Silicate versus carbonate weathering in Iceland: New insights from Ca isotopes

Andrew D. Jacobson [a,*], M. Grace Andrews [a], Gregory O. Lehn [a], Chris Holmden [b]

[a] *Department of Earth and Planetary Sciences, Northwestern University, Technological Institute, 2145 N. Sheridan Road, Evanston, IL 60208, USA*
[b] *Saskatchewan Isotope Laboratory, Department of Geological Sciences, University of Saskatchewan, 114 Science Place, Saskatoon, SK S7N 5E2, Canada*

A B S T R A C T

Several studies have measured riverine fluxes of Ca and carbonate alkalinity in Iceland with the aim of quantifying the role of basalt weathering in the long-term carbon cycle. A major assumption is that all of the Ca and alkalinity originates from the dissolution of Ca-bearing silicate minerals, such as plagioclase and clinopyroxene. However, hydrothermal calcite occurs throughout Iceland, and even trace levels are expected to impact river geochemistry owing to the mineral's high solubility and fast dissolution rate. To test this hypothesis, we used a new, high-precision Ca isotope MC-TIMS method ($\delta^{44/40}$Ca; $2\sigma_{SD} = \pm 0.04$‰) to trace sources of Ca in Icelandic rivers. We report elemental and Ca isotope data for rivers, high- and low-temperature groundwater, basalt, hydrothermal calcite (including Iceland Spar), and stilbite and heulandite, which are two types of zeolites commonly formed during low-grade metamorphism of basalt. In agreement with previous research, we find that rivers have higher $\delta^{44/40}$Ca values than basalt, with a maximum difference of ∼0.40‰. This difference may reflect isotope fractionation in the weathering zone, i.e., preferential uptake of ^{40}Ca during clay mineral formation, adsorption, and other geochemical processes that cycle Ca. However, calcite $\delta^{44/40}$Ca values are also up to ∼0.40‰ higher than bedrock values, and on a diagram of $\delta^{44/40}$Ca versus Sr/Ca, nearly all waters plot within a plausible mixing domain bounded by the measured compositions of basalt and calcite, with glacial rivers plotting closer to calcite than non-glacial rivers. Calcite and heulandite form during hydrothermal alteration of basalt in the deep lava pile and often occur together in metabasalts now exposed at the surface. Because heulandite $\delta^{44/40}$Ca values are ∼1–2‰ lower than basalt, we suggest that ^{40}Ca uptake by heudlandite explains the relatively high $\delta^{44/40}$Ca values of calcite and that calcite weathering in turn elevates riverine $\delta^{44/40}$Ca values. High mechanical erosion rates are known to facilitate the exposure and weathering of calcite, which explains the isotopic contrast between glacial and non-glacial watersheds. Using a mixing model, we find that calcite weathering provides ∼0–65% of the Ca in non-glacial rivers and ∼25–90% of the Ca in glacial rivers, with silicate weathering providing the remainder. Icelandic hydrothermal calcite contains mantle carbon. Noting that zeolite facies metamorphism and hydrothermal fluid circulation are ubiquitous characteristics of basaltic eruptions and assuming that hydrothermal calcite in other basaltic settings also contains mantle carbon, we suggest that the contribution of basalt weathering to long-term CO_2 drawdown and climate regulation may be less significant than previously realized.

1. Introduction

While basalt represents a small fraction of crustal rocks exposed at the Earth's surface (5%; Amiotte Suchet et al., 2003), basalt weathering may have a disproportionately large effect on the long-term carbon cycle because Ca-bearing silicate minerals composing basalt appear to dissolve easily, thereby consuming atmospheric CO_2 at a relatively rapid rate (Amiotte Suchet et al., 2003; Dessert et al., 2003). Several studies have examined basalt weathering in Iceland (Gislason and Arnórsson, 1993; Gislason et al., 1996; Moulton et al., 2000; Stefansson and Gislason, 2001; Arnórsson et al., 2002; von Pogge Strandmann et al., 2006; Georg et al., 2007; Louvat et al., 2008; Gislason et al., 2009; Vigier et al., 2009). Icelandic basalt also contains secondary Ca-bearing minerals, such as calcite and a variety of zeolites, produced during petrogenesis, burial metamorphism, and hydrothermal alteration (Walker, 1960; Saemundsson et al., 1980;

* Corresponding author. Tel.: +1 847 491 3132.
  E-mail addresses: adj@earth.northwestern.edu (A.D. Jacobson),
grace@northwestern.edu (M. Grace Andrews), greg@earth.northwestern.edu
(G.O. Lehn), ceh933@mail.usask.ca (C. Holmden).

Steinthórsson et al., 1987; Neuhoff et al., 1999, 2000; Weisenberger and Selbekk, 2009). Iceland is of course the type locality for Iceland spar, a chemically and optically pure form of calcite (Kristjansson, 2012). Unaltered Icelandic basalt contains ∼0.20 wt% calcite, whereas altered basalt contains ∼8 wt%, with some rocks surrounding active geothermal systems displaying as much as ∼15 wt% (Wiese et al., 2008). Icelandic basalt is not unique in this regard. Many igneous rocks contain accessory calcite (Jacobson and Blum, 2000; White et al., 2005). In watersheds draining granite and schist, the chemical weathering of accessory calcite often dominates riverine Ca and alkalinity fluxes (Mast et al., 1990; Clow and Drever, 1996; Blum et al., 1998; Jacobson et al., 2003; Oliva et al., 2004). Only a few studies have recognized the importance of accessory calcite weathering in Iceland (Raiswell and Thomas, 1984; Georg et al., 2007), but the full implications with respect to the long-term carbon cycle have not been realized. Trace calcite typically contains non-atmospheric carbon (Templeton et al., 1998; White et al., 2005). Therefore, given how the long-term carbon cycle works (e.g., Berner et al., 1983), the dissolution of trace calcite by carbonic acid has no impact on climate change over geologic timescales. The CO_2 that contributes to the formation of hydrothermal calcite in Iceland originates from the mantle (Arnorsson and Barnes, 1983; Marty et al., 1991; Arnórsson, 1995, 2014; Barry et al., 2014). Thus, the possibility exists that riverine fluxes of Ca and carbonate alkalinity from Icelandic watersheds cannot be used to calculate the extent of CO_2 drawdown by silicate weathering without first correcting for the calcite weathering contribution.

High-precision analysis of calcium isotope ratios ($\delta^{44/40}$Ca) offers one way to directly trace proportions of riverine Ca from silicate versus carbonate weathering, although challenges exist to differentiate effects of isotope fractionation from conservative mixing. For example, Ca isotope fractionation occurs during calcite precipitation (Lemarchand et al., 2004; Tipper et al., 2006) and might also occur during ion-exchange with clay minerals (Ockert et al., 2013). Plant uptake is another process that can fractionate Ca isotopes (Bullen et al., 2004; Wiegand, 2005; Page et al., 2008; Cenki-Tok et al., 2009; Holmden and Bélanger, 2010; Cobert et al., 2011; Farkaš et al., 2011; Hindshaw et al., 2011, 2013b; Bagard et al., 2013; Schmitt et al., 2013). Indeed, some authors have attributed patterns of Ca isotope variation in streams and rivers to reflect fractionation during secondary calcite precipitation (Tipper et al., 2006), zeolite and clay formation (Hindshaw et al., 2013a), and plant uptake (Cenki-Tok et al., 2009; Holmden and Bélanger, 2010; Moore et al., 2013). Others have interpreted the isotopic variations in their studied systems to reflect source mixing processes stemming from mineral dissolution, i.e., the release of Ca from bedrock-forming minerals having unique $\delta^{44/40}$Ca values, Ca concentrations, solubilities, dissolution rates, and modal abundances (Jacobson and Holmden, 2008; Moore et al., 2013). Laboratory-scale chemical weathering experiments provide some support for the mixing interpretation. For example, using a column reactor, Ryu et al. (2011) found that the time-dependent pattern of Ca isotope variation during granite weathering could be quantitatively linked to the dissolution of individual, Ca-bearing minerals having distinctive Ca isotope signatures.

