

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

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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

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

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

38 **1 Introduction**

39 Iron and Al (oxyhydr)oxide ($\text{Fe}/\text{Al}_{\text{OOH}}$) concentrations are approximated based on
40 selective chemical extractions techniques. The pool of dithionate-citrate-bicarbonate (DCB)
41 reducible minerals, referred to as 'highly reactive Fe/Al' ($\text{Fe}_{\text{HR}}/\text{Al}_{\text{HR}}$), is one of the most
42 commonly used methods for estimating for both Fe_{OOH} and Al_{OOH} (Raiswell and Canfield
43 2012). There are strong correlations between the concentrations of Fe_{HR} and organic carbon
44 in marine sediments and $\text{Fe}_{\text{HR}}/\text{Al}_{\text{HR}}$ and organic matter in soils (Schrumpp et al., 2013). These
45 correlations are thought to reflect the physiochemical protection of organic matter by Fe_{OOH}
46 and Al_{OOH} (see review by Schrumpp et al., 2013); a process which has been dubbed the
47 'Rusty Carbon Sink' (Lalonde et al., 2012, Barber et al., 2014).

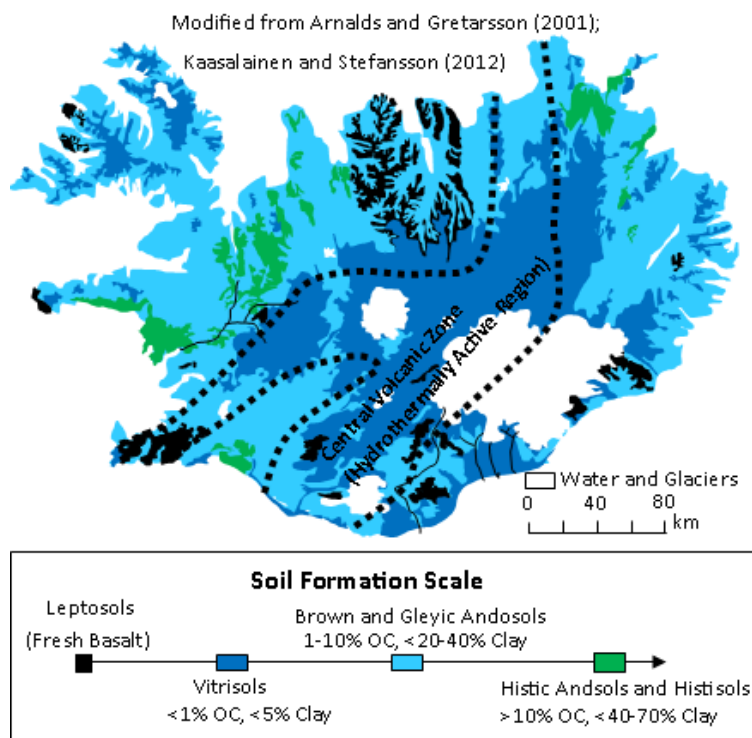
48 The Rust Carbon Sink is not the first hypothesis to propose Fe_{OOH} can have a major
49 impact on Earth's climate cycle. The Iron Hypothesis (Martin, 1990) is the well-studied idea
50 that Fe_{OOH} accumulation in the Southern Ocean controls primary productivity in the region.
51 While much of the research into the Iron Hypothesis has focused on atmospheric dust e.g.
52 Coale et al., 2004; as Martinez-Garcia et al., (2014) the original iron hypothesis also
53 proposed the intensity of glacial weathering on Antarctica itself was a major control of iron
54 export to the ocean. Glacial weathering has been shown to allow for both the formation and
55 large scale export of iron (oxyhydr)oxides to coastal marine environments (Raiswell et al.,
56 2008; Hawkins et al., 2014, Eiriksdottir et al 2015). This raises the question of whether
57 weathering promotes organic carbon burial, in addition to primary production, as a result of
58 enhanced marine Fe_{OOH} discharge.

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

68 **2 Icelandic Geology, Hydrology and Sample Locations**

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

78 Bed rock rheology and chemical composition significantly impact continental
79 weathering rates (Syvitski and Milliman 2007). Therefore, geologically similar and well-
80 characterized catchments are useful when comparing glacial and non-glacial weathering
81 rates. Iceland is a geologically young and active island, formed primarily (>80%) of basaltic
82 lavas, with a mixed mid-ocean ridge/ocean island melt source composition. The remainder of
83 the island is composed of more acidic/rhyolitic lavas (Jakobsson 1972). Iceland was
84 completely covered by a single glacial icesheet ~9 ka ago, which collapsed during the Early
85 Holocene stabilizing to near modern conditions about 6 ka ago (Gislason 1996; Norðhal
86 and Petersson et al., 2005). Since the collapse of the icesheet vegetation and soil formation
87 have created significant chemical differences between glacial and non-glacial catchments,
88 reflected in the distribution of Iceland's major soil/sediment types (Figure 1). Soil formation
89 has been attributed to as the principle cause of a number of chemical differences between
90 the glacial and non-glacial catchments (Gislason et al., 1996; Pogge von Strandmann et al.,
91 2006, 2012; Opfergelt et al., 2013; Opfergelt et al., 2014).



