

BIROn - Birkbeck Institutional Research Online

Hawley, S. and Pogge von Strandmann, Philip A.E. and Burton, K. and Williams, H. and Gislason, S. (2017) Continental weathering and terrestrial (Oxyhydr)oxide export: comparing glacial and non-glacial catchments in Iceland. *Chemical Geology* 462 , pp. 55-66. ISSN 0009-2541.

Downloaded from: <https://eprints.bbk.ac.uk/id/eprint/18989/>

Usage Guidelines:

Please refer to usage guidelines at <https://eprints.bbk.ac.uk/policies.html>
contact lib-eprints@bbk.ac.uk.

or alternatively

Continental Weathering and Terrestrial (Oxyhydr)oxide Export: Comparing Glacial and Non-glacial Catchments in Iceland.

Scott M Hawley^{*1}, Philip A.E. Pogge von Strandmann², Kevin W. Burton¹, Helen M Williams³, Sigurdur R Gíslason⁴

¹ Department of Earth Science, Durham University, Stockton Road, Durham, DH 1 3LE, UK

² London Geochemistry and Isotope Centre (LOGIC), Institute of Earth and Planetary Sciences, University College London and Birkbeck, University of London, Gower Street, London, WC1E 6BT, UK.

³ Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

⁴ Science Institute, University of Iceland, Dunahgi 3, 107 Reykjavik, Iceland

*Corresponding author. E-mail: s.m.hawley@durham.ac.uk, address: Dept. Earth Science, Durham University, DH1 3LE

Abstract

Glaciers enhance terrestrial erosion and sediment export to the ocean. Glaciers can also impact mineral specific weathering rates relative to analogous non-glacial terrains. In tandem these processes affect continent sediment export to the oceans over glacial-interglacial cycles. This study summarizes field data from glacial and non-glacial Icelandic river catchments to quantify the impact of weathering regime on iron and aluminium (oxyhydr)oxide mineral formation and flux rates. Aluminium and iron (oxyhydr)oxides are strong indicators of organic carbon preservation in soils and marine sediments. Tracing changes in (oxyhydr)oxide formation and deposition therefore provides a means of evaluating potential changes in organic carbon sequestration rates over glacial-interglacial cycles. Overall, there are several measurable chemical differences between the studied glacial and non-glacial catchments which reflect the key role of soil formation on terrestrial weathering. One of the noted chemical difference is that weathering in non-glacial catchments is characterized by higher apparent rates of iron and aluminium (oxyhydr)oxide formation relative to glacial catchments. However, the offset in (oxyhydr)oxide formation does not appear to be transferred into river sediment compositions, and physical weathering appears to be the dominant control of river sediment composition and export. Glacial rivers export far more total sediment to nearshore marine environments than analogous non-glacial

rivers suggesting glacial weathering enhances carbon burial by increasing nearshore marine (oxyhydr)oxide accumulation.

Keywords: Climate change; organic carbon burial; iron oxyhydroxides; continental weathering

1 Introduction

Iron and Al (oxyhydr)oxide ($\text{Fe}/\text{Al}_{\text{OOH}}$) concentrations are approximated based on selective chemical extractions techniques. The pool of dithionate-citrate-bicarbonate (DCB) reducible minerals, referred to as 'highly reactive Fe/Al' ($\text{Fe}_{\text{HR}}/\text{Al}_{\text{HR}}$), is one of the most commonly used methods for estimating for both Fe_{OOH} and Al_{OOH} (Raiswell and Canfield 2012). There are strong correlations between the concentrations of Fe_{HR} and organic carbon in marine sediments and $\text{Fe}_{\text{HR}}/\text{Al}_{\text{HR}}$ and organic matter in soils (Schrumpf et al., 2013). These correlations are thought to reflect the physiochemical protection of organic matter by Fe_{OOH} and Al_{OOH} (see review by Schrumpf et al., 2013); a process which has been dubbed the 'Rusty Carbon Sink' (Lalonde et al., 2012, Barber et al., 2014).

The Rust Carbon Sink is not the first hypothesis to propose Fe_{OOH} can have a major impact on Earth's climate cycle. The Iron Hypothesis (Martin, 1990) is the well-studied idea that Fe_{OOH} accumulation in the Southern Ocean controls primary productivity in the region. While much of the research into the Iron Hypothesis has focused on atmospheric dust e.g. Coale et al., 2004; as Martinez-Garcia et al., (2014) the original iron hypothesis also proposed the intensity of glacial weathering on Antarctica itself was a major control of iron export to the ocean. Glacial weathering has been shown to allow for both the formation and large scale export of iron (oxyhydr)oxides to coastal marine environments (Raiswell et al., 2008; Hawkins et al., 2014, Eiriksdottir et al 2015). This raises the question of whether weathering promotes organic carbon burial, in addition to primary production, as a result of enhanced marine Fe_{OOH} discharge.

This study re-examines published physical and chemical weathering data from glacial and non-glacial catchments in Iceland. River waters, sediment and soils are compared to derive generalized patterns of continental weathering in glacial and non-glacial catchments. Novel PHREEQC inverse models are also used to approximate the Fe_{OOH} and Al_{OOH} formation rates based on comprehensive river monitoring datasets. The geologic and geographic nature of Iceland limits the impact of bedrock variability and emphasizes the impact of continental weathering on sediment composition. This allows a more accurate determination of the potential impact of chemical offsets between glacial and non-glacial weathering on (oxyhydr)oxide formation.

2 Icelandic Geology, Hydrology and Sample Locations

Iceland has four characteristics which favour its use as a type locality for linking glacial and non-glacial weathering differences to differences in $\text{Fe}/\text{Al}_{\text{OOH}}$ dynamics. Iceland's geologic and geographic history has combined to create river catchments, which can be chemically differentiated based on their extents of soil formation (Gislason et al., 1996). Iceland's human geography ensures that the catchments are not significantly altered by anthropogenic activity. Icelandic rivers have been intensively sampled providing a large historic chemical database which can be utilized to investigate chemical weathering. Finally, existing thermodynamic scientific studies have defined clear expectations of how chemical weathering should progress in Iceland.

Bed rock rheology and chemical composition significantly impact continental weathering rates (Syvitski and Milliman 2007). Therefore, geologically similar and well-characterized catchments are useful when comparing glacial and non-glacial weathering rates. Iceland is a geologically young and active island, formed primarily (>80%) of basaltic lavas, with a mixed mid-ocean ridge/ocean island melt source composition. The remainder of the island is composed of more acidic/rhyolitic lavas (Jakobsson 1972). Iceland was completely covered by a single glacial icesheet ~9 ka ago, which collapsed during the Early Holocene stabilizing to near modern conditions about 6 ka ago (Gislason 1996; Norðhal and Petersson et al., 2005). Since the collapse of the icesheet vegetation and soil formation have created significant chemical differences between glacial and non-glacial catchments, reflected in the distribution of Iceland's major soil/sediment types (Figure 1). Soil formation has been attributed to as the principle cause of a number of chemical differences between the glacial and non-glacial catchments (Gislason et al., 1996; Pogge von Strandmann et al., 2006, 2012; Opfergelt et al., 2013; Opfergelt et al., 2014).

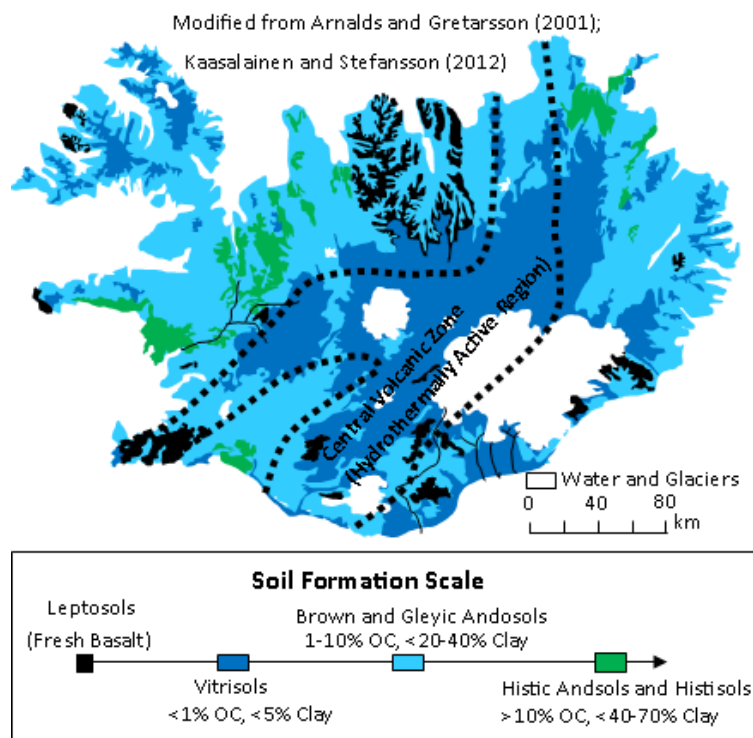


Figure 1. Icelandic soil coverage map as modified from Arnalds and Gretarsson (2001). The Central Volcanic zone defines the general limits of significant hydrothermal groundwater formation as mapped by Kaasalainen and Stefansson (2012).

A number of previous studies have sampled Icelandic soils, sediments, rivers and groundwaters in the context of continental weathering and this study will draw extensively on data from: Gislason and Stefansson (1993), Gislason et al., (1996), Stefansson et al., (2001), Arnorsson et al., (2002), Pogge von Strandmann et al., (2006), Vigier et al., (2006), Vigier et al., (2009), Oskarsson et al., (2012), Pogge von Strandmann et al., (2012), Eiriksdottir et al., (2008), Louvat et al., (2008) and Opfergelt et al., (2014). This previously published work provides what is likely the most complete and extensive data-set on the interplay of weathering regimes and chemical weathering ever collected on a single geologic terrain. Because the chemistry of river waters and sediment can show a high degree of temporal and spatial variability, large sample sets are required to make statistically robust conclusions about the chemical weathering process.

3 Methods

3.1 Field sample collection:

River water and sediment samples from Iceland were collected during September 2003, August 2005 reported in Pogge von Strandmann et al., (2006) and then again by the same methods in August 2012 and August 2013 at locations shown on Figure 2. River samples were collected from near the water surface in the centre of the flow with access

113 facilitated by road bridges. For filtered and suspended sediment samples, 15L of water was
114 collected and filtered shortly after sampling through 0.2µm cellulose-acetate Millipore filters,
115 using a pressurized PFA unit. To prevent sample cross contamination the units were flushed
116 with milli-Q water and at least 2 L of sample which were discarded prior to sample collection.
117 Elemental iron and aluminium concentrations within this filtered water will be referred to as
118 'filtered' iron/aluminium rather than the more commonly used 'dissolved' moniker. The filters
119 were sealed in petri-dishes for immediate storage and transport to controlled lab conditions
120 where the sediment was physically removed with a tephlon spatula and transferred into
121 glass vials. Total suspended sediment (TSS) concentrations were measured separately by
122 filtering a known volume of water through a pre-weighted 0.2µm filter. These filters were also
123 sealed in petri-dishes for transport to the laboratory where they were dried and re-weighed.
124 Total anion samples, utilizing containers cleaned without acids to avoid NO_3^{2-} or Cl^-
125 contamination, were also collected. Temperature, pH, alkalinity and conductivity were
126 measured in the field, and where possible a river bed sediments (RBS) sample was also
127 taken.

