Does temperature or runoff control the feedback between chemical denudation and climate? Insights from NE Iceland

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Abstract

The relative role of temperature and runoff on the chemical denudation rates in seven NE Iceland river catchments were determined through the analysis of river water chemistry collected over a five-year period. Denudation rates are quantified from the instantaneous riverine Na fluxes. As sodium is the major element least incorporated into secondary phases, its denudation rate is directly related to the dissolution rate of the catchments’ primary rocks. Chemical transport in rivers is taken to be analogous to laboratory mixed-flow reactors; dissolution rates in mixed flow-reactors at fixed temperature and flow rate are a function of fluid composition, degree of fluid undersaturation, the Arrhenius activation energy, and reactive surface area. Data analysis suggests that the Na chemical denudation rates of the NE Icelandic catchment rocks increase by 13% for each °C increase in temperature. Of this 13%, 5% stems from the Arrhenius activation energy and 8% stems from the temperature dependence of the fluid pH and aqueous Al activity. Increased runoff raises the height of the water table thus enhancing chemical denudation by increasing the reactive surface area of weathering minerals. Regression of measured Na fluxes indicate that the average active water–rock surface area of the studied catchments increase linearly with runoff such that a 1% rise in runoff produces a 1% increase in reactive surface area and chemical denudation rates. The relative role of temperature versus runoff on chemical denudation depends, therefore, on the relative changes in these two rate controlling parameters. The maximum temperature variation of the studied rivers was 15.4 °C, which would increase Na chemical denudation rates by a factor of 6. In contrast, instantaneous runoff varies by as much as a factor of 250. These observations suggest that runoff dominates the instantaneous variation of the Na chemical denudation rates of the studied catchments.

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1. INTRODUCTION

Continental weathering and denudation is the most important process regulating the long-term carbon cycle and global climate (e.g. Ebelmen, 1845, 1847; Urey, 1952; Garrels and Perry, 1974; Holland, 1978; Walker et al., 1981; Berner et al., 1983; Brady, 1991; Drever and Zobrist, 1992; White and Blum, 1995; Gislason et al., 1996; Louvat and Allègre, 1997; Kump et al., 2000; Wallmann, 2001; Dessert et al., 2003; Berner, 2004; Gislason et al., 2006, 2009). The two major contributing factors linking continental weathering and climate are runoff and temperature (e.g. Amiotte-Suchet and Probst, 1993; Berner and Caldeira, 1997; Dessert et al., 2001, 2003; Gislason et al., 2009; Ferrier et al., 2012). The distinct roles of runoff versus temperature in this process are challenging to identify because these two factors commonly co-vary (e.g. rainfall, and thus runoff tend to increase with increasing temperature). In addition, the overall weathering process consists of large number of distinct reactions including the dissolution of primary material, the precipitation of secondary phases, and physical and chemical transport. To provide insight into the feedback between weathering and climate, this study was initiated to define the distinct roles of runoff and temperature on the chemical denudation rate of seven catchments in NE Iceland over a five year period.
This study focuses on the weathering of basaltic rocks. The significance of basalt weathering on global scale processes has been highlighted in numerous studies (e.g., Bluth and Kump, 1994; Gislason et al., 1996; Brady and Gislason, 1997; Louvat and Allègre, 1997; Taylor and Lasaga, 1999; Dessert et al., 2001; Goddéris et al., 2003; Sak et al., 2004; Pokrovsky et al., 2005; Zakharova et al., 2005; Gislason et al., 2006; Pogge von Strandmann et al., 2006; Vigier et al., 2006; Wolff-Boenisch et al., 2006; Georg et al., 2007; Navarre-Sitchler and Brantley, 2007; Rad et al., 2007; Wimpey et al., 2007; Zakharova et al., 2007; Eiriksdottir et al., 2008; Hausrath et al., 2008; Louvat et al., 2008; Pelt et al., 2008; Pogge von Strandmann et al., 2008; Gislason et al., 2009; Vigier et al., 2009; Gislason and Oelkers, 2010; Pogge von Strandmann et al., 2010; Pearce et al., 2010; Oksarshdottir et al., 2011; Schopka and Derry, 2011; Schopka et al., 2011; Ma et al., 2012). About 30–35% of atmospheric CO₂ consumption due to silicate weathering on land has been attributed to basalts (Gaillardet et al., 1999; Dessert et al., 2003; Gislason et al., 1996; Louvat and Allègre, 1997, 1998; Taylor and Lasaga, 2005a). The abundance of fresh basaltic glass in the riverine suspended material is 25% stems from weathering of volcanic islands (Gislason et al., 1996; Louvat and Allègre, 1997, 1998; Dessert et al., 2003; Louvat et al., 2008).

A number of past studies of the weathering of the basaltic rocks of NE Iceland have been reported in the literature. The mechanical and chemical denudation rates of the glaciated catchments of NE Iceland have been shown to be at or close to steady-state with the exception of the Lagarfljót catchment which drains a reservoir which contains a sediment trap (Eiriksdottir et al., 2008; Louvat et al., 2008). Kardjilov et al. (2006) and Kardjilov (2008) estimated the effect of climate and primary production of vegetation on carbon fluxes in these catchments. The seasonal and annual variation of chemical and mechanical denudation rates of NE Iceland catchments have been reported by Gislason et al. (2006).

