Lithium, magnesium and uranium isotope behaviour in the estuarine environment of basaltic islands

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ABSTRACT

This study presents major and trace elements and uranium (U), lithium (Li) and magnesium (Mg) isotope data for dissolved and suspended particulate material from estuaries draining dominantly basaltic terrains in Iceland (Borgarfjörður) and Sao Miguel (Povoação) in the Azores archipelago. The concentrations of dissolved sodium (Na), calcium (Ca), potassium (K), sulphate (SO_4), Mg and Li, and $^7Li/^6Li$ and $^{26}Mg/^{24}Mg$ isotope ratios vary directly as a function of the dissolved chloride concentration [Cl], indicating that these species are non-reactive in these estuaries. However, U appears to be affected either by colloid flocculation or the formation of Fe-oxyhydroxides in Borgarfjörður. The major element composition of suspended particulate material in the estuary at Borgarfjörður shows that the detrital silicates delivered to the estuarine mixing zone are relatively unweathered. Accordingly, the $\delta^{26}Mg$ isotope composition of the suspended material is indistinguishable from that of the parent basalts. However, the ($^{234}U/^{238}U$) activity ratios of the suspended material are significantly different from the parent basalt indicating rapid equilibration of the U isotopes between particles and seawater. The Li concentration and δ^7Li isotope composition of the suspended load are also observed to increase with increasing [Cl], consistent with ongoing weathering of detrital material and the formation of secondary minerals in seawater. Depending on the particle residence time in the estuary, this process could remove as much as 15–25% of the global riverine input of Li to the ocean.

1. Introduction

On geological timescales the most important climate moderating process is the weathering of calcium (Ca)–magnesium (Mg) silicates (Walker et al., 1981; Berner et al., 1983, 1990; Kump et al., 2000). On land, this process occurs through the chemical weathering of silicate rocks and minerals converting atmospheric carbon dioxide (CO_2) to hydrogen carbonate ions which, along with metal ions, are transported to the oceans by rivers and groundwaters where they are removed via precipitation of calcium carbonate (Gaillardet et al., 1999b; Dessert et al., 2003). Increased temperature and continental runoff enhances both weathering and riverine transport, increasing CO_2 consumption, resulting in lower temperatures due to the negative feedback which the greenhouse gases exert on climate. Thus, records of ancient seawater chemistry potentially provide a means of determining the importance of weathering on the global carbon cycle and its effect on Earth's climate. Many natural long-lived radiogenic isotopes in seawater, such as strontium (Sr) or lead (Pb), are sensitive to changes in the balance of input from continental weathering, and sedimentary archives potentially preserve a record of changes in chemical weathering through geological time (e.g. Palmer and Edmond, 1989). However, changes, for example, in the marine $^{87}Sr/^{86}Sr$ record, cannot be used to reconstruct past CO_2 consumption rates because it is not possible to distinguish changes in the chemical weathering flux from those caused by variations in the composition of the continental source (e.g. Oliver et al., 2003). Consequently, over recent years considerable effort has been made to find new proxies that provide information on both weathering processes and flux, including uranium (U), lithium (Li) and magnesium (Mg) isotopes.

Uranium is delivered to the oceans via rivers and dust, and is removed by uptake into marine sediments and oceanic basalts (Henderson and Anderson, 2003). During rock weathering, the energetic α-decay of ^{238}U results in the preferential release of ^{234}U due to α-recoil effects, so river waters generally have ($^{234}U/^{238}U$) activity ratios (where parentheses denote activity ratio) of greater than 1 (secular equilibrium)

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(Porcelli et al., 2001; Vigier et al., 2002; Swarzenski et al., 2003, 2004; Pogge von Strandmann et al., 2006). Moreover, the $(^{234}U/^{238}U)$ activity ratio is proportional to the surface area of the rock or mineral from which the ^{234}U can be directly recoiled; highest $(^{234}U/^{238}U)$ activity ratios are found in waters which interact with fine-grained soils or glacial tills (Kronfeld and Vogel, 1991; Pogge von Strandmann et al., 2006). Because all rocks older than ca. 1 million years are in secular equilibrium, the U activity ratio in rivers thus records the balance of physical weathering processes (which raise the activity ratio of the water by creating a greater surface area to grain size ratio; Kronfeld and Vogel, 1991; Robinson et al., 2004; Pogge von Strandmann et al., 2006) to chemical weathering (which lowers the activity ratio towards secular equilibrium by rock dissolution and congruent release of both ^{234}U and ^{238}U; Chabaux et al., 2003).

Lithium is conservative in the oceans, with a residence time of ca. 1 million years (Huh et al., 1998), and it is isotopically uniform on a global scale ($\delta^7Li=+31$‰; Tomascak, 2004). The concentration and isotopic composition of seawater is maintained by inputs of high-temperature hydrothermal fluids at oceanic ridges (with $\delta^7Li \approx +6.7$‰; Bray, 2001) and dissolved Li from rivers (average $\delta^7Li=+23$‰; Huh et al., 1998), and low-temperature removal of Li into oceanic basalts and marine sediments. Thus, seawater Li is isotopically heavier than its sources; this is because ^6Li is preferentially retained by secondary minerals (Huh et al., 1998, 2001, 2004). Accordingly, if weathering is congruent, the Li isotopic composition of river water is the same as that of the parent rock, but if weathering is incongruent, and there is secondary mineral formation, river waters are enriched in ^7Li (Huh et al., 2001; Kisakurek et al., 2005; Pogge von Strandmann et al., 2006). Recent work has shown that >90% of dissolved Li in river water is derived from weathering of silicates, even in carbonate dominated catchments (Kisakurek et al., 2005). The Li and Li isotopic composition of river water can therefore be used to obtain information about silicate weathering rates, as well as weathering congruency.

The major source of Mg to the oceans is from the weathering of carbonate and silicate rocks of the continental crust, and it is removed through exchange with Ca during hydrothermal reaction at mid-ocean ridges, the formation of dolomite, and ion exchange reactions with clays (Elderfield and Schultz, 1996). At the present-day, the oceans have a uniform Mg concentration (53 mmol/l; Carpenter and Manella, 1973) and isotope composition ($\delta^{26}Mg=-0.82$‰; Tipper et al., 2006b). Fractionation of Mg isotopes occurs as a result of both secondary mineral formation (Pogge von Strandmann et al., in review, Tipper et al., 2006a) and biological processing (Black et al., 2006), but not during primary rock dissolution (de Villiers et al., 2005; Black et al., 2006; Tipper et al., 2006a). Nevertheless, the range in the $\delta^{26}Mg$ value of river water (−2.5 to −0.5‰; Tipper et al., 2006a,b) is only about half the variation observed in terrestrial rock types. While it is therefore difficult to distinguish Mg isotope variations which arise from weathering processes from those caused by variations in lithology, Mg isotopes should be a powerful tool for assessing weathering congruency and biological activity when used in parallel with Li isotopes.

