1   **Quantifying the impact of riverine particulate dissolution in seawater on**

2   **ocean chemistry**

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15

16   **Abstract**

17   The quantification of the sources and sinks of elements to the oceans forms the basis of our

18   understanding of global geochemical cycles and the chemical evolution of the Earth's surface.

19   There is, however, a large imbalance in the current best estimates of the global fluxes to the

20   oceans for many elements. In the case of strontium (Sr), balancing the input from rivers would

21   require a much greater mantle-derived component than is possible from hydrothermal water flux

22   estimates at mid-ocean ridges. Current estimates of riverine fluxes are based entirely on

23   measurements of dissolved metal concentrations, and neglect the impact of riverine particulate

24   dissolution in seawater. Here we present ^{87}Sr/^{86}Sr isotope data from an Icelandic estuary, which

25   demonstrate rapid Sr release from the riverine particulates. We calculate that this Sr release is

26   1.1-7.5 times greater than the corresponding dissolved riverine flux. If such behaviour is typical

27   of volcanic particulates worldwide, this release could account for 6-45 % of the perceived marine

28   Sr budget imbalance, with continued element release over longer timescales further reducing the

29   deficit. Similar release from particulate material will greatly affect the marine budgets of many

30   other elements, changing our understanding of coastal productivity, and anthropogenic effects

31   such as soil erosion and the damming of rivers.

32

33   **1. Introduction**

34   Continental weathering and erosion is the primary control on the transport of material from the

35   continents to the oceans, and a major component of the cycles of many elements on the Earth's

36   surface. The riverine flux of material from continental weathering is the dominant input of many

37   elements to the oceans. Ocean chemistry is commonly modelled as a combination of these

38   riverine fluxes, hydrothermal exchange at mid-ocean ridges, and sedimentation coupled to burial

39   (Riley & Chester, 1971). Strontium is among the best constrained of the global element cycles

40   over geologic time due to the facility of measuring its isotopic composition, its significant

41   temporal isotope variations, and its preferential incorporation into marine carbonates. The ratio

42   between the radiogenic ^{87}Sr (a product of the decay of ^{87}Rb) and stable ^{86}Sr isotopes increases

43   with the age of the rock substrate. The ^{87}Sr/^{86}Sr isotope composition and Sr concentrations of

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the open oceans is currently homogenous at ~0.7092 (Elderfield, 1986) and ~7.85 mg/L (Bernat et al., 1972), respectively, as the residence time of Sr greatly exceeds the rate of ocean mixing (Broecker & Peng, 1982). This value reflects a balance in inputs and outputs between radiogenic Sr derived from the continents and unradiogenic Sr from mantle-derived material. While spatially homogenous at current levels of precision, seawater $^{87}Sr/^{86}Sr$ has varied significantly over geological time (e.g. Veizer et al., 1999). These changes to seawater $^{87}Sr/^{86}Sr$ have been used to infer changes in inputs and outputs to the oceans in response to climatic and/or tectonic forcings over geological time (e.g. McArthur et al., 2001); although this is contentious (Palmer & Edmond, 1992; Oliver et al., 2003). Strontium isotope compositions have also been used as tracers of inputs from different river catchments into intra-continental seas (Andersson et al., 1991).

Seawater $^{87}Sr/^{86}Sr$ has been increasing at a rate of 0.000054 Myr^{-1} in the Neogene and Pleistocene (Henderson et al., 1994; Hodell et al., 1989). There is a current discrepancy in our scientific understanding of the global Sr cycle, as mass balance calculations indicate that the current input of radiogenic Sr from the continents, assumed to only be transported in dissolved form to the oceans, cannot be balanced by unradiogenic Sr originating from hydrothermal exchange with oceanic crust to satisfy the observed rate of $^{87}Sr/^{86}Sr$ change. The global average dissolved riverine $^{87}Sr/^{86}Sr$ input is approximately 0.7136 (Allègre et al., 2010) while Sr liberated during hydrothermal exchange has a ratio of 0.7029 (Albarède et al., 1981). To balance the input from the world's rivers, the hydrothermal flux would need to be 4-20 times higher than current estimates (Davis et al., 2003; Hodell et al., 1989; Palmer and Edmond, 1989; Vance et al., 2009). A number of mechanisms have been proposed to reconcile this apparent flux imbalance. One

67 possibility is a deglacial weathering pulse that has yet to decay, which means that current

68 dissolved riverine measurements would not be representative of the average over a time period

69 greater than glacial/interglacial cycles (Vance et al., 2009). Potential missing fluxes of

70 unradiogenic Sr include groundwater inputs from volcanic terrains (Allègre et al., 2010) and off-

71 axis exchange with oceanic crust (Elderfield and Gieskes, 1982), with the latter considered to be

72 of insufficient magnitude to play a considerable role (Davis et al., 2003).

73

74 Recent estimates suggest that rivers transport between 15-20 Gt yr^{-1} of suspended material to the

75 ocean each year (Peucker-Ehrenbrink et al., 2010; Walling, 2006), considerably greater than the

76 dissolved riverine and aeolian fluxes combined (Oelkers et al., 2011; 2012). Traditionally it has

77 been assumed that this particulate material undergoes little additional weathering in seawater,

78 because dissolution rates are reduced at low temperatures and because burial is thought to rapidly

79 isolate sediment. Nevertheless, some dissolution of riverine particulate material in the oceans is

80 inevitable, depending upon the saturation states of minerals in seawater, particulate surface area,

81 temperature, and prior weathering history. Experimental determinations of basalt dissolution

82 rates covering the pH and temperature range of modern seawater suggest that ~0.05 % of basaltic

83 particulate material could dissolve in seawater each day, with potentially profound impacts on

84 seawater chemistry (Gislason et al., 2006). More recently, laboratory experiments have shown

85 that there is substantial release of both soluble elements (such as Sr) and insoluble elements

86 (such as Nd) from riverine particulates to seawater over a timescale of days to months (Jones et

87 al., 2012a; 2012b; Pearce et al., 2013). Field evidence also indicates that the dissolution of

88 particles is a significant part of the Nd cycle (Lacan and Jeandel, 2005; Arsouze et al., 2009),

89 including large submarine fans such as from the Ganges/Brahmaputra (Singh et al., 2012). For

90 more soluble elements such as Ca, Mg, and Sr, it is more difficult to observe such release in

91 natural environments. This is due to both their elevated concentrations in seawater, which are

92 several orders of magnitude greater than in the water arriving from estuaries, and the effects of

93 contemporaneous precipitation of secondary minerals and ion-exchange as river-transported

94 particles attempt to equilibrate with their new surroundings (Jones et al., 2012a).