Chemical denudation comprises a large number of coupled dissolution and precipitation reactions. To overcome some of the complexities associated with distinguishing these coupled reactions, this study is focused on the chemical denudation rates of sodium. Sodium is considered in this study because it is the most mobile major element during the chemical weathering of Icelandic basaltic terrains (Gislason et al., 1996; Eiriksdottir et al., 2008); it is the element least incorporated into secondary phases or left behind in leached layers formed on primary minerals and glasses. Sodium chemical denudation rates are thus dominated by the dissolution rates of the Na-bearing minerals and glasses present in the studied river catchments; little contribution to sodium chemical denudation is expected from secondary mineral or saprolite dissolution. Gislason et al. (2009) determined the variation of the annual weathering fluxes of these catchments over the past 40 years and related them to corresponding climate variations in NE Iceland. This study builds on this past work by using the measured riverine elemental fluxes of the basaltic catchments of NE Iceland to deduce the relative role of temperature and runoff on Na chemical denudation rates.

2. GENERAL SETTINGS OF THE STUDY AREA

This study focuses on four glacial river catchments; Jökulsá á Dal at Brú, Jökulsá á Dal at Hjardarhagi, Jökulsá i Fljótshal at Höll, and Lagarfljót at Lagarfoss, and three direct runoff rivers; Fellssá, Grímsá, and Fjardará located in NE Iceland. The locations of these catchments are shown in Fig. 1 (The National Land Survey of Iceland, 2003; The Hydrological Services of the National Energy Authority, 2005a). Jökulsá á Dal at Brú is a sub-catchment of Jökulsá á Dal at Hjardarhagi. The waters of the Jökulsá á Dal, Jökulsá i Fljótshal, and Lagarfljót are a mixture of glacial and direct runoff. The Grímsá and Lagarfljót are dammed, and Lagarfljót drains a lake where the residence time of the water is around 1 year (Tómasson and Hardardóttir, 2001). The glacial river catchments will be referred to as Brú, Hjardarhagi, Höll, and Lagarfljót in the following text. The Hydrological Service of the National Energy Authority has continuously monitored the discharge and suspended load of most of these catchments over the past three to four decades (Pálsson and Vigfússon, 1996; Tómasson et al., 1996; Adalsteinsson, 2000; The Hydrological Services of the National Energy Authority, 2005b; Gislason et al., 2006; Eiriksdottir et al., 2008; Gislason et al., 2009).

The bedrock is predominantly basaltic lavas and hyaloclastite (consisting of mostly basaltic glass) with acidic intrusions connected to extinct central volcanoes (Wood, 1976, 1978; Jóhanesson and Sæmundsson, 1998; Hards et al., 2000; Eiriksdottir et al., 2008). The age of the bedrock increases from the west to the east and the average area-weighted age of the river catchments ranges from 1.3 to 11.2 Ma (Gislason et al., 2006; Kardjilov, 2008). Surface runoff dominates in the Tertiary and Quaternary rocks of the catchments located further east where a large percentage of the pores have been filled with secondary minerals. The secondary minerals found in the Tertiary rocks are mainly zeolites, clays (mainly allophane), and quartz (Walker, 1960; Neuhoff et al., 1999; Fridriksson et al., 2001).

The abundance of fresh basaltic glass in the riverine suspended material is 43% of total suspended sediments in Hjardarhagi and decreases with age to the east and is 24% in Höll (Pálsson, 2003). Suspended material tends to exhibit increased alteration with increasing catchment age from west to east (Pálsson, 2003; Eiriksdottir et al., 2008). The composition of the suspended particles in the rivers of NE Iceland is basaltic with the average silica concentration 51.2 ± 2.1 wt.% (Eiriksdottir et al., 2008).

The Na-containing primary minerals and glasses are mostly basaltic glass and plagioclase but some andesitic-to rhyolitic-glass is present in the interstitial groundmass of crystalline basalt and air-borne volcanic ash in the soil. There are numerous effluents in the studied river catchments including soil water seepage to small direct runoff rivers. Several warm springs (10–20 °C) are located in the study area and two 50–70 °C springs are located in the in Brú and Höll catchments (Sæmundsson and Jóhanesson, 2004). No correction is made for the Na flux of the hot springs in Brú and Hjardarhagi since it is a small proportion of the annual Na flux.

Vegetation in the study area increases from west to east as the bedrock becomes older and less permeable. A large part of the study area is located in the highlands and is poorly vegetated (Kardjilov et al., 2006). Wetland areas...
are present in the Brú, Hjardarhagi, and Höll catchments (Kardjilov, 2008), however, wetlands tend to be sparse in the studied catchments. The Grímsá and Lagarfljót catchments have the richest vegetation, with some forests. The Icelandic soil is rich in air borne glassy volcanic material and the main secondary minerals present are ferrihydrate and allophane (Wada et al., 1992). The soil pH ranges from 4 to 7 (Arnalds, 2004). There is a correlation between soil thickness and the concentration of total dissolved solids (TDS) in the soil water. Thicker soils contain more volcanic glass and therefore more dissolvable material (Sigfusson et al., 2008). Calcite has not been reported in Icelandic soils (Wada et al., 1992).