92

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

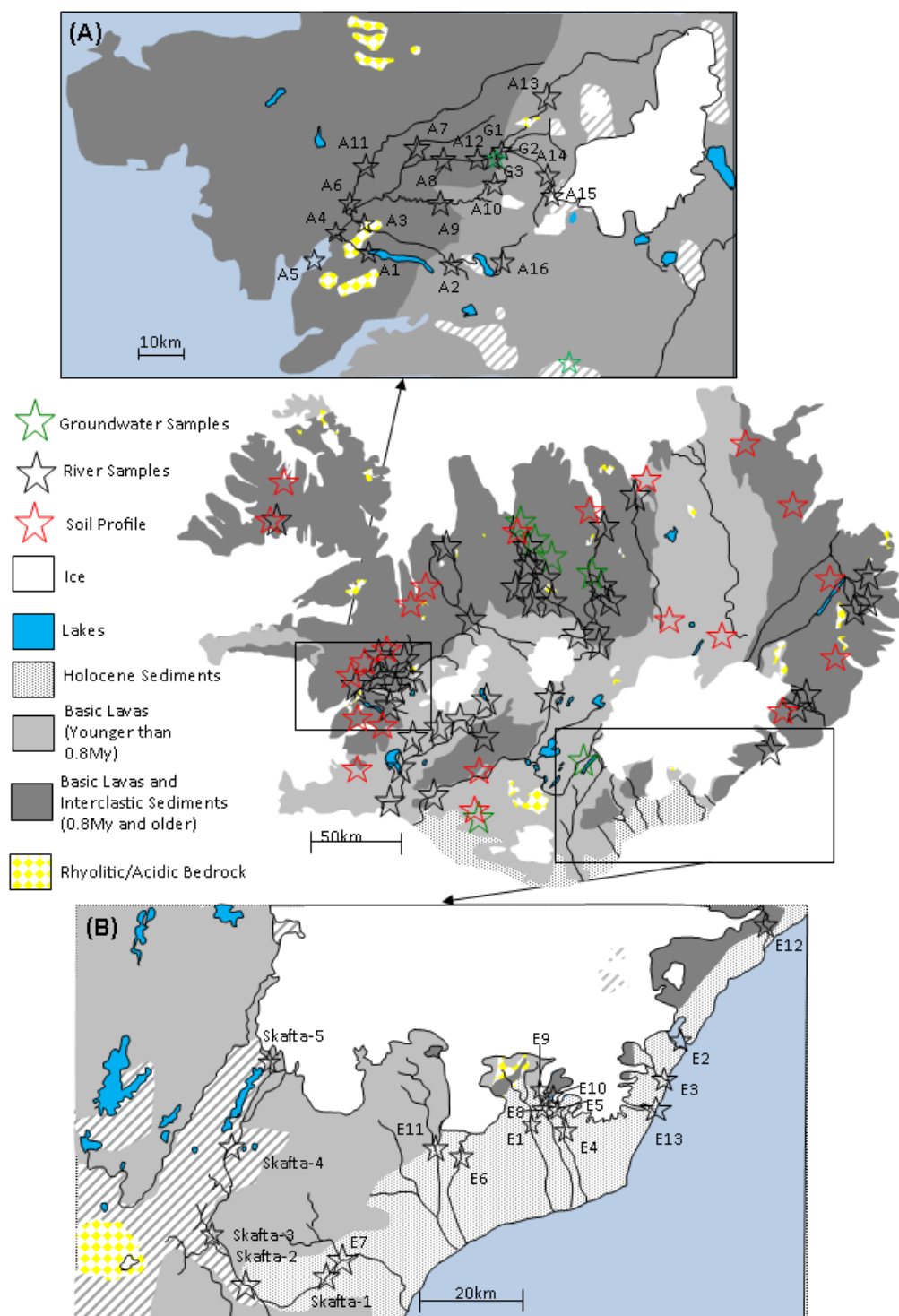
96 A number of previous studies have sampled Icelandic soils, sediments, rivers and
97 groundwaters in the context of continental weathering and this study will draw extensively on
98 data from: Gislason and Stefansson (1993), Gislason et al., (1996), Stefansson et al.,
99 (2001), Arnorsson et al., (2002), Pogge von Strandmann et al., (2006), Vigier et al., (2006),
100 Vigier et al., (2009), Oskarsson et al., (2012), Pogge von Strandmann et al., (2012),
101 Eiriksdottir et al., (2008), Louvat et al., (2008) and Opfergelt et al., (2014). This previously
102 published work provides what is likely the most complete and extensive data-set on the
103 interplay of weathering regimes and chemical weathering ever collected on a single geologic
104 terrain. Because the chemistry of river waters and sediment can show a high degree of
105 temporal and spatial variability, large sample sets are required to make statistically robust
106 conclusions about the chemical weathering process.

107 3 Methods

108 3.1 Field sample collection:

109 River water and sediment samples from Iceland were collected during September
110 2003, August 2005 reported in Pogge von Strandmann et al., (2006) and then again by the
111 same methods in August 2012 and August 2013 at locations shown on Figure 2. River
112 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.



128

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

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

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

141 *3.2 Major and Trace Element Analysis:*

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

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

158 **4. Theory and Model Calculations**

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

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

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

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

192 **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	Ferrosillite: 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	

193

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

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

199 Basaltic glass is the first component of Icelandic basaltic to be chemical weathered in
200 most low temperature environments (Stefansson et al., 2001). The thermodynamics of glass
201 dissolution in Iceland have been studied but the process has only been defined as a function
202 of a theoretical pure $\text{SiAl}(\text{OH})$ form i.e. Gislason and Oelkers (2003), Eiriksdottir et al.,
203 (2015). As our model is dependent on mineral stoichiometry, the inclusion a theoretical glass
204 formula, which does not contain Fe, Ca, Mg, etc., would strongly bias the model predicted
205 impact of glass dissolution. Glass dissolution is a well quantified source of Fe_{OOH} formation
206 (Gislason and Arnorsson 1993). The exclusion of basaltic glass in the model is equivalent to
207 the assumption that Fe and Al will behave in the same way during glass weathering. That is
208 glass weathering is assumed to not lead to preferential Fe_{OOH} vs Al_{OOH} formation. A different
209 stoichiometric problem prevents the inclusion of allophane, one of the most common
210 secondary minerals in Icelandic soils (Oskarsson et al., 2012), in the models.