95

96 Here we present Sr elemental and isotope (^{87}Sr/^{86}Sr) data for riverine particulates from a basaltic

97 catchment, tracing their pathway from the Hvítá River into the Borgarfjörður Estuary in western

98 Iceland (Fig. 1). This catchment is well suited for the study of seawater-particulate interaction as

99 it has sparse vegetation, poorly developed soils, a stable climate, and a relatively homogenous

100 basaltic geology (c.f. Gislason et al., 1996). High physical erosions rates result in the delivery of

101 readily weathered material with a high surface area. The estuary is < 2 m deep over the first 5

102 km from the river mouth and is consequently tidally-dominated and both vertically and

103 horizontally well mixed. The shallow depth results in a high particulate-water ratio, maximizing

104 both the likelihood of continued particulate weathering, and a detectable chemical response in

105 the estuarine waters. The estuary has a natural narrowing, enhanced by Borgarfjörður Bridge at

106 Borgarnes (Fig. 1); consequently sediment input from outside the catchment is minimal.

107 Previous work on this catchment has demonstrated a distinct difference between the particulate

108 and dissolved compositions of several isotopes and elements including Sr (Jones et al., 2012a;

109 Pearce et al., 2010; 2013; Pogge von Strandmann et al., 2008). Crucially, Li isotope data

110 indicates that the river-derived particulates have experienced weathering in this estuary,

111 including both primary phase dissolution and secondary phase precipitation (Pogge von

112 Strandmann et al., 2008).

113

114   This study focuses on particle dissolution in a volcanic estuary for a number of reasons.

115   Estimates suggest that humid, young, and mountainous regions account for 40% of the global

116   dissolved flux and >60 % of the suspended particulate flux, despite comprising just 14 % of the

117   global drainage area (Milliman and Farnsworth, 2011). Proportionally, volcanic terrains exert a

118   much greater global influence on particulate fluxes to the oceans than expected from their

119   geographical extent, due to the combined effects of high relief, high runoff, the presence of

120   rapidly weathered volcanic rocks, and the absence of sedimentary traps (Milliman and Syvitski,

121   1992). The dissolution rates of primary basaltic minerals are, generally, an order of magnitude

122   or more rapid than those of granitic, metamorphic, or recycled sedimentary minerals (Dupré et

123   al., 2003; Gislason and Oelkers, 2003; Wolf-Boenisch et al., 2004; Gudbrandsson et al., 2012).

124   Moreover, particulate material delivered from volcanic islands typically undergoes little

125   weathering during riverine transport due to rapid transit to the oceans, so they are particularly

126   susceptible to dissolution once they arrive in coastal waters. Hence, elemental release from

127   basaltic particles could potentially account for the imbalances identified in the global cycles of a

128   number of elements. For strontium, the ^{87}Sr/^{86}Sr isotope composition of basaltic particulates is

129   less radiogenic than seawater, and thus may potentially account for at least part of the apparent

130   shortfall in the marine Sr budget.

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132   **2. Methods**

133   *2.1 Sampling*

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Three field excursions were conducted in the Borgarfjörður/Hvítá catchment in 2003, 2008, and 2011. Samples were collected in transects along the estuary across the mixing zone of fresh and saline water at high tide (see Fig. 1). The sampling methods from the 2003 field excursion are summarized in Pogge von Strandmann et al. (2008). This sample suite, collected from the Hvítárvellir Bridge to beyond the estuary mouth, represents a range in salinity from riverine water to close to that of pure seawater. Fluid, suspended particles, and some colloid samples were collected. The 2011 transect also started at Hvítárvellir and collected a higher density of samples across the mixing zone, finishing at the bridge at Borgarnes. Surface water samples were collected at a depth of 30 cm, with the exception of sample Bo8b, which was taken using a Niskin sampler at a depth of 2 m (bottom water at this location). Conductivity and temperature were measured on location. The samples were brought to the laboratory the same day and filtered using a peristaltic pump through a 0.2 μm cellulose acetate membrane filter. The samples were then subdivided prior to analysis. The filters were rinsed through with de-ionized water, dried then weighed to estimate the suspended fraction concentration.

The 2008 transect collected bedload material that has been the focus of previous investigations (Jones et al., 2012a; Pearce et al., 2013). The sample locations matched that of the locations in 2003. In the shallow parts of the river and estuary, samples were collected from exposed sandbanks or using a corer to collect material from the top 20 cm of the sediment. In deeper water, samples were collected using a weighted bucket dragged behind the boat over a distance of ~10 m. Repeat passes were conducted to collect sufficient material, which were then homogenized prior to splitting into sample containers. All samples were dried at 40 °C immediately after collection but no other processing was performed.

2.2 Chemical Analyses

The filters and particulate material were flushed with 1L of de-ionized water and dried at 40 °C before digestion in 20 ml savillex® containers at 120 °C for 72 hours using 2 ml 15M HNO_3. After digestion, samples evaporated to dryness at 75 °C and re-diluted to 2 % HNO_3 prior to elemental analyses. The elemental compositions of these samples after digestion were measured in a Thermo Finnigan® ELEMENT XR at the GET in Toulouse, France. An In Re spike was used for calibration purposes, and the total blank contributions (including blank filters) were negligible for the elements presented in here compared to sample concentrations. Dissolved concentrations of major elements and cations in collected fluid samples were conducted on an ICP-SFMS in ALS laboratories, Sweden. Anion concentrations in these samples were measured using ion chromatography techniques using a Dionex® ICS-2000 in Reykjavík, Iceland.

The $^{87}Sr/^{86}Sr$ ratios of each sample were measured using a VG Sector 54 thermal ionization mass spectrometer (TIMS). Liquid and pre-digested solid samples were evaporated, taken up in 3M HNO_3 and run through Sr-spec columns. The purified Sr was then loaded onto outgassed Ta filaments. The samples were run at ^{88}Sr beam potentials of 2V and 100 ratios were collected using a multi-dynamic peak jumping routine. Resulting $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. Six analyses of the NBS 987 standard yielded an average $^{87}Sr/^{86}Sr$ of 0.710243 ± 0.000010 (2 SD). Individual errors did not exceed ± 0.000012 $^{87}Sr/^{86}Sr$. Total blanks for Sr were found to be negligible compared to the Sr amounts from the samples.

2.3 Mixing Calculations

This study focusses on the Sr isotope compositional evolution in Borgarfjörður estuary as river water mixes with seawater. The ^{87}Sr/^{86}Sr ratio of the estuary water in this system, if it was controlled by the mechanical mixing of two sources (the dissolved Sr present in the river and in seawater) would be given by:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{2comp} = \left(F_{river} \times \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{river}\right) + \left((1 - F_{river}) \times \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{x}\right) \qquad \underline{\quad\quad}(1)$$

where $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{2comp}$ refers to the isotopic ratio expected in the samples based on 2-component mechanical mixing, $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{river}$ refers to the isotopic ratio of the Hvítá river end-member (0.70459), and $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{x}$ refers to the isotopic value of non-riverine derived Sr, which in this case is equal to the isotopic ratio of seawater (^{87}Sr/^{86}Sr$_{sw}$ = 0.709198). f_{river} refers to the fraction of dissolved riverine-derived Sr in the water, calculated from dissolved Cl concentrations:

$$f_{river} = \left(\frac{[Cl]_{est} - [Cl]_{sw}}{[Cl]_{river} - [Cl]_{sw}}\right) \times \left(\frac{[Cl]_{river}}{[Cl]_{est}}\right) \underline{\quad\quad\quad\quad\quad\quad\quad\quad}(2)$$

where the suffixes *est*, *sw* and *river* refer to the estuarine sample, the river end-member, and the seawater end-member, respectively. The first part of the equation calculates the relative masses of the two water bodies, which is effectively ~1 in the low salinity mixing zone. The degree to which the Sr composition of Borgarfjörður estuarywater is consistent with the mechanical mixing of the dissolve Sr in the river and the seawater will be assessed in detail below.

3. Results

The measured element concentrations and $^{87}Sr/^{86}Sr$ ratios of all collected fluids are shown in Table 1. The variation of estuary water Sr concentrations are plotted against the corresponding Cl concentrations in Fig. 2. The solid line in this figure illustrates the mechanical mixing line between river and sea water. Both sample sets plot close to the mechanical mixing line, with a slight suggestion of a net removal of Sr in the low-salinity part of the mixing zone. Note that there is a consistent difference in both elemental concentrations and $^{87}Sr/^{86}Sr$ ratio between the 2003 and 2011 samples at Hvítárvellir, which may indicate a greater input of sea-spray derived Sr into the catchment in the 2003 samples.