Air temperature has been monitored at several sites in NE Iceland for the past several decades (The Icelandic Meteorological Office, 2007; Gislason et al., 2009), and climate models, constrained by ground measurements, have been used to calculate average annual temperatures of all the catchments considered in this study from 1998 to 2006 (Kardjilov, 2008). The daily average soil temperature for the period ranged from −2.5 to 15 °C at 10 and 20 cm depth; from 0 to 12 °C at 50 cm and from 1.5 to 8 °C at 100 cm. From May to September, the monthly average soil temperature in the top 100 cm of the soil is similar to monthly average air temperature measured at 2 m height. From October to April, however, the monthly average soil temperature in the top 100 cm of the soil was never below freezing while the average monthly air temperature during the same period was as low as −4 °C (The Icelandic Meteorological Office, 2006).

Critical to any assessment of the effect of temperature on chemical denudation rates is the residence time of water within the catchment. The residence time, which is equivalent to the average time water remains in the catchment, is equal to the ratio of the total water volume in the catchment to the water flux out of the catchment. If the residence time is large compared to seasonal temperature variations, the effect of seasonal temperature change on weathering rates is obscured. The estimation of residence time in regional scale catchments is challenging; a complete hydrological analysis of a catchment requires detailed quantification of input fluxes to the catchment including rainwater, groundwater, and glacial melt water on one hand, and exit fluxes including evaporation, groundwater flow, and riverine run-off on the other hand. Such detailed information is difficult or impossible to obtain. Estimates of the residence time of water in catchments considered in the present study can be made if one assumes that riverine runoff dominates water...
fluxes out of the catchment compared to groundwater flux (e.g. Church, 1996) and evaporation (e.g. Sigurðsson et al., 2007). The runoff of the catchments considered in this study ranged from 1 to 4.5 m/yr. The volume of total pore space of the catchment can be estimated from the product of the average soil depth and the porosity. Taking an average soil porosity of 40%, an average soil depth of 0.75–1.5 m (Óskarsson et al., 2004), and assuming all pores were water saturated, yields residence times of 3 weeks–7 months depending on the catchment. It should be emphasized that such estimates are not possible for the Lagarfljót catchment, which contains a large lake which increases the residence time of water in this catchment to over 1 year (Tómasson and Hardardóttir, 2001).

3. MATERIALS AND METHODS

3.1. Sampling, filtration and analyses

River water samples were collected from seven river catchments in the NE Iceland during 44 sampling trips from November 1998 to November 2003. The water samples were filtered on site after sampling through 0.2 μm Milipore cellulose acetate filters using a peristaltic pump, silicone tubing, and a 142 mm Sartorius filter holder. Water samples collected for major and trace element analyses were acidified with suprapure HNO₃. All the rivers were sampled 44 times except the Fjadárdæli, which was sampled 20 times, and the Brú, which was sampled 24 times. In total 264 samples were collected, but 6 were rejected from consideration due to poor charge balance of their chemical analyses. Discharge, and air and water temperature were measured at the time of sampling.

The composition of collected water samples was measured using an Optima 4300 DV Series ICP-AES and Element 1 model ICP-SFMS located at Analytica-AB, Luleå in Sweden. The analyses done by Analytica-AB were performed according to EPA-method USP 200.7(mod) for ICP-AES and EPA 200.8(mod) for ICP-SFMS, the SLRS-4 a certified reference material, was used for external calibration. Measurements have uncertainties of <10%. River water fluxes of dissolved elements were found by multiplying the chemical concentration of individual elements at the time of sampling and the corresponding instantaneous discharge which has an uncertainty estimated to be 5%. The propagation of variance of the elemental flux was calculated to be 11%.

3.2. Thermodynamic calculations

Aqueous speciation and mineral solubility products in the present study were generated using the PHREEQC 2.11 computer code (Parkhurst and Apello, 2005), calculated using the measured river water temperature at the time of sampling. The PHREEQC.dat database was used for all calculations after adding to it (1) the thermodynamic properties for Al(OH)₄⁻ taken from Arnórsson and Andrésdóttir (1999) and Diakonov et al. (1999) respectively, (2) the equilibrium constants for the reaction H₂SiO₄⁻=H₂SiO₄− + H⁺ taken from WATCH (Arnórsson et al., 1982), and (4) equilibrium constants for the basaltic primary and secondary minerals, as well as hydrated basaltic glass (HBG) found in Icelandic soils as reported by Stefánsson (2001), Stefánsson and Gíslason (2001), Stefánsson et al. (2001) and Wolff-Boenisch et al. (2004a). The thermodynamic properties of An₇₀Ab₃₀, basaltic and rhyolitic glass, and allophe are listed in Table 1. Note that the basaltic and rhyolitic glass reported in Table 1 is not primary volcanic glass but hydrated basaltic glass depleted of non-network forming cations.