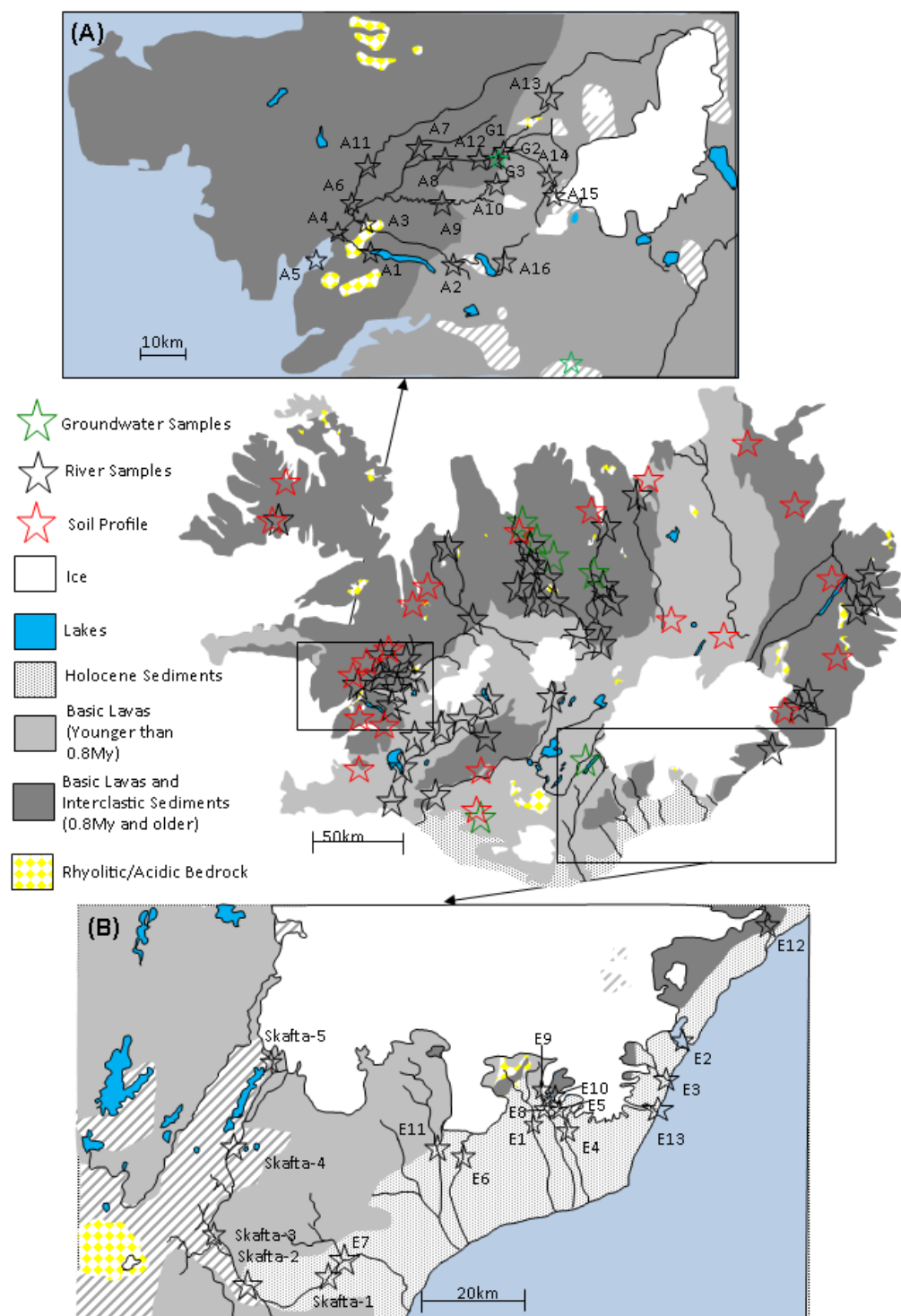


Figure 2. Bedrock Map and River Catchments. The middle figure shows the locations of samples from Gislason et al., (1996), Arnorsson et al., (2002), Oskarsson et al., (2012), and Opfergelt (2014) on a modified version of the Icelandic bedrock map from the Natural History Museum of Iceland. (A) Shows sample locations in the Borgarfjörður region and (B) shows the sample locations in the Vatnajökull region.

We will consistently compare our data with Gislason and Arnorsson (1993), Gislason et al., (1996) and Arnorsson et al., (2002) who sampled at locations shown on Figure 3. The

only significant difference between the methods used in these studies and our methods is that these previous studies utilized a 0.1 μ m cut-off size for filtering their water. Waters filtered at the 0.2 μ m and 0.1 μ m level are predicted to be closely comparable in terms of Fe, based on studies of the relationship between particle size and Fe speciation (e.g. Lyven et al., 2003, Andersson et al., 2006).

3.2 Major and Trace Element Analysis:

Samples from the 2003 and 2005 field seasons were analysed by Pogge von Strandmann et al., (2006) with methods reported therein. Anions and cations from the 2012 and 2013 samples were analysed using a Dionex D-500X ion exchange chromatograph at Durham University. Iron and aluminium concentrations were measured by a Thermo-Fisher X-Series inductively coupled plasma mass spectrometry (ICP-MS) at Durham University, calibrated against multi-element synthetic standards prepared from high purity single element standards. A collision cell was used to reduce oxide formation and improve accuracy. The natural water certified reference material SLRS-5 was used confirm the accuracy of the measurements. External reproducibility for all measurements was better than $\pm 5\%$.

The total carbon concentrations of a selected range of suspended sediment samples were measured during stable carbon and nitrogen analysis on an isotope ratio-mass spectrometer at Durham University. The total carbon concentrations of river bedload sediments were not directly measured but loss-on-ignition values collected during XRD analysis by Pogge von Strandmann et al., (2006) are used to reflect maximum potential carbon concentrations in these samples.

4. Theory and Model Calculations

PHREEQC v. 3.0.6 (Parkhurst and Appelo 1999) parameterized with the Bureau de Recherches Geologiques et Minieres database (Blanc et al., 2011) was used to build an inverse dissolution/precipitation weathering model. The model calculates primary mineral dissolution rates and secondary mineral precipitation rates. This is done by numerically determining the balance of primary mineral dissolution and secondary mineral dissolution needed to recreate the measured river water chemistry of a sample from an initial idealized rainwater solution. In effect this modelling approach provides a way of utilizing the overall chemical patterns of the rivers to investigate chemical weathering rather than depending on one or two element comparisons.

The measured chemical composition (alkalinity, pH Al, Ca, Cl, Fe, K, Mg, NO₃, Na, Si, SO₄) of the river samples was used to define a solution for every filtered water sample.

The Cl concentrations of each sample were then used to define an idealized initial rainwater solution for each sample according to the method developed by Gislason et al., (1996). The idealized Cl derived rainwater solutions are not perfectly charge balanced so a 5% elemental uncertainty was included in the model calculations to account for the charge imbalances. The 5% threshold was set by assuming the charge imbalances reflected analytic uncertainty. All chemical pathways which reproduce the river solutions from the dissolution of primary bedrock phases and precipitating the secondary phases starting from the idealized rainwater solutions were calculated. These pathways were then averaged, yielding a single set of mineral precipitation and dissolution values characteristic of the weathering signature of each sample.

The primary mineralogy of both the primary basaltic bedrock (excluding basaltic glass) and secondary clay and (oxyhydr)oxide phases are well constrained and have been defined based on Jakobsson (1972), Gislason and Arnorsson (1993), Stefansson (2001), and Opfergelt et al., (2013) as reported in Table 1. The inverse models depend on stoichiometric calculation, rather than thermodynamic data, preventing the inclusion of amorphous phases namely, basaltic glass and allophone, which have no set formula. The stoichiometric nature of the model also makes it impossible to differentiate minerals with the same chemical formula. Ferrihydrite and boehmite were excluded from the models on this basis as these minerals have the same chemical formulas (as defined in the PHREEQC database) as goethite and gibbsite, respectively. PHREEQC requires all elements used for charge balance during inverse model calculations to be included in model input phases requiring the addition of CO₂, O₂, Cl₂, NH₃ and SO₂ into the model parametrization.

Table 1 Summary of minerals included in PHREEQC inverse-models.

Charge Balance	Primary Mineral Phase (Dissolved Only)		Secondary Mineral Phases (Precipitate Only)	
CO ₂	Forsterite: Mg ₂ SiO ₄	Hedenbergite: CaFe(SiO ₃) ₃	Imogolite: Al ₂ SiO ₃ (OH) ₄	Goethite: FeOOH
O ₂	Fayalite: Fe ₂ SiO ₄	Ilmenite: FeTiO ₃	Heulandite: Ca _{1.07} Al _{2.14} Si _{6.86} O ₁₈ ·6.17H ₂ O	Boehmite: AlOOH
Cl ₂	Ferrosilite: FeSiO ₃	Albite: NaAlSi ₃ O ₈	Montmorillonite(A): Ca _{0.17} Mg _{0.34} Al _{1.66} Si ₄ O ₁₀ (OH) ₂	
NH ₃	Enstatite: MgSiO ₃	Anorthite: CaAl ₂ Si ₂ O ₈	Montmorillonite (B): Na _{0.34} Mg _{0.34} Al _{1.66} Si ₄ O ₁₀ (OH) ₃	
SO ₂	Diopside: CaMg(SiO ₃) ₂	Sandine: KAlSi ₃ O ₈	Kaolinite: Al ₂ Si ₂ O ₅ (OH) ₄	

The biggest potential problem with utilizing inverse-chemical weathering models is that the results are dependent on knowing the exact chemical formulas of all the mineral

phases. Ideally every potential mineral phase needs to be precisely and accurately defined however this is not possible in the context of Icelandic weathering. Specifically, additional consideration needs to be given for the behaviour of basaltic glass and allophane.