The measured estuary fluid $^{87}Sr/^{86}Sr$ ratios are plotted as grey circles a function of the corresponding aqueous Cl concentrations in Fig. 3. The solid curve in this figure illustrates the Sr isotope compositions consistent with the mechanical mixing between river and estuary water as calculated using Eqns. 1 and 2. Although the estuary water total Sr concentrations plotted in Fig. 2 suggest close to conservative mixing of river and sea water, their $^{87}Sr/^{86}Sr$ ratios deviate markedly from simple two-component mixing (Fig. 3). These same $^{87}Sr/^{86}Sr$ ratios are plotted as a function of the fraction of river water component in the estuary water in Fig. 4. The distribution of the symbols shows a clear deviation from the two component mixing line. The difference between the observed and calculated two-component mixing $^{87}Sr/^{86}Sr$ values are consistently more than an order of magnitude greater than the measurement error of ± 0.000012, indicating that this is a robust and sizeable deviation from simple mixing. The difference between the measured estuary water $^{87}Sr/^{86}Sr$ ratios and those estimated from a two component mixing model are shown as a function of the corresponding Cl concentrations in Fig. 5. This $^{87}Sr/^{86}Sr$ deviation is evident from a Cl concentration of approximately 50 mg/L. At its

maximum, the dissolved $^{87}Sr/^{86}Sr$ ratio in the mixing zone is 690 (± 135) and 3460 (± 920) ppm

(10^{-6}) lower than that predicted by conservative mixing in 2011 and 2003, respectively. Note the

considerably larger errors for the 2003 dataset are due to the inherent uncertainties of using a

riverine end-member from a different spot-sample set. Experimentally derived dissolution rates

of basaltic particulates from Icelandic catchments in seawater have shown both bedload and

suspended sediment from Icelandic river catchments react to change the seawater $^{87}Sr/^{86}Sr$

without a contemporaneous change in Sr concentrations over a period of days to months (Jones

et al., 2012a; 2012b). These laboratory dissolution rates after 1 to 4 days are shown as an

expected deviation from pure mechanical mixing in Fig. 5. Both the 2003 and 2011 sample sets

approach the calculated offset after just one day, the minimum residence time of suspended

particles in the estuary.

The concentration and Sr content of the suspended particulate load are summarized in Table 1.

The suspended load concentration is relatively constant and ranges from 492-650 mg/L in the

estuary. The Sr concentrations of this suspended particulate load also remain close to constant in

the mixing zone and ranges from 146-228 mg/kg. The $^{87}Sr/^{86}Sr$ ratios of these suspended

particles are illustrated as a function of the Cl concentration of their adjacent fluid in Fig. 3. In

contrast with the total concentration of the particles and their total Sr concentration, the $^{87}Sr/^{86}Sr$

ratios of the suspended particles show a dramatic shift towards seawater values in the estuary.

The chemical composition of the bedload samples collected during 2008 are listed in Table 2.

The $^{87}Sr/^{86}Sr$ ratios of these bedload samples are illustrated as a function of the Cl concentration

of their adjacent fluid in Fig. 3. The bedload sample $^{87}Sr/^{86}Sr$ ratios follow a similar trend as the

246   suspended particles but exhibit less of a seawater Sr isotope signal than the corresponding

247   suspended particulate material. The Sr concentrations in the bedload increase away from the

248   river mouth due to the presence of carbonate minerals (Jones et al., 2012a). That study

249   concluded from mass balance equations that up to 14.9 % of the original basaltic Sr has been

250   removed from the non-carbonate bedload.

251

252   **4. Discussion**

253   ***4.1 Estimation of the Sr fraction inputted to the estuary waters from particulate material***

254   The degree to which Sr originating from particulate phases influences the estuarine water

255   chemistry can be estimated from mass balance calculations. By substituting $\left(\frac{^{87}Sr}{^{86}Sr}\right)_{2comp}$ for

256    $\left(\frac{^{87}Sr}{^{86}Sr}\right)_{sample}$ into Eqn. (1) and rearranging, one obtains:

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$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_x = \frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{sample} - \left(F_{river} \times \left(\frac{^{87}Sr}{^{86}Sr}\right)_{river}\right)}{1 - F_{river}} \qquad (3)$$

259   The difference between $\left(\frac{^{87}Sr}{^{86}Sr}\right)_x$ and $\left(\frac{^{87}Sr}{^{86}Sr}\right)_{sw}$ originates from a Sr source other than the

260   conservative mixing of river and sea water. It is assumed in this study that this difference occurs

261   from the conservative transfer of Sr from particulates to the fluid phase, and from the fluid to the

262   particulates. Taking account of this assumption, the fraction of the Sr present in the estuarine

263   water samples originating from particulate weathering (f_{part}) can then be obtained from:

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$$f_{part} = \frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_x - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{sw}}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{part} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{sw}} \hspace{3cm} (4)$$

where the subscript *part* designates the value of the particulate material, where the measured

$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{part} = 0.703294$. The total amount of Sr released from the particles to the fluid is attained

by multiplying the dissolved Sr in the water by f_{part}; the results of this calculation are provided in

Supplementary Table 1. Note that the quantification of the particulate material release is

severely hampered by the difference in element concentrations between the fresh and saline

water. Consequently, the calculations either induce high errors at very low salinity levels, or are

swamped by the seawater signature in high salinity areas. As such, f_{part} values are only reported

over the $100 < Sr < 1000\ \mu g/L$ concentration range. In this mid-mixing zone, measured $^{87}Sr/^{86}Sr$

compositions require that an average 3.98 ($\pm$ 2.7) $\mu g/L$ of Sr be transferred from the particulates

into the water. As these samples were collected at high tide, this Sr must have been liberated

from the particulates to the seawater in a matter of minutes to hours.

Similarly, mass balance calculations can be used to validate if the compositions of the suspended

particle samples collected in 2011 are consistent with these being the source of the unradiogenic

Sr required to balance the Sr composition of the estuary water. Taking account of mass balance

constraints, the fraction of Sr in the particles originating from seawater (f_{sw}) can be calculated

from:

$$f_{sw} = \frac{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{sample} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{basalt}}{\left(\frac{^{87}Sr}{^{86}Sr}\right)_{sw} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{basalt}} \hspace{3cm} (5)$$

where the subscripts *sample*, *basalt*, and *sw* refer to values for suspended particles in the estuary, the basaltic Hvítá river end member, and the isotopic composition of seawater, respectively. As the Sr concentrations in the particles are close to constant, the total mass of Sr transferred to the estuarine waters from the particles ($m_{Sr\ released}$) is approximately:

$$m_{Sr\ released} = f_{sw} \times m_{Sr\ particles} \hspace{3cm} (6)$$

where $m_{Sr\ particles}$ refers to the mass of Sr present in the particles. This assumes that the provenance of the suspended material in the mixing zone is dominantly of terrestrial origin. Therefore, these calculations were only performed up to sample Bo12 (64°34' N, 021°50' W). The depth at Bo12 is <2 m and well within the confines of the estuary, which supports the assumption that the overwhelming majority of suspended particulates in this part of the estuary originate from the Hvítá catchment. This is also the final sample site used for estimating f_{part} above. The seawater component (f_{sw}) is expressed as a percentage in Supplementary Table 1 and Fig. 6 to provide a comparison with the estimates generated from the estuarine water compositions.

