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The stable calcium isotopic composition of rivers draining basaltic catchments in Iceland

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ABSTRACT

Calcium isotopic compositions ($\delta^{44/42}$Ca) were measured in Icelandic rivers draining a range of catchment types. The $\delta^{44/42}$Ca values of the rivers ranged from 0.45‰ to 0.67‰, which in all cases was higher than the $\delta^{44/42}$Ca value of basaltic rock standards (0.42 ± 0.03‰). A single explanation was unable to satisfactorily explain the $\delta^{44/42}$Ca values of all rivers, rather it was found that the rivers formed three distinct groups based on the extent of glacial coverage in each catchment. The Ca isotopic composition of rivers draining catchments with less than 10% glacial cover could be explained by the mixing of water sources: basalt-derived solutes, meltwater (taken to represent meteorological precipitation inputs) and hydrothermal water. However, fractionation of $\delta^{44/42}$Ca in these catchments cannot unequivocally be ruled out. In catchments with greater than 22% glacial cover, Ca isotopic compositions could not be explained by a mixture of water sources and instead reflected a fractionation process, most likely the precipitation of Ca-bearing secondary minerals or the adsorption/ion-exchange of Ca onto mineral surfaces. The fractionation factor (α) for this process was calculated to be 0.9999. The third group of rivers, with partially glaciated (10–21%) catchments, grouped with glaciated catchments with respect to their Sr geochemistry and with non-glaciated catchments with respect to their Ca geochemistry. The difference in the controls of Ca isotope fractionation between glaciated and unglaciated catchments was attributed to different weathering regimes.

1. Introduction

Silicate weathering rates are affected by changes in environmental conditions, such as temperature, runoff and erosion (e.g. White and Blum, 1995; Riebe et al., 2004; West et al., 2005). Since the magnitude of silicate weathering is thought to provide an important negative feedback in the long-term carbon cycle (Walker et al., 1981; Berner et al., 1983), through the reaction of calcium (Ca) and magnesium (Mg) silicates with carbonic acid derived from atmospheric carbon dioxide, it is important to be able to predict exactly how silicate weathering fluxes will be affected by changes in climate.

Basaltic rocks are particularly susceptible to weathering and are thought to constitute 30–35% of atmospheric drawdown by silicate rocks (Dessert et al., 2003), despite a global outcrop area of only 5% (Amiotte Suchet et al., 2003). The weathering flux from oceanic basaltic islands is thought to be particularly important due to the tendency for the islands to be geologically young and have higher meteorological precipitation and runoff, thereby enhancing weathering rates (Gíslason et al., 1996; Louvat and Allègre, 1997, 1998). A 40 year study of basalt weathering in a single locality (Iceland) has already hinted that increasing temperatures lead to increased rates of chemical weathering (Gíslason et al., 2009). This study calculated annual weathering fluxes from regular samples of river water, a common method for obtaining catchment-scale integrated weathering rates. Another approach to study the response of weathering rates and processes to changes in climate is through shorter term studies which compare river water samples taken from different catchments with the same underlying lithology, but which differ in their local environmental conditions (e.g. White and Blum, 1995;

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Gíslason et al., 1996; Oliva et al., 2003). Such an approach has been applied extensively in Iceland where the island is essentially mono-lithological and there are variations in meteorological precipitation, glacial cover and vegetation across the island (e.g. Gíslason et al., 1996).

Previous studies which focussed on the major ion chemistry of Icelandic rivers have shown that the formation of secondary minerals is ubiquitous in these catchments, weathering is incon-gruent, pH (modified by glacial cover and vegetation) is an important control on element release and glaciers affect chemical weathering rates (Gíslason and Eugster, 1987b; Gíslason et al., 1996; Arnórsson et al., 2002).

More recently, two spot sampling campaigns have focussed on isotopic studies of Icelandic river water. The use of isotope tracers has enabled additional information on and/or provided confirma-tion of how basaltic weathering processes are affected by local environmental conditions. For example, using silicon isotopes Georg et al. (2007) found that, due to differences in the amount of meteorological precipitation, the east and the west sides of the island had different weathering regimes. Measurements of ura-nium series nuclides have suggested that weathering processes are close to steady-state and the highest weathering rates are found in those catchments with the shortest weathering timescale (Vigier et al., 2006). The extent of secondary mineral formation, as controlled by several environmental factors such as pH, strongly influences weathering rates: the highest chemical weathering rates are reported from those catchments where the extent of secondary mineral formation, as measured by lithium isotopes, is low (Vigier et al., 2009).

This study investigates the Ca isotopic compositions of the aforementioned two sets of Icelandic river samples, which have previously been analysed for other isotopic systems. In basaltic rocks, calcium is typically present at around 10 wt% and is the most abundant constituent after silicon and aluminium (Arnórsson et al., 2002). The major minerals hosting Ca are plagioclase and pyroxene. As a major constituent of basalt (and all silicate rocks), understanding the release and subsequent biogeochemical cycle of Ca is crucial in order to predict how the cycle may be altered by changing environmental conditions. Nevertheless, there have been relatively few studies on Ca isotope systematics in the terrestrial environment (Bullen et al., 2004; Wiegand et al., 2005; Tipper et al., 2006, 2008; Ewing et al., 2008; Cenki-Tok et al., 2009; Holmden and Bélanger, 2010; Farkaš et al., 2011; Hindshaw et al., 2011; Moore et al., 2013). Only one of these studies (Wiegand et al., 2005) was conducted in a basaltic environment (Hawaii) and highlighted changes in the source of Ca to plants, from primary minerals to atmospheric deposition, as the age of basalt increased from 0.3 to 4100 ka. Fractionation of Ca isotopes occurs during uptake into plants, with vegetation enriched in light Ca and, depending on the extent of vegetation, the upper soil layers are depleted in light Ca (Holmden and Bélanger, 2010; Farkaš et al., 2011; Hindshaw et al., 2013). Previous studies in granitic catchments have suggested that negligible fractionation occurs during the initial stages of weathering (Hindshaw et al., 2011) but that in older sites Ca isotopic differ-ences between soil pools (Bullen et al., 2004) and seasonal changes in the Ca isotopic composition of runoff (Cenki-Tok et al., 2009) may be observed. Although variations in riverine Ca isotopic compositions are small (Tipper et al., 2010), there is evidence that the precipitation of secondary minerals (Tipper et al., 2006) and adsorption onto clays (Ockert et al., 2013) may cause river waters to become fractionated compared to bedrock.

Variations in stable isotope ratios may arise as a result of a fractionation process or the mixing of isotopically different sources. In order to aid in the interpretation of stable Ca isotope ratios, strontium (Sr) radiogenic isotope ratios, which only trace

sources, were also obtained. The radiogenic strontium isotope ratio is commonly used to trace Ca sources due to the similar geochemical behaviour of Ca and Sr (e.g. Capo et al., 1998).

The aim of this study was to investigate whether the previously reported precipitation of secondary minerals and variations in weathering processes in Iceland, inferred from other isotopic and element data, would affect the calcium isotopic composition of river water, and thus help develop the use of Ca isotopes as a viable tracer of catchment scale biogeochemical processes.

2. Sampling locations

Iceland is situated in the north Atlantic ocean on the Mid-Atlantic ridge and over the Iceland hotspot, it is therefore a geologically active island with several active volcanoes and hydro-thermal springs. The climate on Iceland is maritime (cool summers and mild winters) with a mean annual temperature of 2–5 °C. Meteorological precipitation is highly variable with the highest values in the southeast (4000 mm) and the lowest values in the north (400 mm), in the rain shadow of Vatnajökull (Einarsson, 1984). Icelandic rivers have significant seasonal varia-tion in discharge: peak discharge occurs in spring as a result of snow-melt and later in the summer if there is a significant contribution from glacier ice melt. Glaciers cover 11.5% of the area of Iceland with the Vatnajökull icecap alone accounting for 70% of the glacial cover. Vegetation cover is sparse with only 23% of the island vegetated. Iceland is composed of volcanic rocks, predomi-nantly of basaltic composition (80%), but also includes intermedi-ate and silicic compositions and clastic sediments of volcanic origin. As a result of crustal accretion, there is a symmetrical pattern of rocks ages about the axis of the main rift. The oldest rocks (~13 Ma) are found in the north-west and east of the island and the youngest are found near the active volcanic zones. Volcanic eruptions which occur under ice cover tend to prod-uce predominantly basaltic glass (hyaloclastite) (Jakobsson and Gudmundsson, 2008), whereas predominantly crystalline basalt is the main product from volcanoes free of ice. Soils in Iceland are developed from volcanic material and tend to be young and immature. The majority of soils in the non-glaciated catchments are classified as Brown Andosols, which contain significant amounts of the secondary phases allophane (15–30 wt%) and ferrihydrite (1–8 wt%), whereas in the glaciated catchments the most common soil type is Vitrisols, which are dominated by volcanic glass (Arnalds, 2004).