Records of the past variation in seawater $(^{234}U/^{238}U)$, δ^7Li and $\delta^{26}Mg$ are now starting to emerge in the literature (Henderson and Anderson, 2003; de Villiers et al., 2005; Hathorne and James, 2006), and all have been interpreted in terms of past variations in continental weathering. For example, records of seawater $(^{234}U/^{238}U)$, derived from marine sediments and corals, demonstrate that $(^{234}U/^{238}U)$ has remained close to the modern value of 1.146 (Chen et al., 1986) for at least the last 400 kyr (Henderson and Anderson, 2003), which is interpreted to suggest that the balance of physical to chemical weathering on the continents has varied little over recent glacial–interglacial cycles. On longer timescales, records of seawater [Li] and δ^7Li suggest that silicate weathering rates decreased between ~16 and 8 Ma, which may have been responsible for putative increases in levels of atmospheric CO_2 (pCO_2) (Hathorne and James, 2006). However, each of these interpretations relies on the critical assumption that the

weathering signal carried by rivers is transferred to the oceans without modification in the estuarine mixing zone. Therein lies a problem because, to date, there have been no studies on the behaviour of lithium or magnesium isotopes in estuaries, while studies of uranium-series isotopes indicate that uranium can be both removed from or added to the dissolved phase during mixing between freshwater and seawater in some estuaries (e.g. Andersson et al., 2001; Porcelli et al., 2001; Swarzenski et al., 2003), but undergoes no reaction in others (e.g. Toole et al., 1987; Swarzenski et al., 2003).

This study presents U, Li and Mg isotope data for both dissolved and suspended material from estuaries in the predominantly basaltic islands of Iceland and the Azores. These results illustrate the effects of estuarine mixing on the U, Li and Mg isotope composition of the dissolved load. Moreover, both Iceland and the Azores are typical of the high-relief, volcanic and tectonically active islands thought to contribute >45% of the river suspended material to the oceans (Milliman and Syvitski, 1992; Gislason et al., 2004, 2006). Therefore, these results also provide an insight into the behaviour of such suspended material, and how weathering and dissolution of suspended material may contribute to the overall riverine signal to the oceans.

2. Sample localities

2.1. Iceland

The Borgarfjörður estuary lies on the west coast of Iceland (Fig. 1). Its catchment area is 1685 km^2 (Gislason et al., 1996) and consists mainly of young (<3.3 Ma) basaltic rock (Gislason et al., 1996; Tronnes, 2003), some of which is glaciated (the Langjökull icecap). The climate is oceanic boreal; the mean annual temperature is 4 °C and the mean annual precipitation in the sampling area is ~1000 mm. The estuary itself is over 25 km in length and 5 km wide at its broadest point. It is only ~1–2 m deep in the innermost 5 km but water depth increases
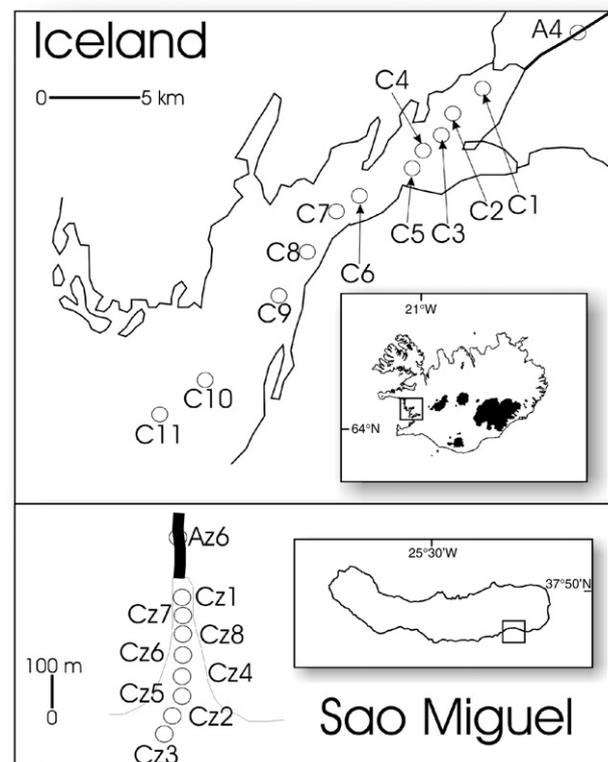

Fig. 1. Maps to show sample locations in Iceland and Sao Miguel. The black areas on the map of Iceland represent permanent ice caps.

rapidly beyond this point, reaching ~100 m at a distance of 10 km. River discharge into the estuary is low so the estuary is tide-dominated and it is both vertically and horizontally well-mixed (pers. comm. Iceland Marine Institute). The geochemistry of the rivers which drain into the estuary has been extensively studied and is discussed elsewhere (Gislason et al., 1996; Pogge von Strandmann et al., 2006).

2.2. Sao Miguel

The island of Sao Miguel is the largest of the islands which make up the Azores archipelago. The climate is maritime and temperate, with mean annual temperatures which range from 13 to 23 °C and mean annual precipitation of ~700 mm (Instituto de Meteorologia). The Povoação estuary is located in the south-east of the island and receives input from the Ribeira do Purgar and Ribeira das Lagos, which merge before they enter the estuary (Fig. 1). Both rivers drain basalt which erupted ~2 million years ago (Moore, 1990). The estuary is well-mixed, and the mixing zone is only about 200 m long and not more than ~1.5 m deep.

3. Sampling and analytical techniques

3.1. Sampling

Samples were collected from Iceland in September 2003 and from the Azores in October 2004. Samples from the Borgarfjörður estuary were collected from a Rigid Inflatable Boat crewed by members of the Borgarnes Rescue team. At each locality, a pre-cleaned 10-litre Go-Flo bottle was placed over the side of the boat on a Kevlar rope and the sample was collected at a depth of ~1 m below the water surface. In situ measurements of pH, temperature and conductivity were made at the same depth. The estuary at Povoação is much smaller, so samples were collected in pre-cleaned 2-litre HDPE bottles at intervals throughout the mixing zone by hand from centre of the flow. Measurements of pH, temperature and conductivity were made at each sample locality. Each water sample was filtered, on the day of collection, through 0.2 μm cellulose acetate filters using a pressurised Teflon unit. The filters from Iceland were retained for analyses of suspended particles. For some samples, the 0.2 μm filtered water was then ultrafiltered, using a Sartorius cross-flow filter unit containing Sartocon polyethersulphone (PESU) slice cassettes, in order to separate the retentate/colloidal fraction (>10 kD) from the truly dissolved (<10 kD) fraction. Possible addition or retention of elements by the cassette was assessed by mass balance (Dupre et al., 1999). No effect was observed for Li, Mg and dissolved organic carbon (DOC), consistent with the findings of Dupre et al. (1999), but U concentrations are 15–20% higher in the <10 kD fraction compared to the <0.2 μm fraction, suggesting that U is added by the cassette. It is thus also possible that there is a contribution from the cassette to the retentate (colloidal) fraction; this cannot be quantified, but is likely to be small.