A recent field study by Moore et al. (2013) demonstrated the importance of conservative mixing for rivers draining schist in the western Southern Alps of New Zealand. Here, rivers have higher $\delta^{44/40}$Ca values and lower Sr/Ca ratios compared to bedrock, with statistically significant differences between glacial and non-glacial catchments. Fractionation during plant uptake was recognizable in rivers draining greywacke watersheds in the eastern Southern Alps. However, after correcting for this effect, rivers on both sides of the mountain range showed similar patterns of $\delta^{44/40}$Ca variation relative to Sr/Ca. Fractionation cannot explain the isotopic contrast between rivers and bedrock because potential mechanisms such as

calcite precipitation and formation of Ca-bearing clay minerals do not occur in this setting, or are insignificant at the watershed scale. Nor can these mechanisms explain the apparent discrimination between elemental Ca and Sr. Instead, rivers conform to the pattern expected for two-component mixing between silicate bedrock having low $\delta^{44/40}$Ca values and high Sr/Ca ratios and hydrothermal calcite having high $\delta^{44/40}$Ca values and low Sr/Ca ratios. Mixing equations reveal that hydrothermal calcite provides ∼60 to >90% of the riverine Ca, even though calcite represents a minor fraction of the bedrock composition.

More recently, Hindshaw et al. (2013a) examined the Ca isotope geochemistry of rivers throughout Iceland. Icelandic rivers have higher $\delta^{44/40}$Ca values and lower Sr/Ca ratios compared to bedrock. The pattern is remarkably similar to that observed for the New Zealand Southern Alps, including contrast between glacial and non-glacial rivers. Hindshaw et al. (2013a) attributed the pattern to Ca isotope fractionation during formation of clays, adsorption onto mineral surfaces, and/or ion-exchange with heulandite, a zeolite mineral known to significantly lower Sr/Ca ratios in groundwater (Fridriksson et al., 2009). However, the authors did not analyze the Ca isotope composition of zeolites, nor did they consider contributions from the weathering of hydrothermal calcite. In this paper, we offer an alternative explanation that synthesizes fractionation and mixing, highlighting in particular the contribution of calcite weathering to the $\delta^{44/40}$Ca and Sr/Ca geochemistry of Icelandic rivers. We report new elemental and Ca isotope data for rivers draining glacial and non-glacial catchments throughout Iceland, including many of the same catchments examined by Hindshaw et al. (2013a). To test hypotheses surrounding mixing versus fractionation control on the Ca isotope composition of rivers and to more broadly examine the role of basalt weathering in the long-term carbon cycle, we also analyzed groundwater, basalt, hydrothermal calcite, and two different zeolites, namely heulandite and stilbite.

2. Geologic and climatic setting

Iceland is located between the latitudes of 63 and 67° N and the longitudes of 25 and 13° W (Fig. 1). The island lies above the Iceland hotspot and along the Mid Atlantic Ridge, which separates the Eurasian and North American plates. Iceland is geologically active and contains several volcanoes and vigorous hydrothermal systems. Basalt composes ∼80–85% of the bedrock (Gislason et al., 1996). Modern and Upper Quaternary rocks are confined to the active volcanic zone, which strikes roughly southwest to northeast through the island (Gislason et al., 1996). The age of the rocks generally increases with distance away from the volcanic zone. The oldest rocks exposed have an age of ∼13 Myr (Moorbath et al., 1968). Glaciers cover ∼11% of Iceland (Norðdahl and Pétursson, 2005). The mean annual temperature is 4 °C. Mean annual precipitation ranges from ∼3000–4000 mm along the south coast to <400 mm in the north. Vegetation covers only 23% of the land surface area (Hindshaw et al., 2013b).

3. Methods

3.1. Field measurements and water sample collection

Nineteen water samples were collected in October and November 2013 (Fig. 1; Table 1). The sample suite includes three non-glacial rivers, seven glacial rivers, and nine groundwaters. Of the groundwater samples, three were collected from natural springs and six were collected from wells maintained by the Iceland GeoSurvey (ISOR). Fig. 1 displays sample locations, and Table 1 provides additional supporting information. Locations were documented with a Garmin 60CSx handheld GPS meter. Temperature (± 0.1 °C) and pH (± 0.02) were measured on-site using an
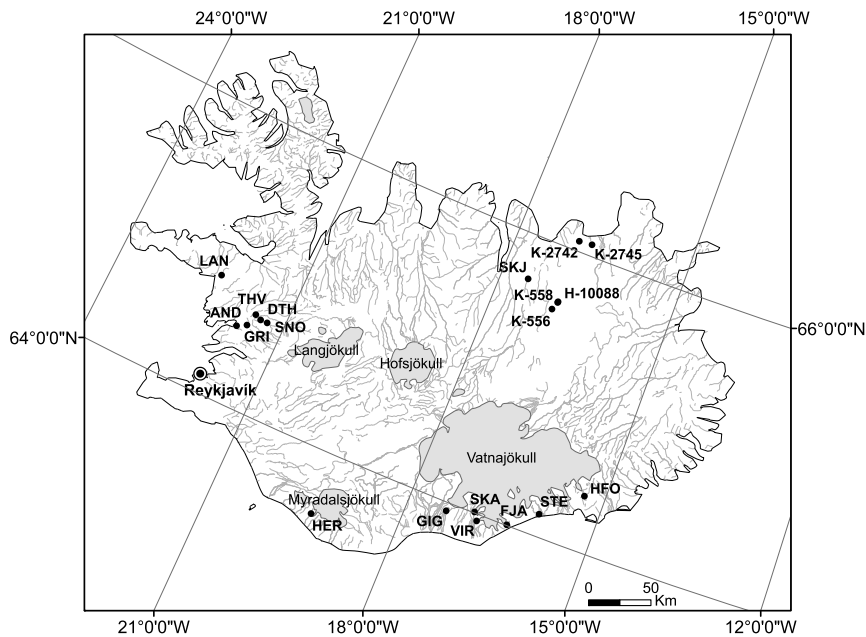
Fig. 1. Map of Iceland showing water sample locations.

Orion 250Aplus portable meter equipped with an Orion ATC probe and an Orion 8104 ROSS Ultra pH electrode. The pH meter was calibrated daily with pH = 4, 7, and 10 certified, NIST traceable buffers. Water samples for the analysis of cation and Si concentrations and Ca isotope ratios were passed through 0.45 µm filter capsules (Versapor membrane), collected in I-CHEM HDPE bottles, and acidified to pH = 2 using ultrapure, concentrated HNO_3. Samples for the analysis of total alkalinity and anion concentrations were passed through 0.45 µm filter capsules (Versapor membrane) and collected in LDPE bottles. Nitrile gloves were worn while sampling. Total alkalinity (Alk) in µeq/L was measured by Gran titration with standardized 0.02N HCl. Total alkalinity is assumed to represent carbonate alkalinity (Alk = HCO_3^- + $2CO_3^{2-}$). Given the pH range of the samples, Alk ≈ HCO_3^-. The uncertainty of the method was less than ±5%, as determined by repeated titrations of a gravimetrically prepared Na_2CO_3 standard.

3.2. Rock and mineral samples: sources and preparation

Rock and mineral samples were obtained from a variety of sources and originate from locations throughout Iceland (Table 2). Six basalt hand samples were obtained from the Icelandic Institute of Natural History. The outer portion of the rock samples was removed with a saw, and a jaw crusher was used to break the inner portion into smaller chips, which were powdered in a shatterbox equipped with a tungsten carbide grinding container. Ten mineral specimens were obtained from the Icelandic Institute of Natural History, the Smithsonian Institution, and the University of Iceland, including eight calcite specimens, one heulandite specimen, and one stilbite specimen. Identifications were confirmed by Raman spectroscopy. The samples were cleaned with MQ water and powdered with a Diamonite mortar and pestle. We also analyzed seven calcite, five heulandite, and four stilbite powders previously collected, prepared, and studied by Fridriksson et al. (2001, 2004, 2009). About half of the calcite samples analyzed in this study are Iceland spars, including one sample from the Helgustadir Mine type locality. In all cases, original sample IDs were preserved to facilitate traceability.