The sources of Icelandic rivers have been grouped into four categories: direct runoff, spring-fed, glacial-fed and lake-derived, with rivers often having more than one source type. Direct runoff rivers are more common in the geologically older areas (NW and E) of Iceland due to a reduction of permeability caused by soil compac-tion and secondary mineral formation (Gíslason et al., 1996).

River water samples were analysed from two previous sam-pling campaigns in Iceland. The first (samples IS-x), sampled rivers around the island in late June/early July 2001 (Fig. 1). The rivers sampled cover a variety of ages, from 0.01 Ma (IS-14 Laxá) to 11.2 Ma (IS-19 Heiðarvatn) and represent a range of glacial cover-age and runoff. Areas with known inputs of hydrothermal water were avoided. These samples have previously been analysed for Os isotopes (Gannoun et al., 2006), U-series (Vigier et al., 2006), Si isotopes (Georg et al., 2007) and Li isotopes (Vigier et al., 2009). The second sampling campaign (samples Ax and Ex), sampled two localities in September 2003 and August 2005. The 'A' set consisted of rivers draining the west of the island which are minimally glaciated, are of Tertiary age (~3.1 Ma) and are situated in one of the most vegetated parts (primarily mosses and grasses) of Iceland. The 'E' set consisted of rivers draining the Vatnajökull
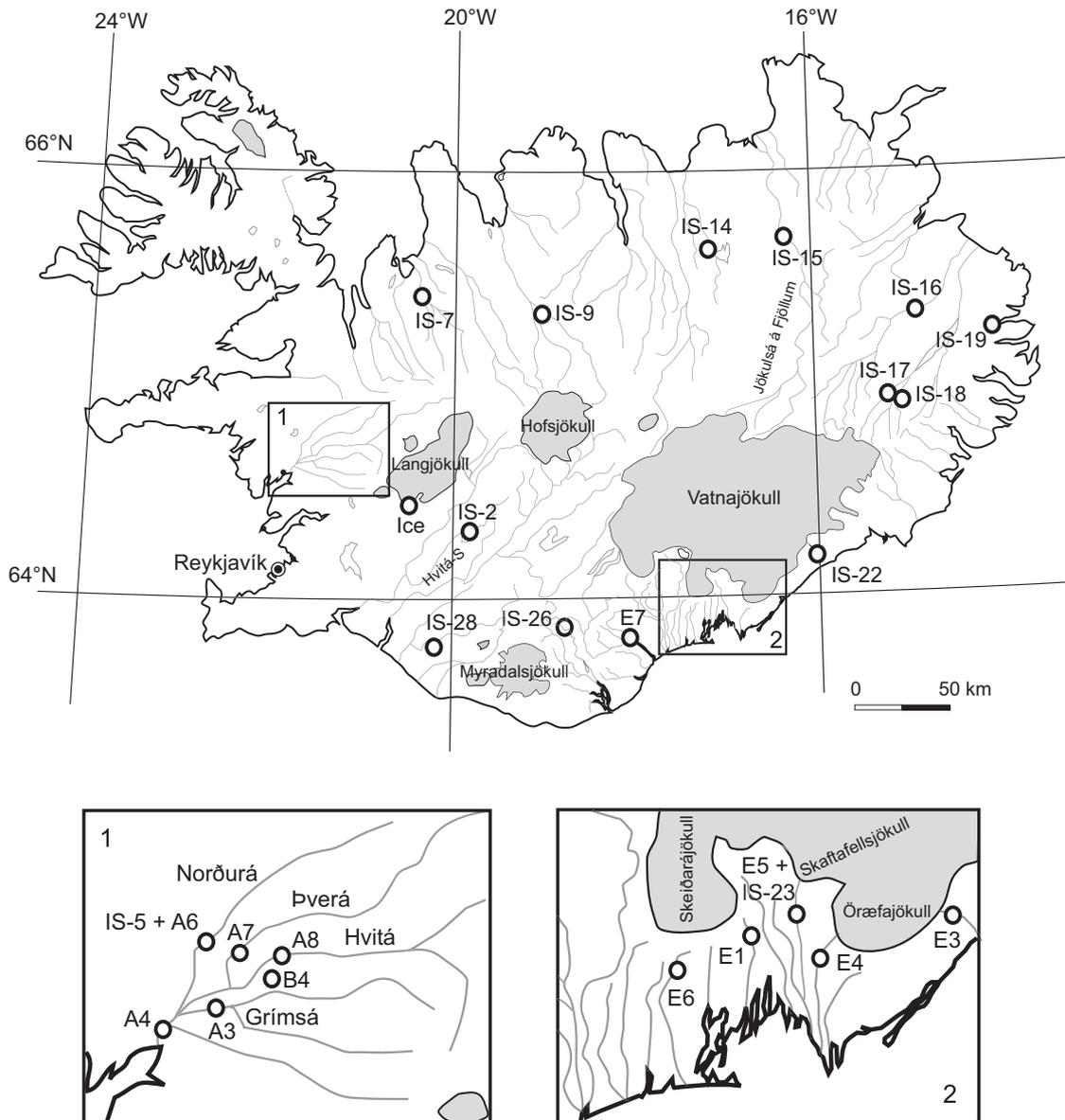
Fig. 1. Map of Iceland showing the river, hydrothermal (B4) and icemelt sampling locations.

icecap to the south. This area is minimally vegetated, young (~1.8 Ma) and is dominated by the Skeiðarársandur outwash plain. This plain experiences transiently extremely high sediment loads (e.g. 1% of the total annual global river suspended sediment flux (180 million tonnes) in less than 42 h, Stefánsdóttir and Gíslason, 2005) as a result of jökulhlaups (sub-glacial flood outbursts as a result of volcanic activity). The most recent event occurred in 1996 (Gjálp jökulhlaup). Sample E3, taken from Fjallsárlón, drains a large end-glacial lake rather than representing a river directly draining a glacier. This lake was approximately 1.5 km^2 at the time of sampling (Schomacker, 2010). This sample was found to be an outlier in terms of its chemical and isotopic behaviour, probably owing to the presence of the lake. These samples have previously been analysed for U-series and Li isotopes (Pogge von Strandmann et al., 2006, 2011), Mg isotopes (Pogge von Strandmann et al., 2008), Mo isotopes (Pearce et al., 2010) and Si isotopes (Opfergelt et al., 2013). Each sampling campaign also sampled ice from the Langjökull ice cap in western Iceland. The melted ice samples are intended to represent meteorological precipitation inputs to the rivers. A hydrothermal spring sample from Deildartunguvegur (B4) was also analysed. Further descriptions of all the sampling locations can be found in the aforementioned papers. In this paper the samples are divided into those from rivers draining catchments with greater than 22% glacial cover (glacial) and those draining catchments with less than 10% glacial cover (non-glacial), consistent with the previous division of 'A' and 'E' samples into non-glacial and glacial respectively (Table 1, Pogge von Strandmann et al., 2008). In addition, we have added a 'partially glaciated' category which includes three rivers with catchments which are between 10% and 21% glaciated.

3. Analytical procedure

Wherever possible, water samples were collected from the middle of the river using a bucket lowered from a bridge. Water samples were immediately filtered through 0.2 μm cellulose acetate filters using a pressurised teflon filtering unit and collected in pre-cleaned (acid-washed) polypropylene (PP) bottles and acidified to pH 2 with ultra-pure nitric acid. Cation concentrations in the dissolved load were measured by inductively coupled plasma-mass spectrometry (ICP-MS). The precision (2σ) of the major cation

Table 1
Element concentrations[a] and Ca and Sr isotope ratios in Icelandic river water samples.