The $^{87}Sr/^{86}Sr$ composition of the suspended load samples from 2011 indicates that <0.1 % of the Sr in the suspended particles originated from seawater in the Hvítá River, but 86 % of the Sr in suspended particles has a seawater signature at the Borgarfjörður Bridge. This observation indicates that the transformation of the Sr isotopic compositions of the particles begins at very low salinity levels (Fig. 6). Note that part of the isotopic evolution could be an artefact due to contamination from residual salts on the filter, even after rinsing with deionized water. However, the dramatic Sr isotopic evolution observed in the particulate material collected from

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the low salinity mixing zone, confirms that this effect is not an artefact of contamination. Logically, one would expect that if there was any deviation from the dissolved mechanical mixing line in the fjord, the particles would be more unradiogenic than their host water due to resuspension through tidal action.

The change in $^{87}Sr/^{86}Sr$ in the suspended particles while maintaining a near constant total Sr concentration indicates the two way transfer of material from and into the particles. In total, the calculations presented above, based on the composition of the suspended particles collected in 2011, indicate that 9-27 μg/L of Sr is transferred from the particles to the estuarine waters in the mixing zone. This mass is 2.5-7.5 times greater than the input to seawater by dissolved riverine transport and approximately 10-30 % of the total particulate Sr concentrations. Nevertheless, these values are substantially greater than the corresponding estimates based on the analysis of the concentrations of the estuary waters. The most likely reasons for this are a longer residence time of particulates in the mixing zone compared to river water, and the formation of, and exchange with Sr-bearing phases within the estuary. Nevertheless, the dramatic compositional change in the suspended material demonstrates that the particulate fraction is the major contributor of Sr to estuarine waters through dissolution and/or exchange of Sr. The larger estimated Sr release deduced from the suspended material compositions compared to that indicated by the estuarine water compositions (1.1 times greater than the dissolved flux) may reflect the larger residence time of the particulates in the mixing zone.

The question remains as to whether the Sr released from particulates is sourced by the dissolution of or exchange from primary igneous minerals, secondary weathering phases, or even

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331   colloids. Data from Hvítárvellir suggests that the Sr concentration of riverine colloids is far too

332   low (0.06 ng/g) for their flocculation to impact seawater chemistry. However, the Sr

333   concentration in Fe-Mn oxyhydroxides (1.8-2.4 μg/g) suggests that these phases may be a

334   significant source, consistent with the observed effects on ^{234}U/^{238}U activity ratios (Pogge von

335   Strandmann et al., 2008). Therefore, at least part of the two-way transfer of Sr between the

336   particulate and fluid phases could stem from adsorption-desorption processes, as shown by Li

337   isotopes (Pogge von Strandmann et al., 2008). Further insight into the mechanism responsible

338   for the reincorporation into the solid phase can be gained from Fig. 7, which illustrates the Sr/Al

339   ratio against the Ca/Al ratio for the bedload particulate material. These concentration ratios plot

340   as a near linear function of one another with a slope of 0.028. This dependence suggests that the

341   re-incorporation of Sr into the solids is due to its co-precipitation with Ca as the particulate

342   material interacted with seawater in the estuary. It seems likely that this precipitating phase is

343   calcite, given its high concentrations in these sediments (Pearce et al., 2013). The fact that this

344   linear correlation is offset from the origin by 0.6 Ca/Al implies that a substantial fraction of Sr in

345   the particulate material is hosted by non-carbonate phases (such as silicates).

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347   *__4.2 Global Implications__*

348   These findings have far-reaching implications for the global element cycles. On a catchment

349   scale, the Hvítá River has a mean discharge of 89 m^{3}s^{-1}, with an annual particulate suspended

350   flux of 200,600 tons and a dissolved Sr flux of 9.54 tons yr^{-1}, based on monthly monitoring

351   (Eiriksdottir et al., 2011). The results described here indicate that a further 10.4-71.5 tons yr^{-1} of

352   Sr will be transferred to the estuarine waters from particulates, assuming a linear covariance

353   between the dissolved and suspended flux throughout the year. In this case, the overall ^{87}Sr/^{86}Sr

354 composition delivered to the ocean (both riverine dissolved and that from particulate dissolution)

355 is calculated to be between 0.70345 and 0.70391, rather than the value of 0.70459 of the riverine

356 dissolved signal alone. If this behaviour is typical for volcanic particulates worldwide, then

357 consideration of the geographic extent of volcanic islands and basaltic terrains (as defined by

358 Allègre et al., 2010 and Dessert et al., 2003) suggests from 42 and 291 x 10^9 g yr^{-1} of Sr could be

359 released in this way. This release could account for between 6 and 45% of the current perceived

360 imbalance in the marine Sr budget, which is of comparable magnitude to the contribution from

361 hydrothermal exchange (Davis et al., 2003). Estimations of annual fluxes based on summer spot

362 sampling from this catchment gave the dissolved Sr flux from Hvítá as 37 tons yr^{-1} (Pogge von

363 Strandmann et al., 2008), underlining the sensitivity of these calculations to the conditions at the

364 time of sampling. Crucially, these calculations only take into account the initial release of Sr in

365 the estuary; whereas reworking of the sediments is likely to continue to react over much longer

366 periods (e.g. Aller 1998), as exhibited by the experimental evidence (Jones et al., 2012a; 2012b;

367 Pearce et al., 2013).

368

369 While these results are conclusive field evidence of 'proof of process', there is some degree of

370 uncertainty associated with the magnitude of this flux, especially when scaled up to a global

371 process. Therefore, these may not necessarily be a fair reflection on the annual fluxes. There are

372 considerable climatic differences between Iceland and other basaltic provinces and outcrops

373 worldwide, which would result in varying degrees of weathering, soil formation, and denudation.

374 Moreover, Iceland hosts several sub-glacial volcanoes that lead to the formation of significant

375 amounts of easily-weathered hyaloclastite (hydrated tuff-like breccia that is rich in volcanic

376 glass, formed through water-lava interaction). Each of these variables would affect the partition

377   of Sr between the solid and fluid phases. Moreover, the relative contributions of mineral and

378   oxyhydroxide dissolution need to be more accurately quantified before firm flux estimates can be

379   made. Despite these uncertainties, the magnitude of these deviations in $^{87}Sr/^{86}Sr$ from a two

380   component mixing curve is clear evidence that the reactions of particulate material upon arrival

381   in coastal waters are a major contributor to the global cycle of Sr.

382

383   **5. Conclusions**

384   These results represent the first direct evidence that the weathering of riverine particulate

385   material upon arrival in coastal areas makes a significant contribution to the overall Sr chemistry

386   of seawater over geological timescales. This is significant as marine $^{87}Sr/^{86}Sr$ values are a

387   default tool for estimating weathering rates over geological time. Moreover, this evidence

388   demonstrates that we may have underestimated the elemental mass of material being transferred

389   from the continents to the oceans. The feedback between climate and weathering is commonly

390   quantified based upon the mass of the alkali earth metals Ca and Mg transferred from the

391   continents to the oceans during weathering, which consume atmospheric CO_2 both during

392   chemical weathering and the precipitation of carbonates (e.g. Walker, et al., 1981; Berner et al.,

393   1983; Berner, 2004; Berner and Kothavala, 2001; Wallmann, 2001). If Ca and Mg behave in a

394   similar fashion to Sr, then the feedback between climate and weathering is stronger than

395   previously presumed (Eiriksdottir et al., 2013).

396

397   As the overwhelming mass of sparingly soluble bio-limiting nutrients such as Fe and P are

398   brought to the oceans in particulate form, the dissolution of these particulates in seawater could

399   provide a new stronger link between continental weathering and marine primary productivity.