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

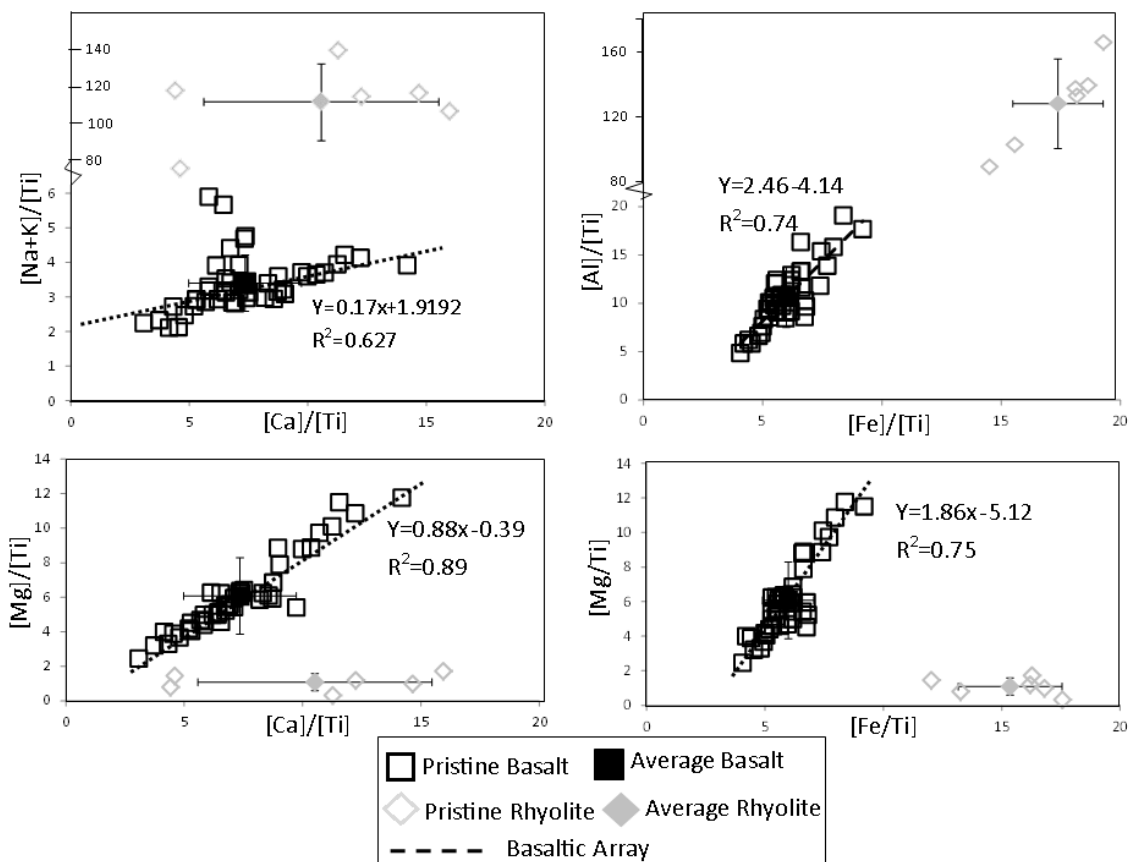
220 In other localities, the inclusion of iron in certain clay minerals would also introduce
221 uncertainty in terms of the model-predicted $\text{Fe}/\text{Al}_{\text{OOH}}$ formation rates. In Iceland, this does
222 not appear to be a significant problem. While Fe-smectites have been identified in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

229 5 Results

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

235 5.1 Icelandic Bedrock

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



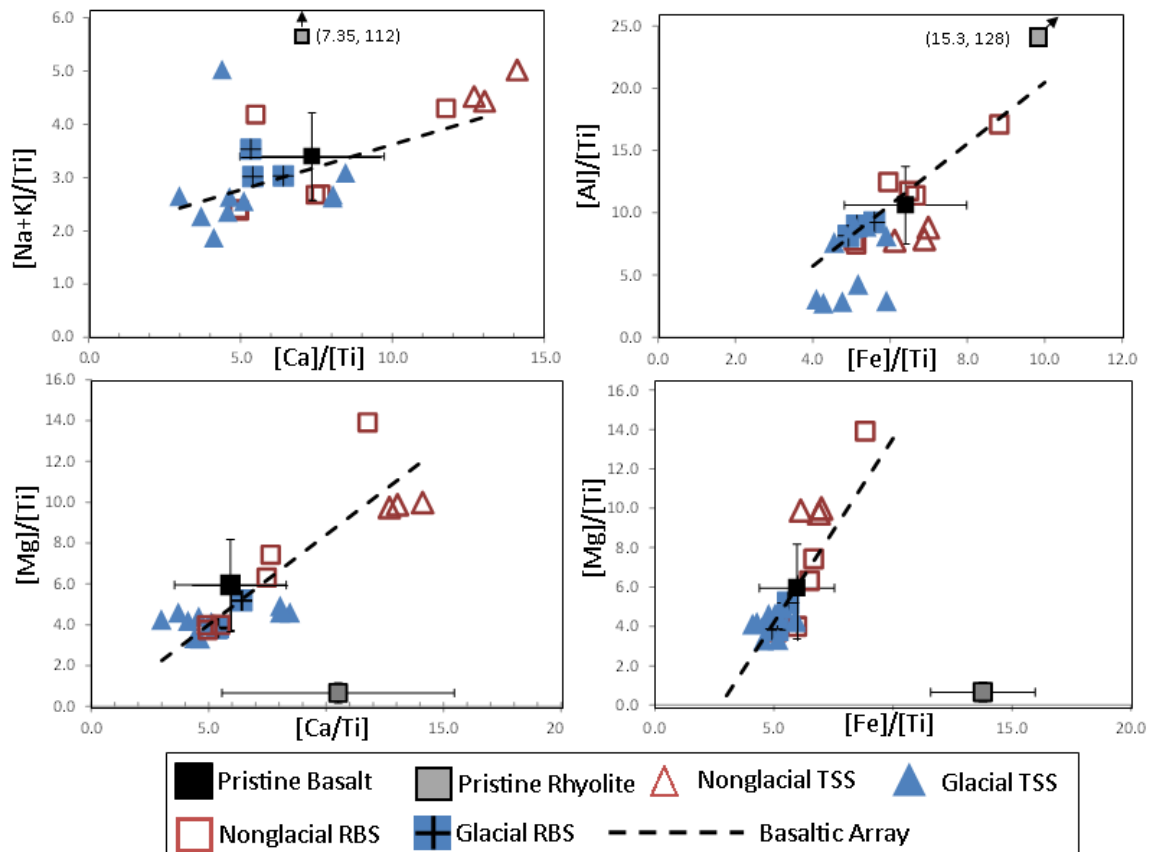
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245 **Figure 3.** data from Jakobsson (1972), Arnorsson et al., (2002), Eiriksdottir et al., (2008), Louvat
246 (2008) and Schuessler et al., (2009). Icelandic basalts display a limited range of variability in Ti
247 normalized elemental space characterized by positive correlations between the various elements.