Sample	Location	Glaciated area (%)	Age[b] (Ma)	Ca (μmol/L)	Na (μmol/L)	Sr (nmol/L)	$\delta^{44/42}$Ca (‰)	2SD	N	^{87}Sr/^{86}Sr
Non-glacial rivers										
A3	Grímsá	0	2.9	112	361	60.8	0.55	0.01	2	0.70650
A4	Hvítá at Ferjukot	< 9	3.7	98.1	309	72.5	0.59	0.04	2	0.70659
A6	Norðurá (Stekkur)	0	5.9	109	283	115	0.51	0.02	2	0.70604
A7	þverá	0	6.6	129	362	178	0.52	0.00	2	0.70521
A8	Hvítá at Kljáfoss	9	1.0	74.3	270	57.4	0.50	0.03	2	0.70617
IS-5	Norðurá	0	5.9	90.2	434	106	0.55	0.07	2	0.70495
IS-7	Vatnsdalsá	0	1.9	131	530	152	0.45	0.00	2	0.70383
IS-14	Laxá	0	0.01	167	965	124	0.48	0.03	2	0.70441
IS-18	Kelduá	6	4.9	46.7	115	45.5	0.53	0.07	2	0.70435
IS-19	Heiðarvatn	0	11.2	50.0	125	41.2	0.57	0.06	2	0.70434
IS-26	Syðri-Ófæra	3	0.3	92.4	404	73.3	0.57	0.02	2	n.m.
IS-28	Rauðilækur	0	3.2	506	1055	977	0.50	0.07	1	0.70449
Partially glacial rivers										
IS-2	Hvítá-S	21	0.7	104	370	73.4	0.50	0.04	2	0.70376
IS-9	Austari-Jökulsá	16	2.9	62.7	223	30.7	0.55	0.11	2	0.70381
IS-15	Jökulsá á Fjöllum	21	0.3	106	479	53.3	0.47	0.03	2	0.70339
Glacial rivers										
E1	Skeiðará	> 50	1.8	106	205	40.3	0.65	0.01	2	0.70397
E3	Fjallsárlón	> 50	1.8	160	65.8	130	0.53	0.03	2	0.70340
E4	Virkisá	> 50	1.8	27.9	117	30.5	0.63	0.05	2	0.70401
E5	Skaftafellsá	> 90	1.7	92.1	132	27.2	0.67	0.06	2	0.70363
E6	Sandgígjukvísl	> 50	1.8	60.9	136	12.5	0.61	0.08	2	0.70407
E7	Skaftá	> 25	1.8	347	341	194	0.62	0.01	2	0.70363
IS-16	Jökulsá á Dal	43	1.7	96.8	142	20.4	0.60	0.03	2	0.70360
IS-17	Jökulsá í Fljótsdal	26	2.1	162	151	62.1	0.54	0.06	2	0.70348
IS-22	Steinavötn	27	0.6	339	263	87.8	0.50	0.06	2	0.70371
IS-23	Skaftafellsá	> 90	1.7	258	319	63.9	0.56	0.01	2	0.70410
Other samples										
O2-L2	Langjökull ice			0.85	43.1	7.6	0.75	0.08	3	n.m.
OU ice	Langjökull ice			0.70	61.1	11.4	n.m.	–	–	0.70919
B4	Hydrothermal			584	23,600	162	0.53	0.03	2	0.70327
	Seawater			9981	469,769	91,303	0.95	0.03	30	0.70925
	Basalt[c]			2,081,000	729,000	2250	0.42[d]	0.03	41	0.70340[e]

n.m., not measured.

[a] Concentration data from Pogge von Strandmann et al. (2006) and Gannoun et al. (2006).
[b] Mean age of basalt rocks in the catchment.
[c] Concentration data are median values in mmol/kg of 83 basalt samples from Arnórsson et al. (2002), Fridriksson et al. (2009) and Koornneef et al. (2012).
[d] Average of basalt standards BHVO-2, BCR-1 and BCR-2.
[e] Average five bed load samples from A and E rivers.

analysis is estimated to be better than 3.2% based on the repeat analysis of the reference standard SLRS-4. For the analysis of Ca isotopes, a volume of water (< 3 mL) containing 3 μg Ca was dried down in teflon beakers together with 22 μL of a 7 ppm ^{43}Ca–^{46}Ca double-spike. The solid residue was re-dissolved in concentrated nitric acid, dried down again and re-dissolved in 3 M nitric acid in preparation for column chemistry. The purification chemistry and analytical procedures used were identical to those previously described by Hindshaw et al. (2011). Briefly, a four-stage ion exchange column chemistry procedure was used in order to remove interfering elements prior to analysis by thermal ionisa-tion mass spectrometry (Triton, Thermo Fischer Scientific) using the ^{43}Ca–^{46}Ca double-spike to correct for instrumental mass bias. Calcium isotope ratios are reported in delta notation relative to the standard NIST SRM 915a

$$\delta^{44/42}\text{Ca}(‰) = 1000 \left\{ \frac{\left(\frac{^{44}\text{Ca}}{^{42}\text{Ca}}\right)_{sample}}{\left(\frac{^{44}\text{Ca}}{^{42}\text{Ca}}\right)_{SRM915a}} - 1 \right\} \quad (1)$$

The external $2\sigma_{SD}$ reproducibility ($n = 79$) of NIST SRM 915b was 0.07‰ and, as this was greater than internal errors (< 0.02‰), this was used as the error for all samples. The measured value for

seawater was $0.95 \pm 0.03‰$ ($n = 30$). An additional secondary correction was applied to account for the drift of the standards with time (Hindshaw et al., 2011).

Radiogenic strontium ratios were measured by two different procedures. For the 'IS' set of samples, a volume of water contain-ing 1 μg Sr was dried down and prepared for column chemistry in an identical way to that described above for Ca. A single column of Sr-spec resin was used to separate Sr from the matrix using a procedure described in Hindshaw (2011). Measurements were performed by thermal ionisation mass spectrometry (TIMS) (Finnigan MAT 252 at the University of Bergen). Aliquots, corre-sponding to 250 ng Sr, were loaded onto degassed double rhenium filaments in nitric form together with 1 μL of tantalum phosphate activator. Data acquisition comprised 70–100 measurements with an 8 s integration time in multi-dynamic mode. The exponential law was applied to correct for instrument mass fractionation and all ^{87}Sr/^{86}Sr ratios were normalised to ^{86}Sr/^{88}Sr = 0.1194. ^{85}Rb was monitored to correct for rubidium interferences on ^{87}Sr. Each turret of samples was bracketed by NBS 987 and a secondary correction to give NBS 987 ^{87}Sr/^{86}Sr ratios of 0.710250 was used. Two measurements of local seawater yielded a ^{87}Sr/^{86}Sr value of 0.709202 ± 73 (2SD). For the 'A' and 'E' samples, chemical separa-tion of Sr followed established methods (e.g. Deniel and Pin, 2001). Between 225 and 450 ng of Sr was used for analysis and loaded on

single Re filaments using approximately 0.7 L of TaF_5 activator (cf. Charlier et al., 2006). Measurements were made using a Thermo Scientific Triton (at the Open University, UK). Data was typically acquired using a signal of 8–10 V of ^{88}Sr for 5–6 h, giving 540 ratios each measured or 16.984 s. The standard NBS 987 gave a value of 0.710256 ± 0.000004 (2σ; $n=23$) and seawater gave a value of 0.709179 ± 0.000002 ($n=17$).

4. Results

The calcium and strontium isotope ratios and concentrations are reported in Table 1.