3.2. Cations, anions and trace elements

Suspended particulate material was washed thoroughly with Milli-Q water to remove any salt particles and dissolved in a mixture of teflon distilled (TD) hydrofluoric (HF) and nitric (HNO_3) acid (cf. Kisakurek et al., 2004). Cation concentrations in the suspended and dissolved loads were measured by inductively coupled plasma mass spectrometry (ICP-MS). Major elements were calibrated against a set of synthetic multi-element standards prepared gravimetrically from high purity single element standard solutions. The accuracy of the analysis was assessed by running the natural water certified reference material SLRS-4, and the seawater salinity standard IAPSO. The following certified reference materials were used for external calibration: BHVO-2, BIR-1, JB-2 and BCR-2. BHVO-2 was also used as a monitoring standard in each batch of analyses. The 2σ external uncertainty of these measurements is better than ±3.2% for major elements and ±5.0% for trace elements. The anion concentrations in the dissolved load were measured by ion chromatography, with an uncertainty of better than ±5% for all anions.

3.3. U, Li and Mg isotopes

For the U-isotope analyses, 100 ml of filtered water were evaporated after spike addition, and then passed through cation exchange resin to separate U. Measurements were made by thermal ionisation mass spectrometry (TIMS) on single rhenium filaments, with a 2σ external error of ±0.024 on the $(^{234}U/^{238}U)$ activity ratio, using a diluted (100 ng/l), spiked NIST U960 standard. U concentrations were also measured in all samples by isotope dilution, with a 2σ external error of better than ±0.7% on the same diluted NIST 960 standard (van Calsteren and Schwieters, 1995; Turner et al., 2001).

For Li isotope analysis, between 0.1 ml and 50 ml of filtered water were evaporated and passed through a cation exchange column to separate Li (James and Palmer, 2000). Measurements were performed by multi-collector ICP-MS (Nu Instruments), using a sample-standard bracketing technique, relative to the L-SVEC standard (Flesch et al., 1973) which has a Li concentration within ±10% of that of the sample (Kisakurek et al., 2004). Results are presented as δ^7Li (where $\delta^7Li = ([(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{L\text{-}SVEC}] - 1) \times 1000$). The 2σ external uncertainty based on repeat measurements ($n=44$) of IAPSO seawater is +31.2±0.90‰ (2σ).

For Mg isotope analysis, between 0.5 and 10 μl of filtered water was dried down and passed through cation exchange columns to separate Mg from matrix elements, including sodium (Na), aluminium (Al) and Ca (Galy et al., 2001; Chang et al., 2003; Tipper et al., 2006a), in order to obtain 50 ng of Mg. Particulate material was also passed through an anion exchange column to remove iron (Fe) (Wiechert and Halliday, 2007). Mg isotope measurements were performed by multi-collector ICP-MS (Nu Instruments, Open University); replicate measurements of some of the particulate samples were made on a Neptune MC-ICP-MS at Bristol University. We adopted a sample-standard bracketing technique, relative to an in-house standard (OU-Mg) (Pearson et al., 2006), which had a Mg concentration within ±5% of that of the sample. However, all data presented here are normalised to DSM-3 (Galy et al., 2003), and are given as $\delta^{25}Mg$ and $\delta^{26}Mg$, in‰ variations from DSM-3 (where $\delta^x Mg = ([(^x Mg/^{24}Mg)_{sample}/(^x Mg/^{24}Mg)_{DSM\text{-}3}] - 1) \times 1000$, and $^x Mg$ is either ^{25}Mg or ^{26}Mg). Secondary standards measured during the course of these analyses include BHVO-2, JB-2, IAPSO seawater and the Cambridge (CAM-1) standard. $\delta^{26}Mg$ values (and their 2σ external uncertainties) are as follows: CAM-1 ($n=23$): −2.78±0.15‰; OU-Mg: −2.91±0.18‰; IAPSO ($n=20$): −0.89±0.18‰; BHVO-2 ($n=5$): −0.25±0.11‰; JB-2 ($n=4$): −0.24±0.12‰.

4. Results and discussion

Sample locations, field measurements (conductivity, pH and temperature) and cation, anion and isotope data for the dissolved load are given in Table 1. Major, trace element and isotope data for the suspended load (Borgarfjörður only) are given in Table 2.

4.1. Major element composition of the dissolved and suspended load

In the absence of biogeochemical processes, the physical mixing of fresh and saline waters in an estuary will result in a linear relationship between the concentration of a dissolved species and the proportion in which the two waters have undergone mixing — provided that the compositions of the end-members remain constant over time, and there are no other sources or sinks of the species in question. The effects of biogeochemical processes on the distribution of a species in an estuary can be assessed by plotting the concentration of the species in a suite of samples against a conservative index of mixing, i.e. a

Table 1
In situ measurements, anion and cation concentrations and isotope ratios of the dissolved load in both estuaries