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

255 *5.2 River Sediment Compositions*

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

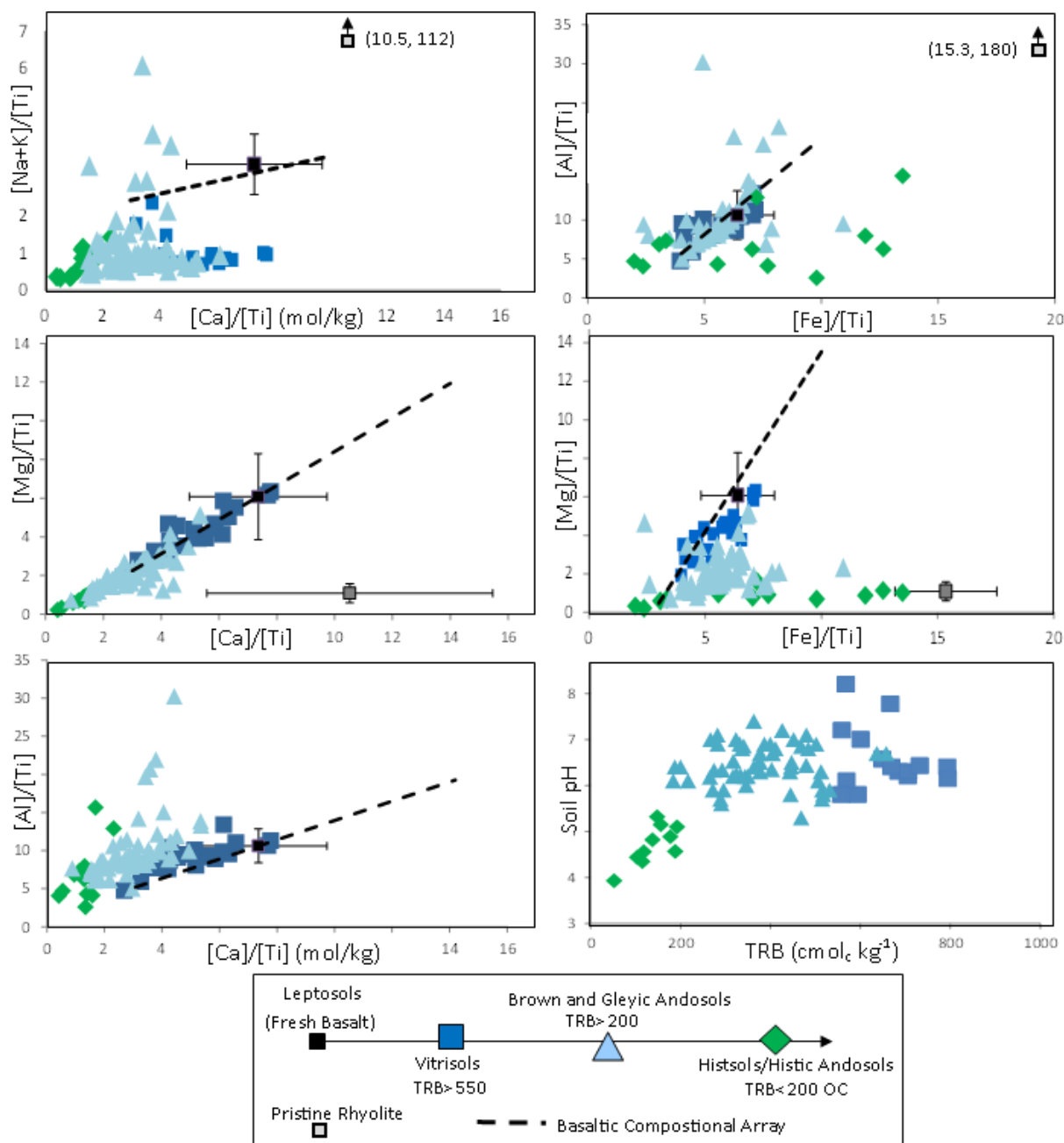


266

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

271 5.3 Soil Formation

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



281

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

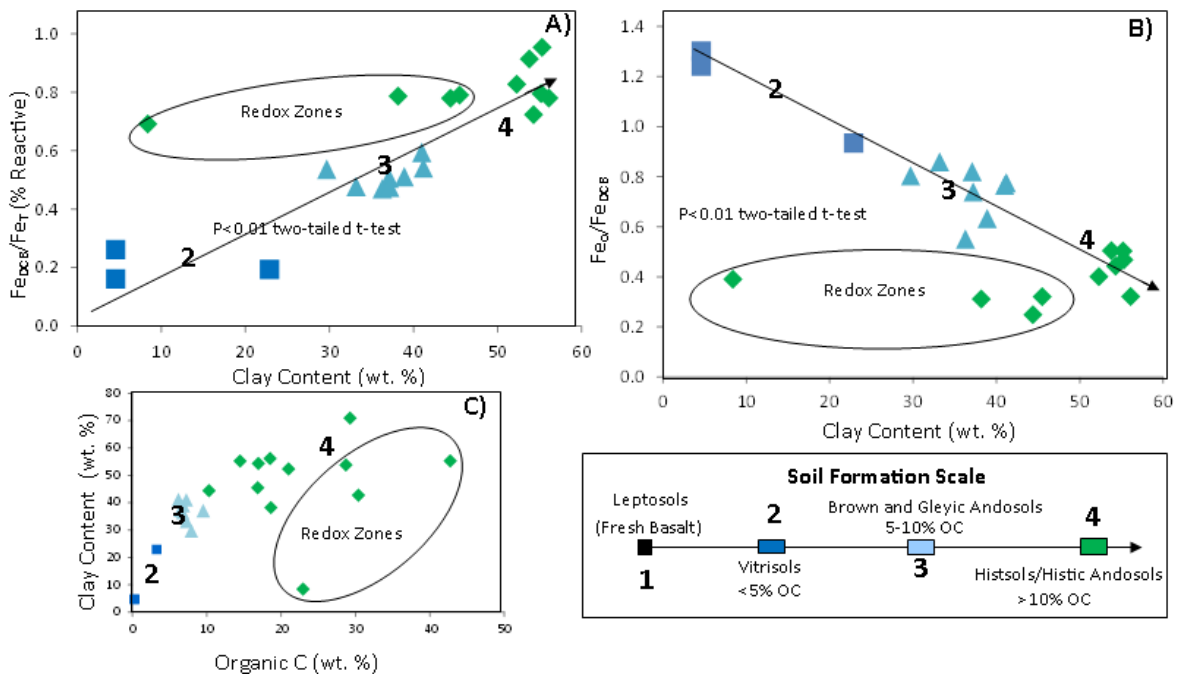
286 There is a general decrease in soil pore-water pH with decreasing TRB. Magnesium and
 287 Ca appear to behave similarly and lie on the basaltic compositional array during chemical
 288 weathering. Nearly all the soils are significantly depleted in $[Na+K]/[Ti]$ relative to basalt.
 289 Aluminium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

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

294 The trends in iron behaviour during weathering can be further explored by examining
295 changes in iron mineralogy during weathering. Two selective iron extractions, sodium-
296 dithionate-bicarbonate (Fe_{DCB}) and oxalate (Fe_O), were used to measure iron concentrations
297 as a function of iron mineralogy in Icelandic soil by Opfergelt et al., (2014). The important
298 difference between the extractions is that Fe_O includes magnetite but not goethite, while