4. THEORETICAL BACKGROUND

A significant amount of ambiguity surrounds the use of the words discharge and runoff in the literature. In the present study discharge refers to the water flow rate measured in rivers in units of volume per time (e.g. m³/s). Runoff refers to the discharge divided by the surface area of the catchment in units of length per time (e.g. mm/yr). As such values of runoff can be compared directly with the quantity of rainfall in the study area. Instantaneous discharge and runoff will be represented by Q and q, respectively, in the discussion below.

For the case of mobile elements such as sodium that are insignificantly incorporated into secondary minerals or leached layers, and are negligibly affected by ion exchange (Clow and Mast, 2010), chemical denudation rates match closely the dissolution rates of the solids containing the element in the catchment rocks (Gíslason et al., 1996; Gíslason, 2001). Sodium in the studied basaltic catchments is contained mostly within basaltic glass and plagioclase (An < 75). A large number of studies have shown that the dissolution rates of volcanic glass and the alkali-rich feldspars (Oelkers et al., 1994; Gautier et al., 1994; Blum and Stillings, 1995; Oelkers and Schott, 1995; Oelkers, 2001; Oelkers and Gíslason, 2001; Gíslason and Oelkers, 2003; Wolff-Boenisch et al., 2004b; Carroll and Knauss, 2005) depend on temperature, the a₁/t /a₁/t⁺ activity ratio of the aqueous solution, and the saturation state of the water with respect to the dissolving phase. These various affects on rates can be quantified using

\[ r = sA_4 \exp \left( -\frac{E_A}{RT} \right) \left( \frac{a_{Al}^4}{a_{Al}^{4+}} \right)^{1/3} \left( 1 - \exp \left( \frac{\Delta G_{Al^4}}{\sigma RT} \right) \right) \]  

where r represents the basaltic glass or feldspar dissolution rate, s refers to the reactive surface area, A₄ designates a pre-exponential factor, E₄ refers to an activation energy, R corresponds to the gas constant, T designates the absolute temperature, and σ symbolizes the Temkin parameter, equal to 1 for basaltic glass when its formula is normalised to one Si atom (Duax et al., 1997) and 3 for the plagioclase (Gautier et al., 1994). \( \Delta G_{Al^4} \) refers to the Gibbs free energy of the reaction dissolving the solid phase in contact with water, which for the case of basaltic glass dissolution is that of hydrated basaltic glass surface layer. Consistent with the pragmatic application of Eq. (1) to experimental dissolution rate studies (e.g. Wolff-Boenisch et al., 2004a), the reactive surface area in this study refers that of the water–solid
interface exposed to weathering rather than the fraction of this interface that is actively dissolving (e.g. Helgeson et al., 1984).

Eq. (1) will be used in the present study to interpret the relative role of temperature versus runoff on the dissolution rates of primary rocks and thus the Na chemical denudation rates of the studied catchments. In accord with Eq. (1) dissolution rates depend on (1) the reactive surface area \(s\), (2) an Arrhenius-type term \(A_i \exp(-E_i/RT)\), (3) an aqueous activity term \((d_i^{aq}/d_i)^{1/3}\), and (4) a saturation-state term \((1 - \exp(H_i^{at}))\). Of the four terms in this rate equation, the Arrhenius-type term can be readily characterized in the laboratory. Activation energies and the ‘pre-exponential’ term \(A_i\) for basaltic glass and 0.17 for the plagioclase. Rearranging Eq. (2) and combining it with Eq. (1) yields:

\[ s = \frac{Q \times c_i}{v_i A_i \exp(-E_i/RT) \left(\frac{d_i^{aq}}{d_i}\right)^{1/3} (1 - \exp(H_i^{at}))} \]  

This equation allows estimation of the reactive surface area in a river catchment assuming one knows (1) the chemical composition of the river water, (2) the activation energy and pre-exponential Arrhenius terms for the mineral or glass containing the ith element, (3) and the fluid flow rate of water flowing from the catchment. These equations will be used below to illuminate the relative roles of temperature and runoff on the Na chemical denudation rates of the glaciated and direct runoff catchments of NE Iceland.

5. RESULTS

The measured concentrations of dissolved riverine major elements, pH, water temperature, and river instantaneous discharge are listed in Annex A. Two representative examples of the dependence of instantaneous discharge on water temperature are shown in Fig. 2. Glacial and direct runoff rivers show distinct discharge versus temperature relationships. Instantaneous discharge in Fig. 2 and the rest of this manuscript are reported as runoff normalized to the catchment area in units of mm/yr to facilitate comparison between individual catchments, with other studies and with previously reported annual discharge values. A direct correlation between instantaneous discharge and temperature is evident in the Hjarðarhagí glacial river; discharge increases with increasing temperature due to glacial melting. In contrast, there is no clear correlation between instantaneous