Subsamples of calcite powders were weighed into acid cleaned Teflon vials and completely dissolved in ultrapure, 6N HCl. Subsamples of zeolite and basalt powders were weighed into acid

cleaned Teflon vials, mixed with a 2:1 solution of ultrapure, concentrated $HF-HNO_3$, and heated at 95 °C on a hotplate for five days. The solutions were dried, re-dissolved in ultrapure, 6N HCl, and refluxed at 95 °C on a hotplate for two days. No insoluble residues were observed. All mineral and rock digestions were dried and re-dissolved in ultrapure, 5% HNO_3.

3.3. Elemental analysis

Elemental data were collected in the Aqueous Geochemistry Laboratory at Northwestern University. Concentrations of cations (Al, Ca, Fe, K, Mg, Na, and Sr) and Si in water samples, as well as Ca and Sr concentrations in rock and mineral digestions, were measured using a Thermo Scientific iCAP 6500 ICP-OES. NIST SRM 1643e was repeatedly analyzed to monitor instrumental performance and overall data quality. Results were within ±5% of reported concentrations. Concentrations of anions (Cl, F, and SO_4) in water samples were measured using a Dionex DX-120 IC equipped with an AS15 anion-exchange column and an ASRS-300 self-regenerating suppressor. Analyses of a NIST-traceable Dionex standard were within ±5% of reported concentrations. For all water samples, Al and Fe were below detection limits. The quality of the water sample data was assessed by calculating the charge balance error [CBE = $(TZ^+ - TZ^-)/(TZ^+ + TZ^-)$], where TZ^+ is the sum of all cations, and TZ^- is the sum of all anions, in equivalents. The average CBE is −0.43%. Omitting one sample (SKJ) with a CBE of −9.1% improves the average CBE to 0.05%.

3.4. Ca isotope ratios

Calcium isotope ratios ($^{44}Ca/^{40}Ca$) were measured using an optimized $^{43}Ca-^{42}Ca$ double-spike MC-TIMS technique recently introduced by Lehn et al. (2013). All analyses were made in the Radiogenic Isotope Clean Laboratory at Northwestern University using a Thermo Fisher Triton MC-TIMS. Sample aliquots containing 50 µg of Ca were weighed into acid-cleaned Teflon vials and spiked. The vials were capped and gently heated at ∼60 °C overnight to ensure complete sample-spike equilibration. The solutions were dried, re-dissolved in 0.5 mL of 1.55N HCl, and eluted through Teflon columns packed with Bio-Rad AG MP-50 cation exchange

Table 1
Field parameters, major ion geochemistry, and Ca isotope composition of water samples

Sample ID	Description	Date (m/d/yr)	Latitude (N)	Longitude (W)	T (°C)	pH	Ca (μmol/L)	K (μmol/L)	Mg (μmol/L)	Na (μmol/L)	Si (μmol/L)	Sr (nmol/L)	Cl (μmol/L)	F (μmol/L)	SO$_4$ (μmol/L)	Alk (μeq/L)	$\log(\Omega_{cal})$	$\delta^{44/40}$Ca (‰)
Non-glacial rivers																		
AND	Andakílsa	11/25/13	64°33.177′	21°43.857′	3.3	7.18	97	8.83	83	281	142	80.6	275	–	27	338	−2.57	−0.92
GRI	Gímsá	11/25/13	64°35.344′	21°34.743′	0.7	6.98	112	9.91	109	355	223	61.5	240	–	27	506	−2.58	−0.73
THV	Thverá	11/25/13	64°40.970′	21°31.154′	0.6	7.41	140	18.5	148	382	230	146	308	–	30	632	−1.95	−0.84
Glacial rivers																		
HER	Héraðsvötn	10/07/13	63°33.044′	19°21.813′	2.5	7.01	115	16.6	94	253	293	55.2	79.3	–	18.2	573	−2.45	−0.76
SKJ	Skjálfandafljót	10/07/13	65°41.348′	17°32.466′	2.6	7.26	134	13.0	91	403	295	57.9	73.8	6.74	52	855	−1.97	−0.88
STE	Steinavötn	11/12/13	64°09.506′	15°56.182′	1.8	7.75	359	2.76	46	139	102	93.2	102	–	154	572	−1.25	−0.82 (−0.85)
FJA	Fjallsá	11/13/13	64°00.304′	16°22.084′	0.1	8.14	202	6.91	44	106	110	178	56.7	–	44	423	−1.25	−0.88
VIR	Virkisá	11/13/13	63°57.183′	16°50.872′	0.6	8.38	96	22.3	52	348	280	102	122	9.43	39	385	−1.37	−0.86
SKA	Skaftafellsá	11/13/13	64°00.480′	16°55.894′	0.1	9.01	112	5.91	18.1	236	117	36.5	76.7	–	31	366	−0.72	−0.61
GIG	Gígjukvísl	11/13/13	63°56.442′	17°22.095′	0.2	8.10	246	11.2	112	427	217	67.5	94.8	6.30	61	987	−0.86	−0.77
Groundwater																		
K-2742	ÍSOR site	10/11/13	66°04.221′	16°57.563′	3.2	9.45	66	–	–	711	169	4.64	237	–	51	558	−0.35	−0.37 (−0.33)
K-2745	ÍSOR site	10/11/13	66°04.793′	16°43.758′	3.9	8.31	145	20.9	116	405	377	82.6	254	–	41	596	−1.03	−1.16 (−1.12)
K-556	ÍSOR site	10/12/13	65°33.150′	16°58.132′	5.9	8.46	177	33.4	196	760	329	87.0	91.3	8.06	76	1324	−0.44	−0.90
K-558	ÍSOR site	10/12/03	65°36.660′	16°55.203′	5.9	8.46	269	42.6	261	904	382	135	158	8.25	208	1460	−0.24	−1.05
H-10088	ÍSOR site	10/09/13	65°37.000′	16°55.000′	19.8	8.24	405	160	166	3209	1922	221	467	36.5	1037	1886	−0.43	−0.87
SNO	Snorralaug	11/25/13	64°39.842′	21°17.468′	21.1	8.73	67	89.4	–	3887	3051	29.8	1016	149	668	1504	−0.05	−1.35 (−1.33)
LAN	Landbrotslaug	11/25/13	64°49.934′	22°19.109′	38.8	7.61	557	59.6	40	6830	2262	665	3442	35.2	624	3300	−0.04	−0.91 (−0.95)
DTH	Deildartunguhver	11/25/13	64°39.810′	21°24.635′	96.5	8.95	77	52.2	–	3432	2124	122	985	142	558	1354	0.14	−0.90
HFO	Hoffell well 1	11/13/13	64°23.516′	15°20.516′	70.2	8.61	216	50.1	–	4509	1031	861	2045	479	590	1324	0.42	−1.02

Duplicate analyses provided in ().
"–" = below detection limit.