299 Fe_{DCB} includes goethite but not magnetite (Poulton and Raiswell 2005). Goethite is a
300 common Fe-oxyhydroxide present during basaltic weathering (Stefansson and Gislason
301 2001), while magnetite is a common primary mineral phase in Icelandic basalts (Gislason
302 and Stefansson 1993). Consequently, $Fe_{DCB}/Total\ Iron\ (Fe_T)$ values reflect the proportion of
303 iron oxyhydroxides to total iron within a sample. The Fe_O/Fe_{DCB} values reflect the balance of
304 magnetite dissolution to goethite formation.

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

313



314

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

320 5.4 Dissolved Load Concentrations

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

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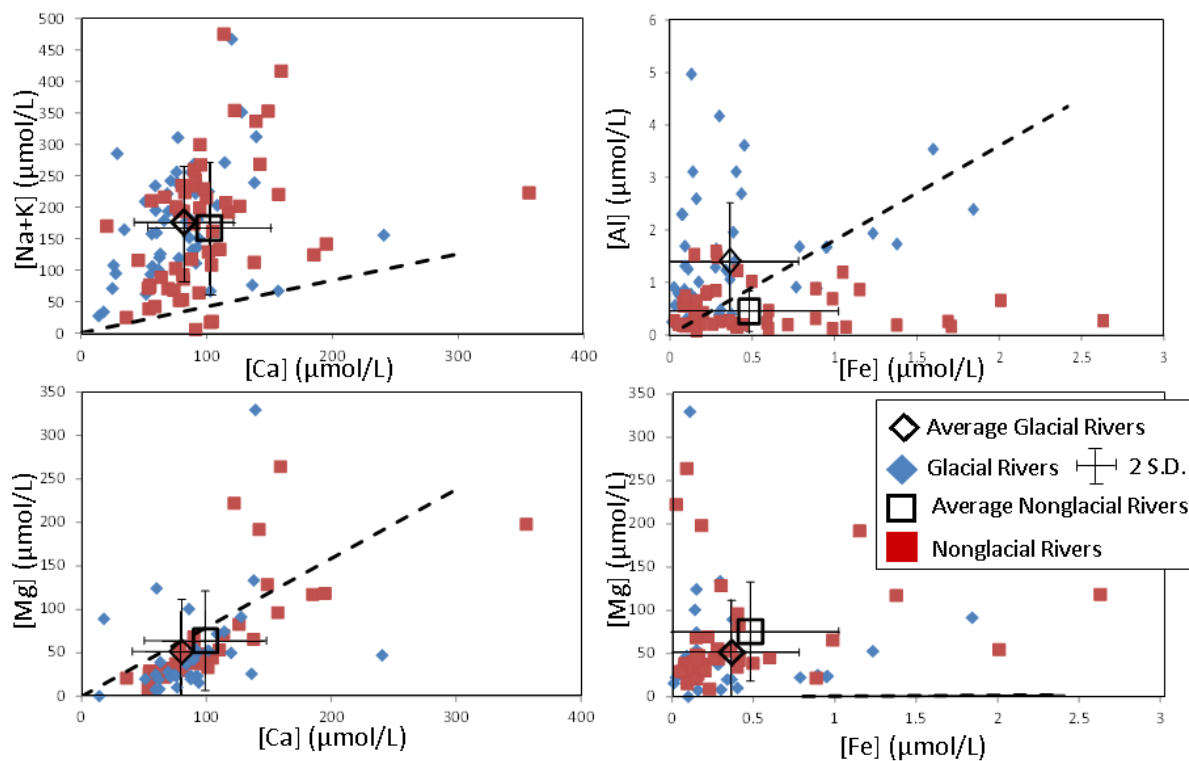
334 **Table 2.** Average River water compositions $\pm\sigma$. *TSS values were only measured by Pogge von
 335 Strandmann et al., (2006), Vigier et al., (2006) and in the new samples reported in the this study. As a
 336 result, only 30 glacial and 30 non-glacial samples were utilized to calculate the pH and TSS values.
 337 **Chlorine concentrations were used to correct the river values for precipitation inputs according to
 338 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		