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>(\log K)</th>
<th>(\Delta H_r) (kJ/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>An70Ab30</td>
<td>(\text{Ca}_2\cdot\text{Na}_3\cdot\text{Al}_1\cdot\gamma\text{Si}_3\cdot\gamma\text{O}_8 = 0.7\text{Ca}^+ + 1.7\text{Al(OH)}_4^- + 2.3\text{H}_2\text{Si}<em>4\text{O}</em>{10})</td>
<td>-18.82</td>
<td>45,435</td>
<td>Stefánsson et al. (2001)</td>
</tr>
<tr>
<td>Basaltic glass</td>
<td>(\text{SiAl}_{0.36}\text{O}<em>2\cdot(\text{OH})</em>{1.08} + 2\text{H}_2\text{O} + 0.36\text{OH}^-)</td>
<td>-2.36</td>
<td>15,101</td>
<td>Gislason and Oelkers, 2003</td>
</tr>
<tr>
<td>Rhyolite glass</td>
<td>(\text{SiAl}_{0.2}\text{O}<em>2\cdot\text{OH}</em>{0.61} + 2\text{H}_2\text{O} + 0.2\text{OH}^-)</td>
<td>-0.94</td>
<td>17,090</td>
<td>Wolff-Boenisch et al. (2004b)</td>
</tr>
<tr>
<td>Allophane</td>
<td>(\text{Al}_2\text{O}_3\cdot\text{Si}<em>2\cdot\text{O}</em>{7.22} + 4.94\text{H}_4\text{SiO}_4 + 2\text{H}^+)</td>
<td>-33.42</td>
<td>139,539</td>
<td>Stefánsson and Gislason (2001)</td>
</tr>
</tbody>
</table>

The calculation of the thermodynamic properties of hydrated basaltic glass and the hydrated rhyolite glass was performed by using the thermodynamic data for amorphous \(\text{SiO}_2\) and \(\text{Al(OH)}_3\). Example of the calculation of the hydrated basaltic glass: \(\log K (\text{SiO}_2\text{am}) + 0.36\log K (\text{Al(OH)}_3 \text{amorph}).\)
The variation of the measured rock derived Na flux in all the studied rivers is shown as a function of instantaneous discharge in Fig. 3. Rock derived Na fluxes, which are equal to the Na chemical denudation rates were calculated from the difference of the total measured Na flux in the river samples and that originating from sea-spray. This latter flux was calculated by assuming all the Cl present in the river waters originated from seawater and multiplying the Cl flux by the Na/Cl ratio of seawater (Bruland, 1983). The proportion of Na originating from sea-spray ranged from 10% to 50% of the corresponding Na total fluxes, the highest sea-spray Na was in catchments close to the shore and decreasing inland. In contrast, the proportion of Na originating from glacial melt waters is negligible. The rock derived Na fluxes of the studied rivers increase with runoff in each catchment. The lowest fluxes were measured during the winter months which experienced both lower rainfall and temperature, and the highest fluxes were measured during the summer for the glacial rivers but during the spring for the direct runoff rivers (see Annex A). The ratio between the highest and lowest measured rock derived Na flux ranged from 176 in the direct runoff Grímsá river to 13 in the partial glacial Lagarfljót river. Note that water fluxes in the Lagarfljót are affected greatly by the presence of a large dam; the presence of this dam limits the seasonal flow variation of the Lagarfljót compared to the other rivers in this study.

Temperature affects significantly solution chemistry of the sampled river waters. The temperature variation of the aqueous activity term \( \left( a_{\text{Al}^3+} / a_{\text{Al}^3+} \right)^{1/3} \) in Eq. (1) in all the studied rivers is shown in Fig. 4. It can be seen that \( \left( a_{\text{Al}^3+} / a_{\text{Al}^3+} \right)^{1/3} \) for all of the studied rivers is a single function of temperature. In contrast, these ratios exhibit a scattered variation with runoff. In total this parameter increases by a factor of \( \frac{176}{24} \) with increasing temperature from 0 to 16°C, with an average increase of 7.4% per degree temperature increase. As can be seen in Fig. 5 the compositions of sampled river waters in all the catchments are characterized by a high proportion of Na derived from sea-spray, which increases with increasing temperature but decreases with increasing runoff.

![Fig. 2. Comparison of instantaneous discharge versus river water temperature at the time of sampling in two representative rivers, the direct runoff Fellsá and the glacial river at Hjardarhagi.](image)

![Fig. 3. Flux of rock derived Na (Na*) versus instantaneous discharge: (a) shown as a linear–linear plot and (b) shown as a log–log plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 4. Water temperature (T\text{water}) versus the aqueous activity ratio \( \left( a_{\text{Al}^3+} / a_{\text{Al}^3+} \right)^{1/3} \) for all river water samples collected in this study. The symbols represent measured river water chemistry but the curve corresponds to a fit of these data with Eq. (4) – see text.](image)
The variation of this term with temperature for basaltic glass and intermediate plagioclase is calculated using parameters reported by Gislason and Oelkers (2003) and Carroll and Knauss (2005) shown in Fig. 7. The activation energies reported for basaltic glass and intermediate plagioclase dissolution are 25.5 and 42 kJ/mol, respectively. As shown in this figure, this Arrhenius term leads to dissolution rates that increase by approximately a factor of two with temperature rising from 0 to 16 °C with an average increase of 5% per degree temperature increase.

