



The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland

N. Vigier^{a,*}, S.R. Gislason^b, K.W. Burton^c, R. Millot^d, F. Mokadem^c

^a CRPG-CNRS, Nancy-Université, 15 rue ND des Pauvres, 54501 Vandoeuvre les Nancy Cedex, France

^b Univ. of Iceland, Iceland

^c The Open University, Milton Keynes, UK

^d BRGM, Metrology, Monitoring, Analysis Division, 3 Av. Claude Guillemin, BP 6009, 45060 Orleans Cedex 2, France

ARTICLE INFO

Article history:

Received 23 July 2009

Accepted 20 August 2009

Available online 9 September 2009

Editor: M.L. Delaney

Keywords:

Li isotopes

basalt

silicate weathering

erosion

ivers

ABSTRACT

This study presents lithium isotope and elemental data for the dissolved phase and suspended and bedload sediments of the major Icelandic rivers. For the dissolved phase, $\delta^7\text{Li}$ values range between 10.1‰ and 23.8‰, while river sediments display lower and much more homogeneous values ($\delta^7\text{Li} = 3.1\text{‰}–4.8\text{‰}$), close to the composition of unweathered Mid-Ocean Ridge Basalt (MORB). High $\delta^7\text{Li}$ values are associated with high K/Li, Na/Li and Mg/Li ratios, in waters draining mainly old and weathered basalt catchments, whereas low $\delta^7\text{Li}$ rivers are located in younger parts of the island. Simple mixing between precipitation, Li-rich hydrothermal springs and basalt weathering is unable to explain the entire range of $\delta^7\text{Li}$ values. Instead, a simple model of Li uptake by secondary minerals, associated with clay–water Li isotope fractionation ($\Delta^7\text{Li}$ ranging from -1‰ to -7.5‰) can explain both water and sediment $\delta^7\text{Li}$ values. A negative correlation is observed between basalt chemical erosion rates and $\delta^7\text{Li}$ measured in Icelandic rivers, and an empirical law is inferred. Comparison with literature data suggests that this relationship may be applicable at a more global scale, and, if confirmed, could be of particular use for estimating the evolution of continental weathering preserved in marine sedimentary records. However, more data are now needed for rivers draining silicates typical of the continental crust, in order to refine large scale modelling.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Lithium has two stable and light isotopes (7.52% ^6Li and 92.48% ^7Li) that fractionate significantly during silicate chemical erosion (weathering). The few studies of rivers undertaken thus far have suggested that dissolved Li is mainly derived from silicates, even in large basins of mixed lithology, and that the Li isotope composition of waters varies with indices of chemical erosion (Huh et al., 1998, 2001; Kisakürek et al., 2005; Pogge von Strandmann et al., 2006). Marine sedimentary records may therefore preserve unique information on past silicate chemical erosion rates, particularly if the relationship between $\delta^7\text{Li}$ in waters and silicate chemical erosion rate can be quantified at a continental scale.

The main evidence for Li isotope fractionation accompanying silicate chemical erosion is firstly, that measured $\delta^7\text{Li}$ ratios of continental waters ($\delta^7\text{Li} = ((^7\text{Li}/^6\text{Li}) / (^7\text{Li}/^6\text{Li})_{\text{LSEV}} - 1) * 1000$) are systematically higher than the rocks they drain and the sediments they carry (suspended and bed load) (Chan and Edmond, 1988; Huh et al., 2001; Rudnik et al., 2004; Kisakürek et al., 2004, 2005).

Secondly, the $\delta^7\text{Li}$ composition of the ocean (31.2‰, e.g. Chan and Edmond, 1988; Millot et al., 2004) is significantly higher than any presently known Li source (the global riverine composition is estimated to possess a $\delta^7\text{Li}$ value of 23.4‰ and that for hydrothermal exchange is ~9‰, Huh et al., 1998; Chan et al., 1993). Two processes have been proposed to account for Li isotope fractionation during weathering: (i) rock or mineral leaching, (ii) the formation of secondary minerals. Some soil studies suggest that ^7Li is preferentially released into solution from fine grained sediments (Rudnik et al., 2004; Kisakürek et al., 2004). This is a priori surprising since ^6Li diffuses much quicker than ^7Li and other studies suggest little isotope fractionation during Li loss from a basalt (Pistiner and Henderson, 2003; Huh et al., 2004). In contrast, both experiments and observations provide evidence for Li isotope fractionation during clay formation, at both low and high temperatures (Taylor and Urey, 1938; Chan et al., 1992, 1993, 1994, 2002; Seyfried et al., 1998; Zhang et al., 1998; James et al., 1999, 2003; Pistiner and Henderson, 2003; Williams and Hervig, 2005; Vigier et al., 2008).

Small catchments or monolithological basins are characterized by fewer variables, and provide a means to deconvolve the primary controls on silicate weathering rates. The volcanic island of Iceland is one of the few regions where river water chemistry and sediment fluxes have been extensively studied and monitored for more than

* Corresponding author.

E-mail address: nvigier@crpg.cnrs-nancy.fr (N. Vigier).

30 years. Geology and rock composition are also well-constrained and anthropogenic inputs are minimal. Weathering in Iceland has then been extensively studied (e.g. Gislason and Eugster, 1987a,b; Louvat, 1997; Stefansson and Gislason, 2001; Arnorsson et al., 2002; Eiríksdóttir et al., 2008). Recent studies have demonstrated a large range in chemical and physical erosion rates (Gislason et al., 1996; Vigier et al., 2006; Georg et al., 2007). Runoff and the age of the basalt appear to be two key controls on weathering. In addition, glass may play a major role because it can dissolve up to 6 times faster than crystalline basalt (e.g. Gislason and Eugster, 1987a,b; Wolff-Boenisch et al., 2006) and is abundant in the hyaloclastites of the central and glaciated part of the island.

This study presents Li isotope data for waters and sediments of the main Icelandic rivers. The samples are the same as those used for constraining chemical erosion rates in Vigier et al. (2006) from dissolved major elements, allowing a direct comparison of chemical erosion and riverine $\delta^7\text{Li}$.

2. Sampling area

The island of Iceland is located on the Mid-Atlantic ridge. A combination of sea-floor spreading and associated volcanism has produced a symmetrical SW–NE zonation in the age of the basalts, from the centre of the island towards the east and north-west coasts. The older basalts (>3 Ma) are located in the north and east of the island, while the most recent basalts are mainly located in the central and volcanically active zone.

The climate in Iceland is oceanic boreal, and less than 25% of the island is vegetated and about 12% is covered by glaciers. Three types of

ivers have been recognized in Iceland: (i) spring-fed rivers, mainly located in the central volcanic part where the high rock permeability precludes significant surface runoff, (ii) glacier-fed rivers, and (iii) direct runoff rivers draining mainly older basalts, where compaction and sealing by secondary minerals reduces the permeability. Soils are generally thin and the main secondary minerals in soils are allophane and ferrihydrite (Arnalds, 2004).

Quaternary volcanic rocks formed under ice during the last 3 Myr are glassy (hyaloclastites) but those formed when the island was ice-free are mostly in the form of crystalline lava flows. Thus, the most recent basalts are characterized by a glassy texture, in contrast with the older northern lava flows which are mainly crystalline.