339

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

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

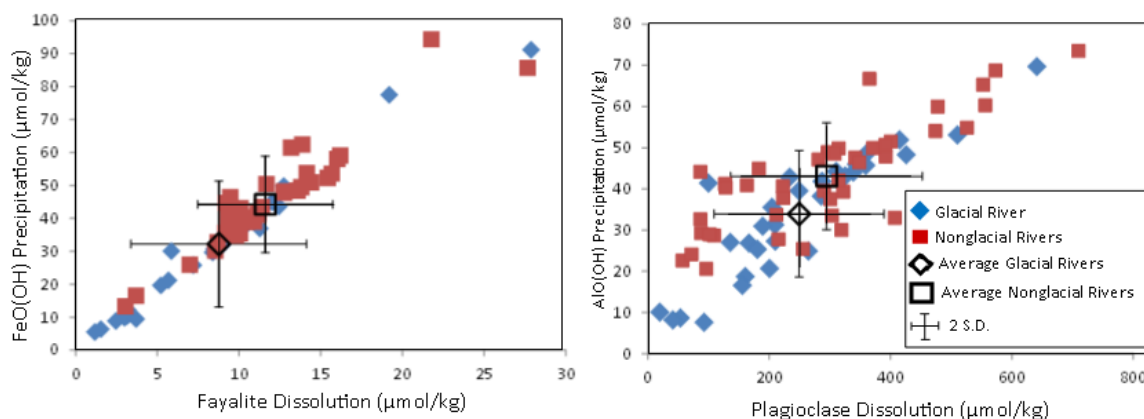


357

358 **Figure 7.** Icelandic rivers composition data from Gislason and Arnorsson (1993), Gislason et al.,
 359 (1996), Arnorsson et al., (2002), Vigier et al., (2006) and Pogge von Strandmann et al., (2006). The
 360 data has been corrected for precipitation inputs. The dashed lines represent the element ratios of
 361 pristine basalt.

362 5.5 Inverse Models and Secondary Mineral Formation Rates.

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



372

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

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

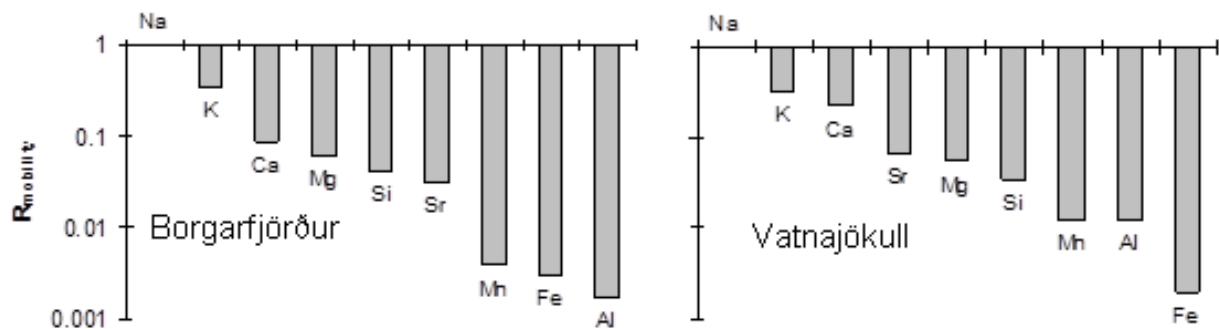
385 6. Discussion

386 6.1 pH and Chemical Weathering Patterns.