Basaltic glass is the first component of Icelandic basaltic to be chemical weathered in most low temperature environments (Stefansson et al., 2001). The thermodynamics of glass dissolution in Iceland have been studied but the process has only been defined as a function of a theoretical pure $\text{SiAl}(\text{OH})$ form i.e. Gislason and Oelkers (2003), Eiriksdottir et al., (2015). As our model is dependent on mineral stoichiometry, the inclusion a theoretical glass formula, which does not contain Fe, Ca, Mg, etc., would strongly bias the model predicted impact of glass dissolution. Glass dissolution is a well quantified source of Fe_{OOH} formation (Gislason and Arnorsson 1993). The exclusion of basaltic glass in the model is equivalent to the assumption that Fe and Al will behave in the same way during glass weathering. That is glass weathering is assumed to not lead to preferential Fe_{OOH} vs Al_{OOH} formation. A different stoichiometric problem prevents the inclusion of allophane, one of the most common secondary minerals in Icelandic soils (Oskarsson et al., 2012), in the models.

Secondary alumina-silica formation in Iceland has been described as involving the formation of 'amorphous sponge-like balls of kaolinite, allophane and imogolite' which are in quasi-equilibrium with gibbsite (Stefansson and Gislason 2001). The precise composition of these alumina-silicate agglomerates appears to vary with changing conditions (Stefansson and Gislason 2001), making it impossible to define a fixed chemical formula for the species. Kaolinite and Imogolite are the endmembers of the kaolinite-allophane-imogolite series so they were included in the model and allowed to vary relative to one another. The overall uncertainty of the Al/Si ratio of the amorphous alumina-silicates however does limit the certainty which can be ascribed to the Al_{OOH} formation rate estimates.

In other localities, the inclusion of iron in certain clay minerals would also introduce uncertainty in terms of the model-predicted $\text{Fe}/\text{Al}_{\text{OOH}}$ formation rates. In Iceland, this does not appear to be a significant problem. While Fe-smectites have been identified in mature Icelandic soils (Stefansson and Gislason 2001), very little iron appears to be directly incorporated into Icelandic clay minerals. Data supporting this assertion will be outlined in subsequent sections, but, in short, the most altered Icelandic soil samples from Opfergelt et al., (2014) are 82.5 and 98 wt. % clay and organic matter, and the iron within these samples is 91% and 95% DCB-extractable, respectively. Consequently, no more than about 5% of iron cycling during chemical weathering is affiliated with the formation of iron bearing clays.

5 Results

All data are presented in figures containing a mixture of new and published data which are cited accordingly. The solid phase concentration data is reported normalized to titanium. Titanium is considered to be immobile during basaltic weathering and behaves conservatively in basaltic soils (Nesbitt and Wilson 1992) favouring its use to normalize against organic matter dilution and/or mobile element leaching.

5.1 Icelandic Bedrock

Pristine Icelandic basaltic lavas from Jakobsson (1972), Arnorsson et al., (2002), Eiriksdottir et al., (2008), Louvat (2008) and Schuessler et al., (2009) are characterized by relatively constant Ti normalized elemental ratios shown on Figure 3. Icelandic rhyolite contains an order of magnitude less total Ti than the basalts, 2.2 mol/kg vs 0.17 mol/kg respectively, which significantly offsets the Ti normalized elemental concentrations between the basalts and rhyolites. There is limited compositional overlap between the basaltic and rhyolitic samples although some of the basaltic samples have [Na+K]/[Ti] values which drift towards more evolved values.

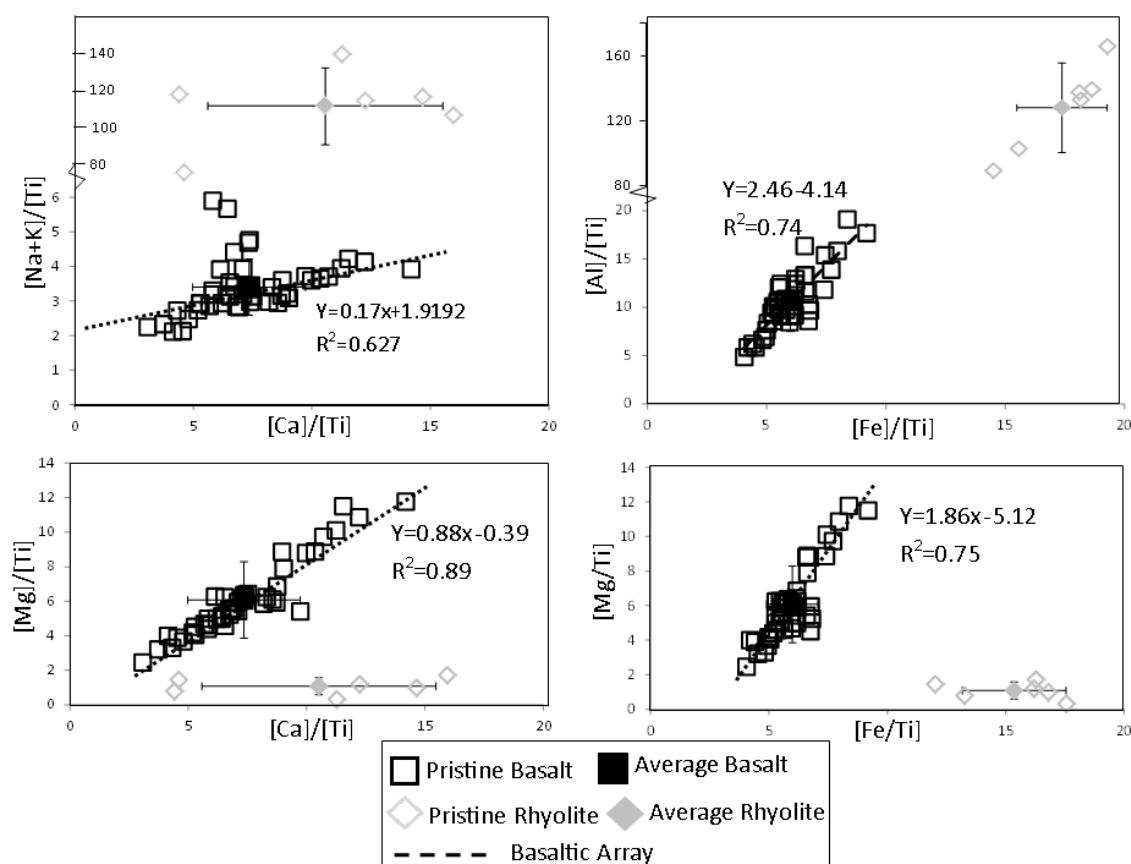


Figure 3. data from Jakobsson (1972), Arnorsson et al., (2002), Eiriksdottir et al., (2008), Louvat (2008) and Schuessler et al., (2009). Icelandic basalts display a limited range of variability in Ti normalized elemental space characterized by positive correlations between the various elements.

The compositional range of pristine Iceland basalt can be constrained to statistically significant correlations between Ti normalized elemental concentrations, shown as the dashed lines on Figure 3. These correlations include elemental pairs such as Mg and Ca, which have a similar mobility during chemical weathering, and elemental pairs such as Mg and Fe which have significantly different elemental mobilities (Gislason et al., 1996). For the remainder of this paper these correlations are used to define the compositional signature of pristine basalt, which will be shown as dashed black lines on the subsequent figures.

5.2 River Sediment Compositions

The compositions of total suspended sediment (TSS) and river bed sediment (RBS) from glacial and non-glacial rivers from Pogge von Strandmann et al., (2006) and Eiriksdottir et al., (2008) are reported relative to the basaltic compositional array in Figure 4. All the sediments have compositions which fall along or near the basaltic compositional array for most elements. The non-glacial TSS samples have mobile element patterns near one endmember of the basaltic compositional array while the glacial TSS samples have mobile element concentrations near the other basaltic endmember. The only potential compositional deviation of the sediments from basaltic values is apparent in Fe/Al space. A number of the glacial samples have lower [Al]/[Ti] ratios relative to their [Fe]/[Ti] ratios than observed in pristine basalt.

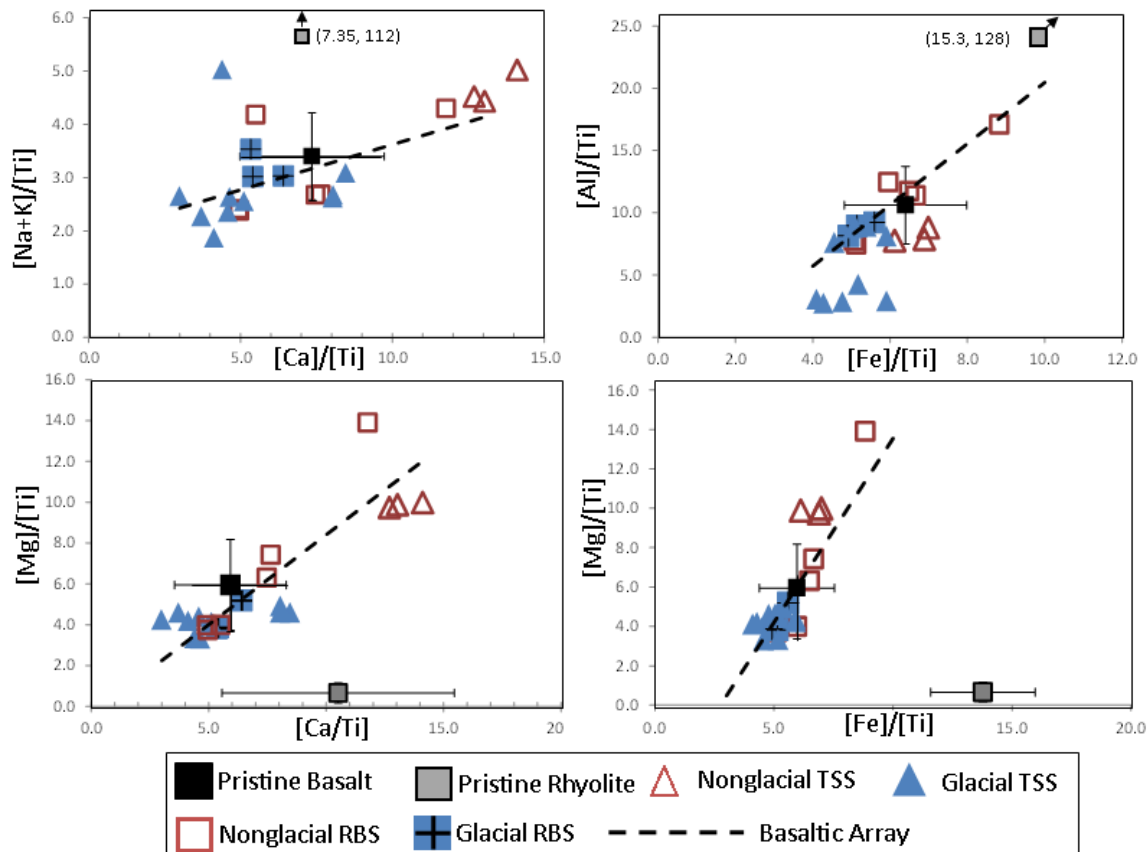


Figure 4. River sediment compositional data from Pogge von Strandmann et al., (2006) and Eiríksdóttir et al., (2008). All the river sediments have elemental compositions consistent with those expected for pristine basalt except in terms of the proportion of $[Al]/[Ti]$ to $[Fe]/[Ti]$ in the glacial sediments.