More than twenty rivers were sampled across Iceland in June/July 2001 (Fig. 1). Catchments from the volcanically active zone in the centre of Iceland, where the hydrothermal contribution to rivers can be significant, were avoided. Glacier-fed rivers have also been sampled, notably the Skaftafellsa River (#23) which is sourced directly by the large Vatnajökull glacier. More details on the samples and their locations can be found in Gannoun et al. (2006) and Vigier et al. (2006).

River monitoring by the University of Iceland and the Hydrological Division of the National Energy Authority provides precise estimates of discharge and corresponding runoff for each watershed studied here. In addition, the Total Suspended Sediment (TSS) load has been regularly recorded for a number of Icelandic rivers over the last four decades (Palsson and Vigfusson, 1991; Gislason et al., 2006; Eiríksdóttir et al., 2008). Both records provide valuable information that can be used to estimate the physical and chemical erosion rates of most of the watersheds of the sampled rivers. For 2001, a wide range of physical erosion rates were inferred for Icelandic catchments,

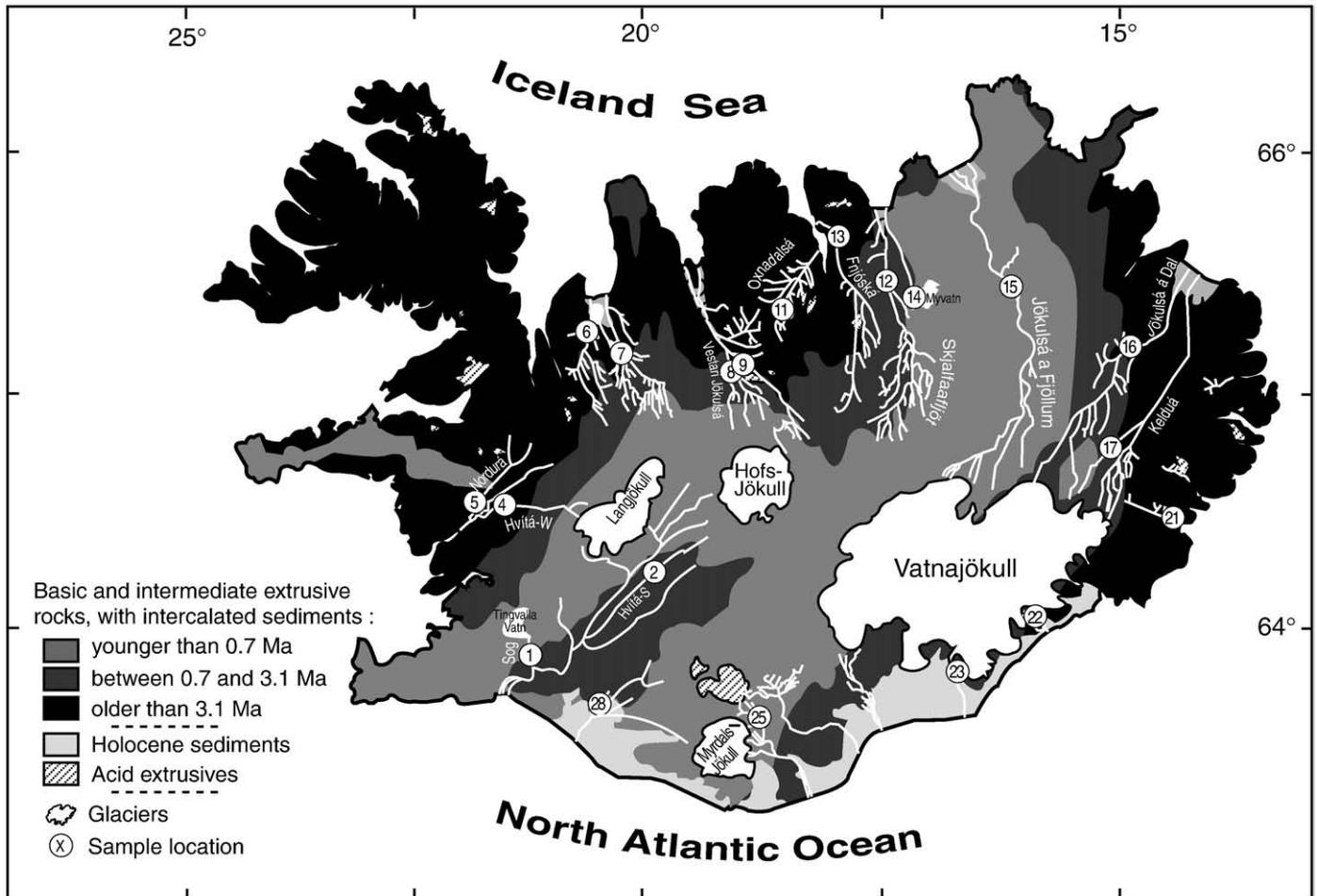


Fig. 1. Map of the Icelandic rivers sampled during June 2001 for Li analyses. Sample numbers refer to sample designation as given in Table 1.

between 21 and 4864 t/km²/yr, with an average of 519 t/km²/yr which compares well with previous estimates (Tomasson, 1986). This is about twice the world average estimated by Milliman and Meade (1983). Chemical erosion rates, which can be estimated from the flux of dissolved elements exported by rivers, are lower than physical erosion rates, ranging from 13 to 333 t/km²/yr. Chemical erosion rates correlate positively with physical erosion rates and runoff, and negatively with the mean age of the drained basalts (e.g. Gislason et al., 1996; Louvat, 1997; Vigier et al., 2006).

3. Analytical procedure

3.1. Li contents

All river samples were filtered on the field using acetate cellulose filters (0.2 μm) which separated the dissolved phase from suspended particles, collected on the filter with ultra-pure water. Li concentrations (along with other major and trace cations) were determined using ICP-MS. For the suspended and bed load sediments, Li contents were calibrated against a number of International rock reference materials including AC-E (granite), WS-E (dolerite), and BIR-1, BCR-2 and BHVO-1 (basalts). The external reproducibility, determined from repeat measurements of BCR-2, is better than 2% (1σ), where the measured concentration of Li in BCR-2 of 9.7 ± 0.2 ppm (1σ) is indistinguishable from the certified value of 9 ± 2 ppm (USGS Certificate of Analysis). For the dissolved load Li was calibrated against an in-house standard (Scottish river water). The external reproducibility, determined by repeat measurement of the natural river water certified reference material SLRS-4, is better than 3%. The measured Li content of SLRS-4 of 0.48 ± 0.01 ppb is similar to the value of 0.54 ± 0.07 ppb obtained by Yeghicheyan et al. (2001) for the same river water.