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

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

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



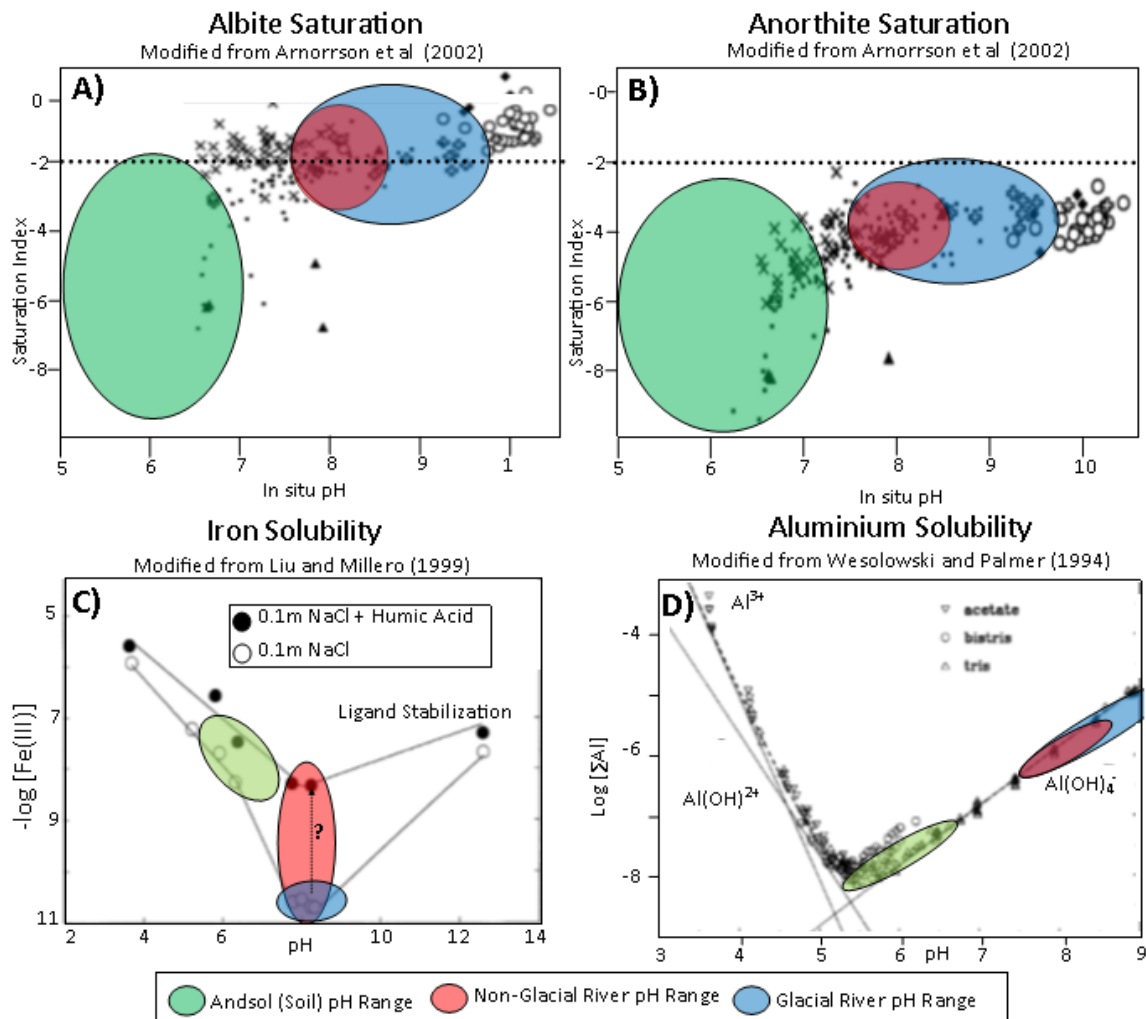
409

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

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

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

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



427

428 **Figure 10.** The andsol pH range is defined based on pore-water solutions from Opfergelt et al.,
 429 (2014) and reflects soils typical of non-glacial catchments in Iceland. A) Albite solubility and B)
 430 Anorthite solubility in Icelandic surface waters modified from Arnorrson et al (2002). At pH>7
 431 albite is near saturated while anorthite is significant under saturated across the pH spectrum.
 432 C) Iron solubility curve modified from Liu and Millero (1999) and D) Al solubility curve
 433 modified from Wesolowski and Palmer (1994). Iron is more soluble in the pH range of soil
 434 porewater than in the pH range of Icelandic rivers whereas Al solubility follows the opposite
 435 trend. The arrow on panel C underscores the relationship between apparent iron solubility
 436 and organic ligand availability with non-glacial rivers potentially falling nearer to the ligand
 437 stabilized values.

438 In many surface water environments, the mobility's of Fe and Al are dominated by
 439 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.