4.1. River water chemistry

The general characteristics of the river water samples are described in Vigier et al. (2006) for the 'IS' set of samples and in Pogge von Strandmann et al. (2006) for the 'A/E' set of samples. In the majority of rivers, Ca is the second most dominant cation after Na, with Ca/Na molar ratios as low as 0.17 (Laxá, IS-14). However, in four of the rivers with glaciated catchments, Ca is the dominant cation, with Ca/Na molar ratios up to 2.43 (Fjallsárlón, E3). Riverine Ca concentrations varied from 27.9 µmol/L in Virkisá (E4) to 506 µmol/L in Rauðilækur (IS-28) and Sr concentrations varied from 12.5 nmol/L in Sandgígjukvísl (E6) to 977 nmol/L in Rauðilækur (IS-28). The Ca and Sr concentrations of a hydrothermal source in the west of the island (B4) were 584 µmol/L and 162 nmol/L respectively. The hydrothermal concentrations were approximately quadruple that of the average riverine concentration (141 µmol/L) for Ca and similar for Sr (113 nmol/L). The meltwater sample taken from Langjökull was very dilute with only 0.85 µmol/L Ca and 11.4 nmol/L Sr.

4.2. Ca isotopes

The Ca isotopic compositions ($\delta^{44/42}Ca$) of Icelandic river water span a range of 0.22‰, with the lowest value (0.45‰) observed in the unglaciated Vatnsdalsá river (IS-7) in the north of the island and the highest value (0.67‰) in the Skaftafellsá river (E5) draining the Vatnajökull icecap. Icelandic rivers are at the high end of the range of $\delta^{44/42}Ca$ values measured in global rivers so far (Tipper et al., 2010) and all values measured are elevated with respect to basaltic rock. A hydrothermal spring sampled at Deildartunguvegur yielded a Ca isotopic composition of 0.53‰ and a melted ice sample from Langjökull had a $\delta^{44/42}Ca$ value of 0.75‰. No Icelandic basalts were measured in this study but it is assumed that the Ca isotopic composition will be close to that of the basalt standards BCR-1, BCR-2, and BHVO-2 which have an average value of 0.42 ± 0.03‰ ($n=41$) (Amini et al., 2009; Wombacher et al., 2009; Simon and DePaolo, 2010; Hindshaw et al., 2011). Due to the proximity of many of the rivers to the sea, seawater inputs could be important. The isotopic composition of seawater used in further discussion is taken to be 0.95 ± 0.03‰ based on 30 measurements of the seawater standard NASS-5 (Hindshaw et al., 2011).

4.3. Sr isotopes

The Sr isotopic compositions ($^{87}Sr/^{86}Sr$) of Icelandic river water span a range of 0.00320, with the lowest value (0.70339) observed in the Jökulsá á Fjöllum river (IS-15) in the north of the island which drains the Vatnajökull icecap and the highest value (0.70659) in the Hvítá river at Ferjukot (A4). The hydrothermal spring had a Sr isotopic composition of 0.70327 and a melted ice sample from Langjökull had a $^{87}Sr/^{86}Sr$ value of 0.70919, which is nearly identical to the Sr isotopic composition of seawater (0.70925). Note that this was a different ice sample from that used to obtain the $\delta^{44/42}Ca$ value of ice-melt. The average of five bed load samples (0.70340 ± 0.00021, 1SD) from different rivers is taken to be representative of the Sr isotopic composition of bedrock.

5. Discussion

5.1. Mixing of different water sources

All of the analysed Icelandic river water samples have Ca and Sr isotopic compositions which are intermediate between basaltic rock, meltwater and seawater, and thus could be explained by mixing between these end-members (Table 1).

The meteorological precipitation in Iceland is strongly influenced by sea salt inputs (Gíslason and Eugster, 1987b; Gíslason et al., 1996), indeed the Ca/Cl and Sr/Cl molar ratios of meltwater from Langjökull (O2-L2) are identical to that of seawater (Ca/Cl=0.018 and Sr/Cl=0.0002). The contribution of meteorological precipitation to the Ca concentration in rivers can be determined using a chloride correction.

$$Ca^* = Ca_r - ((Ca/Cl)_{sw}Cl + 9.71) \tag{2}$$

where Ca^* is the meteorological precipitation corrected Ca concentration, Ca_r is the Ca concentration of the river in µmol/L and $(Ca/Cl)_{sw}$ is the Ca/Cl ratio of seawater. Calcium concentrations in meteorological precipitation are higher than would be expected from just a seawater source, unlike all other major cations (Gíslason et al., 1996). Gíslason et al. (1996) have determined that this additional source can be represented by a constant enrichment of 9.71 µmol/L Ca. The source of the non-marine Ca in meteorological precipitation is unknown, but potential sources include basalt dust, anthropogenic and hydrothermal inputs (Gíslason and Eugster, 1987b). The results of the above calculation indicate that, on average, meteorological precipitation contributes 13% (range=4–46%) to the dissolved load of Ca, identical to the contribution determined for a set of SW Icelandic rivers (Gíslason et al., 1996). As the non-marine source of Ca in meteorological precipitation is unknown, it is not possible to determine meteorological precipitation corrected Ca isotope ratios.

With the assumption that Ca and Sr have similar geochemical behaviour, radiogenic Sr isotopes can help constrain whether the measured river $\delta^{44/42}Ca$ values represent mixtures between rock, meltwater/seawater and hydrothermal end-members because radiogenic isotope ratios are not sensitive to fractionation during chemical processes. No extra non-marine component has been identified in Icelandic meteorological precipitation for Sr, thus the meteorological precipitation correction is

$$^{87}Sr/^{86}Sr^* = \frac{^{87}Sr/^{86}Sr_r \cdot Sr_r - ((Sr/Cl)_{sw}\cdot Cl) \cdot {}^{87}Sr/^{86}Sr_p}{Sr_r - (Sr/Cl)_{sw} \cdot Cl} \tag{3}$$