3.2. Li isotopes

Special caution was taken for ensuring complete dissolution of all samples before the Li separation chemistry. River waters were evaporated in Teflon beakers and the residues were dissolved several times in concentrated nitric acid. Bulk sediments and suspended particles were digested in a mixture of HF–HNO₃–HCl and HClO₄, following the procedure described in Vigier et al. (2001) and previously used for measuring Th isotopes. Cation exchange resin was used to separate Li from the sample matrix, following a procedure modified from that of James and Palmer (2000). The 100% recovery was checked for each sample, considering analytical uncertainties. Li isotopes were measured on pure Li fractions, using the Open University Nu-Instruments MC-ICP-MS for waters and the BRGM Neptune MC-ICP-MS for sediments. A Cetac Aridus desolvating nebuliser was used with the Nu Instruments while a quartz dual spray chamber and a low flow PFA microconcentric nebuliser were used with the Neptune. More details concerning the analytical procedure are described in Millot et al. (2004) and in Vigier et al. (2008). In brief, analyses were performed on 2–3% HNO₃ solutions with Li concentrations of 30 ng/ml, typically yielding a current intensity of 1.5 to 2 × 10⁻¹¹ A for ⁷Li ion (using 10¹¹ Ω resistors). The total duration of data acquisition did not exceed 5–6 min, including sample uptake and peak centering. The analytical protocol employed involves the acquisition of 15 ratios with a 16 s integration time per ratio, and yields an in-run precision of ~0.15% (2σ_m). The sample introduction rate is approximately 80–100 μl/min and the total volume of sample used for each measurement is less than ~600 μl, corresponding to about 15–20 ng of Li. Sample are bracketed by the L-SVEC RM 8545 standard in order to correct isotopic compositions for instrumental mass fractionation. The measured ⁷Li/⁶Li ratio of a sample is normalized to the mean ⁷Li/⁶Li ratio of the two standards run immediately before and after. In addition, during each

sequence of analyses blanks are measured before and after each sample and standard for background correction. Blank values are low, typically 3–4 mV for the ⁷Li (i.e. 0.2%), and 5 min wash time is sufficient to achieve a stable background value. Since blanks are very stable, the background correction applied to samples and standards is made using the average value of the two bracketing blanks.

The accuracy of this procedure has been checked using Li solutions made from LSVEC powder and ⁶Li and ⁷Li spikes of known composition (Li6-N and Li7-N respectively, Carignan et al., 2007), and reference materials. Two analyses of seawater gave δ⁷Li values of 31.25 ± 0.16 and 31.31 ± 0.12 respectively, which closely correspond to published values (e.g. see review in Carignan et al., 2004; Millot et al., 2004). The JB-2 basalt reference material has also been analyzed and gave δ⁷Li values of 5.65 ± 0.12 and 5.73 ± 0.12, which are within the published range for this basalt (Jeffcoate et al., 2004; Carignan et al., 2007; Vigier et al., 2008).

4. Results

4.1. Li contents

The Li contents of Icelandic river waters range between 20 ng l⁻¹ for the Heioarvatn and Geithellnadalur Rivers (#19 and #21), draining old basalts in the eastern part of the island (basalt mean age ~5.9 Ma), and 2.2 μg l⁻¹ for the Vestari Jökulsa River. This range is similar to that observed for rivers in a small watershed located in western Iceland (Pogge Von Strandmann et al., 2006). The mean Li content of Icelandic rivers is 0.6 μg l⁻¹. This is significantly lower than both the Li content of world-wide rivers (Huh et al., 1998) and the Li contents of rivers draining mixed lithology basins of the Himalayas (Kisakürek et al., 2005). This is likely to be due to low Li contents in basalts relative to granites and gneisses, and also to high runoffs in Iceland during the ice melting season. The Li contents of two samples from Geysir hot spring, located in central Iceland, have also been determined and are 389 μg/l and 360 μg/l respectively.

4.2. Li isotopes

Li isotope compositions have been determined for all river waters and some suspended sediment and bedload samples. The δ⁷Li values of the waters range between 10.1‰ for the Skaftafellsa (#23), a glacier-fed river in the south of Iceland, and 23.8‰ for the Vididalsa River (#6) located in northern Iceland. This range is similar to those published for world-wide and Himalayan rivers (Huh et al., 1998; Kisakürek et al., 2005). The δ⁷Li of Geysir hot spring has also been measured and is 5.5‰. The range for sands and suspended sediments is narrow (3.1‰–4.8‰) and close to the values estimated for unweathered MORBs (e.g. Elliott et al., 2006), but contrasts with the values published by Pogge von Strandmann et al. (2006) for other Iceland river sediments (–1.3‰ to 8.9‰).

5. Discussion

5.1. Sources of dissolved Li

In order to constrain the controls on the Li isotope signatures of Icelandic river waters, it is important to first determine the sources of dissolved Li. The Li contents of Icelandic rivers are relatively low (0.02–2.2 μg/l) and even though these rivers mainly drain basalts, alternative Li sources must be considered, in particular hydrothermal waters and atmospheric input.

The rivers studied here are mainly located away from the central and active ridge where most of the hydrothermal activity is known to occur. Nevertheless, Li concentrations are several orders of magnitude greater in hydrothermal waters than in river waters. In the ocean, Li contents of hydrothermal fluids range from 3000 to 9000 μg/l. In

Iceland, the Li content of geothermal waters ranges from 35.9 µg/l (Pogge von Strandmann et al., 2006) to 6600 µg/l (Henley and Ellis, 1983). In the thermal waters of Geysir, which represents the most famous, and one of the largest, hydrothermal fields of Iceland, two aliquots sampled during different seasons yield Li contents of 389 µg/l and 360 µg/l. In contrast with Li concentrations, the $\delta^7\text{Li}$ measured in hydrothermal waters of mid-ocean ridge systems are relatively homogeneous, around $8.7\% \pm 1.4\%$ (Chan et al., 1993). The $\delta^7\text{Li}$ measured at Geysir spring is 5.5%. Taking these values into account, it can be calculated that a hydrothermal source contribution of less than 1% would impose similar $\delta^7\text{Li}$ values for all the rivers studied here. Thus, the wide range of $\delta^7\text{Li}$ values displayed by Iceland river waters a priori suggests that the contribution from hydrothermal inputs must be significantly less than 1%.

It has previously been shown that melted ice from central glaciers can be used as a proxy for atmospheric inputs in Iceland (e.g. Gannoun et al., 2006). The Li content of melted ice is relatively low (<6 ng/l), consistent with the non-volatile nature of Li during low temperature evaporation processes. However, this is not negligible when compared with the Li contents measured in some of the Icelandic rivers, such as the Heioarvatn and Geithellnadalur Rivers (Table 1). It can be reasonably assumed that most of the atmospheric Li comes from marine aerosols and that the $\delta^7\text{Li}$ composition of any precipitation is close to the seawater value (31.2‰, Chan and Edmond, 1988; Millot et al., 2004). In river waters, the highest $\delta^7\text{Li}$ (>21‰) and K/Li values, closest to the composition of precipitation (Fig. 2), are located in the area with the lowest runoff and where the percentages of glacial cover are the lowest at the basin scale (Vigier et al., 2006). Consequently, the high $\delta^7\text{Li}$ values and K/Li ratios measured in these rivers cannot simply be explained by a greater contribution from precipitation.