Table 2
Elemental and Ca isotope data for Icelandic basalt, calcite, heulandite, and stilbite.

| Sample ID	Location	Source	Ca (μmol/g)	Sr (nmol/g)	$\delta^{44/40}Ca$ (‰)
Basalt					
9149 (Tholeiite)	Veidivotn, Heljargja lava	Icelandic Institute of Natural History	2151	1713	−1.06
22038 (Olivine Tholeiite)	Krafla, 1980 lava	Icelandic Institute of Natural History	2020	1079	−1.05
9297 (Tholeiite)	Krafla, 1724–1729 lava	Icelandic Institute of Natural History	1698	1745	−1.06
9265 (Olivine Tholeiite)	Askja, Sudurhraun lava	Icelandic Institute of Natural History	2000	1715	−1.07
709 (Tholeitte)	Askja, 1961 lava	Icelandic Institute of Natural History	1536	2107	−1.04
4685 (Basaltic Andesite)	Hekla, 1970 lava	Icelandic Institute of Natural History	1184	4410	−1.07
Calcite					
500 (spar)	Akrar	Icelandic Institute of Natural History	9918	256	−0.72
6917 (spar)	Hvalstöð	Icelandic Institute of Natural History	10906	1625	−0.95
7906 (spar)	Miðhús	Icelandic Institute of Natural History	9967	575	−0.76
10303 (spar)	Höskuldsstadase	Icelandic Institute of Natural History	9687	1107	−0.88
11622 (spar)	Skardsheidi	Icelandic Institute of Natural History	9916	1597	−0.64
15239 (spar)	Húsafell	Icelandic Institute of Natural History	10045	27.6	−0.62
NÍ 4320	Hvalfjördur	Fridriksson et al. (2004, 2009)	10604	320	−0.69
NÍ 4525	Glerhallvík	Fridriksson et al. (2009)	10163	448	−0.94
NÍ 1582	Teigarhorn	Fridriksson et al. (2004, 2009)	10262	146	−0.59
NÍ 10784	Djúpidalur	Fridriksson et al. (2009)	9928	267	−0.80
Bulandstindur	Búlandstindur	Fridriksson et al. (2009)	9192	159	−0.78
NÍ 14632 (spar)	Helgustadir Mine	Fridriksson et al. (2009)	9908	1112	−1.01
NÍ 14231	Hvalfjördur	Fridriksson et al. (2009)	10130	102	−0.68
B9435	Eskefjord	Smithsonian Institution	9883	1507	−1.18
Sturlugata	–	University of Iceland	9762	588	−1.09
Heulandite					
NÍ 14320	Teigarhorn	Fridriksson et al. (2004, 2009)	1202	58485	−2.01
NÍ 14692	Oddskard	Fridriksson et al. (2004, 2009)	928	15329	−1.79
NÍ 1582	Teigarhorn	Fridriksson et al. (2004, 2009)	857	24640	−1.83
Heul A	Teigarhorn	Fridriksson et al. (2004)	685	23164	−2.24
R4133	Berufjord	Smithsonian Institution	1262	28434	−1.72
Stilbite					
NÍ 14692	Oddskard	Fridriksson et al. (2004, 2009)	1363	27.0	−1.07 (−1.06)
NÍ 10784	Djúpidalur	Fridriksson et al. (2009)	538	358	−1.32
Búlandstindur	Búlandstindur	Fridriksson et al. (2009)	1391	24.6	−0.69
BF-10	Teigarhorn	Fridriksson et al. (2001)	153	18.5	−0.90
B17602	Teigarhorn	Smithsonian Institution	1369	12.8	−0.68

Duplicate analyses are provided in ().

resin to isolate Ca from K and other matrix elements. After drying the purified fractions, two drops of 35% H_2O_2 were added to oxidize organic compounds, and two drops of concentrated 16N HNO_3 were added to convert Ca to nitrate form. Approximately 10–16 μg of Ca was loaded onto single filament assemblies containing degassed Ta ribbon, and 0.5 mg of 10% H_3PO_4 was added before drying at 3.5 amps. Ultrapure reagents were used for all steps, and procedural blanks were negligible. Sample to blank ratios were ~500:1 or better. In the mass spectrometer, a 20V ^{40}Ca ion beam was attained after a 0.5 hr warm-up, and $^{40}Ca/^{42}Ca$, $^{43}Ca/^{42}Ca$, and $^{43}Ca/^{44}Ca$ ratios were measured with a three-hop collector cup configuration for a total of 90 duty cycles requiring an additional 2.5 h. The ^{41}K beam was monitored during the first hop to ensure that ^{40}K did not isobarically interfere with ^{40}Ca. No corrections were required. Runs were carefully monitored to ensure the absence of significant filament reservoir effects, which can manifest as reverse fractionation in the uncorrected ratios and/or trends in the corrected ratios, after processing through the double-spike data reduction equations. Data were corrected for changes in collector cup efficiency (drift) following the protocol discussed in Lehn et al. (2013). All sample (SMP) $^{44}Ca/^{40}Ca$ ratios are reported in delta notation relative to OSIL seawater (SW), where $\delta^{44/40}Ca = [(^{44}Ca/^{40}Ca)_{SMP}/(^{44}Ca/^{40}Ca)_{SW} - 1] \times 1000$. The internal precision of the measurements was ±0.02–0.03‰ ($2\sigma_{SEM}$). During the period of analysis, OSIL SW and NIST SRM 915b were repeatedly analyzed to assess accuracy and reproducibility. The results are $\delta^{44/40}Ca_{SW} = 0.000 ± 0.008‰$ ($2\sigma_{SEM}$, $n = 36$) and $\delta^{44/40}Ca_{915b} = -1.126 ± 0.012‰$ ($2\sigma_{SEM}$, $n = 7$). These data correspond to an external reproducibility ($2\sigma_{SD}$) of ±0.046‰ for OSIL

SW and ±0.031‰ for NIST SRM 915b. The short-term results agree well with long-term data collected over the past two years: $\delta^{44/40}Ca_{SW} = 0.000 ± 0.003‰$ ($2\sigma_{SEM}$, $n = 273$), $\delta^{44/40}Ca_{915a} = -1.862 ± 0.006‰$ ($2\sigma_{SEM}$, $n = 55$), and $\delta^{44/40}Ca_{915b} = -1.129 ± 0.004‰$ ($2\sigma_{SEM}$, $n = 135$). The long-term data correspond to an external reproducibility ($2\sigma_{SD}$) of ±0.042‰ for OSIL SW, ±0.045‰ for NIST SRM 915a, and ±0.045‰ for NIST SRM 915b. Based on all of these results, we adopt a global, $2\sigma_{SD}$ uncertainty of ±0.04‰ for the present dataset, which is identical to the value determined in Lehn et al. (2013). Although the Lehn et al. (2013) method consistently yields excellent results for OSIL SW (a matrix-rich standard), we analyzed a few duplicates of randomly selected samples, mostly waters and one mineral, to confirm that the uncertainty determined from the repeated analysis of standards can be used as a proxy for the uncertainty assigned to matrix-rich samples. For a $2\sigma_{SD}$ uncertainty of ±0.04‰, results could in theory differ by 0.08‰, but as shown in the data tables, duplicates differ by only 0.04‰ or less.

4. Results

Table 1 provides results for the water samples, and Table 2 provides results for the rock and mineral samples. Fig. 2 illustrates the ionic composition of the water samples. $(Na^+ + K^+)$ dominates the cationic charge. In general, $(Na^+ + K^+)$ dominates the cationic charge of groundwater, and Ca^{2+} dominates in glacial rivers. Non-glacial rivers display roughly equal contributions from Ca^{2+} and Mg^{2+}. Bicarbonate (HCO_3^-) dominates the anionic charge. A few groundwater samples show higher contributions from SO_4^{2-}. All
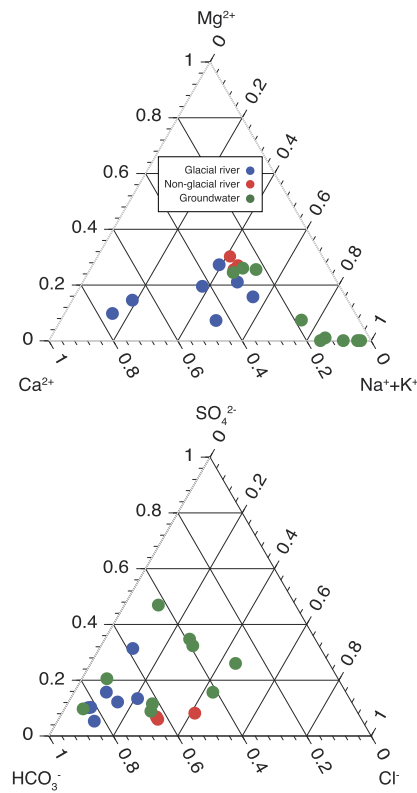
Fig. 2. Ternary diagrams showing the major cation and the major anion composition (in equivalents) of Icelandic glacial rivers, non-glacial rivers, and groundwater.

river samples and most groundwater samples are undersaturated with respect to calcite. Two groundwater samples with elevated temperatures are near equilibrium with respect to calcite, and two samples with the highest temperatures are supersaturated. Many Icelandic rivers contain small amounts of atmospherically derived Ca (Gislason et al., 1996; Hindshaw et al., 2013a). Although dissolved Cl can be employed to correct riverine Ca concentrations for atmospheric inputs, Icelandic precipitation contains a small, unidentified source of Ca (Gislason et al., 1996) with an unknown isotopic composition (Hindshaw et al., 2013a). For this reason, and because the impact of atmospheric deposition on riverine $\delta^{44/40}$Ca values is predictably negligible (Hindshaw et al., 2013a), no corrections were made.

