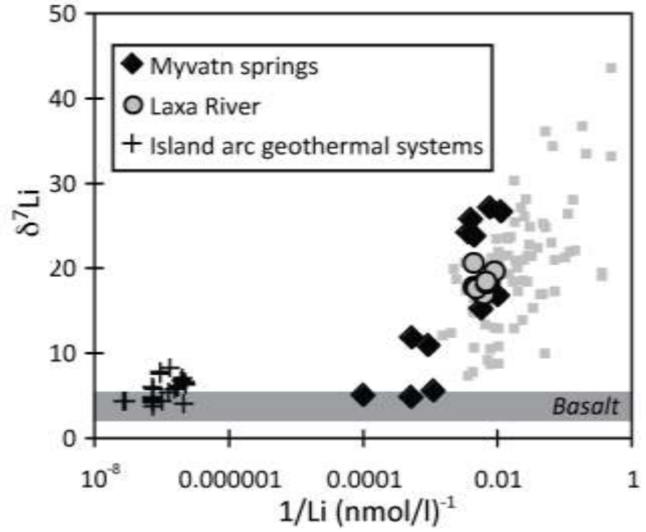

Figure 2. Li isotopes as a function of the reciprocal of the Li concentration. The island arc geothermal systems are from Guadeloupe and Martinique (Millot et al., 2010a). The small grey squares represent other basaltic weathering data from rivers and soil pore waters from Iceland (Pogge von Strandmann et al., 2006; Vigier et al., 2009), the Azores (Pogge von Strandmann et al., 2010), and the Columbia River Basalts (Liu et al., 2015). Typical basaltic $\delta^7$Li compositions shown as grey field (Elliott et al., 2006; Tomascak et al., 2008).

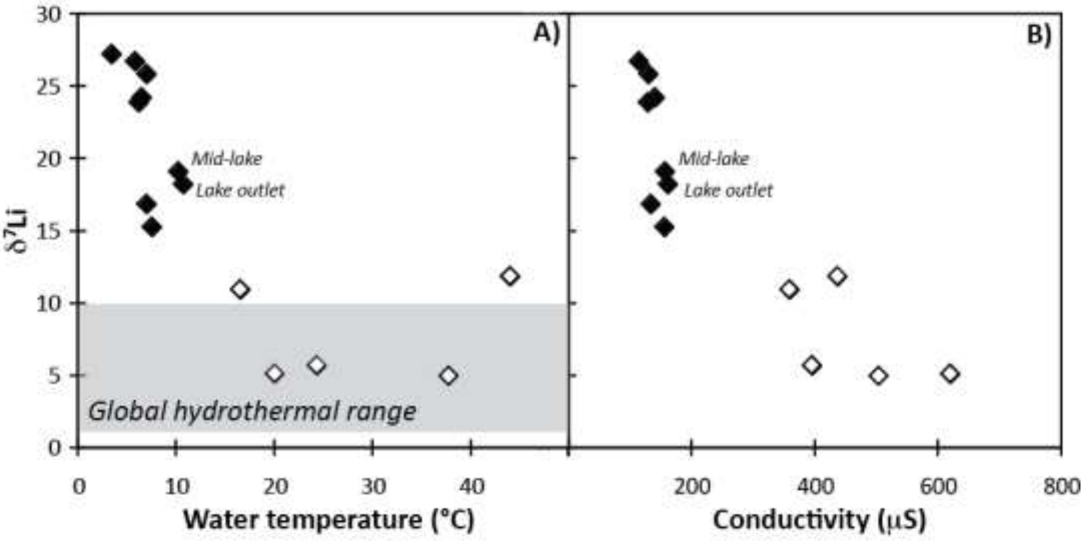

Figure 3. Li isotope ratios from the source springs to Myvatn, plotted against A) water temperature, and B) conductivity. Open symbols are “hot” springs from geothermal fields, while closed symbols are “cold” groundwaters. The grey field

denotes the global hydrothermal range of δ$^7$Li values (Chan et al., 1993; Chan et al., 1994; Henchiri et al., 2014; Millot et al., 2010a; Pogge von Strandmann et al., 2010; Pogge von Strandmann et al., 2006).