The sources of Li in Icelandic rivers can be more precisely constrained by comparing the concentrations of Li and major elements in river waters with three determined endmembers (basalt weathering, precipitation, hydrothermal exchange) (Fig. 2a,b,c). To a first approximation, basalt weathering in Iceland can be assumed to be congruent, as has been demonstrated for some of the youngest Icelandic basins (e.g. Vigier et al., 2006), leading to waters with K/Li, Mg/Li and Na/Li ratios similar to the average drained basalt (Louvart, 1997). The Li contents of the rivers correlate with K, Na and Mg contents ($r^2=0.60\text{--}0.75$, not shown here), suggesting identical

sources for these elements. In mixing diagrams, river waters all plot between the three endmembers considered: precipitation (or glacier-fed waters), hydrothermal springs and basalt weathering (Fig. 2). However, as discussed above, atmospheric inputs are likely to be small when compared to the amount of Li released by basaltic lithologies during weathering. The waters possessing high $\delta^7\text{Li}$ and K/Li values are located in the older and drier parts of the island. These areas are characterized by a significant amount of clays and secondary minerals that have replaced primary minerals in the weathered lava flows. Li uptake by secondary minerals could also be responsible for elevated K/Li, Na/Li and Mg/Li ratios and it is therefore not possible, based on concentrations only, to distinguish between this effect and a mixing process involving the endmembers described above (Fig. 2). Moreover, as illustrated in Fig. 2a and b, it is also difficult, based on concentrations alone, to distinguish between the role of basalt dissolution and the potential impact of any hydrothermal springs drained by these rivers.

Since the range in $\delta^7\text{Li}$ values in river waters (10.1‰–23.8‰) lies between those of hydrothermal (~9‰) and atmospheric inputs (31.2‰), it might be argued that a mixing process involving these two sources could explain the entire range of isotope compositions measured for these waters. In such a case, it would be very difficult to infer precise information concerning low temperature basalt weathering rates from the Li isotope signatures of Icelandic rivers. However, Fig. 3 illustrates that the $\delta^7\text{Li}$ values in river waters cannot be explained by simple binary mixing of these sources. Similarly, mixing between atmospheric inputs and a solution resulting from basalt weathering does not explain the river $\delta^7\text{Li}$ (Fig. 3). River $\delta^7\text{Li}$ values are systematically higher than any of the theoretical mixing lines. The highest $\delta^7\text{Li}$ values correspond to the oldest basins with the lowest runoff and are therefore unlikely to result from a greater contribution from the atmosphere. High $\delta^7\text{Li}$ values, associated with high K/Li or Na/Li ratios, are more consistent with a Li uptake process, during the formation of secondary phases. Fig. 3 shows that the initial solution must have low $\delta^7\text{Li}$ and a high Li content. It might be envisioned that this process occurs in soils and that initial soil solutions would either have isotopic compositions close to that of the source basalt, with or without similar K/Li ratios, or would lie on the mixing curve with precipitation. These data also indicate that negligible isotope fractionation occurs during basalt leaching, as has been suggested in

Table 1
Li isotope composition ($\delta^7\text{Li}$) of Icelandic river waters (w), suspended sediments (p) and bedload sands (s).

Sample #	Name	Age (Ma)	Chem. er. rates ($\text{t km}^{-2} \text{yr}^{-1}$)	Li_w ($\mu\text{g/l}$)	$\delta^7\text{Li}_w$ (‰)	$\delta^7\text{Li}_s$ (‰)	$\delta^7\text{Li}_p$ (‰)	Mg_w^a (ppm)	K_w^a (ppm)	Na_w^a (ppm)
#1	Sog	0.27		0.48	19.4 ± 0.2			1.33	0.61	8.09
#2	Hvita-S	0.67	45.8	0.60	19.5 ± 0.2	3.2 ± 0.2		1.27	0.56	6.67
#4	Hvita-W	1.22	54	0.35	17.4 ± 0.2	4.4 ± 0.2		0.94	0.40	6.26
#5	Nordura	5.9	25	0.07	21.4 ± 0.2			1.39	0.31	5.60
#6	Vididalsa	4.13		0.45	23.8 ± 0.3			3.55	0.77	7.12
#7	Vatnsdalsa	1.88	13.1	0.74	23.6 ± 0.1			2.51	1.09	8.67
#8	Vestari Jökulsa	2.43	28.1	2.20	20.8 ± 0.2	3.3 ± 0.2		4.13	1.14	7.99
#9	Vestari Jökulsa, Goddolum	2.86	18.2	0.18	22.5 ± 0.2	3.7 ± 0.2		0.52	0.35	4.36
#11	Oxnadalsa	5.9		0.05	22.2 ± 0.3	3.1 ± 0.2		0.70	0.31	2.16
#12	Skjalfafljot	1.29	27.2	0.83	21.0 ± 0.2	4.5 ± 0.2		1.72	0.48	6.99
#13	Fnjoska	4.76	18.4	0.06	22.1 ± 0.2			0.81	0.25	3.00
#14	Laxa at Myvatssveit ^b	0.01	742.2	2.09	17.5 ± 0.1	3.9 ± 0.2		3.40	1.24	20.09
#15	Jökulsa a Fjöllum	0.3		1.19	18.1 ± 0.2		3.8 ± 0.2	1.64	0.59	11.01
#16	Jökulsa a Dal	1.71		0.15	17.1 ± 0.2		3.9 ± 0.2	0.79	0.21	3.27
#17	Jökulsa i Fljotsdal	2.14	31.7	0.21	15.4 ± 0.1	4.8 ± 0.2		0.84	0.19	2.73
#19	Heioarvatn	11.17		0.02	19.6 ± 0.2			0.87	0.16	2.87
#21	Geithellnadalur	5.9	51.7	0.02	19.2 ± 0.3	4.5 ± 0.2		0.67	0.14	2.40
#22	Kalfafellsdalur	0.57		0.14	20.8 ± 0.2			0.84	0.09	3.85
#23	Skafafellsa	1.66	129.6	0.35	10.1 ± 0.2		3.9 ± 0.2	0.32	0.33	5.51
#25	Holmsarvatn	0.21	518.2	1.58	10.8 ± 0.3	3.2 ± 0.2		1.10	0.48	5.64
#28	Raudilaekur	3.17		1.10	18.3 ± 0.2			12.00	1.45	16.31

Age and chemical erosion rates are from Vigier et al. (2006).

^a Mg, K and Na concentrations for waters are from Vigier et al. (2006).

^b Sample taken at the output of the Myvatn lake.

a previous study (Pistiner and Henderson, 2003). Indeed a leaching process associated with preferential release of ^7Li in waters (relative to ^6Li) would result in a negative trend on Fig. 3.

A hydrothermal contribution to the rivers cannot be completely ruled out, particularly for glacier fed rivers (Skaftafellsa, #23), while hydrothermal springs may also be located along the course of other rivers. Such a contribution, if significant, would decrease river $\delta^7\text{Li}$

values. However, the main positive trend resulting from secondary mineral formation does not appear to have been significantly disturbed by hydrothermal processes, as expected given the sampling strategy adopted in this study (see Section 2).