The reactive surface area corresponding to each measured instantaneous flux measurement as calculated from Eq. (3) and the data reported in Annex A is shown as a function of instantaneous runoff in Fig. 8. This calculation was performed by equating instantaneous discharge values listed in the Annex with \( Q_s \) the fluid flow rates in Eq. (3). Retrieved reactive surface areas are large. Calculated reactive surface areas based on basaltic glass dissolution rates range from \( 1 \times 10^9 \) to \( 1 \times 10^{13} \) m²; these values depend on both the identity of the catchment and the runoff. Using dissolution rates of intermediate plagioclase as reported by Carroll and Knauss (2005), would give 3–4 times larger reactive surface area. This difference, though not negligible, will not affect the interpretation of the role of temperature versus runoff on chemical denudation described below. A clear trend of increasing reactive surface area with runoff is apparent in each catchment.

Further insight into the nature and significance of the retrieved reactive surface areas can be obtained by normalizing them to the geographic surface area of their respective catchments in accord with

\[
\bar{s} = s/A
\]

where \( \bar{s} \) refers to the geographic surface area normalized reactive surface area, and \( A \) designates the geographic surface area of the catchment. The \( \bar{s} \) is, thus, dimensionless and defines the reactive surface area of the mineral or glass per each unit of geographic surface area, e.g. the number of cm² of reactive surface area beneath 1 cm² of soil. The \( \bar{s} \) is a unique parameter allowing evaluation of the effect of runoff on Na chemical denudation rates independent of temperature; the effect of temperature on rates was accounted for through the Arrhenius and fluid composition in Eq. (1). The \( \bar{s} \) for all studied catchments is shown as a function of instantaneous runoff in Fig. 9. The \( \bar{s} \) increases with runoff in all catchments and ranges in value from 14 to 4000. The lines drawn in Fig. 9 correspond to linear fits of these data starting at the origin. It can be seen that, to a first approximation, \( \bar{s} \) can be described as a linear function of runoff.

The \( \bar{s} \) term is directly related to the Na chemical denudation rate of the catchment through Eqs. (1), (3), and (5). As such the slopes of the lines in Fig. 9 provide insight into how sensitive denudation rates are to increases in runoff. As can be seen in Fig. 9 the slopes of \( \bar{s} \) versus instantaneous runoff \( q \), \( \bar{s}/q \), vary significantly from catchment to catchment. The variation of \( \bar{s}/q \) with the average age of the catchment rocks is illustrated in Fig. 10. The \( \bar{s}/q \) ratio de-
creases systematically with the average age of the catchment rocks; the Bruër river, draining the youngest rocks, has a $s/q$ approximately five times greater than that of the Fjardarar river, which drain the oldest rocks of the catchments considered in this study. As such, an increase in runoff will increase the denudation rate of the Bruër river rocks five times more rapidly than that of the Fjardarar river. It is important to note that average rock age may not be the sole factor influencing this $s/q$ parameter. The youngest studied catchments are (1) glaciated, and (2) their rocks on average less crystalline than those of the older studied catchments. Glaciated catchments typically contain a large quantity of fresh permeable sediments; a small increase in runoff could increase dramatically the fluid–solid surface area in these catchments, as suggested by Fig. 10b. As quantified by Wolff-Boenisch et al. (2006), glassy basaltic rocks react ~5 times faster than their crystalline counterparts.

6. DISCUSSION

6.1. Significance of $s$, the geographic surface area normalized reactive surface area

One of the most important results of this study is the identification and quantification of $s$. As described above,
is generated though Eq. (5) by dividing the total reactive surface area participating in the weathering reaction by the geographic surface area of the whole catchment. Insight into the physical meaning of $s$ can be obtained by comparing it with idealized geometric surface areas. The volume normalized geometric surface area of 0.1 cm cubes or spheres is 60 cm$^{-1}$. A soil consisting of 0.1 cm cubes or spheres with a porosity of 40% would have a volume normalized geometric surface area of 36 cm$^{-1}$. Retrieved values of $s$ vary from 40 to 4000. This suggests that the average depth of the soil column actively participating in chemical denudation ranges from 1cm to 100 cm depending on runoff and the identity of the catchment. Note that this estimate may be considered a minimum estimate because not all minerals in the catchment are Na-bearing. Nevertheless, this estimate compares reasonably with the average estimated thickness of Icelandic soils of 50–200 cm as reported by Oskarsson et al. (2004).

The above discussion suggests that the increase of $s$ with runoff stems from a corresponding increase in the height of the water table. Moreover, the linear correlation between $s$ and runoff suggests a similar linear correlation between runoff and water-table height. It is of interest to note that this latter observation is consistent with Darcy’s Law for fluid flow (cf. Oelkers, 1996), assuming permeability does not vary as a function of depth of the solid column, supporting our use of a linear correlation when fitting the $s$ versus runoff plots.