On a plot of $\delta^{44/40}$Ca versus Sr/Ca, the most noticeable observation is that heulandite has much lower $\delta^{44/40}$Ca values and higher Sr/Ca ratios compared to all other samples (Figs. 3A and B). Heulandite has an average $\delta^{44/40}$Ca value of $-1.92 \pm 0.20\text{‰}$ ($1\sigma_{SD}$) and an average Sr/Ca of 30.1 ± 12.3 nmol/µmol ($1\sigma_{SD}$). Calcite and stilbite are indistinguishable. Calcite has an average $\delta^{44/40}$Ca value of $-0.82 \pm 0.18\text{‰}$ ($1\sigma_{SD}$) and an average Sr/Ca of 0.0652 ± 0.0567 nmol/µmol ($1\sigma_{SD}$). Stilbite has an average $\delta^{44/40}$Ca value of $-0.93 \pm 0.27\text{‰}$ ($1\sigma_{SD}$) and an average Sr/Ca of 0.167 ± 0.565 nmol/µmol ($1\sigma_{SD}$). One basalt sample, a basaltic andesite, has a relatively high Sr/Ca ratio (3.73 nmol/µmol) compared to the other samples, which are tholeiites. Nevertheless, the average Sr/Ca ratio of 1.39 ± 1.18 nmol/µmol ($1\sigma_{SD}$) agrees with average ratios reported elsewhere: 1.08 nmol/µmol (Hindshaw et al., 2013a) and 1.37 nmol/µmol (Fridriksson et al., 2009). Likewise, the average $\delta^{44/40}$Ca value of $-1.07 \pm 0.01\text{‰}$ ($1\sigma_{SD}$), agrees with the value of $-1.05 \pm 0.09\text{‰}$ ($2\sigma_{SEM}$) for BIR-1 reported by Amini et al. (2009). BIR-1 is a USGS standard reference material prepared from Icelandic basalt. Plagioclase and clinopyroxene are the predominant mineralogical reservoirs of Ca and Sr in basalt. For basalts from the Skagafjördur region, calculations suggest that plagioclase Sr/Ca ratios range from 1.72 to 3.77 nmol/µmol, while
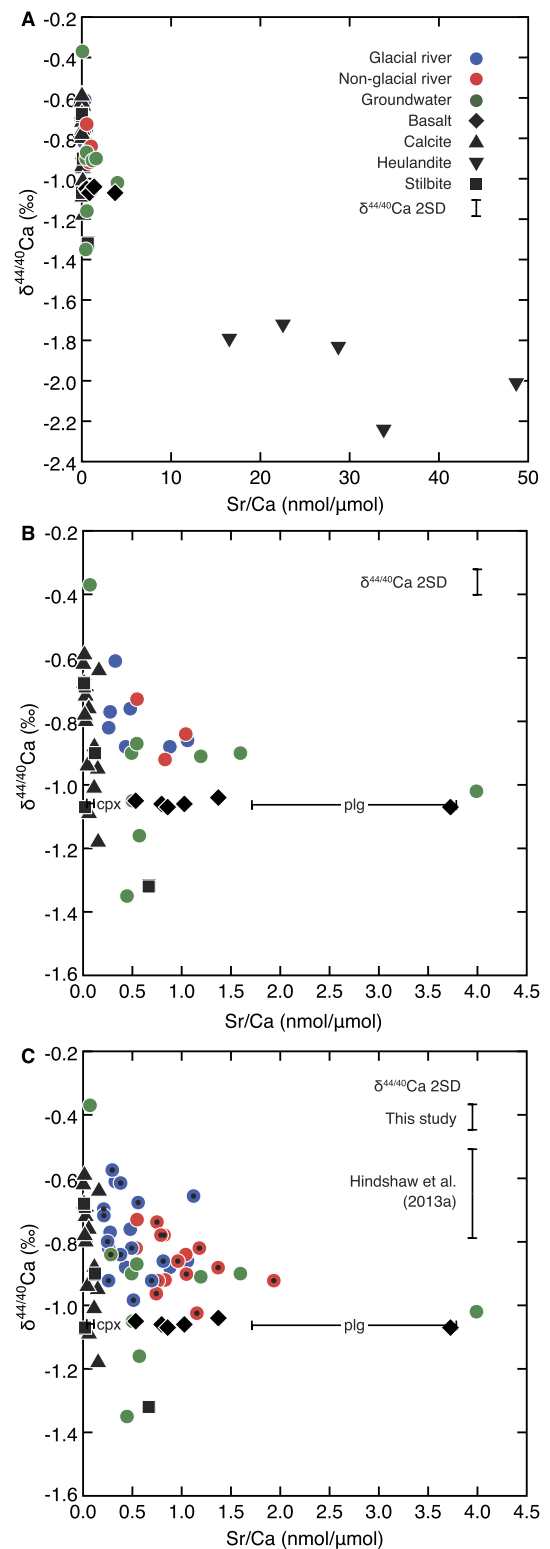
Fig. 3. $\delta^{44/40}$Ca versus Sr/Ca for Icelandic waters, rocks, and minerals. A and B show data measured in the present study. B and C are an inset of A. C includes river and groundwater data reported in Hindshaw et al. (2013a). Symbols for the Hindshaw et al. (2013a) data are denoted with a black dot. Sr/Ca ratios for plagioclase (plg) and clinopyroxene (cpx) are taken from Fridriksson et al. (2009). $\delta^{44/40}$Ca values for plg and cpx reflect the average for bulk Icelandic basalt. See text.

clinopyroxene has a Sr/Ca ratio of 0.0730 nmol/µmol (Fridriksson et al., 2009). Fig. 3B includes data points for these minerals, assuming they have $\delta^{44/40}$Ca values equivalent to the average for basalt, which seems reasonable given that the basalts display no isotopic

variability despite obvious differences in their Sr/Ca ratios. For water samples, Sr/Ca ratios are generally less than or equal to those for basalt, while $\delta^{44/40}$Ca values are higher than those for basalt but no higher than those for calcite and stilbite.