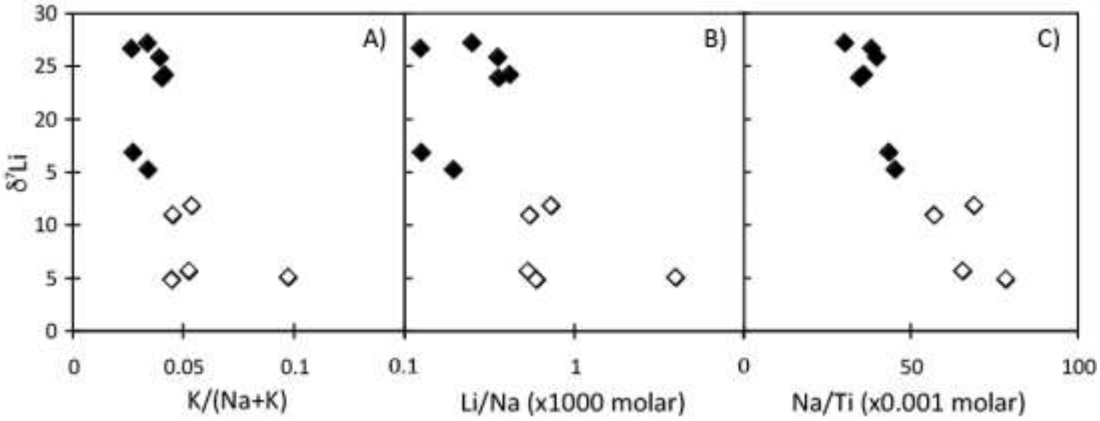

Figure 4. Li isotopes from Myvatn springs plotted against a series of elemental tracers of weathering processes. A) K/(Na+K), a tracer of weathering regime, where higher values indicate transport limitation, and lower values weathering limitation (Edmond et al., 1995; Pogge von Strandmann et al., 2010). B) Li/Na ratios have been proposed as a tracer of silicate weathering residence time in monolithologic catchments (Liu et al., 2015). C) Na/Ti ratios show behaviour of a highly mobile element (Na) relative to an immobile one (Ti). Combined, these relationships show how powerful Li isotopes are at tracing of silicate weathering processes. Open symbols are "hot" springs from geothermal fields, while closed symbols are "cold" groundwaters.

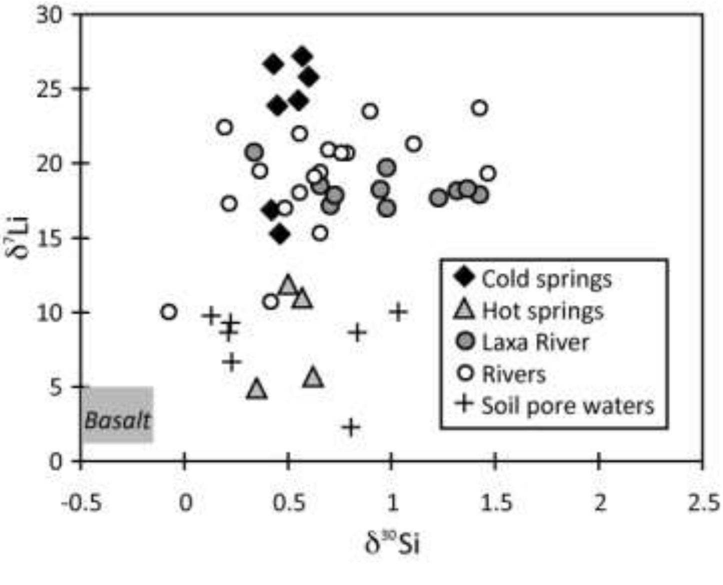

Figure 5. Li isotopes plotted against Si isotopes for the spring samples and Laxa River (Opfergelt et al., 2011), and Icelandic rivers (Georg et al., 2007; Vigier et al., 2009) and soil pore waters (Pogge von Strandmann et al., 2012). The lack of any correlation suggests that the two systems are controlled by different processes.