where subscripts have the same meaning as in Eq. (2). However, applying this formula to the measured river $^{87}Sr/^{86}Sr$ ratios resulted in $^{87}Sr/^{86}Sr$ ratios up to 0.08528 lower than basalt as a result of negative or close to zero Sr concentrations for the majority of the 'A/E' set of samples. Assuming a seawater Sr/Cl ratio for meteorological precipitation may not be valid for these samples since they were taken in autumn when runoff may have more groundwater contribution or is derived from older ice or snow which no longer retains the original seawater ratios. As a result, radiogenic strontium ratios were not corrected for meteorological precipitation and throughout the rest of the paper uncorrected concentrations and ratios are used.
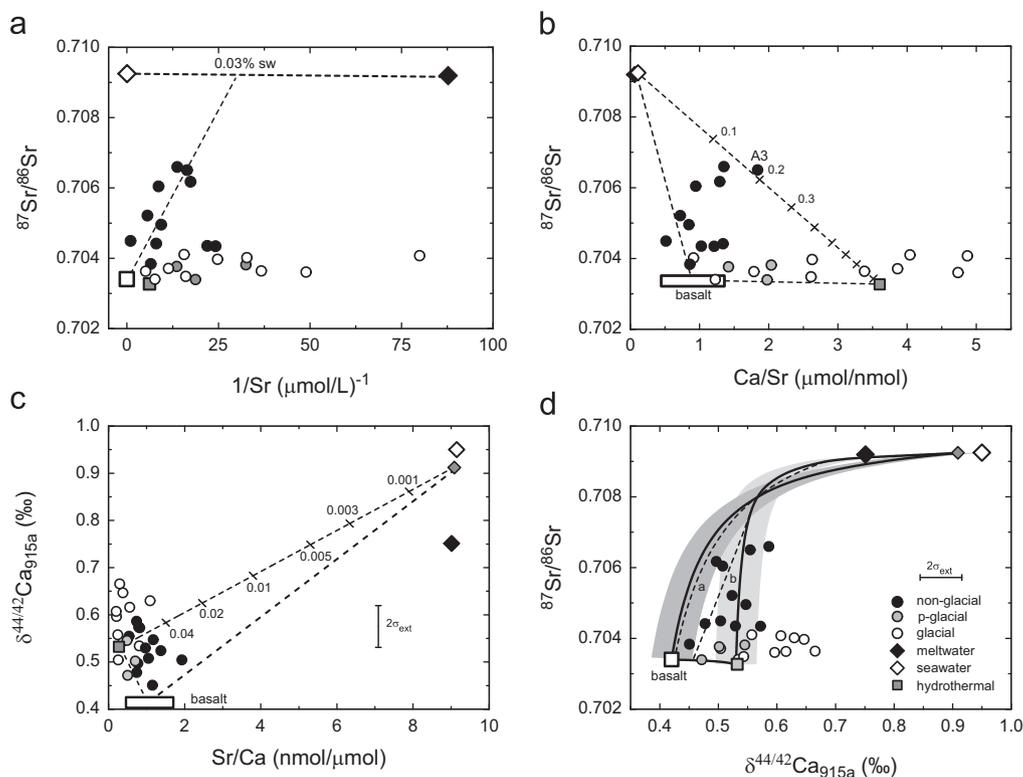
Fig. 2. (a) A plot of $^{87}Sr/^{86}Sr$ vs $1/Sr$. The $^{87}Sr/^{86}Sr$ values of the non-glaciated catchments can be explained by a meltwater-seawater mixture containing 0.03% seawater mixing with Sr derived from basalt rock. (b and c) Plots of $^{87}Sr/^{86}Sr$ vs Ca/Sr and $\delta^{44/42}Ca$ vs Sr/Ca. (d) A plot of $^{87}Sr/^{86}Sr$ vs $\delta^{44/42}Ca$. Mixing lines (dashed lines in b and c and solid lines in d) are indicated between the seawater–meltwater mixture inferred from a (indicated by the grey diamond) and both the basalt rock and hydrothermal end-members and between basalt rock and a hydrothermal source. In b and c the fractional contribution of the hydrothermal end-member is indicated on the hydrothermal-meteorological precipitation mixing line. The range of basalt element ratios is the inter-quartile range of 83 samples (Arnórsson et al., 2002; Fridriksson et al., 2009; Koornneef et al., 2012). In d the 'basalt' end-member concentrations are taken to be those of Vatnsdalsá (IS-7) which is closest in isotopic composition to the basalt and therefore least likely to have been affected by fractionation or mixing processes. The uncertainty in the mixing lines due to uncertainty in the Ca isotopic composition of the hydrothermal and basalt end-members is indicated by grey shading and is taken to be the analytical error (0.07‰). Dashed lines *a* and *b* indicate mixtures between the meteorological precipitation mixture and basalt dissolution with a constant hydrothermal input of 1% and 10% respectively. The chemical and isotopic compositions of the non-glaciated rivers are consistent with a mixture between solutes derived from basalt dissolution and meteorological precipitation. In addition, there is either a significant hydrothermal component or a fractionation process which has shifted element and $\delta^{44/42}Ca$ ratios from the basalt-meteorological precipitation mixing line. The high hydrothermal contributions which would be required if the glaciated catchments were mixtures of water sources are inconsistent with the chemical data, suggesting that mixing with hydrothermal inputs are not responsible for the $\delta^{44/42}Ca$ values of these rivers and that a fractionation process is responsible. The partially glaciated rivers (p-glacial) behave like glacial rivers in terms of Sr chemistry but like non-glacial rivers in terms of Ca chemistry.

Radiogenic strontium data for the river water samples fall into two clear groups: the non-glacial rivers have higher Sr concentrations and $^{87}Sr/^{86}Sr$ values which tend towards the meltwater/seawater end-member whereas the glacial rivers have low Sr concentrations and $^{87}Sr/^{86}Sr$ values which are similar to basalt (Fig. 2a). The range in $^{87}Sr/^{86}Sr$ ratios for the non-glaciated rivers is consistent with a mixture of Sr with a basaltic rock composition and meteorological precipitation which has a composition reflecting a mixture of meltwater and seawater, with an average contribution of seawater of 0.03% (Fig. 2a). This contribution of seawater is in good agreement with Gíslason and Eugster (1987b) who estimated that Icelandic meteorological precipitation was a mixture of 0.01% seawater with pure water.

Iceland is geothermally active and hydrothermal inputs could be significant. The non-glaciated catchments are isotopically and chemically consistent with a three end-member mixture between solutes derived from basalt rock, a meteorological precipitation input and hydrothermal water (Fig. 2). However, if the Ca/Sr (or Sr/Ca) ratio is a conservative tracer then certain rivers e.g. Grímsá (A3) would require nearly a 20% hydrothermal contribution (Fig. 2b and c). This is inconsistent with chemical data such as sodium concentrations (Table 1) and previous studies (Pogge von Strandmann et al., 2006; Vigier et al., 2009) which determined that these rivers had less than 1% contribution from hydrothermal inputs based on isotopic tracers sensitive to hydrothermal inputs.

Alternatively, the Sr/Ca ratio may not be conservative, leading to an overestimation of hydrothermal inputs. The fact that a greater number of non-glacial rivers plot on a hydrothermal-meteorological precipitation mixing line in a $^{87}Sr/^{86}Sr$ vs $\delta^{44/42}Ca$ plot (Fig. 2d) compared to the same mixing line in a $^{87}Sr/^{86}Sr$ vs Ca/Sr plot (Fig. 2b) supports the contention that mixing is not conservative and that the Ca/Sr ratio and $\delta^{44/42}Ca$ are fractionated. In summary, the four panels of Fig. 2 can be interpreted in two ways for the non-glacial rivers: either the geochemical tracers are conservative and there is a significant (up to 20%) hydrothermal component, or the tracers (Sr, Ca and $\delta^{44/42}Ca$) are non-conservative and are affected by a fractionation process.

5.2. Potential isotope fractionation processes

The glacial (and partially glacial) rivers have a minimal contribution from atmospheric sources (Fig. 2a and b). Some of the glacial rivers would be consistent with solutes derived from basalt rock mixing with a hydrothermal source, but for most of the rivers draining catchments with greater than 22% glacial cover, the Ca isotopic composition cannot be explained by a simple mixture of water sources (Fig. 2c and d). These rivers would have to be 100% hydrothermal, which is inconsistent with the solution chemistry (e.g. Na concentrations, Table 1) of the glacial rivers. Instead, it is highly probable that a fractionation process is occurring.

Fractionation of stable isotopes can occur during various stages of their biogeochemical cycle during (1) release from primary minerals, (2) precipitation of secondary minerals, (3) uptake by vegetation and (4) adsorption onto mineral surfaces.

It is unlikely that the primary dissolution of basalt is responsible for the Ca isotope fractionation observed in the glaciated catchments since fractionation during primary dissolution would also be expected to be observed in catchments with no glacial cover. Recent studies have shown that the weathering of granite, where the main Ca-bearing mineral is plagioclase, is congruent with respect to calcium isotopes (Hindshaw et al., 2011; Ryu et al., 2011). Together with pyroxene, plagioclase is the main source of Ca in basalt, thus it is reasonable to assume that the weathering of crystalline basalt will also induce no Ca isotope fractionation during the primary dissolution step. There have been no experimental studies of Ca isotope fractionation during basaltic glass dissolution, but Wimpenny et al. (2010) demonstrated no isotopic fractionation during basaltic glass dissolution for both Mg and Li isotopes.

Calcium is fractionated during uptake by plants (Cobert et al., 2011; Hindshaw et al., 2013), but the vegetation cover on Iceland is relatively sparse, covering only 23% of the surface area of the island. Additionally, the catchments with the Ca isotopic compositions most removed from rock are the rivers draining to the south of Vatnajökull where there is no significant vegetation cover.

Thus, the most probable cause of Ca isotope fractionation is either the precipitation of secondary phases or the adsorption of Ca onto secondary phases. These two processes are grouped together in the following discussion since at present it is not possible to distinguish between them with the available data. The fractionation of Ca isotopes during the formation of secondary phases in the riverine environment has previously been invoked for the Marsyandi catchment in the Himalayas (Tipper et al., 2006) and recent experimental studies have indicated that light Ca isotopes preferentially adsorb to secondary clays in the marine environment (Ockert et al., 2013) which would result in the residual fluid becoming isotopically heavier. In Iceland, there have been numerous studies focussed on identifying the alteration products of both basaltic glass and crystalline basalt weathering. The main Ca-bearing secondary phases have been identified as Ca-smectites, Ca-zeolites and calcite (e.g. Gíslason and Eugster, 1987b; Crovisier et al., 1992; Gíslason et al., 1996; Stefánsson and Gíslason, 2001).