To facilitate discussion of the results, we re-plot data in Fig. 3B together with results reported in Hindshaw et al. (2013a) (Fig. 3C). Hindshaw et al. (2013a) also employed TIMS but measured $\delta^{44/42}$Ca values relative NIST SRM 915a, whereas we measured $\delta^{44/40}$Ca values relative to OSIL SW. To convert the Hindshaw et al. (2013a) data to the seawater scale, first we subtracted 0.95‰, which is the $\delta^{44/42}$Ca value that the authors reported for seawater relative to SRM 915a. Second, we divided the $\delta^{44/42}$Ca values by 0.488, which assumes that all isotopic variation is mass-dependent and follows a kinetic (exponential) law (e.g., Ryu et al., 2011). This assumption is reasonable because significant radiogenic ^{40}Ca enrichments are not expected for K-poor, relatively young Icelandic basalts, and mass fractionation in nature (as well as in the mass spectrometer) is mostly kinetic (Russell et al., 1978; Holmden et al., 2012). Hindshaw et al. (2013a) reported an external reproducibility ($2\sigma_{SD}$) of 0.07‰. Converted to the $\delta^{44/40}$Ca scale, the error bars are thus ±0.14‰. The two datasets agree well. Including the Hindshaw et al. (2013a) dataset shows that glacial rivers tend to have higher $\delta^{44/40}$Ca values and lower Sr/Ca ratios than non-glacial rivers.
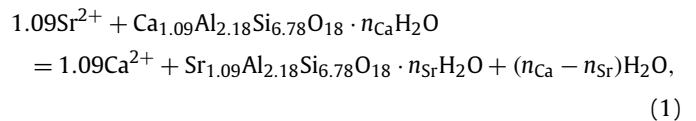
5. Discussion

While there are many potential explanations for the riverine data, several are easy to eliminate. For example, atmospheric deposition, plant growth, and calcite precipitation are unlikely candidates because atmospheric inputs of Ca are negligible (Hindshaw et al., 2013a), watersheds are largely unvegetated (Hindshaw et al., 2013a and this study), and rivers are undersaturated with respect to calcite (Hindshaw et al., 2013a and Table 1). Similarly, no studies have documented Ca isotope fractionation during mineral dissolution. According to the one hydrothermal water sample analyzed by Hindshaw et al. (2013a), conservative mixing between Ca from basalt weathering and hydrothermal water could elevate $\delta^{44/40}$Ca values. However, because the riverine data plot close to the presumed hydrothermal water end-member, this hypothesis implies that all rivers receive the vast majority of their dissolved Ca from hydrothermal sources. While Iceland experiences pervasive geothermal activity, and studies have identified the importance of hydrothermal inputs to specific rivers and small catchments (Gislason et al., 1996), it is difficult to justify that all rivers are affected. Hindshaw et al. (2013a) ultimately rejected this hypothesis based on a Li isotope study showing that hydrothermal water contributions to rivers are on the order of $\sim$1% by volume (Vigier et al., 2009). Given the relatively modest Ca concentration of hydrothermal water and the small isotopic contrast between basalt and hydrothermal water, 1% inputs are insufficient to explain the observed patterns. Similar studies focused on Mg isotopes also suggest minimal contributions from hydrothermal water (von Pogge Strandmann et al., 2008). The new data reported here show that groundwater is compositionally variable across Iceland and mostly plots in the same field as rivers (Figs. 3B and C). Accordingly, there is no unique hydrothermal end-member. Lastly, glacial rivers have lower Sr/Ca ratios and higher $\delta^{44/40}$Ca values than all but one groundwater sample, which further implies that direct hydrothermal Ca inputs are negligible.

5.1. The fractionation hypothesis

Having ruled out hydrothermal groundwater inputs as a factor controlling riverine $\delta^{44/40}$Ca values, Hindshaw et al. (2013a) ultimately concluded that secondary Ca-bearing minerals, such as

clays and zeolites, fractionate Ca isotopes as well as Ca/Sr ratios. Indeed, nearly all of the rivers analyzed by Hindshaw et al. (2013a) are supersaturated with respect to Ca-montmorillonite and laumonite, a common zeolite, and we can reasonably assume the same applies to the samples analyzed in the present study. Formation of smectite, as well as kaolinite and illite, may fractionate Ca isotopes (Ockert et al., 2013), and as shown here, the zeolitite mineral heulandite has very low $\delta^{44/40}$Ca values, consistent with the preferential incorporation of ^{40}Ca. Previous work by Fridriksson et al. (2009) has demonstrated that heulandite also has a high affinity for Sr and can dramatically lower Sr/Ca ratios in Icelandic groundwater via the following equilibrium, ion-exchange reaction:

$$1.09Sr^{2+} + Ca_{1.09}Al_{2.18}Si_{6.78}O_{18} \cdot n_{Ca}H_2O$$
$$= 1.09Ca^{2+} + Sr_{1.09}Al_{2.18}Si_{6.78}O_{18} \cdot n_{Sr}H_2O + (n_{Ca} - n_{Sr})H_2O,$$

$$(1)$$

where nCa and nSr are the stoichiometric coefficients of water in homoionic Ca- and Sr-heulandites, respectively. Experiments are required to determine the magnitude of the Ca isotope fractionation factor associated with Eq. (1), but assuming that heulandite initially has a basaltic $\delta^{44/40}$Ca value, the effect could be on the order of $\sim$1–2‰. Regardless of the exact fractionation factor, heulandite formation could explain why rivers have higher $\delta^{44/40}$Ca values and lower Sr/Ca ratios compared to basalt.

Hindshaw et al. (2013a) offered several additional observations to support the fractionation hypothesis. For example, $\delta^{44/42}$Ca values for glacial rivers were found to follow a Rayleigh-type fractionation law, where clays, zeolites, and/or mineral surfaces removed 90% of the weathering-derived Ca, with a preference for ^{42}Ca over ^{44}Ca. Noting a positive correlation between $\delta^{44/42}$Ca values and suspended sediment concentrations, which serve as proxy for discharge, the authors attributed Ca isotope variations within and between glacial catchments to "reservoir effects" (Tipper et al., 2012). According to this idea, removal of Ca will have a larger isotopic effect on a dilute pool of Ca versus a more concentrated pool. Higher suspended concentrations may also provide more surface area to facilitate Ca adsorption and attendant isotope fractionation. However, $\delta^{44/42}$Ca values for non-glacial rivers did not conform to a Rayleigh-type fractionation law, nor did the authors observe a correlation between $\delta^{44/42}$Ca values and suspended sediment concentrations. Hindshaw et al. (2013a) attributed differences between non-glacial and glacial rivers to differences in the weathering systematics of crystalline versus glassy basalt. Non-glacial rivers drain older, crystalline basalt, whereas glacial rivers drain younger, glassy basalt. The authors proposed that the assemblage of secondary minerals might differ between non-glacial and glacial catchments and that mixing and back reactions with secondary minerals formed during dissolution of crystalline basalt might explain the lack of evidence for Rayleigh-type fractionation in non-glacial rivers.

5.2. The mixing hypothesis

Here, we propose an alternative hypothesis to explain the variability of $\delta^{44/40}$Ca values and Sr/Ca ratios in Icelandic rivers, and in particular, the contrast between glacial and non-glacial rivers. It is based on the possibility of conservative mixing of Ca and Sr ions released during the chemical weathering of basalt and calcite. Mixtures of two components in Fig. 3 define straight lines. There is, however, more than one potential mixing line between basalt and calcite. This is due to the variability of calcite $\delta^{44/40}$Ca values on one hand, and the variability of basalt Sr/Ca ratios on the other. Most likely, the Sr/Ca ratios released by silicate weathering depend on the relative contributions from plagioclase and clinopyroxene. Variations are expected given that the modal abundances
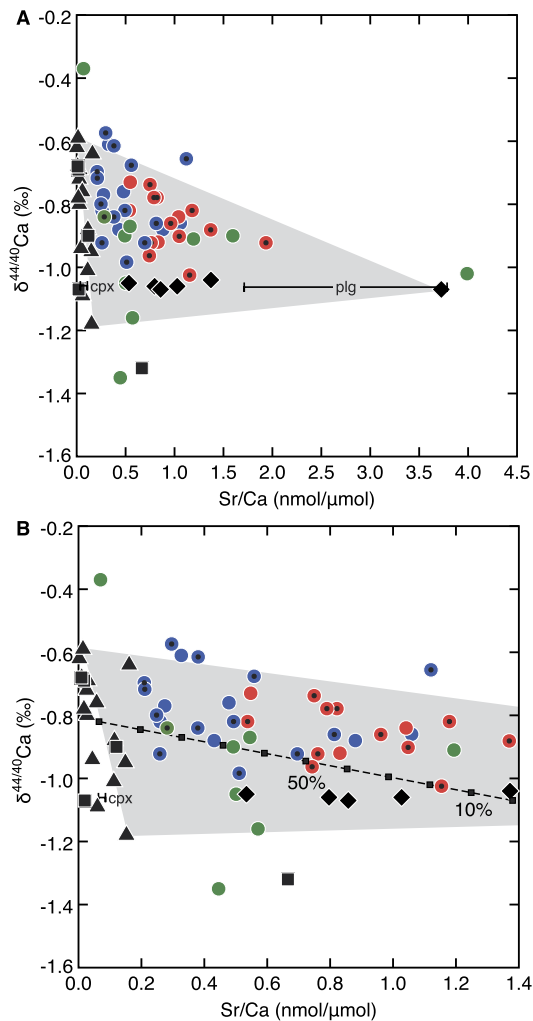
Fig. 4. $\delta^{44/40}$Ca versus Sr/Ca for Icelandic waters, rocks, and minerals. Symbols and error bars are identical to Fig. 3. Note that A and B have different x-axis scales. The shaded region represents a mixing domain defined by the range of data for basalt and calcite. B includes a two-component mixing line connecting the average values for basalt and calcite. The percentages denote contributions of riverine Ca from calcite weathering. See text.