5.2. Assessing the link between riverine $\delta^7\text{Li}$ and silicate erosion rates

As illustrated in Fig. 3, it is difficult to account for the $\delta^7\text{Li}$ values measured in river waters by mixing processes alone. In the older parts of Iceland, high $\delta^7\text{Li}$ values in rivers are associated with low Li contents. These older terrains are characterized by low chemical erosion rates and basalt porosity has been significantly reduced by the precipitation of secondary minerals (e.g. Gislason et al., 1996). In contrast, in the younger areas, chemical erosion rates are greater, corresponding to a more congruent weathering process, due in particular to the higher susceptibility to weathering of glassy hyaloclastites. Taken together, these observations strongly suggest a link between the nature and the intensity of silicate chemical erosion and Li isotope signature in river waters. In fact, excepted the water sampled at the output of the Myvatn lake, a negative correlation can be observed between $\delta^7\text{Li}$ and chemical erosion rates estimated based on major elements measured for the same samples (Fig. 4, Vigier et al., 2006). This is the first direct correlation between both parameters and confirm the initial suggestion of Huh et al. (2001), that the $\delta^7\text{Li}$ composition of river waters could yield precious information on chemical erosion rates, both past and present. An empirical law linking $\delta^7\text{Li}$ and silicate chemical erosion rate (w) can be inferred from the data shown in Fig. 4:

$$\delta^7\text{Li} = -4.8(\pm 1.8) \cdot \ln(w) + 36(\pm 5.9) \quad (1)$$

If this law fits well the data for silicate chemical erosion rates lower than $100 \text{ t km}^{-2} \text{ yr}^{-1}$, i.e. for most of the basins world-wide (Gaillardet et al., 1999), it would need to be refined for higher weathering rate areas. In order to use this relationship for global scale bio-geochemical modelling, more data are needed in order to confirm if this law is representative of silicate chemical weathering at a larger scale, and in particular for other rock types and other climate regimes.

Indeed, if secondary mineral formation is the key process, reducing the levels of cation fluxes to the ocean and resulting in high river $\delta^7\text{Li}$ values, then quantitative application of this system necessitates the determination of Li isotope fractionation accompanying the formation of different Li rich secondary minerals formed during continental weathering. However, as suggested by Vigier et al. (2008), Li isotope fractionation is expected to be broadly similar for all tri- and dioctahedral clays, and solution chemical composition has no effect on isotope fractionation during smectite formation. If this is confirmed, then the law described by Eq. (1) may be representative at a much larger scale than simply that of Iceland. It is instructive to note that, by combining silicate weathering rates reported by Gaillardet et al. (1999) and $\delta^7\text{Li}$ values reported by Huh et al. (1998), most of the large rivers, draining lithologies typical of continental crust, display high $\delta^7\text{Li}$ and correspond to very low chemical erosion rates. The Amazon, Ganges, Orinoco, Lena, Huanghe, and the Qiantang Rivers all display (at their outlet) $\delta^7\text{Li}$ values greater than 21‰ for corresponding

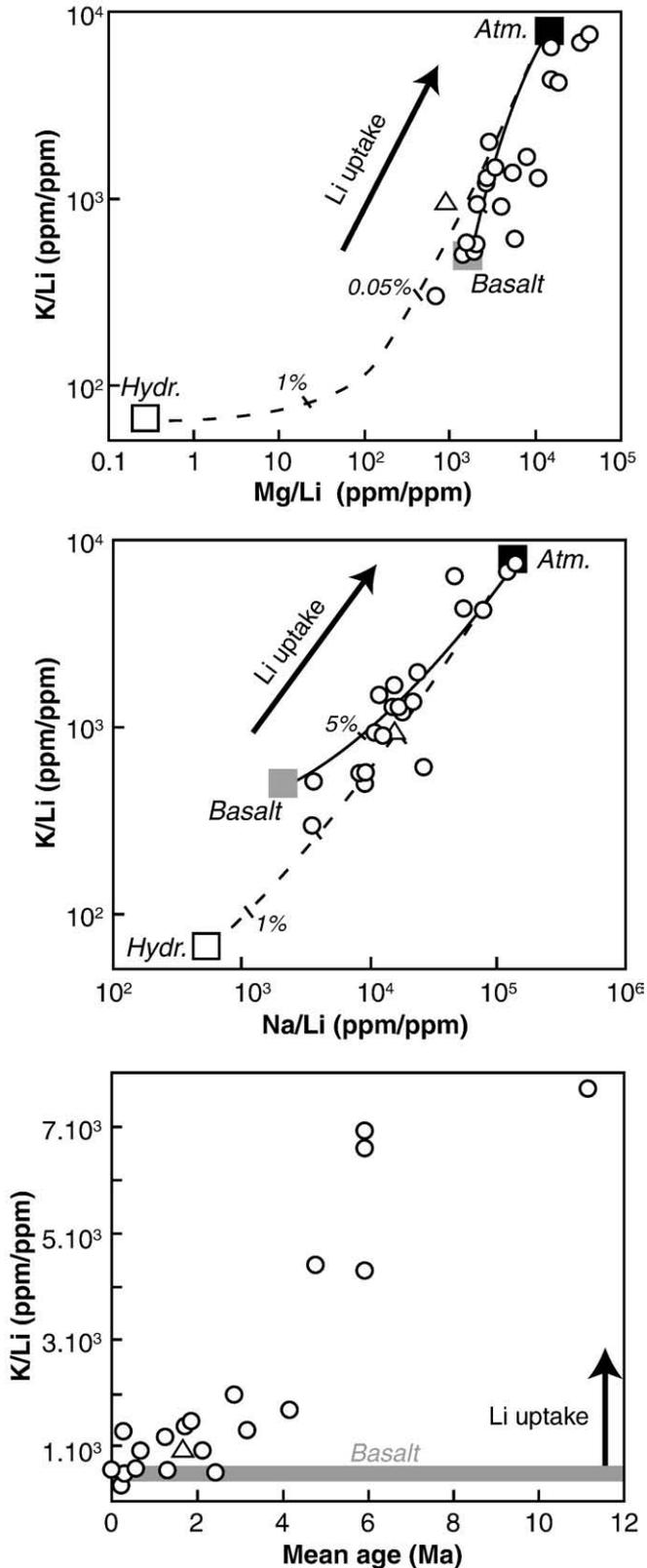


Fig. 2. Dissolved K/Li versus Mg/Li, Na/Li (ppm/ppm) and the mean age of the drained basalts for the main Icelandic rivers. The mean compositions of atmospheric input (Atm.), hydrothermal springs (Hydr.) and drained basalts (Basalt) are also reported (data from analyses of melted Icelandic glacier ice, Pogge von Strandmann (pers. comm.), and Louvat (1997), respectively). Dashed lines represent theoretical mixing curves between hydrothermal springs and atmospheric inputs, and plain lines represent theoretical mixing curves between a water resulting from the congruent weathering of basalts and atmospheric inputs. Arrows represent Li uptake by secondary minerals from a water resulting from the congruent weathering of basalts. The slope of these arrows and the slope defined by the data are close to unity, implying that when Li is taken up by clays, K, Na and Mg are similarly taken up. The triangle is for the glacier fed river Skaftafellsa (#23).