5.3 Soil Formation

The compositions of Icelandic soil samples from Óskarsson et al., (2012) and Opfergelt et al., (2014) are reported relative to the basaltic compositional array on Figure 5. All the samples are from soil profiles that lie above basaltic bedrock as shown on Figure 2. Air borne volcanic ash, primary composed of basaltic ash, is also a major component of most Icelandic soils (Óskarsson et al., 2012). The samples are colour coded according to their Total Reserve in Bases ($TRB = \sum Na^+ + K^+ + Ca^{2+} + Mg^{2+} \text{ cmol}_c \text{ kg}^{-1}$). In general soil formation leads to the loss of base cations, an increase in organic carbon concentration, and the transformation of primary magnetite into secondary (oxyhydr)oxides i.e. ferrihydrite and goethite.

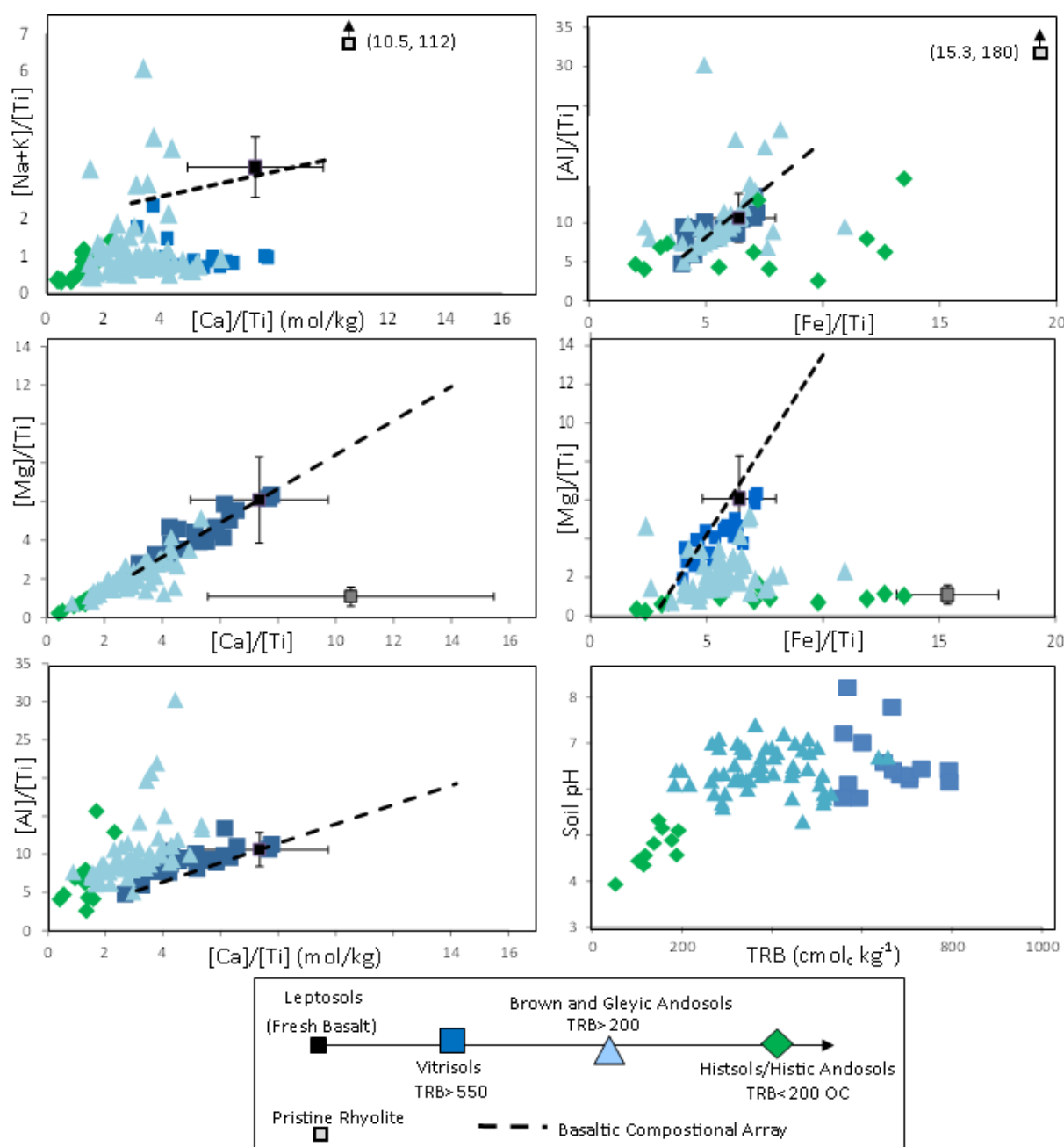


Figure 5. Icelandic soil composition data from (Oskarsson et al., 2012; Opfergelt et al., 2014). The dashed black lines reflect the compositional range of typical Icelandic basalt as defined in Section 3.2. The soils are colour coded according to their Total Reserve in Bases ($TRB = \sum Na^+ + K^+ + Ca^{2+} + Mg^{2+} \text{ cmol}_c \text{kg}^{-1}$).

There is a general decrease in soil pore-water pH with decreasing TRB. Magnesium and Ca appear to behave similarly and lie on the basaltic compositional array during chemical weathering. Nearly all the soils are significantly depleted in $[Na+K]/[Ti]$ relative to basalt. Aluminium is preferentially retained in the soils relative to Ca and Mg during chemical weathering. Iron is also preferentially retained in soils during chemical weathering relative to Mg and Ca. There is no clear and systematic pattern in the behaviour of Fe relative to Al

during chemical weathering although the soils with the lower TRB concentrations have significantly higher Fe/Al values than pristine basalt.

The trends in iron behaviour during weathering can be further explored by examining changes in iron mineralogy during weathering. Two selective iron extractions, sodium-dithionate-bicarbonate (Fe_{DCB}) and oxalate (Fe_{O}), were used to measure iron concentrations as a function of iron mineralogy in Icelandic soil by Opfergelt et al., (2014). The important difference between the extractions is that Fe_{O} includes magnetite but not goethite, while Fe_{DCB} includes goethite but not magnetite (Poulton and Raiswell 2005). Goethite is a common Fe-oxyhydroxide present during basaltic weathering (Stefansson and Gislason 2001), while magnetite is a common primary mineral phase in Icelandic basalts (Gislason and Stefansson 1993). Consequently, $\text{Fe}_{\text{DCB}}/\text{Total Iron (Fe}_\text{T})$ values reflect the proportion of iron oxyhydroxides to total iron within a sample. The $\text{Fe}_{\text{O}}/\text{Fe}_{\text{DCB}}$ values reflect the balance of magnetite dissolution to goethite formation.

Soil $\text{Fe}_{\text{DCB}}/\text{Fe}_\text{T}$ values show a strong positive correlation with soil clay content, increasing to in excess of 0.8 in soils with at least 60 wt.% clay (Figure 6A). Soil $\text{Fe}_{\text{O}}/\text{Fe}_{\text{DCB}}$ shows a negative correlation with clay content in all but the most weathered soils. A few of the strongly weathered samples have unusually low $\text{Fe}_{\text{O}}/\text{Fe}_{\text{DCB}}$ values given their clay content and these samples do not follow the correlation between clay content and organic carbon defined by others (Figure 26 B/C). Field characterizations of the outlying samples by Opfergelt et al., (2014) suggests that they are all from reducing horizons within the soil profiles.

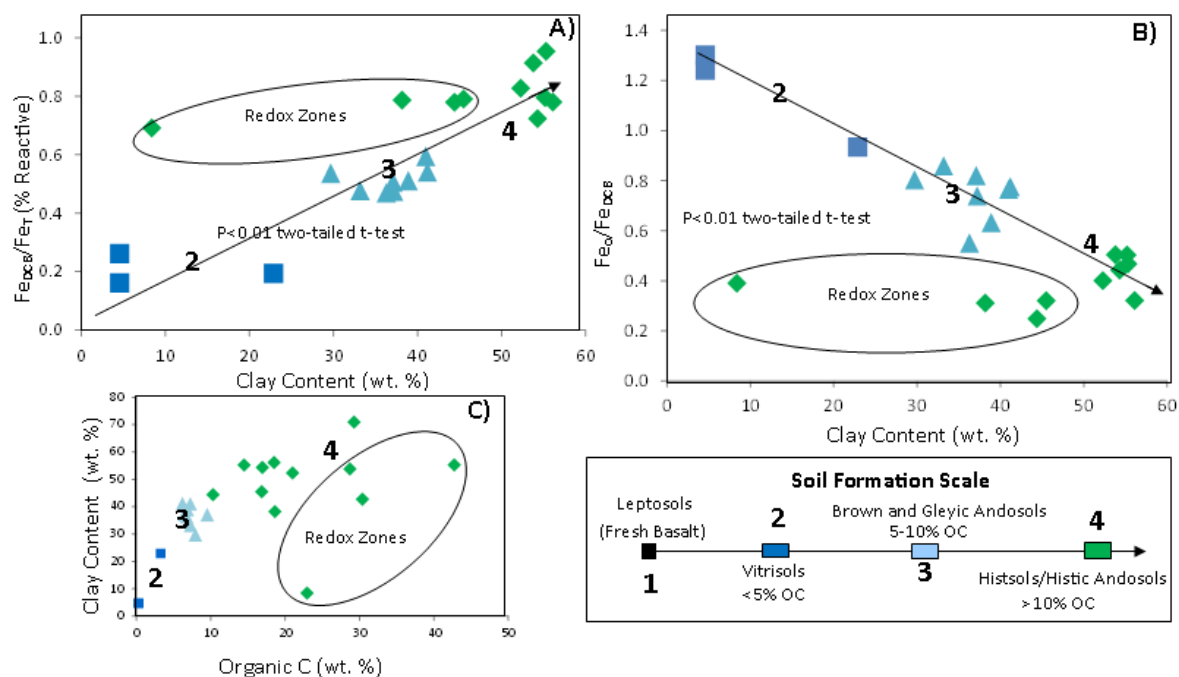


Figure 6. Data from Opfergelt et al., (2014). (A) The $Fe_{DCB}/Total\ Iron\ (Fe_T)$ values, reflecting the proportion of iron oxyhydroxides to total iron within soil samples, and (B) the Fe_O/Fe_{DCB} values, reflecting the balance of magnetite dissolution to goethite formation are plotted versus the clay content of soil samples from 1) leptosol, 2) vitrisols, 3) brown and gleyic andosols and 4) histisols/histic andosols. (C) The clay content increases with the organic carbon content

5.4 Dissolved Load Concentrations

The chemical composition of Icelandic glacial and non-glacial rivers reported by Gislason et al., (1996), Arnorsson et al., (2002), Vigier et al., (2006), Pogge von Strandmann et al., 2006, Louvat et al., (2008), as well as new measurements (data in Supplementary Information) are summarized in Table 2.2. The data in the table includes the measured values as well as values that have been corrected for precipitation inputs. Glacial and non-glacial rivers, on average, have significantly different Cl concentrations (90 μ M vs. 150 μ M respectively, $P < 0.05$). Icelandic river waters receive nearly all their Cl in affiliation with marine aerosols associated with precipitation allowing Cl to be used to correct rivers for rainwater inputs (Gislason et al., 1996).