and compositions of plagioclase and clinopyroxene differ among different basalt flows. Considering this variability, a population of potential mixing lines can be drawn, which collectively define a triangular mixing domain (Fig. 4A). The bulk of the riverine samples (both glacial and non-glacial) and most groundwater samples plot within the proposed mixing domain.

Several studies have demonstrated that the weathering of small amounts of calcite, even as low as ~0.1 wt%, in granite and other felsic silicates can dominate riverine Ca loads (Mast et al., 1990; Clow and Drever, 1996; Blum et al., 1998; Jacobson et al., 2003; Oliva et al., 2004; Moore et al., 2013), so it is not surprising that the higher amounts of calcite in Icelandic basalt might have a similar, if not greater, impact. Given the rapid dissolution rate and high solubility of calcite, significant contributions from stilbite dissolution are not expected. Differences in mechanical erosion rates readily explain the distinction between glacial and non-glacial watersheds. High mechanical erosion rates characteristic of glacial watersheds are well known to enhance the exposure and weathering of trace calcite (e.g., Raiswell and Thomas, 1984; Anderson et al., 2000). The correlation between glacial meltwater discharge, suspended sediment concentrations, and $\delta^{44/40}$Ca values, which Hindshaw et al. (2013a) attributed to fractionation during Ca adsorption to mineral surfaces and "reservoir effects," can also

be explained through variations in the relative mixing proportions between basalt and calcite, with periods of higher discharge representing higher erosion rates and thus more calcite exposure. We interpret scatter among the river water data to reflect heterogeneity in the Ca and Sr geochemistry of calcite and basalt end-members from watershed to watershed, as discussed above. If Ca isotope fractionation is occurring, then the effects are smaller than the domain of potential mixtures and cannot be resolved.

Two-component mixing equations are required to calculate the exact proportions of riverine Ca from basalt and calcite. However, the calculations are prone to large uncertainties because the mixing end-members vary. Nonetheless, we can attempt to make some semi-quantitative arguments assuming that Ca and Sr behave conservatively. The mixing line plotted in Fig. 4B connects the average values for basalt and calcite reported above and shows theoretical percentages of riverine Ca originating from calcite weathering. The percentages were calculated using the following standard, two-component mixing equations (e.g., Moore et al., 2013):

$$(\text{Sr/Ca})_m = f_c (\text{Sr/Ca})_c + (1 - f_c)(\text{Sr/Ca})_b \tag{2}$$

$$\delta^{44/40}\text{Ca}_m = f_c \delta^{44/40}\text{Ca}_c + (1 - f_c)\delta^{44/40}\text{Ca}_b, \tag{3}$$

where f is the mole fraction of Ca, and the subscripts m, c, and b refer to the mixture, calcite, and basalt, respectively. By orthogonally extrapolating measured data points to the nearest position on the mixing line, we can roughly estimate actual percentages that apply to the river water samples. Calcite weathering contributes anywhere from none to practically all of the riverine Ca. In slightly more specific terms, we find that calcite weathering supplies ~0–65% of the Ca in non-glacial rivers and ~25–90% of the Ca in glacial rivers. Employing different $\delta^{44/40}$Ca values for the calcite end-member does not substantially change the interpretation. Employing lower Sr/Ca ratios for basalt reduces the calcite weathering contribution, but this does not seem particularly realistic as it eliminates calcite weathering as a factor influencing non-glacial rivers. It follows that implementing higher Sr/Ca ratios for basalt increases the calcite weathering contribution. Although highly general, we note that our average estimates are consistent with the application of a conventional Ca/Si mass-balance method showing that calcite weathering contributes ~45–80% of the Ca in Icelandic glacial rivers (Georg et al., 2007). Given that hydrothermal calcite contains mantle carbon (Arnorsson and Barnes, 1983; Marty et al., 1991; Arnórsson, 1995, 2014; Barry et al., 2014), these results imply that riverine Ca and alkalinity fluxes, especially from glacial watersheds, should be corrected for calcite weathering contributions before calculating long-term atmospheric CO_2 consumption rates.

5.3. Role of heulandite and clays?

If the Ca isotope geochemistry of Icelandic rivers reflects the mixing of Ca from basalt and calcite weathering, then the question arises what role, if any, does Ca isotope fractionation by heulandite play? The progressive burial of basalt during its formation results in low-grade zeolite facies metamorphism in deeper parts of the volcanic pile (Walker, 1960; Saemundsson et al., 1980; Steinthórsson et al., 1987; Neuhoff et al., 1999, 2000). This type of burial metamorphism, which has been well documented, yields depth-controlled and regionally extensive "zeolite zones" defined by the predominance of specific zeolite minerals (Walker, 1960; Saemundsson et al., 1980; Steinthórsson et al., 1987; Neuhoff et al., 1999, 2000; Weisenberger and Selbekk, 2009). The zeolites, along with calcite and other secondary minerals, fill primary porosity and partially replace primary phases. Importantly, the stilbite-heulandite zone occurs at temperatures between 90 and 110 °C, relatively deep in the pile (Kristmannsdóttir and Tómasson, 1978),

and the geochemistry of heulandite and groundwater indicate that the ion-exchange reaction (Eq. (1)) occurs at temperatures between 55 and 85 °C (Fridriksson et al., 2009).

The location of heulandite formation, the mineral's ability to fractionate Sr/Ca and $^{44}Ca/^{40}Ca$ ratios during ion-exchange, and the relatively high temperature at which the reaction occurs all suggest a predominant control on groundwater (especially hydrothermal) rather than river water. We are unaware of any studies reporting formation of heulandite in soils or beneath glaciers. Any occurrence of heulandite in glacial sediment may reflect that glaciers have incised downward into previously metamorphosed basalt (Neuhoff et al., 2000). We hypothesize that the residual ^{44}Ca-enriched reservoir produced by ion-exchange with heulandite largely determines the isotopic composition of stilbite and calcite, which occur in association with heulandite and with each other (Fridriksson et al., 2001, 2009). However, it is difficult to discern whether stilbite and calcite directly record the isotopic composition of hydrothermal groundwater or impart their own fractionation effects. Iceland supports shallow and deep groundwater systems that can interact in complex ways (Arnórsson et al., 2007), and we do not have sufficient information to determine the origin and history of the groundwater samples analyzed. Some samples with cool temperatures may represent water that exclusively circulated through soils and the shallow subsurface, whereas others could reflect water that was once hydrothermal. Nonetheless, we tentatively suggest that the extent of Ca isotope fractionation among heulandite, stilbite, and calcite correlates with their relative affinities for Ca. Heulandite has an extremely low affinity for Ca and preferentially incorporates lighter Ca isotopes. Because stilbite and calcite have higher affinities for Ca, these minerals may be less isotopically selective by comparison.