Locality	Latitude	Longitude	TDS (mg/l)	Conductivity (mS/cm)	pH	T (°C)	DOC (mg/l)	TOC (Colloid) (mg/l)	Na (mmol/l)	Mg (mmol/l)	K (mmol/l)	Ca (mmol/l)	Cl (mmol/l)	SO$_4$ (mmol/l)	Li (µmol/l)	U (nmol/l)	U (colloid) (nmol/l)	δ^7Li (‰)	δ^{25}Mg (‰)	δ^{26}Mg (‰)	(^{234}U/^{238}U)
A4 (Iceland)	N 64°36.199'	W 21°42.481'	34.7	0.058	7.93	9.0	0.40	0.37	0.309	0.0762	0.012	0.098	0.36	0.005	0.0418	0.0161	0.0023	21.1	−0.12	−0.23	1.57±2
C1 (Iceland)	N 64°34.290'	W 21°49.299'	33.4	0.113	7.92	7.7			0.325	0.262	0.013	0.106	0.41	0.008	0.0382	0.0630		18.3	−0.14	−0.28	1.49±1
C2 (Iceland)	N 64°33.584'	W 21°51.107'	47.2	0.118	7.95	8.0			0.562	0.0832	0.019	0.107	0.86	0.010	0.0566	0.0142		23.1	−0.28	−0.55	1.32±2
C3 (Iceland)	N 64°33.207'	W 21°51.792'	1419	2.57	7.94	8.8			23.8	0.110	0.639	0.669	18.4	2.27	1.36	0.0178		31.7	−0.35	−0.68	1.18±2
C4 (Iceland)	N 64°32.924'	W 21°52.529'	3570	6.06	8.08	9.4			49.7	2.76	1.32	1.29	51	3.22	3.03	0.507		31.8	−0.35	−0.69	1.23±1
C5 (Iceland)	N 64°32.623'	W 21°53.270'	4900	8.54	8.16	9.6			72.9	5.72	194	1.81	115	6.00	4.37	1.20		32.1	−0.33	−0.65	1.16±2
C6 (Iceland)	N 64°31.686'	W 21°56.450'	6460	10.9	8.22	9.8			116	13.4	3.03	2.84	151	7.44	6.92	3.28		32.3	−0.37	−0.73	1.16±2
C7 (Iceland)	N 64°31.240'	W 21°57.647'	7660	13.0	8.25	10.4			163	18.7	4.15	3.91	200	8.44	10.3	4.48		32.0	−0.35	−0.69	1.15±1
C8 (Iceland)	N 64°30.035'	W 21°59.427'	10930	17.7	8.27	10.7			207	23.8	5.08	4.86	275	11.2	13.0	6.17		31.9	−0.35	−0.69	1.15±1
C9 (Iceland)	N 64°29.019'	W 22°01.071'	15400	24.8	8.28	11.1			292	33.2	7.24	6.9	385	15.5	17.5	8.13		31.5	−0.35	−0.70	1.16±1
C10 (Iceland)	N 64°26.523'	W 22°05.955'	21700	36.1	8.26	11.8			398	46.3	10.4	9.51	531	23.1	22.4	11.5		32.0	−0.36	−0.72	1.15±1
C11 (Iceland)	N 64°26.050'	W 22°08.966'	23500	37.5	8.29	12.1			419	48.7	10.8	10.1	542	23.8	23.5	11.3		31.7	−0.42	−0.82	1.15±1
Az6 (Sao Miguel)	N 37° 44.785'	W 25° 14.676'	106	0.22	8.24	16.7	0.80	0.14	0.763	0.289	0.14	0.27	0.487	0.0408	0.200	0.324	0.0414	18.2	0.27	0.54	1.27±1
Cz1 (Sao Miguel)			1040	1.28	7.88	18.4			7.18	1.03	0.28	0.41	8.75	0.411	1.18	0.70		28.2	−0.22	−0.43	1.23±1
Cz7 (Sao Miguel)			3690	6.42	8.15	17.2			57.6	6.79	1.41	1.49	79.2	3.56	5.91	2.23		30.5	−0.33	−0.64	1.17±1
Cz8 (Sao Miguel)			7640	13.0	8.21	17.5			110	12.9	2.66	2.59	140	5.63	10.2	3.85		30.8	−0.34	−0.69	1.16±2
Cz6 (Sao Miguel)			10520	17.6	8.29	17.9			159	18.4	3.54	3.66	203	8.74	13.9	5.36		31.5	−0.49	−0.85	1.15±1
Cz4 (Sao Miguel)			16900	27.6	8.34	18.6			266	30.9	6.37	6.22	340	13.7	22.2	8.56		32.1	−0.42	−0.84	1.16±1
Cz5 (Sao Miguel)			18900	30.8	8.32	19.3			306	35.3	7.41	6.98	391	16.6	23.9	9.53		31.8	−0.38	−0.76	1.15±1
Cz2 (Sao Miguel)			23900	38.5	8.27	19.8			375	43.6	9.07	8.70	478	21.7	28.8	11.7		31.0	−0.42	−0.84	1.15±1
Cz3 (Sao Miguel)			27200	48.6	8.29	20.6			444	51.7	10.6	10.3	547	23.3	34.0	13.8		31.4	−0.48	−0.84	1.15±1

Internal uncertainty is given for U activity ratios. T=temperature, DOC=dissolved (<10 kD) organic carbon, TOC=total organic carbon (in colloids).

Table 2
Element concentrations and isotope ratios of the suspended load, including major element concentrations of fresh basalt taken from the Borgarfjörður catchment (Gislason et al. 1996)

|	Na$_2$O (wt.%)	MgO (wt.%)	Al$_2$O$_3$ (wt.%)	K$_2$O (wt.%)	CaO (wt.%)	Li (μg/g)	U (μg/g)	δ^{7}Li (‰)	δ^{25}Mg (‰)	δ^{26}Mg (‰)	(^{234}U/^{238}U)
Hvita basalt	2.14	9.94	15.6	0.16	12.64						
Nordura basalt	3.02	4.54	14.5	0.47	10.28						
A4	1.96	5.51	17.8	0.234	10.7	5.49	0.196	0.9	−0.11	−0.21	1.04±2
C1		5.90*				5.11*	0.293	−0.18	−0.09	−0.18	1.11±1
C2		5.40*				5.23*	0.517	1.2	−0.15	−0.27	1.09±1
C3	1.86	5.95	15.6	0.216	10.1	6.58	0.668	1.0	−0.05	−0.10	1.14±1
C4	2.05	6.58	16.6	0.343	10.7	8.33	0.669	4.6	−0.08	−0.15	1.09±1
C5	1.96	5.88	15.0	0.33	9.64	7.14	0.607	2.2	−0.11	−0.22	1.10±1
C6	2.20	6.30	16.6	0.30	10.5	7.67	0.498	3.1	−0.18	−0.32	1.13±1
C7						7.41*	0.354	4.2	−0.10	−0.20	1.09±2
C8	2.30	6.05	16.1	0.423	10.2	8.92	0.524	5.0	−0.23	−0.41	1.13±1
C9	1.09	2.32	6.09	0.223	3.78		0.194	8.0	−0.11	−0.22	1.07±2
C10		5.80*					0.314	9.8	−0.15	−0.28	1.17±1
C11	2.12	3.33	5.92	0.247	5.63		0.146	8.7	−0.17	−0.32	1.12±2
Az6	4.01	0.74	8.37	6.9	3.38	5.95	0.264	8.3			1.05±2

Internal uncertainty is given for U activity ratios.
*Sample concentrations were determined from MC-ICP-MS intensities (uncertainty ± 10%).

component whose concentrations in estuarine waters are controlled only by physical mixing. Here, we utilise Cl concentrations [Cl] for this purpose.

The dissolved load concentrations of Na, K, Ca and sulphate (SO$_4$) in both estuaries, fall on a single line that joins the sample with lowest [Cl] to the sample with highest [Cl]. This indicates that, as expected, these species are non-reactive in the Borgarfjörður and Povoação estuaries; they show conservative behaviour.

The major element (Na$_2$O, Al$_2$O$_3$, K$_2$O and CaO) composition of the suspended load of the Icelandic estuary (Table 2) is not significantly different from that of the suspended load of the river which enters it (sample A4), and is generally within the range reported for basalts in the catchment area (Gislason et al., 1996). However, there is a linear decrease in Ca/Na and Mg/Na of the suspended load as distance into the estuary increases, with the suspended load of the river and of the sample furthest from land acting as end-points (Fig. 2). This suggests progressive alteration of the suspended load with interaction with seawater. The Na$_2$O concentrations are approximately constant, suggesting that this trend is not due to contamination by NaCl, rather there is progressive loss of MgO and CaO from the suspended load. This trend may be associated with weathering of the suspended load described in Section 4.2, although it is generally assumed that Na is more mobile than Ca or Mg (Gislason et al., 1996). The major element composition of Norðurá
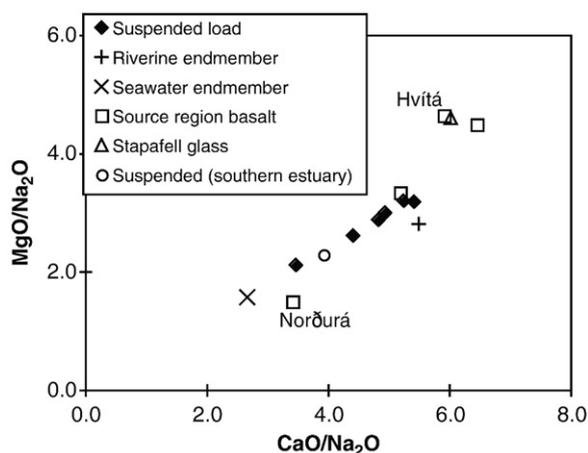
Fig. 2. CaO/Na$_2$O vs. MgO/Na$_2$O (wt.%/wt.%) of suspended particulate material from the Borgarfjörður estuary. Also shown for comparison are values for local basalt (including from the Hvítá and Norðurá source rivers) (Gislason et al., 1996), Stapafell glass (Oelkers and Gislason, 2001) and samples of particulate material from an estuary in the south of Iceland (Stefansdottir and Gislason, 2005).