18

400 Experimental and field studies demonstrate that elements such as Nd are similarly released from

401 particulate material into seawater, despite its preference for the solid phase (e.g. Pearce et al.,

402 2013; Singh et al., 2012). Such observations suggest that particulate weathering in estuaries is a

403 major contributor of these and other elements to seawater, lending weight to the "Boundary

404 Exchange" hypothesis where sediment-seawater reactions in shelf environments are a significant

405 source of the dissolved constituents in seawater (Jeandel, 1993; Lacan and Jeandel, 2005;

406 Jeandel et al., 2007; 2011; Siddall et al., 2008; Arsouze et al., 2009; Horikawa et al., 2011; Cater

407 et al., 2012; Wilson et al., 2012). These findings also add weight to previous studies, where

408 current land-to-ocean fluxes are proposed to be out of equilibrium following a recent

409 deglaciation (Vance et al., 2009). As glacial retreats expose substantial quantities of finely

410 ground material, the reactions of the particles in seawater provide an efficient mechanism for the

411 enhanced global weathering rates in addition to changes in the dissolved transport.

412 Anthropogenic changes to sediment fluxes through soil erosion and the damming of rivers are

413 likely to affect elemental and nutrient fluxes to coastal waters to a much greater extent than has

414 been previously considered, which may have deleterious consequences for coastal ecosystems.

415

422

<u>References</u>

424 Albarède, F., Michard, A., Minster, J., Michard, G., 1981. $^{87}Sr/^{86}Sr$ ratios in hydrothermal
425   waters and deposits from the East Pacific Rise at 21°N. Earth Planet. Sci. Lett. 55, 229-
426   236.

427 Allègre, C., Louvat, P., Gaillardet, J., Meynadier, L., Rad, S., Capmas, F., 2010. The
428   fundamental role of island arc weathering in the oceanic Sr isotope budget. Earth Planet.
429   Sci. Lett. 292, 51–56.

430 Aller, R. 1998. Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors.
431   Mar. Chem. 61, 143-155.

432 Andersson, P.S., Wasserburg, G.J., Ingri, J., 1992. The sources and transport of Sr and Nd
433   isotopes in the Baltic Sea. Earth Planet. Sci. Lett. 113, 459-472.

434 Arsouze, T., Dutay, J.-C., Lacan, F., Jeandel, C., 2009. Reconstructing the Nd oceanic cycle
435   using a coupled dynamical-biogeochemical model. Biogeosciences 6, 1–18.

436 Bernat, M., Church, T., Allègre, C.J., 1972. Barium and strontium concentrations in Pacific and
437   Mediterranean seawater profiles by direct isotope dilution spectrometry. Earth Planet.
438   Sci. Lett. 16, 75-80.

439 Berner, R.A., 2004. The Phanerozoic Carbon Cycle. Oxford University Press, Oxford.

440 Berner, R.A., Kothavala, Z., 2001. GEOCARB III. A revised model of atmospheric CO_2 over
441   Phanerozoic time. Am. J. Sci. 301, 182-204.

442 Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate-silicate geochemical cycle and

443   its effect on atmospheric carbon dioxide over the past 100 million years. Am. J. Sci. 283,

444   641-683.

445 Broecker, W.S., Peng, T.H., 1982. Tracers in the Sea (Eldigio Press, Lamont Doherty Geological

446   Observatory).

447 Cater, P., Vance, D., Hillenbrand, C.D., Smith, J.A., Shoosmith, D.R., 2012. The neodymium

448   isotopic composition of water masses in the eastern Pacific sector of the Southern Ocean.

449   Geochim. Cosmochim. Acta, 79, 41-59.

450 Davis, A., Bickle, M., Teagle, D., 2003. Imbalance in the oceanic strontium budget, Earth

451   Planet. Sci. Lett. 112, 173-187.

452 Dessert, C., Dupré, B., Gaillardet, J., François, L.M., Allègre, C.J., 2003. Basalt weathering laws

453   and the impact of basalt weathering on the global carbon cycle, Chem. Geol. 202, 257-

454   273.

455 Dupré, B., Dessert, C., Oliva, P., Goddéris, Y., Viers, J., Francois, L., Millot, R., Gaillardet, J.,

456   2003. Rivers, chemical weathering and Earth's climate. C.R. Geosci. 335, 1141-1160.

457 Eiriksdottir, E.S., Gislason, S.R., Snorrason, Á., Harðardóttir, J., Þorláksdóttir, S.B.,

458   Eyþórsdóttir, K.G., 2011. Efnasamsetning, Rennsli og Aurburður Straumvatna á

459   Versturlandi V. Gagnagrunnur Jarðvísindastofnunar og Veðurstofunnar (Science Institute

460   Report 04, Haskóli Íslands).

461 Eiriksdottir, E.S., Gislason, S.R., Oelkers, E.H., 2013. Does temperature or runoff control the

462   feedback between chemical denudation and climate? Insights from NE Iceland.

463   Geochim. Cosmochim. Acta 107, 65-81.

464   Elderfield, H. & Gieskes, J.M., 1982. Sr isotopes in interstitial waters of marine sediments from

465   Deep Sea Drilling Project cores, Nature 300, 493-497.

466   Elderfield, H., 1986. Strontium isotope stratigraphy. Palaeogeogr. Palaeoclimatol. Palaeoecol.

467   57, 71-90

468   Gislason, S.R., Arnórsson, S., Ármannsson, H., 1996. Chemical weathering of basalt in SW

469   Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. Am. J. Sci. 296, 837-

470   907.

471   Gislason, S.R., Oelkers, E.H., 2003. The mechanism, rates and consequences of basaltic glass

472   dissolution: II. An experimental study of the dissolution rates of basaltic glass as a

473   function of pH and temperature. Geochim. Cosmochim. Acta 67, 3817-3832.

474   Gislason, S.R., Oelkers, E.H., Snorrason, A., 2006. Role of river-suspended material in the

475   global carbon cycle. Geology 34, 49-52.

476   Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2011. An experimental

477   study of crystalline basalt dissolution from $2 \leq pH \leq 11$ and temperatures from 5 to 75

478   °C. Geochim. Cosmochim. Acta, 75, 5496-5509.

479   Henderson, G.M., Martel, D.J., O'Nions, R.K., Shackleton, N.J., 1994. Evolution of seawater

480        $^{87}Sr/^{86}Sr$ over the last 400 ka: the absence of glacial/interglacial cycles, Earth Planet. Sci.

481   Lett. 128, 643–651.

482   Hodell, D., Mueller, P., McKenzie, J., Mead, G., 1989. Strontium isotope stratigraphy and

483   geochemistry of the late Neogene ocean, Earth Planet. Sci. Lett. 92, 165-178.

484   Horikawa, K., Martin, E.E., Asahara, Y., Sagawa, T., 2011. Limits on conservative behaviour of

485   Nd isotopes in seawater assessed from analysis of fish teeth from Pacific cores. Earth

22

486   Planet. Sci. Lett., 310, 119-130.

487   Jeandel, C. 1993. Concentration and isotopic composition of Nd in the South Atlantic Ocean.

488   Earth Planet. Sci. Lett. 117, 581-591.

489   Jeandel, C., Arsouze, T., , F., Techine, P. and Dutay, J.C. 2007. Isotopic Nd compositions and

490   concentrations of the lithogenic inputs into the ocean: A compilation, with an emphasis on

491   the margins. Chem. Geol. 239, 156-164.

492   Jeandel, C., Peucker-Ehrenbrink, B., Jones, M.T., Pearce, C.R., Oelkers, E.H., Godderis, Y.,

493   Lacan, F., Aumont, O. and Arsouze, T. 2011. Ocean Margins: The missing term for

494   oceanic element budgets? EOS 92, 217-219.