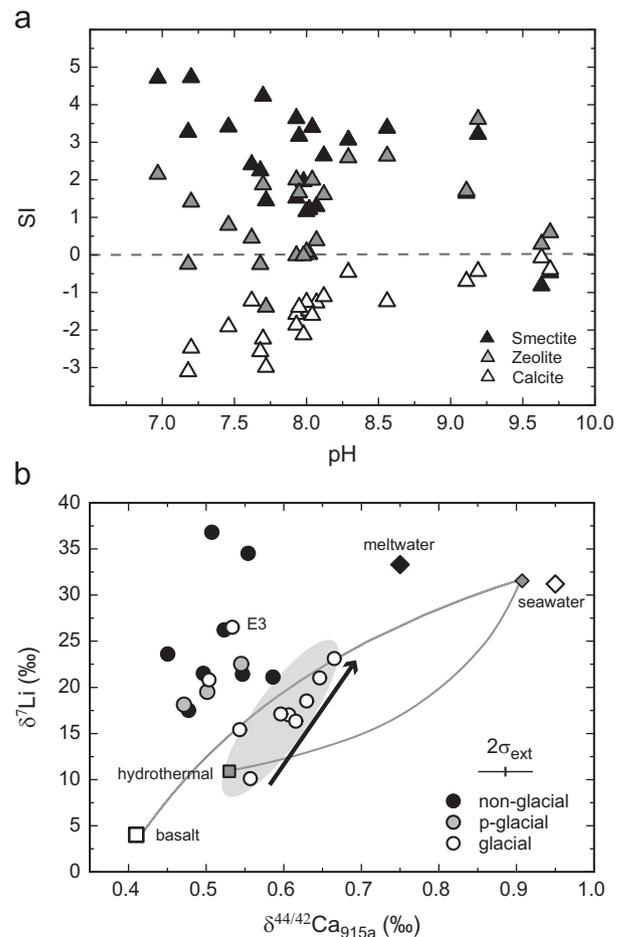### 5.2.1. Saturation indices

In order to assess the likelihood of secondary mineral formation in this set of Icelandic rivers, saturation indices for smectite, zeolite and calcite were calculated using Phreeqc (Parkhurst and Appelo, 1999) using the wateq4f database. Montmorillonite-Ca ($Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$) and laumontite ($CaAl_2Si_4O_{12} \cdot 4 H_2O$) were chosen as representative phases for smectite and zeolite respectively. Measured pH, temperature, cation and anion concentrations were used as inputs. The saturation indices for the two main Ca-bearing primary phases plagioclase (anorthite) and pyroxene (diopside) were also computed. These calculations only account for crystalline phases, however palagonite, which is an alteration product of basalt containing predominantly amorphous smectite phases and is a precursor of crystalline smectite, is expected to be present in all catchments (Stroncik and Schmincke, 2002).

All rivers are under-saturated with respect to plagioclase and pyroxene, though pyroxene approaches saturation at high pH values (pH > 9, not shown). In terms of secondary phases; calcite is under-saturated in all rivers, zeolite is over-saturated in all bar five rivers (E4, E6, IS-5, IS-18 and IS-19) and smectite is

over-saturated in all bar two rivers (E3 and E5). The calculated saturation indices for secondary phases are consistent with calculations of secondary mineral crystallization sequences for basalt dissolution, whereby smectite-group minerals are first to precipitate and with a longer reaction time, zeolites and eventually calcite will precipitate (Crovisier et al., 1992).

The Ca/Sr ratios of glacial waters are higher than that of basalt which requires the formation of a secondary phase which incorporates a greater proportion of Sr relative to Ca. Therefore, the precipitation of calcite can be ruled out as a cause of Ca isotope fractionation because calcite precipitation would result in river water with a lower Ca/Sr ratio compared to basalt (DePaolo, 2011) and this is not observed (Fig. 2b).

As the first Ca-bearing phase likely to precipitate, the formation of smectite could be responsible for fractionating Ca isotopes. The δ^7Li values of Icelandic rivers were previously shown to be controlled by the degree of smectite formation (Pogge von Strandmann et al., 2006). For the glacial rivers, δ^7Li and $\delta^{44/42}Ca$ values are positively correlated (Fig. 3b, $R^2 = 0.97$ ($p < 0.01$, $n = 8$)). This correlation suggests that in the glaciated catchments, similar to Li, secondary precipitation of smectite could be controlling the observed isotopic fractionation of Ca, where the

Fig. 3. (a) Calculated saturation indices for three Ca-bearing secondary phases (smectite, zeolite and calcite). Saturation indices were calculated using Phreeqc. (b) δ^7Li and $\delta^{44/42}Ca$ are positively correlated for glaciated catchments (grey shading) suggesting that, like Li (Vigier et al., 2009), river Ca isotopic compositions are controlled by the formation of secondary phases. Reference mixing lines between a seawater–meltwater mixture containing 0.03% seawater and basalt and hydrothermal sources are indicated in grey. The arrow indicates seasonal variations in the $\delta^{44/42}Ca$ ratio of the river Skaftafellsá (E5, IS-23). The head of the arrow represents a sample taken later in summer than the tail of the arrow. Sample E3 drains a lake at the front of the glacier.
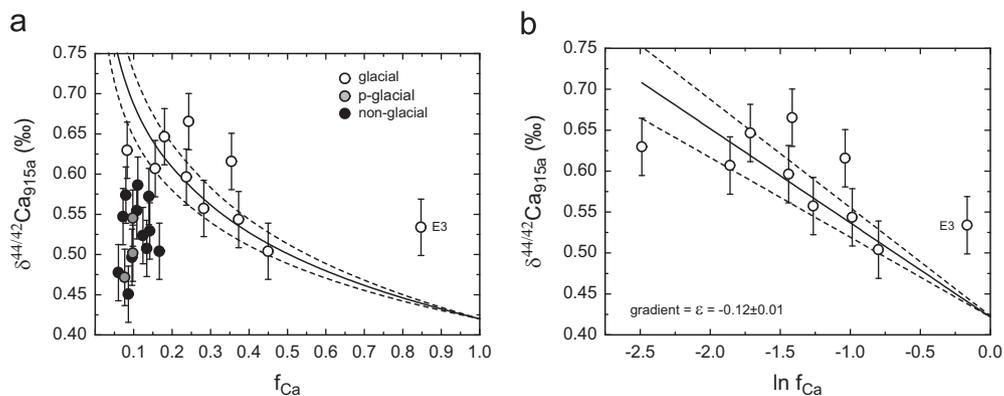
Fig. 4. (a) The Ca isotopic composition versus the fraction of Ca remaining in solution based on a calculation of Ca mobility. The solid line represents a Rayleigh-type fractionation with a fractionation factor ϵ of −0.12. The fractionation factor is calculated from the gradient of a plot of river $\delta^{44/42}$Ca compositions versus the natural logarithm of the fraction remaining in solution (b). The dashed lines in both graphs represent the 95% confidence limits. All lines have been forced through a rock composition of 0.42‰ and sample E3 was not included in line fitting. Error bars are 0.07‰.

light isotope is preferentially incorporated into smectite, leaving the residual river water enriched in heavy Ca (Fig. 3b).

The fractionation of Li isotopes may not solely be due to smectite formation, zeolite formation may also fractionate Li isotopes, either as a result of precipitation (Chan et al., 1992) or due to ion-exchange (Taylor and Urey, 1938). A study of the behaviour of Sr in ground water in northern Iceland (Fridriksson et al., 2009) showed that all the ground water samples had Ca/Sr ratios which were higher than bedrock and concluded that this was either caused by the precipitation of zeolites, or by ion-exchange between water and secondary zeolites, specifically heulandite, which was shown to have a strong affinity for Sr compared to Ca. Zeolites are common in Iceland as a result of zeolite facies metamorphism in the volcanic zone and all of the glacial river samples in this study drain the Vatnajökull ice cap which covers several active volcanoes and geothermal areas (Björnsson, 2002), thus zeolites are expected to be present under Vatnajökull. The median molar Ca/Sr ratio of the ground waters in northern Iceland (Ca/Sr = 5000) is comparable to the hydrothermal water measured in this study (Ca/Sr = 3604). Hydrothermal water chemistry is ultimately derived from bedrock and the fact that the $\delta^{44/42}$Ca ratio is 0.11‰ higher than basalt is a strong indication that the same process which elevates Ca/Sr ratios also fractionates Ca isotopes. The glacial catchments are fractionated from basalt in a similar manner to the hydrothermal end-member (Fig. 2b–d). Therefore, a similar ion-exchange process may be occurring in the glacial waters emanating from Vatnajökull to that observed in ground water in northern Iceland.