6.2. Residence times and water temperature

A major assumption of the data analysis presented in this study is the use of the water temperature of the rivers at the time of sampling to represent the temperature of the overall weathering process. There is little doubt that water in these catchment experiences a range of temperatures during its passage from rain or glacial melt water to the sampling site. Air, soil, and water temperature in NE Iceland is seasonal; during the study, the air temperatures averaged from $-4$ °C in January and $10$ °C in July at low elevation in the study area, but $-8$ to $5$ °C at higher elevations (Björnsson, 2003). The degree to which the measured water temperature is representative of that experienced during its passage through the catchment depends strongly on its residence time. As described above, by assuming that the full 50–200 cm average soil depth of studied catchments was water saturated, the residence time of water in the studied catchments was estimated to be 3 weeks–7 months. The interpretation of reactive surface area retrieved in Section 6.1, however, suggests that, assuming negligible contribution from undersaturated pores, the average water column height in the catchments ranged from 1 to 100 cm in depth with an average height of $\sim 10$ cm. This observation suggests that a better estimate of residence time may be roughly five times shorter than that of our original estimate or from 4 days to 7 weeks. This latter estimate seems to support use of the measured sampled water temperature in our analysis.

6.3. What is the relative influence of temperature versus runoff on chemical weathering?

The results presented above illustrate the distinct influence of temperature and runoff on the Na chemical denudation rates in seven NE Iceland river catchments. The two
major contributors of temperature to the dissolution rates, the Arrhenius and the fluid chemistry terms in Eq. (1) combine to increase rates by 13% per °C, similar to that observed in laboratory experiments. This compares closely with the measured annual chemical denudation rate of Ca and HCO₃ of the same catchments (Gislason et al., 2009) which increased by 6–14% for each °C rise in temperature.

Runoff is found to be linearly correlated to weathering rates through the $\delta$ parameter. This linear correlation passes through the origin for all catchments consistent with the absence of chemical denudation in the absence of runoff. As such, a 1% increase in runoff increases denudation rates by 1% in all studied catchments. Again, this agrees well with the measured annual chemical denudation rate of Ca.

Fig. 9. Retrieved reactive surface area normalized by the geographic surface area of the river catchments ($\delta$) versus instantaneous runoff ($q$) in the studied rivers. The symbols represent instantaneous surface areas but the lines represent a linear least squares fit of the data; this fit was constrained to pass through the origin in all plots. The slope and $R^2$ goodness of fit parameter is listed in each plot.
and calculated Na chemical denudation rates is apparent. Note Eq. (6) is based on the assumption that the dissolution of a single phase, in this case basaltic glass, is responsible for the rock derived Na in the studied rivers and that no Na is incorporated into secondary minerals. Treating Na denudation with this approach is justified because the dissolution mechanism and activation energy of plagioclase, the only other significant source of rock derived Na in these catchments is similar to that of basaltic glass. The generalization of Eq. (6) for its application to other elements and other catchments may require provision for the differing dissolution mechanisms of other primary minerals, multiple sources of the element, secondary mineral precipitation, and the variation of mineral dissolution and precipitation rates with fluid saturation state at close-to-equilibrium conditions.

Consistent with Eq. (6) and the results shown in Fig. 11, a $1\degree C$ increase in temperature will increase Na chemical denudation rates by 13\%, whereas a 1\% increase in runoff will lead to 1\% increase in Na chemical denudation rates. As such the degree to which temperature or runoff dominates the feedback between climate and Na denudation depends on the relative change of these two rate controlling factors. For the case of the NE Icelandic rivers, measured water temperatures ranged from 0 to 15.4 $\degree C$. A 15 $\degree C$ temperature increase will increase chemical denudation rates by a factor of 6 at a constant runoff. In contrast, instantaneous runoff in NE Icelandic rivers increased by as much as 250-fold from lowest to highest. Due to this large variation in runoff, it was the most significant factor influencing chemical denudation in our study area. It is clear that the degree to which temperature or runoff dominates variations in chemical denudation in other catchments will depend on the relative variation of these parameters.

### 6.4. Relevance to the chemical weathering rates of other catchments

Constant temperature sodium chemical denudation rates determined in this study are found to be proportional to runoff. This observation is equivalent to the total aqueous concentration of sodium being runoff independent consistent with the chemostatic behaviour observed in many natural catchments (e.g. Godsey et al., 2009; Clow and Mast, 2010). A number of studies have proposed mechanisms to account of the chemostatic behaviour of catchments (e.g. Clow and Mast, 2010; Maher, 2010, 2011). Processes that could induce such behaviour include (1) the fluid phase approaching equilibrium with the primary phases in the catchment, (2) secondary phases buffering the concentration in the fluid phase, and (3) an increase in mineral-fluid surface area with increasing runoff. The interpretation of Na chemical denudation rates described above is consistent with the last of these processes as the Na bearing primary minerals and glasses are strongly undersaturated, and Na is negligibly incorporated into secondary phases in our study area. The concentration data for other elements, including Si and Ca in Annex A exhibit close to chemostatic behaviour. In the case of these elements, the slowing of primary mineral dissolution rates as
equilibrium is approached, and the contribution of secondary mineral dissolution/precipitation could play a role.