Table 2. Average River water compositions $\pm\sigma$. *TSS values were only measured by Pogge von Strandmann et al., (2006), Vigier et al., (2006) and in the new samples reported in the this study. As a result, only 30 glacial and 30 non-glacial samples were utilized to calculate the pH and TSS values. **Chlorine concentrations were used to correct the river values for precipitation inputs according to methods established in Gislason et al., (1996).

	Uncorrected Value		Cl Corrected value	
	Glacial n=50	Nonglacial n=57	Glacial n=50	Nonglacial n=57
Al (μM)	1.4 \pm 1.1	0.5 \pm 0.4	1.4 \pm 1.1	0.5 \pm 0.4
Ca (μM)	81 \pm 40	102 \pm 49	80 \pm 40	99 \pm 49
Cl (μM)	90 \pm 49	150 \pm 98	-	-
Fe (μM)	0.4 \pm 0.4	0.5 \pm 0.5	0.4 \pm 0.4	0.5 \pm 0.5
K (μM)	10 \pm 6	15 \pm 7	8 \pm 6	12 \pm 8
Mg (μM)	59 \pm 59	75 \pm 57	51 \pm 60	64 \pm 57
Na (μM)	236 \pm 107	280 \pm 108	168 \pm 86	149 \pm 103
TSS* (mg/L)	980 \pm 676	204 \pm 213		
pH*	8.36 \pm 0.95	7.91 \pm 0.47		

The precipitation corrected values for the individual samples location are shown in Figure 7. The dashed lines on Figure.7 correspond to the elemental ratio of pristine basalt, as defined in Section 5.1, such that the bulk dissolution of basalt during chemical weathering would result in the river waters having compositions corresponding to the lines. Overall the rivers do not have compositions consistent with such bulk dissolution. Preferential elemental mobility appears to increase along the trend $\text{Fe}/\text{Al} < \text{Mg}$, $\text{Ca} < \text{Na} + \text{K}$. At the immobile end of this trend Fe and Al appear to behave significantly differently in glacial and non-glacial catchments. All the glacial samples possess an Al/Fe ratio that is equal to or greater than the Al/Fe ratio of basalt. The non-glacial rivers mostly display the opposite trend and are characterized by lower Al/Fe ratios than basalts across a range of Fe concentrations.

In addition to the purely chemical differences, glacial and non-glacial rivers are physically offset in terms of their total suspended sediment concentrations (TSS). Glacial rivers contain on average 4.8 times more TSS than the non-glacial rivers. The average TSS offset is consistent with a long-term record of Icelandic River data by Louvat et al., (2008). Louvat et al., (2008) found that in rivers which had been sampled a minimum of 23 times over a minimum of 7 years, glacial samples contained 923 \pm 606 mg/L TSS while non-glacial samples contained on average 150 \pm 85 mg/L TSS.

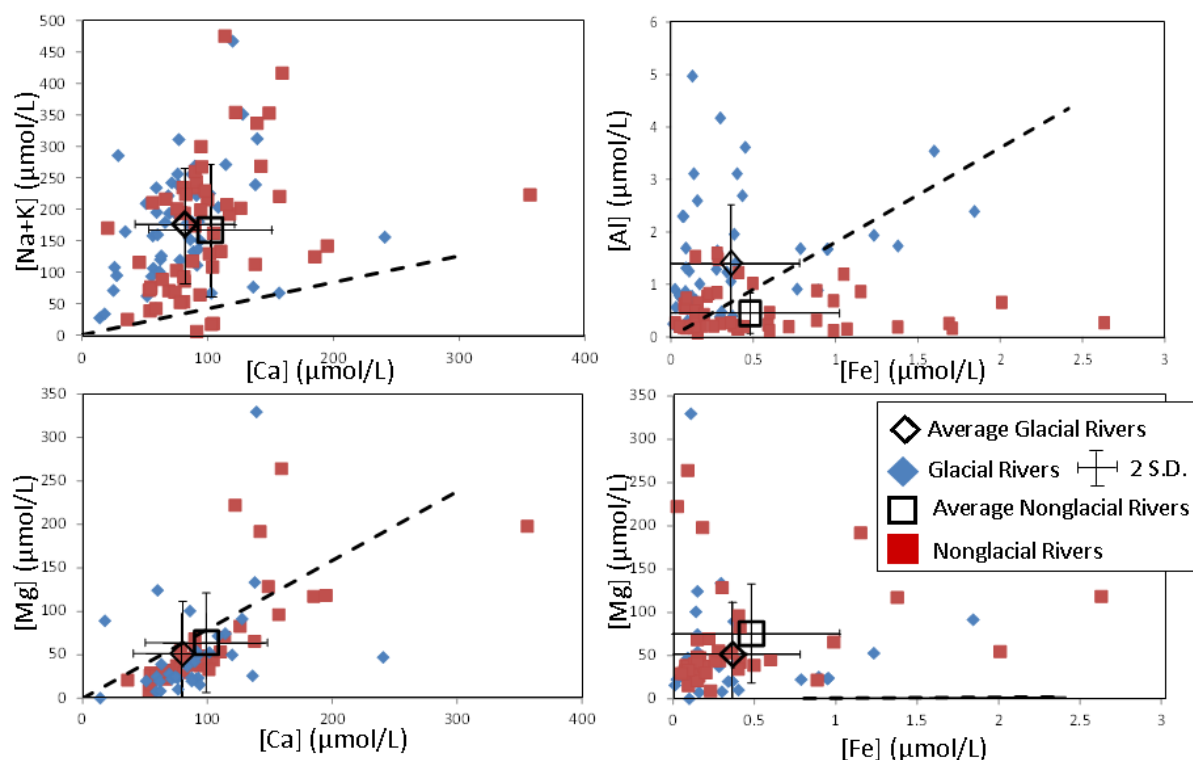


Figure 7. Icelandic rivers composition data from Gislason and Arnorsson (1993), Gislason et al., (1996), Arnorsson et al., (2002), Vigier et al., (2006) and Pogge von Strandmann et al., (2006). The data has been corrected for precipitation inputs. The dashed lines represent the element ratios of pristine basalt.

5.5 Inverse Models and Secondary Mineral Formation Rates.

The inverse chemical weathering model predicted Fe_{OOH} and Al_{OOH} formation rates are shown as functions of primary mineral dissolution rates on Figure 8 for glacial and non-glacial catchments. The rates are shown in molar unit concentrations, which encapsulates the general principle that chemical weathering scales with hydrologic discharge during continental weathering (e.g. Anderson et al., 1997; Eiríksdóttir et al., 2008). On average, non-glacial weathering appears to significantly enhance both Fe ($P < 0.02$ two-tailed t-test) and Al ($P < 0.05$ two-tailed t-test) (oxyhydr)oxide formation relative to glacial weathering. The offset in Fe_{OOH} formation rates constitutes a 37% increase in iron formation in non-glacial catchments relative to glacial catchments: $32 \mu\text{mol/kg}$ to $44 \mu\text{mol/kg}$.

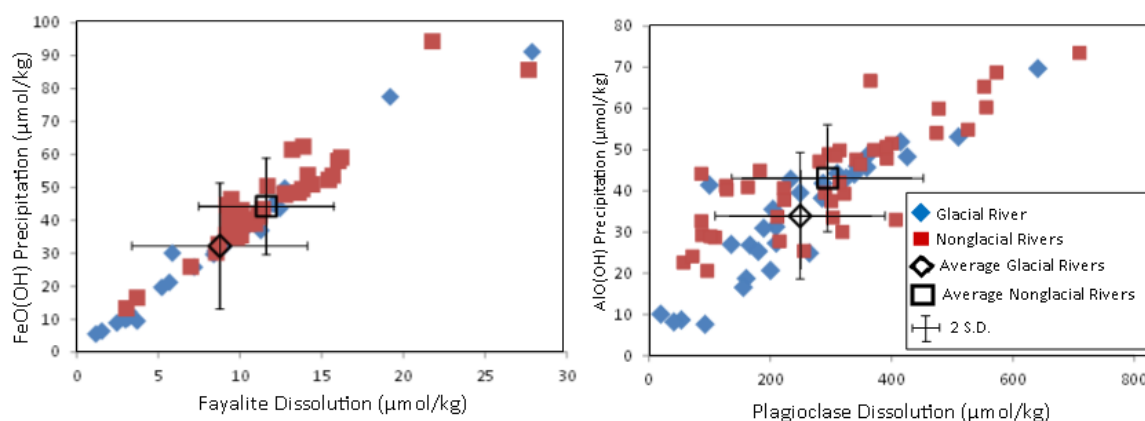


Figure 8. PHREEQC Model calculated reactive oxide formation rates. On average, non-glacial weathering significantly enhances Fe_{OOH} formation ($P < 0.02$) and Al_{OOH} formation ($P < 0.05$).

Sensitivity testing was conducted to determine which chemical factors were most important in terms of controlling $\text{Fe}/\text{Al}_{\text{OOH}}$ formations. The model $\text{Fe}/\text{Al}_{\text{OOH}}$ formation estimates are not sensitive to the measured Fe or Al concentrations of the samples; either doubling or removing the Al and Fe concentrations in the river waters from the model inputs changes the $\text{Fe}/\text{Al}_{\text{OOH}}$ formation estimates by less than the rounding uncertainty associated with the reported data i.e. $< 0.1 \mu\text{mol/kg}$). The estimates are far more sensitive to the concentrations of Mg and Ca. 'The Fe_{OOH} formation estimates effectively scale on a 1:1 basis while Al_{OOH} formation estimates scale with Ca. This is because, as shown on Figure 8, the model predicted Fe_{OOH} formation rates are almost entirely controlled by olivine dissolution while the Al_{OOH} formation rates are mostly controlled by plagioclase dissolution.

6. Discussion

6.1 pH and Chemical Weathering Patterns.