Secondary mineral precipitation reactions are likely to occur in the non-glaciated catchments too, but any fractionation of Ca isotopes could not unequivocally be distinguished from mixing with hydrothermal inputs (Fig. 2c).

5.2.2. Estimation of the fractionation factor

Assuming that the precipitation of a Ca containing secondary mineral is responsible for the observed fractionation of Ca isotopes in glaciated catchments, it is possible to calculate a fractionation factor for this process. We assume a Rayleigh-type fractionation of the form

$$\delta^{44/42}\text{Ca} = \delta^{44/42}\text{Ca}_0 + \epsilon \ln f_{Ca} \qquad (4)$$

$$\epsilon = 1000(\alpha - 1) \qquad (5)$$

where $\delta^{44/42}$Ca is the Ca isotope ratio measured in the river; $\delta^{44/42}$Ca$_0$ is the starting isotopic composition of the river, assumed to be the same as basaltic rock (0.42‰); α is the fractionation factor and f_{Ca} is the fraction of Ca remaining in solution.

Rayleigh-type fractionation has previously been applied to model Ca isotope fractionation during the precipitation of $CaSO_4$ in both arid deserts (Ewing et al., 2008) and hydrothermal settings (Amini et al., 2008).

Sodium is only present in secondary phases in Iceland in trace amounts (Stefánsson and Gíslason, 2001) and thus the Ca/Na ratio can be used to indicate uptake of Ca into secondary phases. The fraction of Ca remaining in solution was estimated using an equation equivalent to the calculation of Ca mobility relative to Na (cf. Gíslason et al., 1996)

$$f_{Ca} = \frac{(\text{Ca}/\text{Na})_{river}}{(\text{Ca}/\text{Na})_{rock}} \qquad (6)$$

This calculation assumes that the release of Ca and Na from basalt is congruent. Although laboratory experiments have indicated that the dissolution of basaltic glass is congruent (Gíslason and Eugster, 1987a) the dissolution of crystalline basalt is incongruent (Gíslason et al., 1996). The greatest uncertainty in the calculation of f_{Ca} arises from determining a (Ca/Na)$_{rock}$ ratio for each catchment. Tholeiitic basalts tend to have lower Ca/Na ratios than alkali basalts (Arnórsson et al., 2002) and the exact type of basalt in each catchment is unknown. Instead a common (Ca/Na)$_{rock}$ molar ratio was assumed for all catchments of 2.87 based on the median of 83 basaltic rocks from Iceland analysed by Arnórsson et al. (2002) and Koornneef et al. (2012). Another source of uncertainty is the fact that precipitation corrected Ca/Na ratios were not used in this calculation. This is because, similar to Sr, the precipitation correction for Na gave negative, or close to zero concentrations for the majority of the 'A/E' set of samples. However, for the 'IS' catchments, the calculated values of f_{Ca} only increase by an average of 0.06 units if meteorological precipitation corrected ratios are used. In addition, the non-meteorological precipitation corrected values of f_{Ca} for the 'A' catchments agree very well with Ca mobility values previously calculated using meteorological precipitation corrected data by Gíslason et al. (1996). Other studies, however, have concluded that the fraction of Ca incorporation into secondary minerals is much lower, and could be as low as 5% (Crovisier et al., 1992; Georg et al., 2007). The glaciated and unglaciated catchments clearly form two separate groups (Fig. 4a): the unglaciated catchments have relatively low and constant f_{Ca} values and a range of $\delta^{44/42}$Ca ratios whilst in the glaciated catchments, as the f_{Ca} value decreases, the $\delta^{44/42}$Ca ratio increases. The fractionation factor for the glaciated catchments is calculated from the gradient of a plot of $\delta^{44/42}$Ca versus $\ln f_{Ca}$ (Fig. 4b), where the analytical error of the $\delta^{44/42}$Ca measurements (0.07‰) is taken into account when calculating the uncertainty in the value of the gradient. We obtain a value of ϵ of −0.12 ± 0.01 (95% uncertainty

limit, $\alpha = 0.9999$). This value is comparable to fractionation factors calculated for the precipitation of $CaSO_4$ (0.9996, Ewing et al., 2008; 0.9995, Amini et al., 2008) and calcite (0.9995–1.0000 (apparent equilibrium α, dependent on reaction rate), DePaolo, 2011).

5.2.3. What controls the degree of fractionation in the glaciated catchments?

Calcium and lithium isotope variations in glaciated catchments ($> 22\%$ glacial cover) appear to be linked, thus the controls of Li isotopic fractionation may also be applicable to Ca. Since many variables may differ between rivers (for example variations in the exact basaltic composition), we will focus the following discussion on two samples taken from exactly the same location. The glacial river Skaftafellsá (IS-23 and E5) was sampled in both sampling campaigns and provides some evidence for seasonal variations in riverine isotopic compositions. The values measured in June were lower in $\delta^7 Li$ and $\delta^{44/42} Ca$ (10.1‰ and 0.56‰) than the values measured in September (23.1‰ and 0.67‰ respectively) (Fig. 3b).

Changes in discharge could be one reason for isotopic variation: in studies from rivers with large seasonal variations in discharge, it has been shown that during high discharge periods Ca and Li isotopic values are closer to bedrock values than at low discharge periods (Kisakürek et al., 2005; Tipper et al., 2010). For Li, the difference was interpreted to reflect a change in weathering intensity with more intense weathering at high discharge: the high weathering intensity results in greater dissolution of primary minerals relative to the formation of secondary minerals and the isotopic value of the dissolved load converges with that of the local bedrock (Kisakürek et al., 2005). In the Strengbach catchment in France the same relationship of $\delta^7 Li$ values with discharge was observed with $\delta^7 Li$ values most removed from rock at low discharge, consistent with increased precipitation of Li in secondary phases due to longer water–rock interaction times (Lemarchand et al., 2010). For Ca, the seasonal variations were interpreted be consistent with changes in calcite precipitation or, alternatively, seasonal changes in the contribution of groundwater (Tipper et al., 2006, 2010). The lack of discharge data for this set of rivers means that we cannot directly test whether discharge has a direct control on the isotopic compositions of these glacial rivers. However, it has been shown that in Icelandic rivers draining glaciers, total suspended sediment (TSS) is high during high discharge periods (Eiriksdottir et al., 2008). In the glaciated catchments the highest $\delta^{44/42} Ca$ values are found at high TSS and therefore at high discharge (Fig. 5) i.e. sample E5 was taken at higher discharge than sample IS-23. This is opposite to what may be expected from the above discussion where $\delta^7 Li$ (and $\delta^{44/42} Ca$) values most removed from bedrock were measured at low discharge where weathering intensity/rate is thought to be higher (Kisakürek et al., 2005; Vigier et al., 2009). This apparent contradiction can be resolved by considering a 'reservoir effect' (Tipper et al., 2012). Here, the amount of secondary mineral precipitation relative to a starting pool has to be considered rather than a ratio between the rates of primary mineral weathering and secondary mineral precipitation. Thus, the values most fractionated from bedrock arise because they derive from dilute water and only a small amount of secondary mineral has to precipitate to account for a large percentage loss of the initial pool. Conversely, although concentrated rivers may have a greater amount of secondary precipitation, the starting pool is larger so the effect of the same amount of secondary mineral precipitation on fractionating river $\delta^{44/42} Ca$ from bedrock values is smaller. Alternatively, in rivers with high TSS, the high surface area may provide ample adsorption or ion-exchange sites, if these reactions preferentially remove light Ca then the remaining river water Ca would evolve to $\delta^{44/42} Ca$ values higher than bedrock.
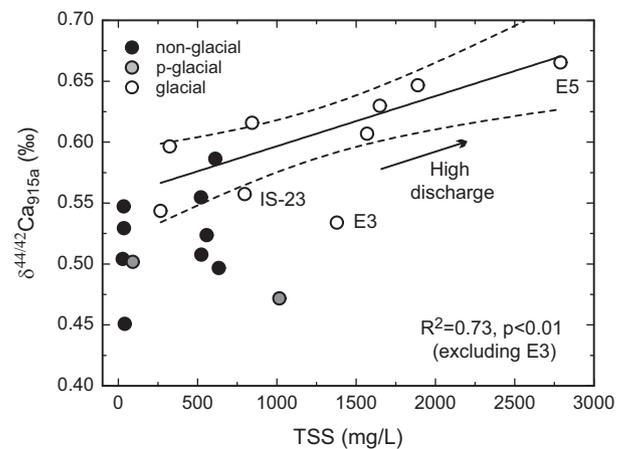
Fig. 5. In the glaciated catchments high total suspended sediment fluxes (TSS), indicative of high discharge conditions (Eiriksdottir et al., 2008), are associated with the $\delta^{44/42} Ca$ values most removed from bedrock (0.42‰). This trend, which could indicate fractionation during adsorption, is not observed for the non-glaciated and partially glaciated catchments. E5 and IS-23 are the two samples from the same river (Skaftafellsá) taken at different times of the year.