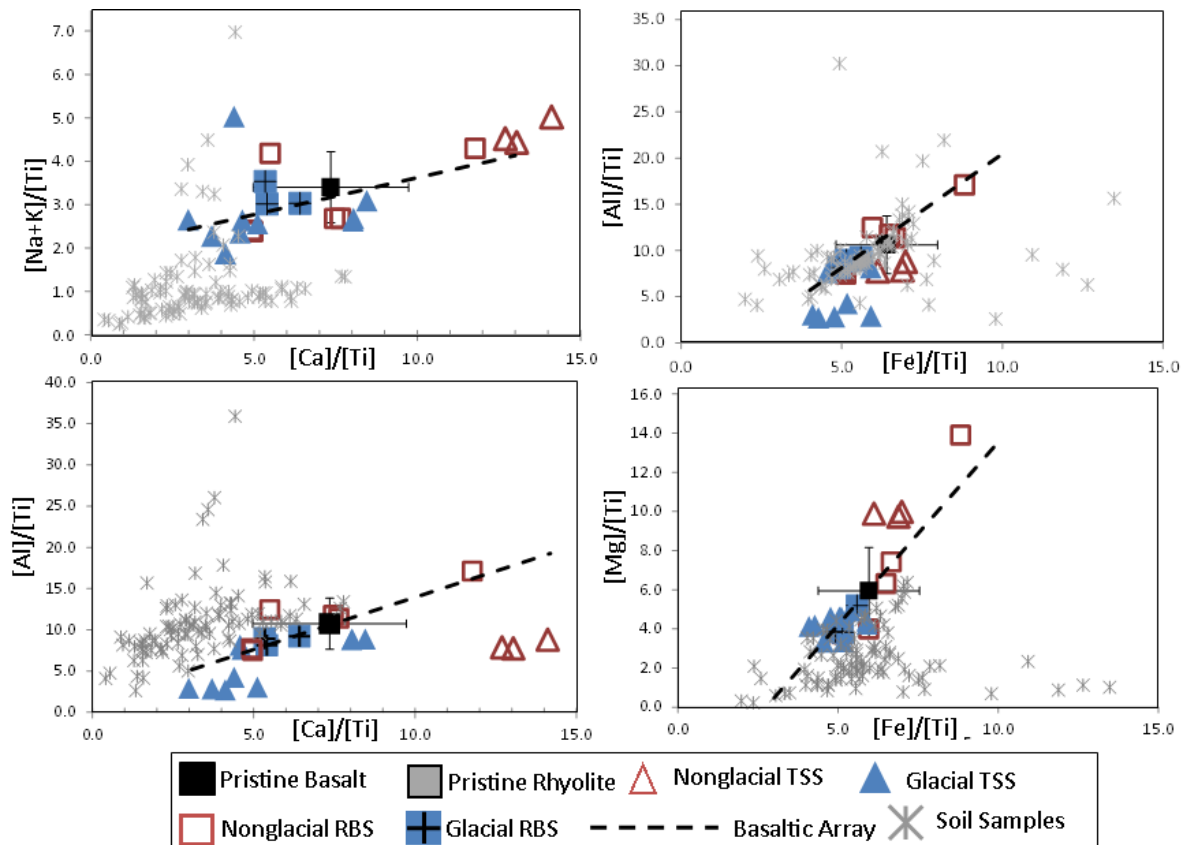
The influence of pH-dependent mineral reactions during soil formation on overall chemical weathering patterns is also reflected in the inverse-weathering Fe_{OOH} and Al_{OOH} formation rate estimates. The inverse weathering models predict Fe_{OOH} formation is mainly coupled to olivine dissolution and 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.

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

480 *6.3 Soils and River Sediments.*

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

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



494

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

499 The dominance of physical weathering on river sediment chemistry is not a new idea
 500 especially in the context of Fe_{OOH} . Poulton and Raiswell (2005) and Poulton and Canfield
 501 (2005) found that the Fe_{OOH} concentrations of river sediment from glacial and non-glacial
 502 catchments from around the world were best explained by physical weathering. Specifically,
 503 Fe_{OOH} concentrations were found to correspond to sediment surface area irrespective of
 504 bedrock lithology or soil formation intensity. This is consistent with more recent studies which
 505 have found high Fe_{OOH} export from glacial systems characterized by high rates of physical
 506 weathering e.g. Bhatia et al., (2013); Hawkins et al., (2014).

507 6.4 Physical Weathering, Fe_{OOH} export and Earth's Climate

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

513 and other terrains (Poulton and Canfield 2005) so the idea isn't new. Additionally, any
514 number of previous studies have stated: chemical weathering patterns do differ between
515 glacial and non-glacial catchments in Iceland e.g. Gislason et al., (1996); Pogge von
516 Strandmann et al., (2006, 2012); Opfergelt et al., (2013); Opfergelt et al., (2014), but
517 because of the environmental behaviour of Fe and Al physical processes control the
518 secondary Fe/ Al_{100H} flux rates (Poulton and Canfield 2005). This confirms Martin (1990)'s 27
519 year old claim that in general physical sediment erosion by glaciers enhances marine Fe_{100H}
520 accumulation.

521 What is important to note is a significant new idea has gained traction since the
522 original proposal of the Iron Hypothesis. It is now widely understood that Fe_{100H} promotes not
523 only primary production but also carbon burial. Marine carbon burial accounts for the
524 sequestration of about 309 Tg C yr⁻¹ (Burdgie 2007) and it accounts for about half of the total
525 annual geologic sink of carbon (Ciais et al., 2013). Its estimated that 20% of organic carbon
526 in marine sediments is directly stabilized by Fe_{100H} (Lalonde et al., 2012) so significant
527 changes in Fe_{100H} export equate to significant changes in Earth's climate. This is a statement
528 that is worth re-iterating because it demands a significant shift in the importance which can
529 be attributed to studying Fe_{100H} fluxes from glacial systems. For example Hawkins et al.,
530 (2014) concludes: "We contend that the consideration of meltwater Fe fluxes, which
531 supplements iron from icebergs, is critical for understanding iron cycling and primary
532 productivity in polar waters." Such a statement falls short of what we are contending as the
533 true significant of the work by Hawkins et al., (2014), Raiswell et al., (2008) and others which
534 is: we contended that the consideration of meltwater Fe fluxes, which supplements iron from
535 icebergs, is critical for understanding **carbon burial** and **Earth's climate**.

536 **7. Summary and Conclusions.**

537 Direct chemical measurements of Icelandic sediments and soils and inverse
538 stoichiometric modelling of chemical weathering in Icelandic catchments support the
539 assertion that the chemical weathering process does differ between glacial and non-glacial
540 catchments. The differences appear to be products of the soil formation process and, more
541 specifically, the relationship between pore-water pH and mineral weathering. However, as
542 many authors have concluded before us, these chemical differences don't appear to have a
543 significant effect on Fe_{100H} and Al_{100H} delivery to the ocean, because physical processes are
544 more important in the context of sediment export rates. This allows us to conclude not just
545 that glacial weathering is a significant source of (oxyhydr)oxides to the ocean, but that glacial
546 weathering promotes the accumulation of significantly more (oxyhydr)oxides in nearshore
547 marine environments than analogous non-glacial weathering. We assert that this difference

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

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