River basalt (Gislason et al., 1996) is close to that of the altered suspended load (Fig. 2); this may be because of alteration of adjacent Norðurá rhyolites, or alteration of the Norðurá basalt itself.

4.2. Uranium and uranium isotopes

With the exception of one sample (C2) which has slightly low [U], dissolved uranium appears to display conservative behaviour in both estuaries (Fig. 3). However, the tie lines which join the sample with the lowest [Cl] to the sample with highest [Cl] are offset because the high [Cl] end-member for Borgarfjörður has a lower U concentration than the high [Cl] end-member sampled in the Povoação estuary. The most likely explanation for this is input of submarine hydrothermal fluids with high U/Cl in seawater around Sao Miguel (Table 3), although we note that the offset is small when the error on [Cl] is taken into account (Fig. 3).

Uranium has been reported to behave conservatively in a number of estuaries, including the Zaire (Martin et al., 1978), the Seine (Schmidt, 2005), the Anadyr (Ray et al., 1996), the Mississippi (Swarzenski and McKee, 1998) and several UK rivers (Toole et al., 1987). However, studies of other river systems have provided evidence for non-conservative behaviour; these include the Ogeechee (Windom et al., 2000), the Amazon and Fly rivers (Swarzenski et al., 2004), the Ganges–Brahmaputra (Carroll and Moore, 1993), the Delaware and Chesapeake rivers (Church et al., 1996) and the Kalix in Sweden (Andersson et al., 1995, 1998, 2001; Porcelli et al., 1997, 2001). Non-conservative behaviour may be linked to a number of processes. These include scavenging by Fe-Mn oxyhydroxides or organic particles, removal of uranium in anoxic bottom waters because of reduction of U(VI) to U(IV), and input of uranium due to resuspension of bottom sediments (Swarzenski et al., 2004). More recent studies, which include measurement of uranium in colloidal phases, indicate that flocculation of colloid phases can result in significant removal of colloid-bound uranium in the low salinity (low [Cl]) zone (Porcelli et al., 1997). Furthermore, Andersson et al. (2001) have shown that variations in colloid composition (i.e. Fe-oxyhydroxides vs. clays vs. organic material) can lead to removal and addition of uranium to the dissolved (<0.2 μm) phase across a range of [Cl].

The rivers which enter both of the estuaries studied here contain relatively little colloidal U: only ~13% of U is found in the 10 kD–0.2 μm fraction (Table 1). They also contain very little organic carbon, both in the truly dissolved (<10 kD) fraction (0.4–0.8 mg/l, Table 1) and in the retentate (colloidal) fraction (0.14–0.37 mg/l). By contrast, estuaries which are reported to be strongly affected by U-removal in the low salinity zone have a far higher proportion of colloid-bound U and far
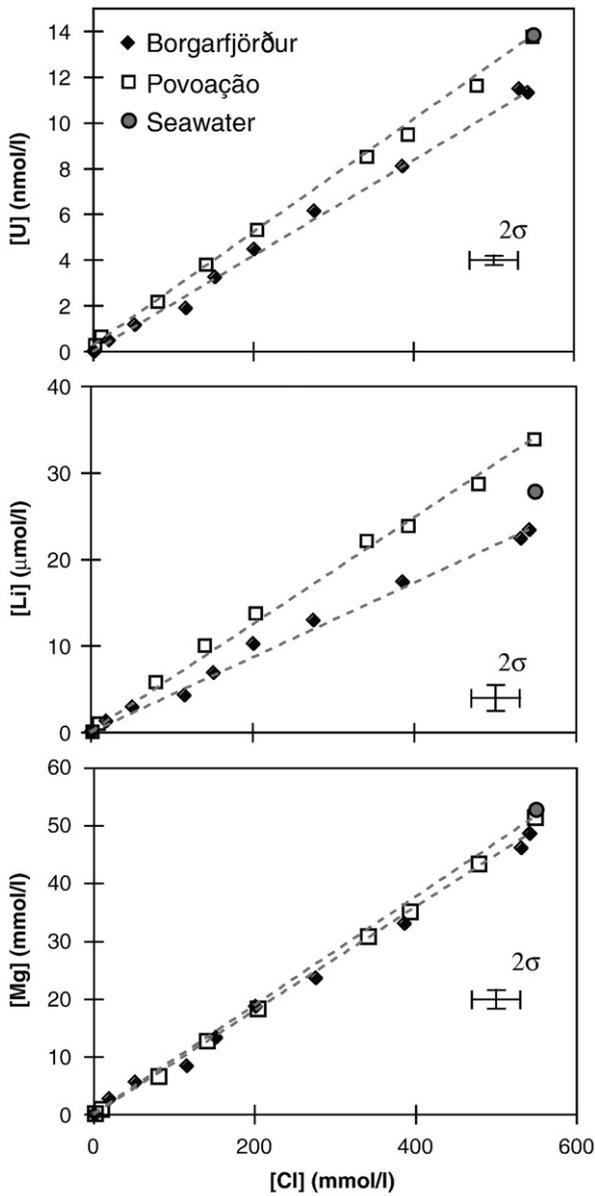
Fig. 3. Concentrations of dissolved U, Li and Mg vs. Cl. Dashed lines link the sample with lowest [Cl] to that with the highest [Cl], for each estuary. Data for seawater are also shown for comparison (Angino and Billings, 1966; Carpenter and Manella, 1973; Chen et al., 1986). Error bars show the external reproducibility (2σ).
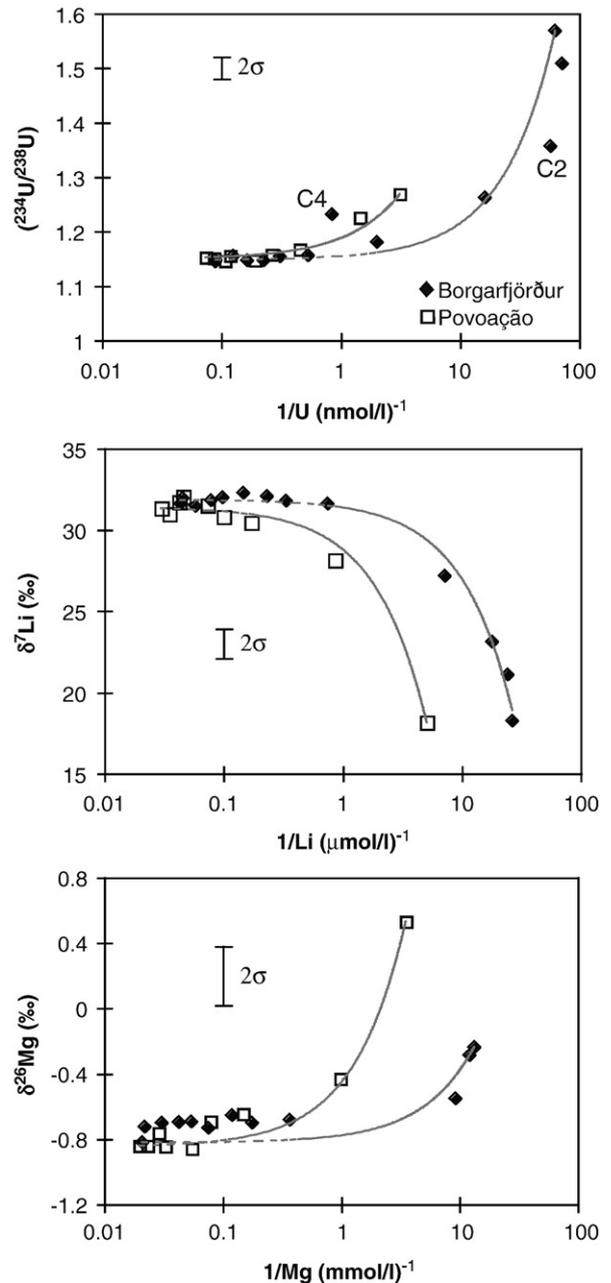
Awout (Dupre et al., 1999), 25 mg/l in the Mengong (Viers et al., 1997) and 10 mg/l in the Kalix (Andersson et al., 1995, 1998; Porcelli et al., 1997). Thus our data, considered together with those from previous studies, strongly suggest that the presence or absence of colloid phases exerts a strong control on the behaviour of dissolved uranium in estuaries. Where colloids are scarce, uranium acts conservatively, but where they are dominant (i.e. in the tropics, or where there are swamps or mires in catchment areas), uranium generally exhibits non-conservative behaviour.