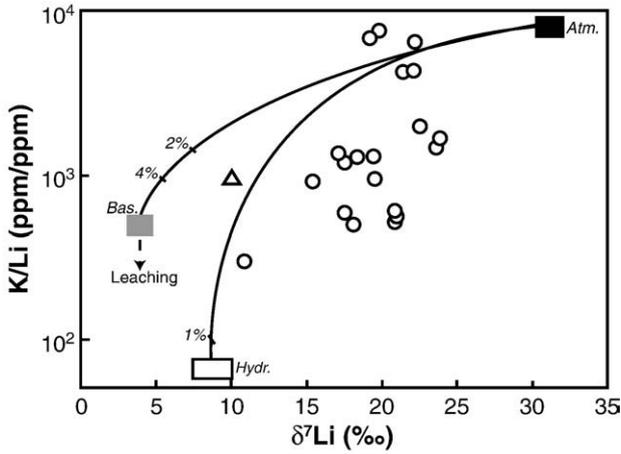


Fig. 3. K/Li versus $\delta^7\text{Li}$ measured in the dissolved phases of the main Icelandic rivers, with same end-members as in Fig. 1. The black arrow represents the evolution of water composition in the case of leaching from a basaltic rock, assuming no associated Li isotope fractionation. Mixing lines do not fit the river data: measured $\delta^7\text{Li}$ are systematically larger than predicted by mixing processes.

chemical erosion rates lower than $14 \text{ t km}^{-2} \text{ yr}^{-1}$. Thus, most of the large rivers draining continental silicates plot on broadly the same trend to that defined by the Icelandic rivers (see Fig. 4). This may imply that Li isotopes do not fractionate during the leaching of Li rich mineral phases present on continents, in particular biotites. However, this would need to be checked experimentally. In order to derive a more general law, it would be necessary to measure $\delta^7\text{Li}$ on the same water samples as those used for estimating chemical erosion rates and to perform systematic studies of granitic catchments.

5.3. Modelling clay–water Li isotope fractionation

On a regional scale, the $\delta^7\text{Li}$ values of the dissolved phase in Icelandic rivers are highly variable. In contrast, the corresponding suspended and bedload sediments display much more homogeneous $\delta^7\text{Li}$ values, close to the composition of unweathered MORB. Where data for both phases are available, such a relationship, between dissolved and sediment loads has been observed for most rivers to date, in particular for Himalayan catchments and the Orinoco basin (Huh et al., 2001; Kisakürek et al., 2005). A simple Rayleigh fractionation model can explain the relationship between these phases, taking into account both the steady-state nature of the erosion processes in Iceland and clay formation. Li is first leached from the basaltic source rocks (e.g. in soils) without significant isotope fractionation, resulting in a dissolved phase with the same $\delta^7\text{Li}$ as the unweathered parent rock (i.e. $\delta^7\text{Li} \approx 4\text{‰}$). When secondary minerals are formed, they incorporate a significant fraction of the dissolved Li. These secondary minerals possess a light $\delta^7\text{Li}$ isotope composition, thus their formation will both deplete the residual waters in ^6Li , and drive their $\delta^7\text{Li}$ values to heavier compositions. It is possible to verify if such a single process could produce both water and sediment river data, using the following equations:

$$\delta_w = \delta_w^i + 1000 \cdot (\alpha - 1) \cdot \ln f_w \tag{2}$$

$$\delta_s = \delta_w + 1000 \cdot \ln \alpha \tag{3}$$

$$\bar{\delta}_s = [(\delta_w^i / 1000 + 1) \cdot (f_w^\alpha - 1) / (f_w - 1) - 1] \cdot 1000 \tag{4}$$

where δ_w and δ_s are the $\delta^7\text{Li}$ of the dissolved phase and sediment respectively, f_w is the fraction of residual dissolved Li, and α is the clay–water Li isotopic fractionation factor ($\delta^7\text{Li}_{\text{clay-water}} = 1000 \ln(\alpha)$). The composition of the cumulated or “bulk” sediment ($\bar{\delta}_s$), as

described by Eq. (4), is calculated assuming a steady-state process such that the erosion products carried by the river reflect the source rock composition (e.g. Négreil et al., 1993):

$$\delta^7\text{Li}_{\text{rock}} = f_s \cdot \bar{\delta}_s + f_w \cdot \delta_w \tag{5}$$

where $\delta^7\text{Li}_{\text{rock}}$ is constant and equivalent to the value of unweathered MORB. This steady-state has recently been demonstrated in Iceland from U-series isotopes measured in rivers (Vigier et al., 2006), and from major and trace element data (Eiriksdottir et al., 2008).

As shown in Fig. 5, this simple model of Li uptake by secondary minerals can explain all the river data (waters and sediments) when $\delta^7\text{Li}_{\text{sediment-water}}$ ranges between -1‰ and -7.5‰ , and f_w is less than $\sim 20\%$. The precise mechanisms responsible for the isotopic composition of river waters and sediments are likely to be more complex than those proposed here, but this model presents an alternative to the leaching model proposed for explaining soil profiles and water data (e.g. Rudnik et al., 2004; Kisakürek et al., 2004). The degree of Li isotope fractionation required to explain the data is significantly lower than the estimation of Chan et al. (1992) (-17‰) for a clay mixture composed of smectite, zeolite, palagonite and oxyhydroxides formed at 4°C on the ocean seafloor. However, isotope fractionation associated with weathering in Iceland may be influenced by other types of secondary minerals. Moreover adsorption processes and coefficients are likely to be different in seawater and continental environments. Recent experimental study shows that the incorporation of Li into the octahedral sites of a smectite at temperatures lower than 90°C is associated with Li isotope fractionations ranging between 8.8‰ and 10.9‰ (Vigier et al., 2008). In parallel, Li adsorption on smectite may be associated with lower or negligible isotope fractionation (Pistiner and Henderson, 2003; Vigier et al., 2008). Further experiments are needed to resolve the present lack of knowledge concerning the processes and phases that fractionate Li isotopes at low temperatures.

Overall, the Li isotope composition of river waters appears to be related to chemical erosion rates and secondary mineral phase formation. Several studies have shown that the stability of secondary phases in Iceland is dependent upon a number of interrelated factors, the principal of which are elemental supply via leaching, water

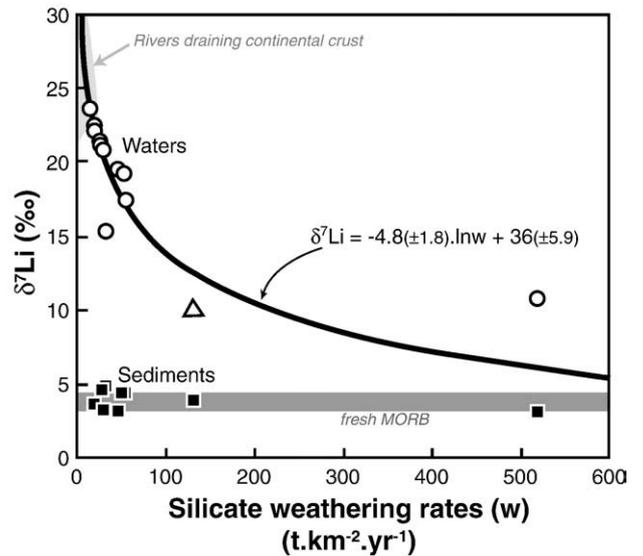


Fig. 4. Chemical erosion rates estimated from major elements in Icelandic river waters (Vigier et al., 2006) versus $\delta^7\text{Li}$ measured in the same waters (open symbols) and in the corresponding river sediments (black symbols). The lake sample (#14) is not represented. The curve and equation represent the best fit for the Icelandic water data. The published values for river waters draining large areas of continental crust are shown for comparison (shaded field) (Amazon, Orenoque, Ganges, Lena, Huanghe, Qiantang; Huh et al., 1998; Gaillardet et al., 1999) (see text for more details).