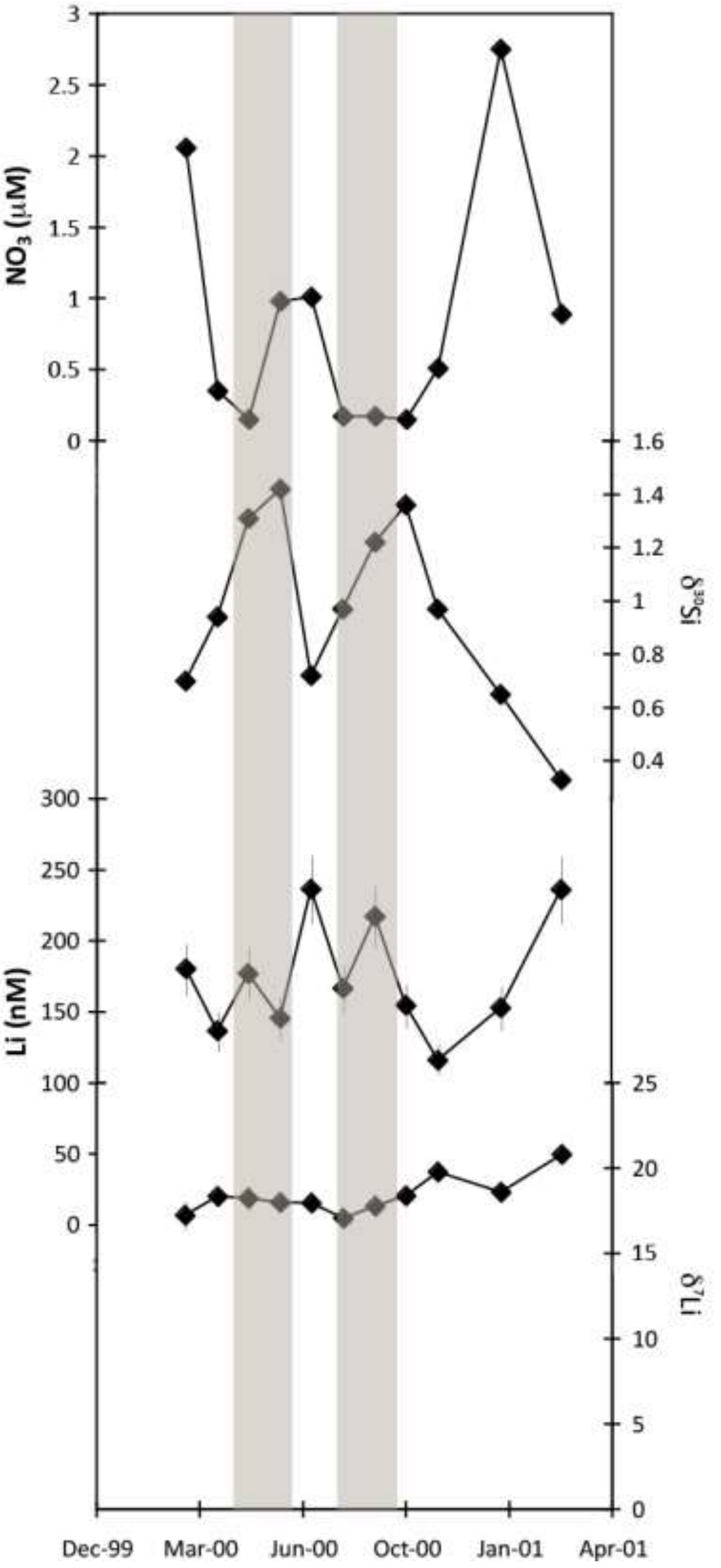

Figure 6. Time series from the Laxa River outflow from Lake Myvatn. The NO$_3$ and $\delta^{30}$Si data (Opfergelt et al., 2011) clearly respond to seasonal productivity changes (times of spring and autumn diatom blooms highlighted in grey). In

contrast, Li concentrations and isotope ratios are unaffected by primary productivity. The small variability in both is likely due to changes in input to the lake. This clearly indicated that Li isotopes are unaffected by primary productivity.