Gislason et al., (1996) proposed the relative mobility's of elements during Icelandic weathering decreased along the trend: $\text{Na} > \text{K} > \text{Ca}$, $\text{Mg} > \text{Al} > \text{Fe}$. This is not entirely consistent with the soil, river sediment or river water data. Figure 9 which shows the average elemental mobility patterns of rivers in the non-glacial Borgarfjörður and glacial Vatnajökull catchment regions (see Figure 2). In non-glacial catchments iron is at least as mobile as Al, and in the glacial catchments the mobility is Ca is closer to K than Mg. In total these patterns most likely reflect the role soil formation has on continental weathering.

The mobility of Ca relative to Na decreases from the glacial to the non-glacial catchments via of a process which does not seem to impact K or Mg. The most plausible explanation for the shift in Ca relative to Na is a change in a plagioclase weathering. The

predicted stabilities of albite (Na-plagioclase) and anorthite (Ca-plagioclase) differ across the typical pH range of Icelandic surface and ground waters (Arnorsson et al., 2002). As shown on Figure 10, anorthite is always under-saturated while albite is near saturated above pH values of 7 (Stefansson et al., 2011; Arnorsson et al., 2002). A shift toward more acidic conditions would therefore be expected to result in a decrease in the mobility of Ca relative to Na. The absolute pHs of the rivers do not cover the appropriate range of values, but Icelandic soil porewater do span the correct range. Chemical weathering in Icelandic soils is associated with decreasing soil pore-water pH (see Figure 5). The pore water in immature soils covers a similar pH range to the Icelandic rivers, but mature soils are characterized by soil pH values as low as 4 (Opfergelt et al., 2014). If plagioclase weathering is dominantly occurring within soils, then the reduction in Ca mobility relative to Na is inductive of the pH controlled shift in continental weathering between glacial and non-glacial patterns.

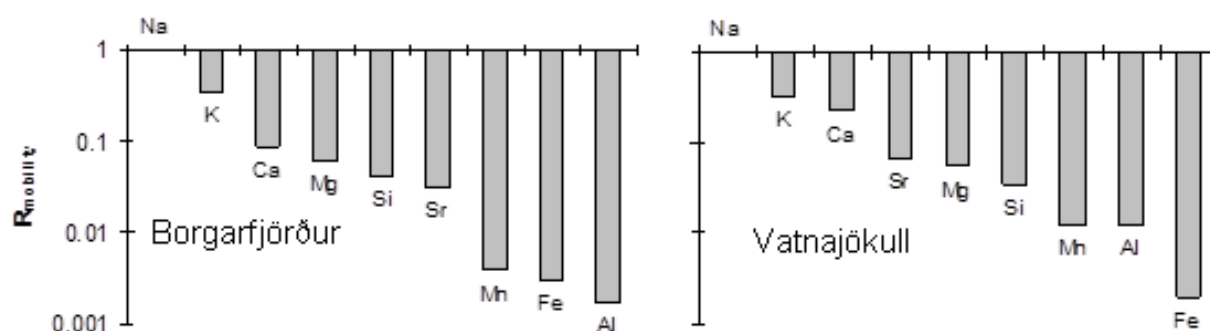


Figure 9 Relative mobility of major cations during basalt weathering in the Borgarfjörður and Vatnajökull catchments. $R_{\text{mobility}} = (X_{\text{water}} / Na_{\text{water}}) / (X_{\text{RBS}} / Na_{\text{RBS}})$

A key aspect of the dynamics of Ca and Na in Icelandic soil and surface water systems is that the solubility of the elements is not pH dependent. Once in solution the migration of Ca and Na between (sub)glacial, soil, and/or river environments is not highly impacted by pH boundaries. This provides a clear contrast when it comes to evaluating the environmental behaviour of Al and Fe.

Temporarily ignoring organic matter dynamics, the solubility's of Fe and Al are both strongly pH dependent. Across the pH range of our river samples, pure Al is about four orders of magnitude more soluble than pure Fe (Wesolowski and Palmer 1994; Liu and Millero 1999). As pH values decrease towards acidic pore water values, the solubility of Fe increases while the solubility of Al decreases (see Figure 10). If, like was the case with plagioclase, most chemical weathering reactions occur in affiliation with soil formation Al mobility would be expected to be higher than Fe in glacial rivers. Additionally, Fe and Al would be expected to be effectively immobile in non-glacial rivers. This is because while

acidic pore waters will favour iron dissolution this dissolved iron would be expected to precipitate as soon as it entered the rivers.

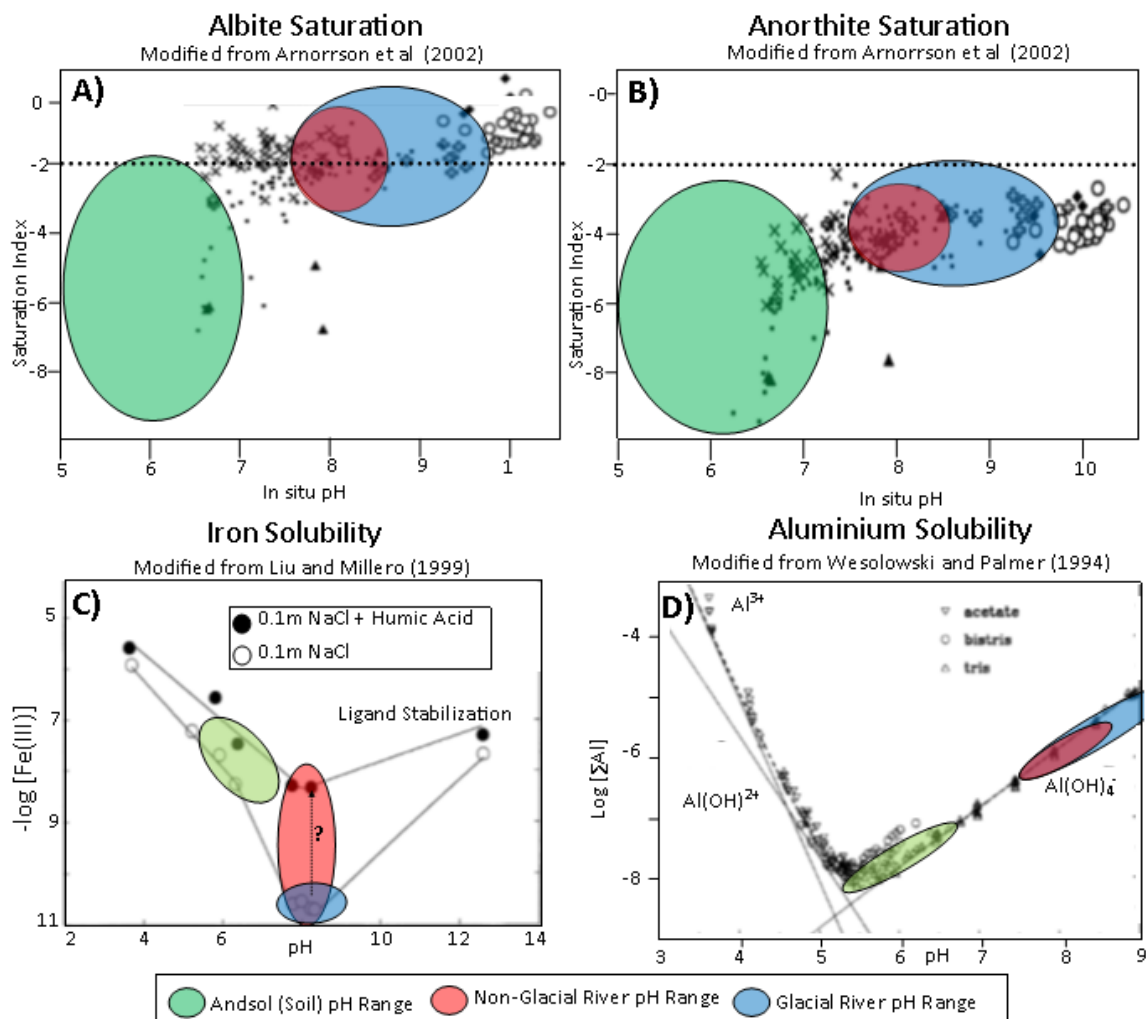


Figure 10. The andsol pH range is defined based on pore-water solutions from Opfergelt et al., (2014) and reflects soils typical of non-glacial catchments in Iceland. A) Albite solubility and B) Anorthite solubility in Icelandic surface waters modified from Arnorrson et al (2002). At pH>7 albite is near saturated while anorthite is significant under saturated across the pH spectrum. C) Iron solubility curve modified from Liu and Millero (1999) and D) Al solubility curve modified from Wesolowski and Palmer (1994). Iron is more soluble in the pH range of soil porewater than in the pH range of Icelandic rivers whereas Al solubility follows the opposite trend. The arrow on panel C underscores the relationship between apparent iron solubility and organic ligand availability with non-glacial rivers potentially falling nearer to the ligand stabilized values.

In many surface water environments, the mobility's of Fe and Al are dominated by organic matter availability rather than the actual solubility's of Fe and Al. (Perdue et al.,

1976; Liu and Millero 1999). The presence of organic matter would be predicted to drive systems to the extremes i.e. high Fe mobility in non-glacial rivers and high Al mobility in glacial rivers as organic matter stabilized the preferentially released element. This pattern of extremes can be identified within the individual samples reported on Figure 7, but on average non-glacial rivers do not contain significantly more iron than glacial rivers (see Table 2.2). Overall, the data appears to be better explained by the aforementioned inorganic solubility patterns. The apparent limited influence of organic matter in non-glacial rivers can in part be explained by the known relationship between organic matter accumulation and soil formation in Iceland. Opfergelt et al., (2011) showed that while Al was complexed to organic matter in organic rich porewaters, in most soil solutions Al was found to be un-complexed. In most non-glacial catchments the total drainage area associated with organic rich soils is limited (See Figure 1) so, at least in Iceland, the Al flux associated with soil formation is not necessarily driven by organic matter. Additionally the overall organic matter concentrations of both glacial and non-glacial river catchments in Iceland are relatively low. Pogge von Strandmann et al., (2008) found dissolved organic carbon (DOC) concentrations of 30-50 $\mu\text{mol/L}$ in glacial rivers in Iceland and DOC concentrations of 100-141 $\mu\text{mol/L}$ in non-glacial rivers. The higher concentrations are very similar to the concentration of humic acid used in the experiments by Liu and Millero (1999) shown on Figure 10. While organic matter does increase the apparent solubility of Fe at this level the overall apparent solubility of Fe remains very low and less than Al.