With the exception of sample C4, all samples with Cl concentrations of >20 mM have a (^{234}U/^{238}U) activity ratio which is within error of seawater (1.144; Chen et al., 1986). The activity ratio of sample C4 is rather higher (1.23) because a small river with high (^{234}U/^{238}U) (1.67) enters the estuary close to this sample locality (Pogge von Strandmann et al., 2006). River water and seawater have distinct (^{234}U/^{238}U) activity ratios and U concentrations; Fig. 4 shows that the (^{234}U/^{238}U) activity

higher concentrations of dissolved organic carbon. For example, 30–90% of dissolved U is found in the 3 kD–0.2 µm (colloidal) fraction at the mouth of the Kalix estuary (Andersson et al., 1995, 1998, 2001; Porcelli et al., 1997), while >90% of U in the Amazon estuary is in the 10 kD–0.4 µm fraction (Swarzenski et al., 1995, 2004). Similarly, concentrations of dissolved organic carbon are as high as 40 mg/l in the

Table 3
Element/Cl ratios in hydrothermal springs from around the island of Sao Miguel

	Li/Cl ($\times 10^6$)	U/Cl ($\times 10^6$)	[Cl] (mmol/l)
This study			
Cald. R. Grande	45700	0.85	0.82
Cruz and Franca (2006)			
Cald. Velha	1690		0.43
Agua Prata	6840		0.40
Terra Nostra	390		8.39
Seawater	51.3	0.025	547

Fig. 4. Element-isotope mixing diagrams for U, Li and Mg. Grey lines represent conservative mixing between the sample with highest [U], [Li] or [Mg], and the sample with lowest [U], [Li] or [Mg]. Error bars show the show the external reproducibility (2σ).

ratio and U concentration of most samples, from both estuaries, reflects simple mixing of these two end-members. One sample from the Borgarfjörður estuary (C2) has either lower [U] or a lower $(^{234}U/^{238}U)$ activity ratio than predicted by simple mixing. This could be due to removal of U from the colloid phase, which is thought to have the same $(^{234}U/^{238}U)$ activity ratio as the dissolved phase (Porcelli et al., 1997; Riotte et al., 2003), but as the concentration of U in colloids in rivers entering the Borgarfjörður estuary is relatively low (~14%; Table 1), this process can only account for ~45% of the U lost. Desorption of U from suspended particulate material (which has a $(^{234}U/^{238}U)$ activity ratio of 1.04–1.17) could lower the $(^{234}U/^{238}U)$ activity ratio of the dissolved phase, but this would presumably increase the concentration of dissolved U, which is not observed. The most likely explanation is removal of dissolved U during precipitation of Fe-oxyhydroxides. This process does not alter the $(^{234}U/^{238}U)$ activity ratio, which would scavenge dissolved U from solution without altering the $(^{234}U/^{238}U)$ activity ratio (Andersson et al., 1998, 2001; Swarzenski et al., 2003), and has been observed to occur at low [Cl] in a number of estuaries (Maeda and Windom, 1982; Andersson et al., 1998).

The uranium concentration of the suspended load in the Borgarfjörður estuary is 0.15–0.67 ppm (Table 2), which is within the range of basalts from the Snæfellsnes lava field to the north of the catchment area (Smit, 2001). The $(^{234}U/^{238}U)$ activity ratios of the suspended particles in the estuary are, however, distinct from those of both basalt and the particles in the river water which enters the estuary (sample A4). The latter have activity ratios of 1.04; that is, they are essentially in secular equilibrium, whereas the suspended particles in the estuary have $(^{234}U/^{238}U)$ activity ratios which are indistinguishable from the value for seawater (1.144; Chen et al., 1986), even at very low [Cl]. This suggests either that all of the U in the suspended load is exchangeable with seawater U, or that the river-born particles, or their ferro-manganese coatings, rapidly adsorb U from seawater (in which case, on average, all of the uranium in ~500 ml of seawater is scavenged onto 1 g of suspended particles) (Andersson et al., 2001; Swarzenski et al., 2004).

4.3. Li and Li isotopes

Dissolved lithium exhibits conservative behaviour in both the Borgarfjörður and the Povoação estuary (Fig. 3), which is consistent with results from other studies (Angino and Billings, 1966; Stoffyn-Egli, 1982), including the well-mixed St. Lawrence, the partially-mixed Scheldt (Stoffyn-Egli, 1982) and the salt-wedge Mississippi Rivers (Colten and Hanor, 1984). Dissolved Li has also been shown to behave conservatively in the Gulf of Papua where, in contrast, particulate Li is trapped in aluminosilicate muds on the shelf (Brunskill et al., 2003). As for U, the high [Cl] end-member of Povoação has higher [Li] than the high [Cl] end-member of Borgarfjörður. Again, this is likely to be due to local input of Li from submarine hydrothermal vents, which surround the island. The Li/Cl ratio of these springs is 2–3 orders of magnitude greater than seawater (Table 3). Meanwhile, a plot of δ^7Li vs. 1/[Li] (Fig. 4) indicates a systematic increase in δ^7Li with increasing [Li] (i.e. with increasing [Cl]). The trend in this δ^7Li–Li mixing distribution appears to approximate linearity which would indicate conservative mixing. Thus, our data imply that the Li and Li isotope signature of river water is transferred to the ocean without modification in the estuarine mixing zone.