The observations on Na chemical denudation rates described above suggest that the catchments considered in this study exhibit a nearly homogeneous behaviour such as illustrated in Fig. 12. In this schematic illustration the catchment soils are homogeneous in terms of (1) mineralogy, (2) porosity, (3) permeability, and (4) surface area, and all reactions assumed to occur in the water saturated region below the water table. A doubling of rainfall would double the height of the water table, for example from water Table 1 to water Table 2. Runoff from the system would double, consistent with Darcy’s law, such that the residence time of the water in the soil would remain constant. The doubling of the water table height would also double the water–solid interfacial surface area, thus doubling the chemical denudation of the primary minerals and glasses consistent with the observations on Na reported.
above. Such a simple model may also be applicable to young volcanic soils, andosol, and recent soils loaded with glacial deposits (Arnalds, 2004; Sigfusson et al., 2006). The simple model described, above, however, is based on the assumption that the soil mineralogy is stratigraphically homogeneous. Soils in many catchments are characterized by a stratigraphic control of secondary minerals in which less reactive secondary minerals are present near the top and more reactive primary minerals deep in the soil column (e.g. White et al., 1996; White and Brantley, 2003; Brantley et al., 2007). In such cases, the model described in Fig. 12 is likely not applicable and increasing rainfall and runoff could dilute the chemical flux originating from the dissolution of the deep secondary minerals.

The dependence of chemical denudation rates on temperature in this study is controlled to a large extent on (1) the activation energies of the dissolving primary minerals and glasses and (2) the degree to which rates depend on aqueous solution chemistry. As the activation energies and rate equations for the dissolution of primary minerals depend on the mineral identity (e.g. Schott et al., 2009), primary lithology will strongly affect the variation of chemical denudation rates on temperature.

7. CONCLUSIONS

The results summarised above suggest that to a first approximation the effects of temperature and runoff on chemical denudation rates can be decoupled by treating them as if they were laboratory flow reactors. By distinguishing the effects of temperature and runoff on chemical denudation rates it should be possible to predict, using comprehensive climate models, the past and future evolution of chemical denudation rates both on a catchment and on a global scale. Such predictions would enable improved interpretation of the feedback between climate and weathering over geological timescales. The degree to which the equations generated in this study describe the annual elemental weathering fluxes of these catchments will be explored in a subsequent study.

Table 2

Physical and chemical parameters describing the studied catchments including the size of the river catchments, percent glacial cover, area weighted age of the catchments rocks, calculated geometric reactive surface area ($s$, Eq. (3)) versus runoff ($q$), geometric surface area normalized to the geographic surface area of the catchments (Eq. (5)) versus runoff ($q$), calculated residence time range of the water on each catchment and a catchment dependent constant, $a$ (Eq. (6)) – see text.

<table>
<thead>
<tr>
<th>River catchment</th>
<th>Catchment size (km²)</th>
<th>Glacial cover (%)</th>
<th>Rock age (Myr)</th>
<th>$s/q$^* (myr)</th>
<th>$s/q$ (yr/ mm)</th>
<th>Residence time** (days)</th>
<th>$a$ (mol/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bru´ 2089</td>
<td>68</td>
<td>1.32</td>
<td>1.00E+09</td>
<td>0.48</td>
<td>4–90</td>
<td>3.26E+22</td>
<td></td>
</tr>
<tr>
<td>Hjarðarhagi</td>
<td>3338</td>
<td>43</td>
<td>1.71</td>
<td>1.55E+09</td>
<td>0.47</td>
<td>5–70</td>
<td>4.39E+22</td>
</tr>
<tr>
<td>Hóll 560</td>
<td>27</td>
<td>2.14</td>
<td>1.18E+08</td>
<td>0.21</td>
<td>2–29</td>
<td>4.10E+21</td>
<td></td>
</tr>
<tr>
<td>Fellá 125</td>
<td>0</td>
<td>5.9</td>
<td>1.04E+07</td>
<td>0.08</td>
<td>0.1–15</td>
<td>4.61E+20</td>
<td></td>
</tr>
<tr>
<td>Grímá 507</td>
<td>0</td>
<td>6.45</td>
<td>5.86E+07</td>
<td>0.12</td>
<td>0.2–33</td>
<td>2.07E+21</td>
<td></td>
</tr>
<tr>
<td>Lagarfjót*** 2777</td>
<td>6</td>
<td>5.99</td>
<td>4.11E+08</td>
<td>0.15</td>
<td>4.12E+21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fjardará 56</td>
<td>0</td>
<td>11.2</td>
<td>4.14E+06</td>
<td>0.09</td>
<td>0.2–39</td>
<td>1.60E+20</td>
<td></td>
</tr>
</tbody>
</table>

^* Area weighted average rock age (Gislason et al., 2009).

** Estimated residence time.

*** Due to the presence of a large lake on the catchment, the residence time likely exceeds 1 year.

![Fig. 12. Schematic illustration of the catchments considered in the present study – see text. The height of the water column is given by either $h$ or $2h.$](image-url)
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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.12.034.

REFERENCES