495   Jones, M.T., Pearce, C.R., Oelkers, E.H., 2012a. An experimental study of the interaction of

496   basaltic riverine particulate material and seawater. Geochim. Cosmochim. Acta 77, 108-

497   120.

498   Jones, M.T.,Pearce,C.R.,Jeandel,C.,Gislason,S.R.,Eiriksdottir,E.S.,Mavromatis,V., Oelkers,

499   E.H., 2012b. Riverine particulate material dissolution as a significant flux of strontium to

500   the oceans. Earth Planet. Sci. Lett. 355–356, 51–59.

501   Lacan, F., Jeandel, C., 2005. Neodymium isotopes as a new tool for quantifying exchange fluxes

502   at the continent-ocean interface. Earth Planet. Sci. Lett. 232, 245–257.

503   McArthur, J.M., Howarth, R.J., Bailey, T.R., 2001. Strontium Isotope Stratigraphy: LOWESS

504   Version 3: Best Fit to the Marine Sr-Isotope Curve for 0–509 Ma and Accompanying

505   Look-up Table for Deriving Numerical Age, *J. Geol*. **109**, 155-170.

506   Milliman, J.D., Farnsworth, K.L., 2011. River Discharge to the Coastal Ocean: A Global

507   Synthesis. Cambridge University Press.

508 Milliman, J.D., Syvitski, J., 1992. Geomorphic/tectonic control of sediment discharge to the

509   ocean: the importance of small mountainous rivers. J. Geol. 100, 525-544.

510 Oelkers, E.H., Gislason, S.R., Eiriksdottir, E.S., Jones, M.T., Pearce, C.R. and Jeandel, C. 2011.

511   The role of riverine particulate material on the global cycles of the elements. Appl.

512   Geochem. 26, S365-S369.

513 Oelkers, E.H., Gislason, S.R., Eiriksdottir, E.S., Jones, M.T., Pearce, C.R., Jeandel, C.,

514 2012. Riverine particulate material dissolution in seawater and its implications for the global

515   cycles of the elements. C.R. Geosci. 344, 646-651.

516 Oliver, L., Harris, N., Bickle, M., Chapman, H., Dise, N., Horstwood, M., 2003. Silicate

517   weathering rates decoupled from the ^{87}Sr/^{86}Sr ratio of the dissolved load during

518   Himalayan erosion. Chem. Geol., 201 (1-2), 119-139.

519 Palmer, M., Edmond, J., 1989. The strontium isotope budget of the modern ocean, Earth Planet.

520   Sci. Lett. 92, 11-26.

521 Palmer, M. R., Edmond, J. M., 1992, Controls over the strontium isotope composition of river

522   water: Geochim. Cosmochim. Acta, 56, 2099–2111.

523 Pearce, C.R., Burton, K.W., Pogge von Strandmann, P.A.E., James, R.H., Gislason, S.R., 2010.

524   Molybdenum isotope behaviour accompanying weathering and riverine transport in a

525   basaltic terrain. Earth Planet. Sci. Lett. 295, 104-114.

526 Pearce, C.R., Jones, M.T., Oelkers, E.H., Pradoux, C., Jeandel, C., 2013. The effect of

527   particulate dissolution on the neodymium (Nd) isotope and Rare Earth Element (REE)

528   composition of seawater. Earth Planet. Sci. Lett. 369, 138-147

529   Peucker-Ehrenbrink, B., Miller, M.W., Arsouze, T., Jeandel, C., 2010. Continental bedrock and

530   riverine fluxes of strontium and riverine particulate material dissolution in seawater

531   neodymium isotopes to the oceans. Geochem. Geophys. Geosy. 11, Q03016.

532   Pogge von Strandmann, P.A.E., James, R.H., van Calsteren, P., Gislason, S.R., Burton, K.W.,

533   2008. Lithium, magnesium and uranium isotope behaviour in the estuarine environment

534   of basaltic islands. Earth Planet. Sci. Lett. 274, 462-471.

535   Riley, J.P., Chester, R., 1971. Introduction to Marine Chemistry. Academic Press, London.

536   Siddall, M., Khatiwala, S., van der Flierdt, T., Jones, K., Goldstein, S.L., Hemming, S.,

537   Anderson, R.F., 2008. Towards explaining the Nd paradox using reversible scavenging in

538   an ocean general circulation model. Earth Planet. Sci. Lett. 274, 448-461.

539   Singh, S.P., Singh, S.K., Goswami, V., Bhushan, R., Rai, V.K., 2012. Spatial distribution of

540   dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and

541   mixing of water masses. Geochim. Cosmochim. Acta, 94, 38-56.

542   Vance, D., Teagle, D., Foster, G., 2009. Variable Quaternary chemical weathering fluxes and

543   imbalances in marine geochemical budgets, Nature 458, 493-496.

544   Veizer, J., Alab, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Cardena, G.A.F., Diener, A.,

545   Ebneth, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O.G., Strauss, H.,

546   1999. $^{87}Sr/^{86}Sr$, ^{13}C and ^{18}O evolution of Phanerozoic seawater. Chem. Geol. 161, 59-88.

547   Walker, J.C.G., Hays, P.B., Kasting, J.F., 1981. A negative feedback mechanism for the long-

548   term stabilization of Earth's surface temperature. J. Geophys. Res. 86, 9776-9782.

549   Walling, D.E., 2006. Human impact on land–ocean sediment transfer by the world's rivers.

550   Geomorphology 79, 192–216.

551 Wallmann, K., 2001. Controls on the Cretaceous and Cenozoic evolution of seawater

552 composition, atmospheric CO_2 and climate. Geochim. Cosmochim. Acta 65, 3005-3025.

553 Wilson D.J., Piotrowski, A.M., Galy. A., McCave N., 2012. A boundary exchange influence on

554 deglacial neodymium isotope records from the deep western Indian Ocean. Earth. Planet.

555 Sci. Let., 341-344, 36-47.

556 Wolf-Boenisch, D., Gislason, S.R., Oelkers, E.H., Putnis, C.V., 2004. The dissolution rates of

557 natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from

558 25 to 74 °C. Geochim. Cosmochim. Acta 68, 4843-4858.

559

560 **<u>Legends</u>**

561 **Fig. 1**. A map of western Iceland, showing the sample locations in the Hvítá River and the

562 Borgarfjörður Estuary. The 2003 (<u>black circles</u>) and 2011 (<u>grey </u>circles) transects collected

563 dissolved and suspended samples. The 2003 samples correspond to A4 and C1-11 from previous

564 studies (Pogge von Strandmann et al., 2008). The 2008 transect (black triangles) collected

565 bedload samples.

566

567 <u>**Fig. 2.** A log-log comparison of dissolved [Sr] and [Cl] concentrations measured in the 2011</u>

568 <u>samples (grey circles) and 2003 samples (black circles). The black line represents the pure</u>

569 <u>mechanical mixing line between the seawater and river water end-members, with the grey shaded</u>

570 <u>area representing the error on this line due to uncertainties associated with the true riverine end-</u>

571 <u>member.</u>

572

Fig. 3. The measured $^{87}Sr/^{86}Sr$ from the dissolved (grey circles) and suspended (grey squares) samples from 2011, and bedload (black triangles) fractions from 2008 against estuarine water dissolved chloride concentrations. The solid curves represent the predicted $^{87}Sr/^{86}Sr$ from mechanical two-component mixing of the riverine and seawater end-members, with associated measurement and analytical errors of this line represented by the grey area within the dashed lines. Errors for individual points are well within the size of the symbols.

Fig. 4. The measured $^{87}Sr/^{86}Sr$ compared with the fraction of river-derived [Sr] concentrations. As with Fig. 2, the black line represents the seawater – river water mechanical mixing line, with the grey shaded area representing the error on this line due to analytical uncertainties.