The influence of pH-dependent mineral reactions during soil formation on overall chemical weathering patterns is also reflected in the inverse-weathering Fe_{OOH} and Al_{OOH} formation rate estimates. The inverse weathering models predict Fe_{OOH} formation is mainly coupled to olivine dissolution and Al_{OOH} formation is primarily coupled to plagioclase dissolution. This is a key result in terms of validating the models as the pattern is consistent with independent predictions of mineral weathering patterns in Iceland e.g. Arnorsson et al., (2002). Furthermore, the absolute stabilities of olivine and plagioclase are predicted to decrease with decreasing pH (Stefansson et al., 2001). As a result, the higher weathering rates in non-glacial catchments are best explained by the increased weathering intensity of acidic non-glacial soils relative to alkaline glacial environments. It is worth noting that this is not a result of the way the inverse models were parametrized. All the models were parametrized with the same initial rainwater pH (5.5 consistent with mean Icelandic precipitation; Gislason et al., 1996) and run to their respective final riverine pHs (which aren't significantly different) preventing the introduction of any pH bias during model parameterization. The models are reproducing the weathering trend based only on the residual chemical patterns of soils formation transferred into the rivers from soil drainage.

Overall it would appear that soil formation has a measurable impact on continental weathering including riverine chemistry. In the case of glacial/non-glacial differences, soil formation promotes Al_{OOH} and Fe_{OOH} formation in non-glacial systems. But this does not imply non-glacial weathering increases $\text{Fe}/\text{Al}_{\text{OOH}}$ export to nearshore marine environments.

6.3 Soils and River Sediments.

There is a fundamental difference between mineral formation and mineral transport. Icelandic soils trap Fe_{OOH} as it forms (Figure 6) opening the possibility that much of the Fe_{OOH} formed during non-glacial weathering never reaches the ocean. This possibility is underscored by the lack of chemical similarity between non-glacial river sediment and mature soils.

Figure 11 shows the compositions of the glacial and non-glacial sediments relative to the composition of the Icelandic soils. All the river sediments are chemically more similar to pristine basalt than to Icelandic soil material. Additionally, the compositions of the river sediment cannot be explained through the mixing of soils with different compositions. All the river sediments have higher Na+K, Mg, and Ca concentrations relative to their Fe and Al concentrations than all the soil samples. This is consistent with physical processes controlling both glacial and non-glacial river sediments independently of chemical soil formation process.

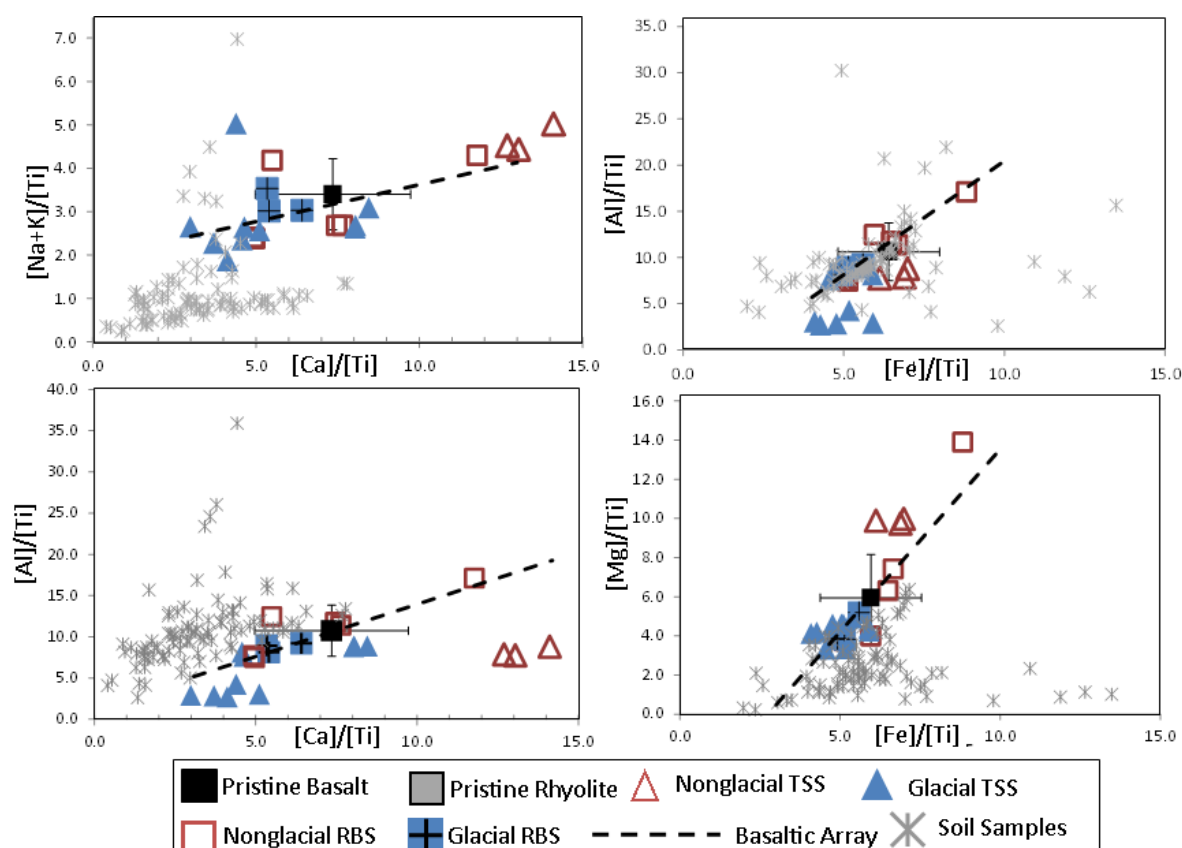


Figure 11 Icelandic river sediment and soil compositions. The river sediment data from Figure 2.5 is combined with the soil data from Figure 2.6: RBS=riverbed Sediment; TSS= total suspended sediment. The solid black lines reflect the composition of pristine Icelandic basalt. The soils are generally depleted in the mobile elements (Na, K, Mg, Ca) relative to the sediments.

The dominance of physical weathering on river sediment chemistry is not a new idea especially in the context of Fe_{OOH} . Poulton and Raiswell (2005) and Poulton and Canfield (2005) found that the Fe_{OOH} concentrations of river sediment from glacial and non-glacial catchments from around the world were best explained by physical weathering. Specifically, Fe_{OOH} concentrations were found to correspond to sediment surface area irrespective of bedrock lithology or soil formation intensity. This is consistent with more recent studies which have found high Fe_{OOH} export from glacial systems characterized by high rates of physical weathering e.g. Bhatia et al., (2013); Hawkins et al., (2014).

6.4 Physical Weathering, Fe_{OOH} export and Earth's Climate

One important aspect of this study is that, whereas previous studies have shown glacial terrains can be a significant source of Fe_{OOH} , we have directly compared analogous glacial and non-glacial terrains in a way which allows us to conclude glacial terrains export more Fe_{OOH} than equivalent non-glacial terrains. However, our conclusion has previously been implied based on studies of Antarctica (Martin 1990), Greenland (Bhatia et al., 2013)

and other terrains (Poulton and Canfield 2005) so the idea isn't new. Additionally, any number of previous studies have stated: chemical weathering patterns do differ between glacial and non-glacial catchments in Iceland e.g. Gislason et al., (1996); Pogge von Strandmann et al., (2006, 2012); Opfergelt et al., (2013); Opfergelt et al., (2014), but because of the environmental behaviour of Fe and Al physical processes control the secondary Fe/ Al_{OOH} flux rates (Poulton and Canfield 2005). This confirms Martin (1990)'s 27 year old claim that in general physical sediment erosion by glaciers enhances marine Fe_{OOH} accumulation.

What is important to note is a significant new idea has gained traction since the original proposal of the Iron Hypothesis. It is now widely understood that Fe_{OOH} promotes not only primary production but also carbon burial. Marine carbon burial accounts for the sequestration of about 309 Tg C yr^{-1} (Burdgie 2007) and it accounts for about half of the total annual geologic sink of carbon (Ciais et al., 2013). It is estimated that 20% of organic carbon in marine sediments is directly stabilized by Fe_{OOH} (Lalonde et al., 2012) so significant changes in Fe_{OOH} export equate to significant changes in Earth's climate. This is a statement that is worth re-iterating because it demands a significant shift in the importance which can be attributed to studying Fe_{OOH} fluxes from glacial systems. For example Hawkins et al., (2014) concludes: "We contend that the consideration of meltwater Fe fluxes, which supplements iron from icebergs, is critical for understanding iron cycling and primary productivity in polar waters." Such a statement falls short of what we are contending as the true significance of the work by Hawkins et al., (2014), Raiswell et al., (2008) and others which is: we contended that the consideration of meltwater Fe fluxes, which supplements iron from icebergs, is critical for understanding **carbon burial** and **Earth's climate**.

7. Summary and Conclusions.

Direct chemical measurements of Icelandic sediments and soils and inverse stoichiometric modelling of chemical weathering in Icelandic catchments support the assertion that the chemical weathering process does differ between glacial and non-glacial catchments. The differences appear to be products of the soil formation process and, more specifically, the relationship between pore-water pH and mineral weathering. However, as many authors have concluded before us, these chemical differences don't appear to have a significant effect on Fe_{OOH} and Al_{OOH} delivery to the ocean, because physical processes are more important in the context of sediment export rates. This allows us to conclude not just that glacial weathering is a significant source of (oxyhydr)oxides to the ocean, but that glacial weathering promotes the accumulation of significantly more (oxyhydr)oxides in nearshore marine environments than analogous non-glacial weathering. We assert that this difference

is not tangentially related to climate change via primary productivity but directly relates to carbon sequestration via marine carbon burial.

Acknowledgements

This research was funded by the European Union FP-7 Marie Curie MetTrans Initial Training Network. We would like to thank the students, researchers and technicians at the University of Iceland for assistance in sampling and field logistics and Chris Otley at Durham University for supporting the new chemical analyses. We would also like to thank James Baldini and Martyn Tranter for his reviews of manuscript during preparation for submission.