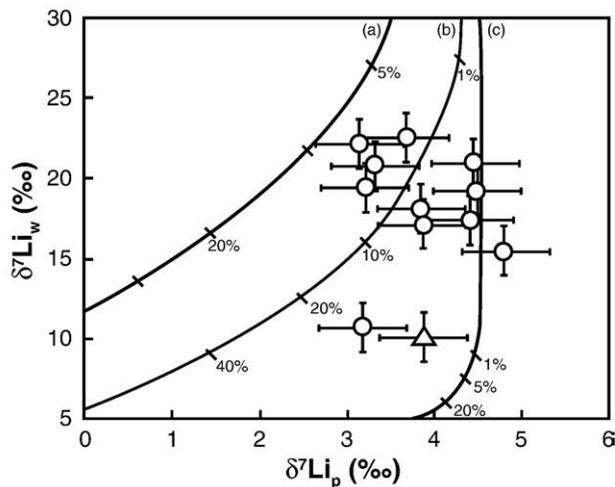


Fig. 5. $\delta^7\text{Li}$ of the dissolved ($\delta^7\text{Li}_w$) and sediment ($\delta^7\text{Li}_p$) loads of the main Icelandic rivers. The curves represent Rayleigh evolution in the case of Li uptake from an initial solution with the same isotopic composition of the source basalts (see Eqs. (2)–(5) in text), and clay–water Li isotope fractionation of (a) -7.5% , (b) -5% and (c) -1% .

temperature, pH and residence time. For most of the samples studied here, taken from the lower reaches of their respective catchments, a steady state is likely to have been achieved such that soil residence times are constant and clay formation is compensated for by chemical and physical erosion. However, a steady state may not always be attained, for example in glacier-fed rivers (such as the Skaftafellsa River (#23)) or in groundwaters, where high pH results as much from the isolation from atmospheric CO_2 , as from chemical weathering. In such cases, there may be no simple relationship with chemical weathering rates, even if secondary minerals such as Fe–Mg–Ca smectites and zeolites are stable.

These observations indicate that the model presented in this study enables the link between secondary mineral formation, chemical erosion rates and the Li isotope composition of residual waters to be quantified, and the data also suggest that secondary mineral formation acts as a key control on the cation flux to the ocean. The relationship between water chemistry and secondary mineral formation is consistent with the U-series data from the same rivers, where soil development and sediment residence time have also been shown to be a major influence on chemical erosion and river water chemistry.

6. Summary and conclusion

The Li isotope compositions of the dissolved phase and suspended and bedload sediments of the main Icelandic rivers have been determined by MC-ICP-MS. For the dissolved phase, $\delta^7\text{Li}$ range between 10.1‰ and 23.8‰, while river sediments display a narrower range of values (3.1‰–4.8‰), close to that of unweathered MORB. High $\delta^7\text{Li}$ values are associated with high K/Li, Na/Li and Mg/Li ratios, and characterise the waters draining mainly old and weathered basalts. Rivers with low $\delta^7\text{Li}$ are located in the younger parts of the island. It is shown that source-mixing alone, between precipitation, Li-rich hydrothermal springs and basalt weathering, cannot explain the entire range of $\delta^7\text{Li}$ values. Instead, the Li isotope compositions of both waters and sediments can be explained by a steady-state erosion process where the formation of secondary minerals is associated with significant Li isotope fractionation. The data obtained in this study, combined with chemical erosion rates previously determined on the same samples provide the first direct evidence for a relationship between $\delta^7\text{Li}$ and chemical erosion rates. An empirical law between chemical erosion rate and $\delta^7\text{Li}$ can be defined, and comparison with literature data suggests that this law may be applicable at a more

global scale and may be of particular use for estimating past changes in continental weathering. Further data are now needed in order to determine if this law can be applied to different rock types and different climatic regimes.

Acknowledgements

We would particularly like to thank Christian France-Lanord (CRPG) for fruitful discussion, and Peter Van Calsteren, Louise Thomas and Mabsie Gilmour (OU) for their technical help during water analyses. This project has been funded by the Open University and by the “Reliefs de la Terre” INSU-CNRS program.

References

- Arnalds, O., 2004. Volcanic soils of Iceland. *CATENA* 56 (1–3), 3–20.
- Arnorsson, S., Gunnarsson, I., Stefansson, A., Andresdottir, A., Sveibjornsdottir, A., 2002. Major element chemistry of surface- and ground waters in basaltic terrain, N-Iceland. I. Primary mineral saturation. *Geochim. Cosmochim. Acta* 66 (23), 4015–4046.
- Carignan, J., Cardinal, D., Eisenhauer, A., Galy, A., Rehkämper, M., Wombacher, F., Vigier, N., 2004. A reflection on Mg, Cd, Ca, Li and Si isotopic measurements and related reference materials. *Geostand. Geoanal. Res.* 28, 139–148.
- Carignan, J., Vigier, N., Millot, R., 2007. Three secondary reference materials for Li isotope measurements: Li7-N, Li6-N and LiCl-N solutions. *Geostand. Geoanal. Res.* 31, 7–12.
- Chan, L.-H., Edmond, J.M., 1988. Variation of lithium isotope composition in the marine environment: a preliminary report. *Geochim. Cosmochim. Acta* 52, 1711–1717.
- Chan, L.-H., Edmond, J.M., Thompson, G., Gillis, K., 1992. Lithium isotopic composition of submarine basalts: implications for the lithium cycle to the ocean. *Earth Planet. Sci. Lett.* 108, 151–160.
- Chan, L.-H., Edmond, J.M., Thompson, 1993. A lithium isotope study of hot springs and metabasalts from mid ocean ridge hydrothermal systems. *J. Geophys. Res.* 98, 9653–9659.
- Chan, L.-H., Gieskes, J.M., You, C.F., Edmond, J.M., 1994. Lithium isotope geochemistry of sediments and hydrothermal fluids of the Gaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta* 58, 4443–4454.
- Chan, L.-H., Alt, J.C., Teagle, D.A.H., 2002. Lithium and lithium isotope profile through the upper oceanic crust: a study of seawater–basalt exchange at ODP Sites 504B and 896A. *Earth Planet. Sci. Lett.* 201, 197–201.
- Elliott, T., Thomas, A., Jeffcoate, A., Niu, A., 2006. Lithium isotope evidence for subduction enriched mantle in the source of mid-ocean-ridge basalts. *Nature* 443, 565–568.
- Eiriksdottir, E.S., Louvat, P., Gislason, S.R., Óskarsson, N., Hardardóttir, J., 2008. Temporal variation of chemical and mechanical weathering in NE Iceland: evaluation of a steady-state model of erosion. *Earth Planet. Sci. Lett.* 272, 78–88.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Gannoun, A., Burton, K.W., Vigier, N., Gislason, S.R., Rogers, N., Mokadem, F., Sigfusson, B., 2006. The influence of weathering process on riverin osmium isotopes in a basaltic terrain. *Earth Planet. Sci. Lett.* 243, 732–748.
- Georg, R.B., Reynolds, B.C., West, A.J., Burton, K.W., Halliday, A.N., 2007. Silicon isotope variations accompanying basalt weathering in Iceland. *Earth Planet. Sci. Lett.* 261, 476–490.
- Gislason, S.R., Eugster, H.P., 1987a. Meteoric water–basalt interactions. II: a field study in N.E. Iceland. *Geochim. Cosmochim. Acta* 51 (10), 2841–2855.
- Gislason, S.R., Eugster, H.P., 1987b. Meteoric water–basalt interactions. I: a laboratory study. *Geochim. Cosmochim. Acta* 51 (10), 2827–2840.
- Gislason, S.R., Arnorsson, S., Armannsson, H., 1996. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* 296, 837–907.
- Gislason, S.R., Oelkers, E.H., Snorrason, A., 2006. Role of river-suspended material in the global carbon cycle. *Geology* 34 (1), 49–52.
- Henley, R.W., Ellis, A.J., 1983. Geothermal systems ancient and modern: a geochemical review. *Earth Sci. Rev.* 19, 1–50.
- Huh, Y., Chan, L.-H., Zhang, L., Edmond, J.M., 1998. Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta* 62, 2039–2051.
- Huh, Y., Chan, L.-H., Edmond, J.M., 2001. Lithium isotopes as a probe of weathering processes: Orinoco River. *Earth Planet. Sci. Lett.* 194, 189–199.
- Huh, Y., Chan, L.-H., Chadwick, O., 2004. Behavior of lithium and its isotopes during weathering of Hawaiian basalts. *Geochem. Geophys. Geosys.* 5. doi:10.1029/2004GC000729.
- James, R.H., Palmer, M., 2000. Marine geochemical cycles of the alkali elements and boron: the role of sediments. *Geochim. Cosmochim. Acta* 64, 3111–3122.
- James, R.H., Rudnicki, M.D., Plamer, M., 1999. The alkali element and boron geochemistry of the Escanaba Trough sediment-hosted hydrothermal system. *Earth Planet. Sci. Lett.* 171, 157–169.
- James, R.H., Allen, D.E., Seyfried, Jr., 2003. An experimental study of oceanic crust and terrigenous sediments at moderate temperatures (51 to 350 °C): insights as to