Fig. 5. The difference between the observed $^{87}Sr/^{86}Sr$ in dissolved field estuarine water samples and the calculated $^{87}Sr/^{86}Sr$ ratios at a given Cl concentration, based on mechanical two-component mixing (corresponding to the curve in Fig. 2). The model curves represent the calculated deviations from this mechanical mixing, based on experimental release rates from Hvítá bedload (Jones et al., 2012a) and suspended particulates from northeast Iceland (Jones et al., 2012b) in seawater after 1-4 days.

Fig. 6. The estimated % seawater signal between the suspended particles (based on $^{87}Sr/^{86}Sr$) and dissolved [Cl] concentrations from the same sample. [Sr] vs [Cl] concentrations are shown for comparison.

595 **Fig. 7.** The Sr/Al concentration ratios plotted against the corresponding Ca/Al concentration

596 ratios of the bedload particulate material. The symbols correspond to measured concentrations

597 while the line represents the least squares fit of the data.

598

599 **Table 1.** Location and chemical data of the water and suspended samples collected in 2011 and

600 2003. n.a. denotes "not analysed" and b.d.l. denotes "below detection limit".

601

602 **Table 2.** The chemical data of the bedload samples collected in 2008. The "corresponding site"

603 labels match those used in Pogge von Strandmann et al. (2008). * denotes that all Fe is assumed

604 to be as Fe^{3+}.

605

606 **Supplementary Information**

607 Supplementary Table 1 is a summary of the analyses that calculated the relative release of Sr,

608 based on equations 1-6.

- We conducted a suite of field investigations in Borgarfjörður estuary in west Iceland.
- Dissolved, suspended and bedload $^{87}Sr/^{86}Sr$ values show clear Sr release from particulates.
- Magnitudes of Sr dissolution agree with experimentally derived values.
- Sr release from sediments must occur within hours of first contact with saline water.
- Global Sr flux estimates of comparable magnitude to mid-ocean ridge Sr exchange.

Table

2011 Data

Site	Latitude	Longitude	Date	Time	Distance from Hvítaávellir (km)	Water Temp. (°C)	pH	Conductivity (mS)	Salinity (% of S.W.)	Suspended Fraction (mg/L)	Alkalinity (meq/L)	Cl (mg/L)	SO₄ (mg/L)	Si (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (µg/L)	Mn (µg/L)	Li (µg/L)	Br (mg/L)	B (mg/L)	Sr (µg/L)	Dissolved ^{87}Sr/^{86}Sr	Suspended Sr (mg/kg)	Suspended ^{87}Sr/^{86}Sr
HvA	64°36'11.0"	021°42'37.5"	25/08/2011	14:55	0.00	7.7	8.08	0.06	0.03	562	0.390	5.3	0.4	6.51	6.7	0.5	3.1	1.1	0.022	71.5	1.67	0.18	0.014	0.005	3.6	0.704589	228.3	0.703294
HvB	64°36'11.0"	021°42'37.5"	25/08/2011	15:25	0.00	7.6	8.08	0.07	0.02	560	0.385	4.4	0.2	6.43	6.6	0.4	3.0	1.1	0.008	61.3	1.16	0.14	0.013	0.004	3.6	n.a	n.a	n.a
Bo1	64°35'36.8"	021°44'06.5"	25/08/2011	16:10	1.57	7.5	8.08	0.06	0.02	507	0.393	4.4	0.2	6.29	6.9	0.4	3.0	1.1	0.009	59.9	0.57	0.17	0.003	0.003	3.6	0.704631	177.9	n.a
Bo6	64°34'27.1"	021°48'09.7"	25/08/2011	17:00	5.43	8.6	7.81	0.08	0.04	505	0.450	7.4	0.8	6.38	8.7	0.5	3.1	1.4	0.013	61.0	1.95	0.23	0.014	0.005	5.7	0.706233	159.2	0.703430
Bo2	64°34'24.1"	021°48'16.7"	25/08/2011	16:40	5.54	9.5	7.80	0.07	0.16	506	0.402	30.7	5.5	6.50	21.3	1.0	3.1	2.6	0.009	51.0	4.97	0.56	0.074	0.015	13.1	0.708060	180.3	n.a
Bo5	64°34'25.0"	021°48'21.2"	25/08/2011	16:55	5.60	9.8	7.81	0.14	0.11	499	0.406	21.9	3.9	6.46	16.9	0.9	3.1	2.2	0.013	52.0	4.46	0.45	0.072	0.009	10.6	0.707776	174.9	0.703940
Bo7	64°34'22.4"	021°48'29.4"	25/08/2011	17:05	5.72	9.5	7.78	0.24	0.21	486	0.407	41.6	7.8	6.51	27.6	1.3	3.3	3.2	0.010	52.1	4.29	0.74	0.123	0.018	16.3	0.708309	163.5	0.704309
Bo4	64°34'23.7"	021°48'32.2"	25/08/2011	16:52	5.73	9.5	7.81	0.13	0.11	501	0.396	20.6	3.5	6.49	16.0	0.8	3.0	2.1	0.009	49.8	3.55	0.75	0.063	0.008	10.2	0.707751	175.2	n.a
Bo3	64°34'22.6"	021°48'39.3"	25/08/2011	16:50	5.82	9.9	7.82	0.27	0.18	505	0.460	34.0	6.1	6.41	23.9	1.1	3.1	2.8	0.011	50.5	4.41	0.62	0.112	0.014	14.2	0.708167	180.3	0.703960
Bo8	64°34'19.6"	021°48'34.9"	25/08/2011	17:10	5.83	9.8	7.78	0.14	0.10	489	0.401	20.1	4.3	6.56	18.0	1.1	3.1	2.4	0.020	62.4	4.51	0.84	0.077	0.010	11.1	0.707912	151.8	0.703987
Bo8-bottom	64°34'19.6"	021°48'34.9"	25/08/2011	17:12	5.83	9.6	7.77	0.13	0.10	747	0.400	20.1	3.4	6.54	15.6	0.8	3.0	2.1	0.011	52.1	2.84	0.17	0.072	0.009	10.0	0.707705	299.0	0.703795
Bo9	64°34'16.3"	021°48'48.7"	25/08/2011	17:15	6.04	9.6	7.78	0.18	0.14	493	0.453	27.2	6.1	6.74	22.6	1.1	3.3	3.1	0.019	61.0	3.26	0.82	0.104	0.012	14.8	0.708179	155.8	0.704135
Bo10	64°34'12.1"	021°49'03.2"	25/08/2011	17:20	6.26	9.6	7.77	0.93	1.28	492	0.431	247.6	24.7	6.45	131.0	5.4	7.4	16.1	0.014	55.8	3.93	8.17	0.739	0.061	89.2	0.709010	151.9	0.704966
Bo11	64°34'07.5"	021°49'13.6"	25/08/2011	17:25	6.45	9.3	7.81	3.62	4.35	494	0.492	843.5	174.6	6.38	471.0	18.0	21.0	57.4	0.010	48.5	4.14	8.39	2.622	0.213	326.0	0.709083	157.1	0.705353
Bo12	64°34'01.5"	021°49'29.4"	25/08/2011	17:29	6.74	9.5	7.84	4.14	4.92	496	0.502	954.8	183.7	6.12	578.0	20.6	23.9	66.5	0.009	49.4	5.02	9.88	3.314	0.238	376.0	0.709095	145.9	0.705300
Bo13	64°33'54.2"	021°49'47.6"	25/08/2011	17:32	7.05	9.5	7.98	n.a	14.75	499	0.770	2861.2	574.4	5.37	1700.0	65.1	70.4	213.0	0.005	41.8	7.86	21.10	10.427	0.715	1200.0	0.709180	202.3	0.706315
Bo14	64°33'46.4"	021°50'07.1"	25/08/2011	17:36	7.41	9.9	8.00	n.a	23.19	517	0.901	4498.2	980.1	4.62	2880.0	102.0	111.0	336.0	b.d.l	36.2	8.64	54.83	17.023	1.113	1920.0	0.709161	150.1	0.706441
Bo15	64°33'23.0"	021°50'56.7"	25/08/2011	17:40	8.36	10.1	8.11	n.a	41.67	651	1.389	8084.8	n.a	3.06	5550.0	199.0	205.0	642.0	0.005	18.1	8.00	85.64	31.602	2.179	3610.0	0.709186	146.5	0.707647
Bo16	64°32'26.0"	021°53'00.8"	25/08/2011	17:45	10.74	10.6	8.12	n.a	53.92	n.a	1.623	10460.9	n.a	2.08	7450.0	268.0	278.0	861.0	b.d.l	12.0	7.32	109.19	43.646	3.019	4920.0	0.709197	143.9	0.708104
Bo17	64°31'59.6"	021°53'31.2"	25/08/2011	17:52	11.57	10.5	8.08	n.a	58.78	n.a	1.836	11402.8	n.a	1.50	8460.0	306.0	315.0	977.0	b.d.l	10.6	6.95	111.30	48.553	3.620	5610.0	0.709198	139.1	0.708359