References

- Anderson S.P., Drever J.I., Humphrey N.F. (1997) Chemical weathering in glacial environments. *Geology* **25**: 399-402.
- Andersson K, Dahlqvist R., Turner D., Stople B., Larsson T., Ingri J., Andersson P. (2006) Colloidal rare earth element in a boreal river: Changing sources and distributions during the spring tide *Geochimica et Cosmochimica Acta* **70**: 3261-3274.
- Arnalds O. and Gretarsson E. (2001) Soil Map of Iceland, second editions. Agricultural Research Institute, Reykjavik. Available from: <www.rala.is/desert>
- Arnorsson S., Gunnarsson I., Stefansson A., Andresdottir A., Sveinbjornsdottir A.E. (2002). Major element chemistry of surface- and groundwaters in basaltic terrain, N-Iceland. I. Primary mineral saturation. *Geochimica et Cosmochimica Acta* **66**(23): 4015-4046.]
- Barber A, Lalonde K., Mucci, A., Gelinas Y. (2014) The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment. *Marine Chem.* **162**: 1-9
- Bhatia M.P., Kujawinski E.B., Das S.B., Breier C.F., Henderson P.B., Charette M.A. (2014) Greenland meltwater as a significant and potentially bioavailable source of iron to the ocean. *Nature Geosci.* **6**, 2013, 271-278.
- Blanc Ph., Lassin A., Piantone P. Nowak C. THERMODDEM PHREEQC database. Bureau de recherches géologiques et minières. Available from <<http://thermoddem.brgm.fr/spip.php?rubrique13>>
- Burdige D.J. (2007) Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? *Chemical Reviews* **107**: 467-485.
- Ciais P and Sabine C. (2013). *Carbon and Other Biogeochemical Cycles*. In: Climate Change 2013: The Physical Sciences Basis. Contribution of Working Group 1 to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, United Kingdom.
- Coale K.H., Johnson K.S., Chavez F.P., Buesseler K.O., Barber R.T., Brzezinski M.A., Cochlan W.P., Millero F.J., Falkowski P.G., Bauer J.E., Wanninkhof R.H., Kudrka R.M., Altabet M.A., Hales, B.E., Takahashi T., Landry M.R. Bidigare R.R., Wnand X., Chase Z., Strutton P.G., Friederich G.E., Gorbunov M.Y., Lance V.P., Hilting A.K., Hiscock M.R., Demarest M., Hiscock W.T., Sullivan K.F., Tanner S.J., Gordon R.M., Hunter C.N., Elrod V.A., Fitzwater S.E., Jones J.L., Tozzi S., Koblizek M., Roberts A.E., Herndon J., Brewster J., Ladizinsky N., Smith G., Cooper D., Timothy D., Brown S.L., Selph K.E., Sheridan C.C., Twining B.S., Johnson Z.I. (2004)

- 588 Southern Ocean iron enrichments experiment: carbon cycling in high- and low-si waters.
589 *Science*, **304**: 408-414.
- 590 Conway T.M. and John S.G. (2014). Quantification of dissolved iron sources to the North Atlantic
591 Ocean. *Nature*. **511**: 212-217.
- 592 Eiríksdóttir E.S., Louvat P., Gislason S.R., Oskarsson N., Hardardóttir J. (2008) Temporal variation of
593 chemical and mechanical weathering in NE Iceland: Evaluation of a steady-state model of
594 erosion. *Earth and Planetary Science Letters*. **272**: 78-88.
- 595 Eiríksdóttir E.S., Gislason S.R., Oelkers E.H. (2013). Does temperature or runoff control the feedback
596 between chemical denudation and climate? Insights from NE Iceland. *Geochim. Cosmochim. Acta*.
597 **107**: 65-81.
- 598 Gislason S.R. and Arnorsson S. (1993) Dissolution of primary basaltic minerals in natural waters:
599 saturation state and kinetics. *Chemical Geology* **105**: 117-135.
- 600 Gislason S.R., Arnorsson S., Armannsson H. (1996) Chemical weathering of basalt in southwest
601 Iceland: effects of runoff, age of rocks and vegetative/glacial cover. *American Journal of*
602 *Science*, **296**: 837-907.
- 603 Gislason S.R. and Oelkers E.H. (2003). Mechanism, rates and consequences of basaltic glass
604 dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of
605 pH and temperature. *Geochimica et Cosmochimica Acta* **67** (20):3817-3832.
- 606 Hawkins J.R., Washam J.L., Tranter M., Raiswell R., Benning L.G., Statham P.J., Tedstone A.,
607 Neinow P., Lee K., Telling J., (2014). Ice sheets as a significant source of highly reactive
608 nanoparticulate iron to the oceans. *Nature Communications*. 5:3929. DOI: 10.1038.
- 609 Jakobsson S.P. (1972) Chemistry and distribution pattern of Recent basaltic rocks in Iceland. *Lithos*.
610 **5**: 365-386.
- 611 Kaasalainen H. and Stefansson A. (2012) The chemistry of trace elements in surface geothermal
612 waters and steam, Iceland. *Chemical Geology*. **330-331**: 60-85.
- 613 Lalonde K., Mucci A., Ouellet A., Gelinás Y. (2012) Preservation of organic matter in sediments
614 promoted by iron. *Nature*. **483**: 198-200.
- 615 Liu X. and Millero F.J. (1999). The solubility of iron hydroxide in sodium chloride solutions.
616 *Geochimica et Cosmochimica Acta*. **63** (19/30):3487-3497.
- 617 Louvat P, Gislason S.R. Allegre C.J. (2008) Chemical and mechanical erosion rates in Iceland as
618 deduced from river dissolved and solid material. *Am. J. Sci.* **308**: 679-726.
- 619 Lyven B., Hasselöv M., Turner D.R., Halrðaldsson C., Andersson K. (2003) Competition between iron-
620 and carbon-based colloidal carriers for trace metals in a freshwater assessed using flow field-
621 flow fractionation coupled to ICPMS. *Geochimica et Cosmochimica Acta* **67**(20):3791-3802.
- 622 Martin J.H. (1990) Glacial-interglacial CO₂ change: the iron hypothesis. *Paleoceanography*. **5**(1):1-13
- 623 Nesbitt H.W. and Wilson R.E. (1992) Recent chemical weathering of basalts. *American Journal of*
624 *Science*. **292**: 740-777.
- 625 Norddahl H. and Petursson H.G. (2005) Relative sea-level changes in Iceland: new aspects of the
626 Weichselian deglaciation of Iceland. *Iceland-Modern processes and past environments*.
627 Elsevier. 25-78.
- 628 Opfergelt S., Georg R.B., Burton K.W., Guicharnaud R., Siebert C., Gislason S.R., Hallidat A.N.
629 (2011) Silicon isotope in allophane as a proxy for mineral formation in volcanic soils. *Applied*
630 *Geochemistry*. **26**: S115-S118.

- 631 Opfergelt S., Burton K.W., Pogge von Strandmann P.A.E., Gislason S.R., Halliday A.N. (2013)
 632 Riverine silicon isotope variations in glaciated basaltic terrains: implications for the Si delivery
 633 to the ocean over glacial-interglacial intervals. *Earth and Planetary Science Letters*. **369-370**:
 634 211-219.
- 635 Opfergelt S., Burton K.W., Georg R.B., West A.J. Guicharnaud R.A., Sigfusson B., Siebert C.,
 636 Gislason S.R., Halliday, A.N. (2014). Magnesium retention on the soil exchange complex
 637 controlling Mg isotope variations in soils, soil solutions and vegetation in volcanic soils,
 638 Iceland. *Geochimica et Cosmochimica Acta* **125**: 110-130.
- 639 Oskarsson B.V., Riishuus M.S., Anrads O. (2012). Climate-dependent chemical weathering of
 640 volcanic soils in Iceland. *Geoderma*. **189-190**:635-651.
- 641 Parkhurst D.L., Appelo C.A.J. (1999) User's guide to PHREEQC-a computer program for speciation,
 642 beach-reaction, one-dimensional transport and inverse geochemical calculations. U.S.
 643 Geological Survey Water-Resources Investigations Report, p.312.
- 644 Perdue E.M., Beck K.C., Melmut-Reuter J. (1976) Organic complexes of iron and aluminium in natural
 645 waters. *Nature*. **260**: 418-420.
- 646 Pogge von Strandmann P.A.E., Burton K.W., James R.H., van Calsteren P., Gislason S.R., Mokaden
 647 F. (2006) Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic
 648 terrain. *Earth and Planetary Science Letters*. **251**: 134-147.
- 649 Pogge von Strandmann P.A.E., Opfergelt S., Lai Y.-J., Sigfusson B., Gislason S.R., Burton K. (2012)
 650 Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil
 651 and pore water profile in Iceland. *Earth and Planetary Science Letters* **339-340**:11-23
- 652 Poulton S.W. and Canfield D.E. (2005) Development of a sequential extraction procedure for iron:
 653 implications for iron partitioning in continentally derived particulates. *Chemical Geology* **214**:
 654 209-221.
- 655 Poulton S.W. and Raiswell R. (2005) Chemical and physical characteristics of iron oxides in riverine
 656 and glacial meltwater sediments. *Chemical Geology*. **218**:203-221.
- 657 Raiswell R., Benning L.G., Tranter M., Tulaczyk S. (2008) Bioavailable iron in the Southern Ocean:
 658 the significance of the iceberg conveyor belt. *Geochemical Transactions*. **9**:7.
- 659 Raiswell R. and Canfield D.E. (2012) The iron biogeochemical cycle past and present. *Geochemical*
 660 *Perspectives*, European Association of Geochemistry, 1(1)
- 661 Schuessler J.A., Schoenber R, Sigmarsson O. (2009) Iron and lithium isotope systematics of the
 662 Hekla volcano, Iceland- Evidence for iron isotope fractionation during magma differentiation.
 663 *Chemical Geology*. **258**: 78-91.
- 664 Schrumpf M., Kaiser K., Guggenberger G., Persson T., Kogel-Knabner I., Schulze E.-D. (2013)
 665 Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates
 666 and attachment to minerals. *Biogeosciences*. **10**: 1675-1691.
- 667 Sholkovitz E.R. and Copland D. (1981) The coagulation, solubility and adsorption properties of Fe,
 668 Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochimica et Cosmochimica Acta*. **45**:
 669 181-189.
- 670 Stefansson A. (2001) Dissolution of primary mineral of basalt in natural waters I. Calculation of
 671 mineral solubilities from 0C to 350C. *Chemical Geology* **172**: 225-250.
- 672 Stefansson A. and Gislason S.R. (2001) Chemical weathering of basalts, southwest Iceland: Effects
 673 of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *American*.
 674 *Journal of Science*. **301**: 513-556.
- 675 Stefansson A., Gislason S.R., Arnorsson S. (2001) Dissolution of primary minerals in natural waters II.
 676 mineral saturation state. *Chemical. Geology*. **172**: 251-276.

- 677 Syvitski J.P.M., Milliman J.D. (2007). Geology, geography and humans battle for dominance over the
678 delivery of fluvial sediment to the coastal ocean. *Geology* **115**: 1-19.
- 679 Vigier N., Burton K.W., Gislason S.R., Rogers, N.W., Duchene S., Thomas L., Hodge E., Schaefer B.
680 (2006) The relationship between riverine U-series disequilibria and erosion rates in a basaltic
681 terrain. *Earth and Planetary Science. Letters.* **249**: 258-273.
- 682 Vigier N., Gislason S.R., Burton K.W., Millot, R., Mokadem F. (2009) The relationship between
683 riverine lithium isotope composition and silicate weathering rates in Iceland. *Earth and*
684 *Planetary Science. Letters.* **287**: 434-411.
- 685 Wesolowski D.J. and Palmer D.A. (1994) Aluminium speciation in equilibria in aqueous solution: V.
686 Gibbsite solubility at 50C and pH 3-9 in 0.1 molal NaCl solutions (a general model for
687 aluminium speciation; analytical methods). *Geochimica et Cosmochimica Acta* **58**(14): 2947-
688 2969.