Finally, a related question pertains to the role of clay minerals. Ion-exchange on clay mineral surfaces fractionates Ca isotopes in marine porewaters (Ockert et al., 2013), and there is some evidence suggesting a similar phenomenon occurs in aquifers (Jacobson and Holmden, 2008). However, we are unaware of any studies conclusively demonstrating the contribution of clays to the Ca isotope geochemistry of rivers. In Iceland, clays do not strongly partition Ca from Sr, and there is no evidence that Ca and Sr exhibit different mobilities as a function of bedrock age (Fridriksson et al., 2009). Also, the lack of Si isotope fractionation in some Icelandic watersheds suggests that the extent of clay mineral formation is insufficient to impact dissolved elemental budgets (Georg et al., 2007). Even in watersheds where clay minerals remove ~50% of the Si released by weathering, the corresponding loss of Ca is only ~0 to 5% (Georg et al., 2007), which is much lower than the estimate of 90% inferred from the Ca isotope fractionation hypothesis presented by Hindshaw et al. (2013a).

6. Conclusions and implications

Two studies (Hindshaw et al., 2013a and the present study) have shown that Icelandic rivers have higher $\delta^{44/40}Ca$ values compared to basaltic bedrock. Hindshaw et al. (2013a) attributed the pattern to isotope fractionation during formation of zeolites and clays, as well as Ca adsorption onto mineral surfaces. Indeed, as reported here, the zeolite heulandite has very low $\delta^{44/40}Ca$ values compared to basalt. We, on the other hand, attribute the pattern to conservative mixing of Ca released during the weathering of basalt and hydrothermal calcite. We suggest that the Ca isotope composition of heulandite reflects the preferential incorporation of ^{40}Ca during equilibrium isotope exchange at hydrothermal temperatures, and we go on to propose that the residual ^{44}Ca-enriched waters determine the $\delta^{44/40}Ca$ values of hydrothermal calcite, which are higher than those for basalt. In other words, fractionation and mixing are not mutually exclusive processes. We find

that high temperature Ca isotope fractionation at depth establishes conditions where mixing controls isotopic variability at the surface.

If correct, the mixing hypothesis could have several implications. For example, much emphasis has been placed on quantifying Ca isotope fractionation factors, but isotopic differences between surface runoff and bedrock do not necessarily imply mass-dependent fractionation during weathering. In terrestrial systems, only two mechanisms are known to fractionate Ca isotopes: plant growth (e.g. Wiegand, 2005; Holmden and Bélanger, 2010; Bagard et al., 2013; Hindshaw et al., 2013b; Schmitt et al., 2013) and calcite precipitation (e.g., Tipper et al., 2006). Plant growth only seems to mask the underlying elemental and isotopic patterns attributable to silicate and carbonate weathering at the watershed scale, which can be corrected under favorable circumstances (Moore et al., 2013). Very good evidence exists that secondary calcite formation fractionates Ca isotopes in watersheds draining carbonate bedrock (Tipper et al., 2006), but the striking similarity between the data presented here and in Moore et al. (2013) implies a different scenario for silicate watersheds, especially those with accessory calcite. Three basic observations collectively identify mixing as the dominant control: carbonate minerals are more soluble and dissolve faster than silicate minerals (e.g., Lerman and Wu, 2008), the weathering of accessory calcite has been repeatedly demonstrated to affect the geochemistry of rivers draining silicate watersheds (e.g., Garrels and Mackenzie, 1967; Drever and Hurcomb, 1986; Mast et al., 1990; Clow and Drever, 1996; Blum et al., 1998; Jacobson et al., 2003; Oliva et al., 2004; Moore et al., 2013), and accessory calcite has higher $\delta^{44/40}Ca$ values and lower Sr/Ca ratios compared to Ca-bearing silicate minerals (Table 2; Ryu et al., 2011; Moore et al., 2013), although factors controlling the Ca isotope composition of metamorphic calcite merit further investigation.

Fantle and Tipper (2014) recently estimated that the $\delta^{44/40}Ca$ value for the global riverine flux is ~0.20 to 0.25‰ higher than expected, based on their literature review of the average $\delta^{44/40}Ca$ values for carbonate and silicate rocks and the proportions of Ca in global runoff attributed to carbonate and silicate weathering. This apparent discrepancy has been used to argue that an unknown fractionation mechanism must exist because according to the authors, there is no evidence for the importance of mixing at a global scale. However, with mixing identified as the predominant control in two very different settings – a basaltic island (this study) and an uplifting mountain range comprising schist and greywacke (Moore et al., 2013) – a case can be made for the opposite scenario. The fractionation hypothesis assumes that the Ca isotope composition of silicate rocks accurately represents the contribution of silicate weathering to the $\delta^{44/40}Ca$ value of the global riverine flux. However, as demonstrated here and in Moore et al. (2013), the $\delta^{44/40}Ca$ value of rivers draining silicate rocks is a few tenths of a per mil higher than the $\delta^{44/40}Ca$ value of silicate bedrock because much of the Ca originates from the dissolution of accessory calcite, which has even higher $\delta^{44/40}Ca$ values than rivers. Of the many studies that have attempted to identify trace calcite in silicate rocks, we are aware of only one that produced a negative result (de Souza et al., 2010).

Finally, given that Ca is a key crustal element involved in the drawdown of atmospheric CO_2, one higher order aim of Ca isotope research is to illuminate how the long-term carbon cycle works. While basaltic terrains represent only about 5% of the continental surface area, basalt weathering may compose 30–35% of the global, atmospheric CO_2 consumption flux (Dessert et al., 2003). Much of the significance attributed to basalt weathering reflects the assumption that contributions from carbonate weathering are negligible to nonexistent, but application of the Ca isotope tracer suggests otherwise. Our data indicate that up to 90% of the Ca in Icelandic rivers originates from the weathering of

hydrothermal calcite as opposed to Ca-bearing silicate minerals. Because the carbon in Icelandic calcite originates from the mantle rather than the atmosphere (Arnorsson and Barnes, 1983; Marty et al., 1991; Arnórsson, 1995, 2014; Barry et al., 2014), it seems likely that atmospheric CO_2 consumption estimates based on riverine Ca and alkalinity fluxes are lower than previously proposed. Given that zeolite facies metamorphism, hydrothermal fluid circulation, and calcite precipitation are ubiquitous characteristics of basaltic eruptions, our findings for Iceland may apply generally to other basaltic settings. If true, then basaltic terrains may not necessarily represent atmospheric CO_2 consumption "hot spots". After accounting for the calcite weathering contribution, long-term CO_2 drawdown rates could be more similar to those for granite, all else being equal. Similarly, it remains widely perceived that high mechanical erosion rates in rapidly uplifting mountain ranges inherently equate to the rapid drawdown of atmospheric CO_2 by silicate weathering (e.g., Larsen et al., 2014), but Ca isotope data reveal that long-term atmospheric CO_2 consumption rates in such environments are not significantly elevated above those for tectonically stable areas (Moore et al., 2013). Thus, if neither lithological variations nor tectonic uplift can dramatically alter the global atmospheric CO_2 flux, then the question remains what mechanisms, if any, could? By process of elimination, internal climatic feedbacks emerge as a compelling candidate. In particular, the relationship between atmospheric CO_2 concentrations, temperature, and the hydrologic cycle could be important (Li et al., 2014; Maher and Chamberlain, 2014). High atmospheric CO_2 concentrations elevate temperature, leading to a more vigorous hydrologic cycle, which in turn promotes more extensive silicate weathering and deeper regolith development. As atmospheric CO_2 concentrations decline, the hydrologic cycle feedback diminishes. Tectonically stable cratons and areas experiencing minimal hydrothermal activity are predicted to play the most important role because they lack appreciable contributions from calcite weathering.

Acknowledgements

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