- chemical processes in near-shore ridge-flank hydrothermal systems. *Geochim. Cosmochim. Acta* 67, 681–691.
- Jeffcoate, A., Elliott, T., Thomas, A., Bouman, C., 2004. Precise, small sample size determinations of lithium compositions of geological reference materials and modern seawater by MC-ICPMS. *Geostand. Geoanal. Res.* 28, 161–172.
- Kisakürek, B., Widdowson, M., James, R.H., 2004. Behaviour of Li isotopes during continental weathering: the Bidar laterite profile, India. *Chem. Geol.* 212, 27–44.
- Kisakürek, B., James, R.H., Harris, N.B.W., 2005. Li and $\delta^7\text{Li}$ in Himalayan rivers: proxies for silicate weathering? *Earth Planet. Sci. Lett.* 237, 387–401.
- Louvat, P., 1997. Etude géochimique de l'érosion fluviale d'îles volcaniques à l'aide des bilans d'éléments majeurs et traces, Doctorat Thesis, IPGParis.
- Millot, R., Guerrot, C., Vigier, N., 2004. Accurate and high-precision measurement of lithium isotopes in two reference materials by MC-ICP-MS. *Geostand. Geoanal. Res.* 28, 153–159.
- Milliman, J.D., Meade, R.H., 1983. World-wide delivery of river sediment to the oceans. *J. Geol.* 91, 1–21.
- Négrel, P., Allègre, C.J., Dupré, B., Lewin, E., 1993. Erosion sources determined by inversion of major and trace element ratios and strontium isotopic ratios in river: the Congo Basin case. *Earth Planet. Sci. Lett.* 12, 59–76.
- Pálsson, S., Vigfusson, G.H., 1991. *Nidurstödur svifaurswmaelinga 1963–1990*, Reykjavik.
- Pistiner, J.S., Henderson, G., 2003. Lithium isotope fractionation during continental weathering processes. *Earth Planet. Sci. Lett.* 214, 327–339.
- Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P., Gislason, S.R., Mokadem, F., 2006. Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain. *Earth Planet. Sci. Lett.* 251, 134–147.
- Rudnik, R.L., Tomascak, P.B., Njo, H.B., Gardner, L.R., 2004. Extreme lithium isotopic fractionation during continental weathering revealed in saprolites from South Carolina. *Chem. Geol.* 212, 45–57.
- Seyfried Jr., W.E., Chen, X., Chan, L.-H., 1998. Trace element mobility and lithium isotope exchange during hydrothermal alteration of seafloor weathered basalt: an experimental study at 350 °C, 500 bars. *Geochim. Cosmochim. Acta* 62, 949–960.
- Stefansson, A., Gislason, G.R., 2001. Chemical weathering of basalts, SW Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.* 6 (513–556), 2001.
- Taylor, S.R., Urey, H.C., 1938. Fractionation of the lithium and potassium isotopes by chemical exchange with zeolites. *J. Chem. Phys.* 6, 429–438.
- Tomasson, H., 1986. Glacial and volcanic shore interactions. Part 1: on land. In: Sigbjarnarson, G. (Ed.), *Iceland Coastal and River Symposium Proceedings*. University of Iceland, Reykjavik, pp. 7–16.
- Vigier, N., Bourdon, B., Turner, S., Allègre, C.J., 2001. Erosion timescales derived from U-decay series measurements in rivers. *EPSL* 193, 549–563.
- Vigier, N., Burton, K.W., Gislason, S.R., Rogers, N.W., Duchene, S., Thomas, L., Hodge, E., Schaefer, B., 2006. The relationship between riverine U-series disequilibria and erosion rates in a basaltic terrain. *Earth Planet. Sci. Lett.* 249, 258–273.
- Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S., France-Lanord, C., 2008. Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle. *Geochim. Cosmochim. Acta* 72, 780–792.
- Williams, L.B., Hervig, R.L., 2005. Lithium and boron isotopes in illite-smectite: the importance of crystal size. *Geochim. Cosmochim. Acta* 69, 5705–5716.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2006. The effect of crystallinity on dissolution rates and CO₂ consumption capacity of silicates. *Geochim. Cosmochim. Acta* 70, 858–870.
- Yeghicheyan, D., Carignan, J., Valladon, M., Bouhnik Le Coz, M., Le Cornec, F., Castrec-Rouelle, M., Robert, M., Aquilina, L., Aubry, E., Churlaud, C., Dia, A., Deberdt, S., Dupré, B., Freyrier, R., Gruau, G., Hénin, O., de Kersabiec, A.-M., Macé, J., Marin, L., Morin, N., Petitjean, P., Serrat, E., 2001. A compilation of silicon and thirty one trace elements measured in the natural river water reference material SLRS-4 (NRC-CNRC). *Geostand. Newsl. Geost. Geoanal. Res.* 25, 465–474.
- Zhang, L., Chan, L.H., Gieskes, J.M., 1998. Lithium isotope geochemistry of pore waters from Ocean Drilling Program Sites 918 and 919, Irminger Basin. *Geochim. Cosmochim. Acta* 62, 2437–2450.