2003 Data

Site	Latitude	Longitude	Date	Time	Distance from Hvítaávellir (km)	Temp. (°C)	pH	Conductivity (mS)	Salinity (% of S.W.)	Suspended Fraction (mg/L)	Alkalinity (meq/L)	TDS (mg/L)	Cl (mg/L)	SO₄ (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Li (µg/L)	Sr (mg/L)	Dissolved ^{87}Sr/^{86}Sr	Suspended Sr (mg/kg)	Suspended ^{87}Sr/^{86}Sr	Colloid Sr (mg/kg)	Colloid ^{87}Sr/^{86}Sr	Suspended Fe-Mn Leachate Sr (mg/kg)	Suspended Fe-Mn Leachate ^{87}Sr/^{86}Sr
A4	N 64°36.199'	W 21°42.481'	09/09/2003	09:30	0.00	9.0	7.93	0.07	0.1	610	0.473	34.7	12.8	0.5	7.1	0.5	3.9	1.9	0.3	6.4	0.705155	192	0.703344	0.00056	0.704567	1.78	0.704555
C1	N 64°34.290'	W 21°49.299'	09/09/2003	08:20	6.43	7.7	7.92	0.07	0.2	n.a	n.a	33.4	14.5	0.8	7.5	0.5	4.2	6.4	0.3	6.9	0.706343	n.a	0.703347	n.a	n.a	n.a	n.a
C2	N 64°33.584'	W 21°51.107'	09/09/2003	08:40	8.42	8.0	7.95	0.09	0.2	n.a	n.a	47.2	30.5	1.0	12.9	0.7	4.3	2.0	0.4	11.6	0.706593	n.a	0.703485	n.a	n.a	n.a	n.a
C3	N 64°33.207'	W 21°51.792'	09/09/2003	09:10	9.21	8.8	7.94	2.89	5.4	n.a	n.a	1419	652.3	218.1	547.2	25.0	26.8	2.7	9.4	346.6	0.709118	210	0.706838	n.a	n.a	n.a	n.a
C4	N 64°32.924'	W 21°52.529'	09/09/2003	09:45	10.00	9.4	8.08	7.15	13.3	n.a	n.a	3570	1808.1	309.3	1142.6	51.6	51.7	67.1	21.0	788.5	0.709127	201	0.707744	n.a	n.a	n.a	n.a
C5	N 64°32.623'	W 21°53.270'	09/09/2003	10:00	10.84	9.6	8.16	9.81	19.1	n.a	n.a	4900	4077.1	576.3	1676.0	75.9	72.5	139.0	30.3	1147.8	0.709166	195	0.708191	n.a	n.a	n.a	n.a
C6	N 64°31.686'	W 21°56.450'	09/09/2003	10:10	13.94	9.8	8.22	12.91	24.8	n.a	n.a	6460	5353.4	714.7	2666.8	118.5	113.8	325.7	48.0	1962.7	0.709176	199	0.708359	n.a	n.a	n.a	n.a
C7	N 64°31.240'	W 21°57.647'	09/09/2003	10:30	15.18	10.4	8.25	15.27	29.7	n.a	n.a	7660	7090.6	810.7	3747.3	162.3	156.7	454.5	71.5	2637.4	0.709182	212	0.708505	n.a	n.a	n.a	n.a
C8	N 64°30.035'	W 21°59.427'	09/09/2003	10:40	17.71	10.7	8.27	21.79	41.2	n.a	n.a	10930	9749.6	1075.6	4758.9	198.6	194.8	578.5	90.2	3469.8	0.709191	n.a	n.a	n.a	n.a	n.a	n.a
C9	N 64°29.019'	W 22°01.071'	09/09/2003	11:05	19.90	11.1	8.28	30.80	58.6	n.a	n.a	15400	13649.4	1488.9	6713.0	283.1	276.6	806.9	121.5	4775.3	0.709194	77.9	0.708576	n.a	n.a	n.a	n.a
C10	N 64°26.523'	W 22°05.955'	09/09/2003	11:20	25.94	11.8	8.26	44.20	87.2	n.a	n.a	21700	18825.5	2218.9	9149.9	406.6	381.2	1125.3	155.5	6247.3	0.709194	n.a	n.a	n.a	n.a	n.a	n.a
C11	N 64°26.050'	W 22°08.966'	09/09/2003	11:45	28.33	12.1	8.29	47.10	90.6	n.a	n.a	23500	19215.5	2286.2	9632.7	422.3	404.8	1183.7	163.1	6799.3	0.709194	14.2	0.708699	n.a	n.a	n.a	n.a

Table

2008 Bedload	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5	Bed 6
Corresponding site	A4	C4	C5	C6	C7	C8
Lat.	N 64°36.199′	N 64°32.924'	N 64°32.623'	N 64°31.686'	N 64°31.240'	N 64°30.035'
Long.	W 21°42.481′	W 21°52.529'	W 21°53.270'	W 21°56.450'	W 21°57.647'	W 21°59.427'
BET (m^2g^{-1})	6.358	11.14	9.603	9.756	12.38	8.404
SiO_2 (%)	46.74	46.29	45.81	46.82	44.94	45.30
Na_2O (%)	2.67	2.40	2.19	2.28	2.72	2.20
MgO (%)	8.17	9.00	9.00	8.51	7.20	9.75
Al_2O_3 (%)	15.24	13.06	13.07	13.70	13.24	11.46
P_2O_5 (%)	0.14	0.12	0.13	0.12	0.17	0.13
K_2O (%)	0.28	0.39	0.33	0.38	0.49	0.38
CaO (%)	14.02	14.02	14.14	13.96	14.63	14.35
TiO_2 (%)	1.45	1.49	1.56	1.44	1.49	1.57
MnO (%)	0.24	0.20	0.20	0.19	0.16	0.18
Fe_2O_3* (%)	10.81	11.46	11.90	11.52	12.42	12.99
Sr (mg kg^{-1})	152.90	159.94	162.64	154.90	196.53	175.92
$^{87}Sr/^{86}Sr$	0.703180	0.703591	0.703668	0.703569	0.705118	0.704637

Supplementary material for on-line publication only