The Li concentration of suspended particulate matter in the Borgarfjörður estuary is within the range of Icelandic basalts (2.68–8.78 ppm; Maclennan et al., 2001; Stracke et al., 2003). However, more remarkable is the observation that as the Li content of the particles increases, the δ^7Li composition of the particles also increases (Fig. 5). The linear relationship between δ^7Li and 1/[Li] suggests that the suspended material is weathering in the estuarine environment, and thus the Li in suspended particles can be regarded as a two-component system, and the covariation reflects a mixture of basaltic Li and seawater Li which is incorporated in alteration minerals. Extrapolation to the most Li-rich rock of
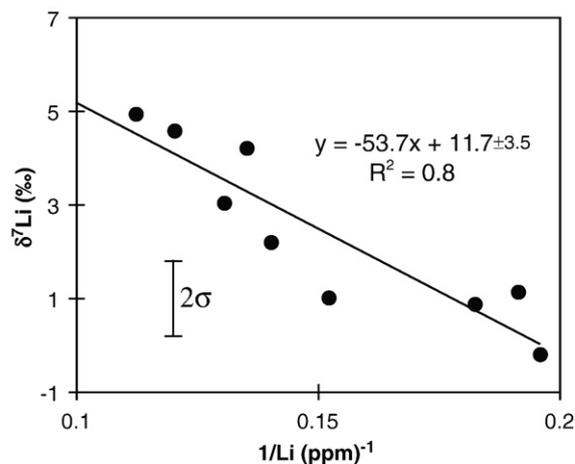

Fig. 5. Element-isotope mixing diagram for Li suspended particulate material from the Borgarfjörður estuary. The correlation is >99% significant ($p=0.01$). Error bars show the external reproducibility (2σ).

Fig. 5 gives an empirical δ^7Li value of about 11.7‰ for the end-member alteration products. This corresponds to an apparent isotopic fractionation factor, $\alpha_{mineral\text{-}fluid}$, of 0.981±0.003 for the clay mineral–seawater system at ambient water temperature, which is identical to the value (0.981) reported by Chan et al. (1992) for weathered seafloor basalts from the Mid-Atlantic Ridge and East Pacific Rise. Thus, Fig. 5 strongly suggests that detrital silicates continue to undergo weathering in the estuarine environment; the wider implications of this are discussed in Section 4.5.

4.4. Mg and Mg isotopes

The concentration of dissolved Mg in both estuaries varies directly as a function of [Cl] (Fig. 3) indicating conservative behaviour. The $\delta^{26}Mg$ value of the riverine end-member in Iceland (−0.23‰) is close to that of local basalt (−0.29‰; [Pogge von Strandmann et al., submitted]) and other terrestrial basalts (−0.41 to+0.09‰; Teng et al., 2007; Wiechert and Halliday, 2007). The river which enters the Povoação estuary has much higher $\delta^{26}Mg$ (+0.54‰), but this value is within the range reported for Icelandic rivers (−0.96 to+0.64‰; [Pogge von Strandmann et al., submitted]), and may have been affected by the formation of secondary minerals or biological processes which preferentially remove light Mg isotopes from solution (Black et al., 2006). For both estuaries, the $\delta^{26}Mg$ value of the dissolved phase can be explained in terms of simple mixing between a river end-member with relatively high $\delta^{26}Mg$ and low [Mg], and a high [Cl] end-member which has relatively low $\delta^{26}Mg$ (−0.82‰; Tipper et al., 2006b) and high [Mg] (Fig. 4). Like Li, these data thus indicate that the Mg elemental and isotopic signature of the dissolved load is transferred from the continents to the ocean without modification in the estuarine mixing zone.

The Mg concentration of the suspended particles is towards the lower end of the range reported for Icelandic basalt (2.68–5.99 wt.%; Gislason et al., 1996) and the $\delta^{26}Mg$ values (−0.41 to −0.1‰) are within the range reported for terrestrial basalts (−0.41 to +0.09‰; Teng et al., 2007; Wiechert and Halliday, 2007). However, unlike Li, there is no obvious correlation between the Mg concentration and the $\delta^{26}Mg$ value of the suspended particles, and thus no evidence for uptake of dissolved Mg from seawater.

4.5. The behaviour of riverine suspended material in the estuarine environment and the implications for oceanic isotope budgets

Iceland and the Azores are both basaltic volcanic islands representative of the high-relief, volcanic and tectonically active islands which

contribute >45% of suspended material to the oceans (Milliman and Syvitski, 1992). These islands dominate the suspended material flux to the oceans due to the combined effect of high-relief, high runoff, the presence of rapidly weathering volcanic rocks, and an absence of sedimentary traps. Experimental work on suspended riverine material from the 1996 outburst flood from the Vatnajokull glacier in Iceland also clearly shows that such material dissolves in seawater (Gislason et al., 2002; Stefansdottir and Gislason, 2005), and the Li isotope and elemental data for suspended particles presented here provide the first field-based evidence for continued weathering of basaltic particles in the estuarine environment and into the marine realm.

The question then is to what extent the continued weathering and dissolution of volcanic material affects the overall U, Li and Mg isotope signal to the oceans. Calculations based on experimentally determined basaltic glass dissolution rates at the pH and temperature range of Icelandic ocean waters (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003), together with measurements of the surface area of river suspended material from Iceland (Stefansdottir and Gislason, 2005) indicate that ~0.05% of this material dissolves in seawater each day (Gislason et al., 2006). Crucially, even severely weathered basaltic material continues to dissolve when exposed to seawater (Stefansdottir and Gislason, 2005). Nevertheless, our data indicate that dissolution of suspended basalt particles is not an important source of Li, Mg or U to the oceans, constituting <2% of the input from the riverine dissolved load (Table 4). As a consequence, simple dissolution of basalt particles has little impact on the overall isotopic signature of the riverine input; mass balance calculations indicate that even for Li, for which the difference between the isotopic composition of the dissolved load (δ^7Li=21.1‰; Table 1) and the particulate load (δ^7Li=0.9‰; Table 2) is greatest, the change to dissolved input is only ~0.1‰, which is within analytical uncertainty.