5.2.4. What creates the difference between glaciated and unglaciated catchments?

We have shown that the Ca isotopic compositions of glaciated and unglaciated catchments are affected by different factors, forming two different 'weathering regimes', one where Ca isotope fractionation is observed and one which is dominated by mixing of water sources (although fractionation cannot be completely ruled out). Secondary mineral formation has been documented all over the island and are therefore expected to occur in the unglaciated catchments, indeed these catchments have the lowest Ca/Na ratios suggesting extensive removal of Ca. Why then is there a difference in fractionation behaviour?

Glacial cover is not the only environmental parameter which differs between the three groups of catchments. A special feature of the glaciated catchments in Iceland is that beneath all the large ice caps there are active volcanoes. When these volcanoes erupt they tend to produce basaltic glass (hyaloclastite) rather than crystalline basalt (Gíslason et al., 1996; Sigmarsson and Steinthórsson, 2007). Regular jökulhlaups (15 in the last 200 yr) ensure that the floodplain areas where the jökulhlaups emerge have a constant supply of fresh material to weather. Even without jökulhlaups, the majority of glaciers in Iceland are surge glaciers which create sediment pulses during and just after each surge (Björnsson et al., 2003; Striberger et al., 2011). Thus, the glacial rivers drain areas which have a high amount of glacially ground sediments containing (altered) basaltic glass whereas the rivers draining non-glaciated catchments tend to drain crystalline basalt. Importantly, the weathering of crystalline basalt is slower than that of basaltic glass (Gíslason and Eugster, 1987a; Wolff-Boenisch et al., 2006) and the factors controlling the dissolution rate are different (Gíslason and Oelkers, 2003; Gudbrandsson et al., 2011). The non-glaciated catchments are situated away from the central rift zone and the age of the bedrock is older (Table 1), any glass which was once present is likely weathered. The assemblage of secondary minerals is likely to differ between crystalline basalt and basaltic glass catchments and different secondary minerals could have different fractionation factors. In addition, secondary minerals have different affinities for Ca and Sr (Fridriksson et al., 2009) and this could explain the difference in Ca/Sr ratios observed between glaciated and non-glaciated catchments. That Rayleigh fractionation behaviour is not observed in the non-glaciated catchments may simply be because mixing processes are also involved and that there is a more complex suite of

processes (including back-reactions) operating, whereas the glaciated catchments are essentially dominated by the weathering of a single phase (basaltic glass).

The three 'partially glacial' catchments provide some evidence that different weathering processes are responsible for the glacial/non-glacial split. Their strontium chemistry follows that of the glacial catchments (Fig. 2b) whereas their Ca chemistry follows that of the non-glacial catchments (Fig. 4a). Apart from indicating that Sr is not a suitable analogue for Ca in these settings, these catchments may indicate a 'transition' between two different weathering regimes. These rivers are situated in the driest parts of the island and thus, despite being glaciated, have comparatively low discharge compared to the other glaciated catchments, which would affect water–rock interaction time and weathering processes.

Geographical differences in weathering processes have previously been invoked to explain the Si isotope data of the 'IS' set of rivers. Georg et al. (2007) found that two different types of weathering regime (a steady-state regime and a regime described by Rayleigh fractionation) were required to explain Si isotope variations. They found an east–west divide between weathering regimes and suggested that this was a result of meteorological precipitation differences between the two sides of the island. However, the Ca isotope data cannot similarly be explained by an east–west divide. The discrepancy is probably due to the considerably lower amount of Ca removal (0–5%) used in the calculation of Si losses, compared to the levels of Ca loss calculated in this study which approach 90%.

A recent study employing Ca isotopes in the Southern Alps, New Zealand also noted differences in weathering behaviour between glaciated and unglaciated catchments, namely that although all rivers exhibited linear mixing between carbonate and silicate end-members, the relative proportion of silicate-derived Ca was greater in the glaciated catchments. However, these findings are not directly transferable to this study because, unlike in Iceland, no Ca-bearing secondary mineral phases were detected and thus fractionation could be ruled out as a cause of Ca isotope variation.

Although we have no clear explanation for the contrasting behaviour of glaciated and non-glaciated catchments, we speculate that the difference arises due to a difference in the main weathering processes occurring in each. This mechanism provides support for the key role of the precipitation of secondary minerals in controlling riverine geochemistry (Goddéris et al., 2006; Maher et al., 2009).

6. Conclusions

The Ca isotopic compositions ($\delta^{44/42}$Ca) of Icelandic rivers were up to 0.26‰ heavier than basaltic rock. A single mechanism was unable to explain the $\delta^{44/42}$Ca values of all rivers: rather, the rivers formed three distinct groups. Catchments with less than 10% glacial cover were influenced by meteorological precipitation, as revealed by their elevated ^{87}Sr/^{86}Sr values. In addition, mixing with a significant hydrothermal (up to 20%) input or a fractionation process is required to explain the $\delta^{44/42}$Ca and Sr/Ca ratios of these catchments. In contrast, a simple mixture of water sources could not account for the $\delta^{44/42}$Ca values observed in the catchments with more than 22% glacial cover. The $\delta^{44/42}$Ca of the glaciated catchments were controlled by a fractionation process, most likely due to the precipitation of Ca-containing secondary phases such as smectite or zeolite and/or adsorption or ion-exchange with these secondary phases. The third group of rivers, with 10–21% glacial cover, had intermediate geochemical behaviour. They had Sr chemistry similar to glacial rivers and Ca

chemistry similar to non-glacial rivers, indicating that, in these rivers, Sr cannot be used as a proxy for Ca behaviour. Although the exact reasons for the contrasting behaviour of glaciated and non-glaciated catchments are unclear, a possible explanation could be a difference in the weathering regime. The glaciated catchments are dominated by reactive basaltic glass (as a result of sub-glacial volcanic eruptions due to their location near the main rift zone), whereas the non-glaciated catchments predominantly contain crystalline basalt. These two types of basalt weather differently both in terms of weathering rates and likely in the nature of secondary minerals formed. Additionally, glaciation itself exerts a major control on the nature of secondary minerals formed by elevating pH and decreasing the temperature of river water, augmenting the underlying differences in weathering regime.

Many world rivers are affected by meteorological precipitation with a significant sea-salt component and due to the significant Ca isotopic difference between seawater and crystalline rocks, a potential meteorological precipitation input must be considered for all rivers exhibiting elevated $\delta^{44/42}$Ca values. If the fractionation observed in the glaciated catchments is confirmed to have its origins in the rare global occurrence of sub-glacial volcanism then the release of isotopically heavy Ca to the ocean by this mechanism may be unique to Iceland and therefore unlikely to affect the global riverine Ca budget. Nevertheless, on a catchment scale, secondary mineral formation is a key processes controlling the $\delta^{44/42}$Ca composition of river water.

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