However, weathering of basaltic material involves not only dissolution of primary minerals, but also the formation of secondary mineral phases. The effect of secondary mineral formation on Mg and Mg isotopes is not yet clear (this study; Galy et al., 2002; Young et al., 2002; Tipper et al., 2006a), but there is strong evidence from this study (Fig. 5) and others (Chan et al., 1992; Huh et al., 2004) that Li is enriched in secondary minerals, and that ^{6}Li is incorporated in preference to ^{7}Li. In the case of Borgarfjörður, the Li concentration of the particles increases by ~3 ppm during the estuarine mixing process (Table 2, Fig. 5). Given that the flux of particulate material entering Borgarfjörður is 1×10^{10} g/day (Table 4), and assuming that the residence time of a particle in the estuary is 1 day, this means that 3×10^4 g/day of Li is taken up into secondary minerals. This is more than 6 times the amount of Li which enters the estuary in the dissolved phase over the same period (Table 4).
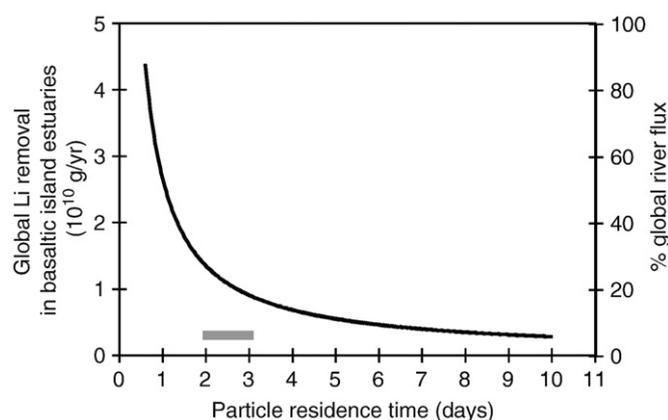
The wider implication of this result is that weathering of basaltic islands is a net sink, rather than a source, of Li to the oceans. On a global basis, given that the riverine sediment flux from basaltic islands is 9×10^{15} g/yr (Milliman and Syvitski, 1992), our data for Borgarfjörður imply that 2.7×10^{10} g/yr of lithium is removed from the oceans in estuaries which drain basaltic islands, a value which is close to half of the global riverine input (5.6×10^{10} g/yr; Huh et al., 1998). Clearly, this

Fig. 6. Rate of removal of dissolved lithium in basaltic island estuaries as a function of the residence time of particles in the estuary. Removal rate is also shown as a percentage of the global riverine input (Huh et al., 1998). Grey bar shows the most likely residence time of particles in Borgarfjörður (see text for details).

would have a profound impact on the oceanic mass balance of lithium, but is it correct?

Our estimate of the rate of Li uptake into secondary minerals is strongly dependent on the residence time of the particles in the estuary (Fig. 6) — the longer the particle resides in the estuary, the lower the Li uptake per unit of time. As far as we are aware, there are no data for particle residence time in the Borgarfjörður estuary; our own measurements of the particulate Li concentration of water samples collected at different times at the same locality indicate that the particle residence time is longer than one tidal cycle (i.e. >12 h), but we cannot constrain the upper limit (Pogge von Strandmann, 2006). Model simulations of particle transport in the Portsmouth Harbour region of the Great Bay estuarine system, which, like Borgarfjörður, is shallow, well-mixed and tide-dominated, suggest that <20% of particles entering at any time remain in the estuary after 10 tidal cycles (~5 days) (Bilgili et al., 2005). However, this is likely to be an upper estimate in the case of Borgarfjörður, because Portsmouth Harbour possesses a complex channel geometry with side bays and creeks, connected to the main channel by narrow channels between several small islands. By contrast, Borgarfjörður (and basaltic islands in general) is characterised by simple channel geometry and a lack of sediment traps (cf. Fig. 1).

Thus, assuming that the best estimate for the residence time of a particle in an estuary draining a basaltic island is 2–3 days, we can conclude that continued weathering of riverine particles in estuaries draining basaltic islands is an overall sink, rather than a source, of Li in the oceans. As a result, the global riverine flux of Li to the oceans may be some 15–25% lower than previously thought (Fig. 6). In turn, the δ^7Li value of the input flux (hydrothermal flux+riverine flux) shifts from 16‰ to between 14.0 and 14.7‰. (For a hydrothermal flux of 4.1×10^{10} g Li /yr (Hathorne and James, 2006), which has δ^7Li=+6.7‰ (Bray, 2001); the river flux has a δ^7Li value of +23‰; Huh et al., 1998). This shift is small, but it is of the order of the apparent change in the δ^7Li composition of seawater recorded by the shells of planktonic foraminifera over the past 10 Myr (Hathorne and James, 2006).

These results may also have implications for global climate. Recent work indicates that climate change is likely to have a significant effect on both the nature and flux of suspended material to the oceans. Firstly, the delivery of suspended material by rivers appears to be far more climate dependent (i.e. sensitive to changes in river discharge/runoff) than the riverine dissolved load (Gislason et al., 2006). Second, there is an inverse relationship between the degree of weathering of the riverine suspended load and the suspended sediment concentration (Gaillardet et al., 1999a). Thus, during climate intervals characterised by warm temperatures and high precipitation/runoff, delivery of suspended material to the oceans will increase and the material itself will

Table 4
Concentration of Li, Mg and U in the particulate and dissolved phase of the river which enters the Borgarfjörður estuary

	Li	Mg	U
Concentration in suspended particles	5.49 µg/g	33 mg/g	0.196 µg/g
Concentration in dissolved phase	0.29 µg/l	1.85 mg/l	3.83 ng/l
Input flux (dissolution of particles)	27 g/day	1.65×10^5 g/day	1 g/day
Input flux (dissolved phase)	4730 g/day	3×10^7 g/day	62 g/day

Input fluxes are calculated based on an average daily discharge of 1.63×10^{10} l/day (Iceland National Energy Authority) and suspended particulate material concentration of 610 mg/l (Pogge von Strandmann et al., 2006).

be less weathered. As a result, weathering of riverine particulate material in the estuarine environment is likely to be enhanced, drawing down atmospheric CO_2 and thus providing a strong negative feedback for the stabilisation of Earth's temperature through the greenhouse effect.

5. Conclusions

The Li and Mg elemental and isotope data for the dissolved phase of water samples from estuaries in Iceland and the Azores reveal that the isotope signature of riverine input is transferred to seawater without fractionation in the estuarine mixing zone. Dissolved U shows contrasting behaviour, behaving conservatively in the Povoação estuary (Azores), whereas removal of U seems to occur at low [Cl] in the Borgarfjörður estuary (Iceland), likely because of scavenging by Fe-oxyhydroxides in the low salinity zone and/or colloid flocculation.

The major element composition of suspended material in the Borgarfjörður estuary (Iceland) suggests that this material is not significantly weathered relative to the basalts from the source river catchment (cf. Gislason et al., 2006), although there is a systematic decrease in MgO and CaO relative to Na_2O. The $\delta^{26}Mg$ isotope composition of the suspended material is indistinguishable from that of the parent basalts. However, the $(^{234}U/^{238}U)$ activity ratio of the suspended particles is higher than that of the parent basalts (1.04), but indistinguishable from the $(^{234}U/^{238}U)$ value of seawater ($\sim$1.14). These data suggest either that uranium is rapidly exchanged between suspended particles and seawater, or that U in seawater is rapidly adsorbed onto particle coatings. The Li concentration and δ^7Li isotope value of the suspended particles are both observed to increase with increasing [Cl], which suggests that weathering of detrital silicates continues in seawater.

The continued dissolution of suspended particulates in these estuaries is not a significant source of dissolved U, Mg or Li to the oceans. However, during the weathering process, significant quantities of Li are taken up into secondary minerals such that weathering on basaltic islands may constitute an overall sink, rather than a source, of Li to the oceans. Depending on the particle residence time in the estuary, this sink may be as large as 15–25% of the global riverine input.

Acknowledgements

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