Title:
Exposure Age and Climate Controls on Weathering in Deglaciated Watersheds of Western Greenland

Authors and Affiliations:
C.A. Scribner\textsuperscript{a}, E.E. Martin\textsuperscript{a*}, J.B. Martin\textsuperscript{a}, K.M. Deuerling\textsuperscript{a}, D.F. Collazo\textsuperscript{a}, A.T. Marshall\textsuperscript{a}
\textsuperscript{a} Department of Geological Sciences, University of Florida, Gainesville, FL 32611 USA
cscribner@ufl.edu, eemartin@ufl.edu, jbmartin@ufl.edu, kdeuer@ufl.edu, adamtmarshall@ufl.edu

* Corresponding Author: Ellen E. Martin, eemartin@ufl.edu, 352-392-2141

© 2015. This manuscript version is made available under the Elsevier user license
http://www.elsevier.com/open-access/userlicense/1.0/
Abstract:

Fine-grained sediments deposited by retreating glaciers weather faster than the global average and this weathering can impact the global carbon cycle and oceanic fluxes of nutrients and radiogenic isotopes. Much work has focused on subglacial and proglacial weathering of continental ice sheets, but little is known about weathering and resulting fluxes from deglacial watersheds, which are disconnected from the ice sheets and discharge only annual precipitation and permafrost melt. We investigate the effects of exposure age and precipitation on weathering intensity in four deglacial watersheds on Greenland that form a transect from the coast near Sisimiut towards the Greenland Ice Sheet (GrIS) near Kangerlussuaq based on evaluations of major ion compositions, Sr isotope ratios, and mineral saturation states of waters and sediments. The transect is underlain by Archean orthogneiss and is characterized by gradients in moraine ages (~7.5-8.0 ky inland to ~10 ky at the coast) and water balance (-150 mm/yr inland to +150 mm/yr at the coast). Anion compositions are generally dominated by HCO$_3^-$, but SO$_4^{2-}$ becomes increasingly important toward the coast, reflecting a switch from trace carbonate dissolution to sulfide mineral oxidation. Coastal watersheds have a higher proportion of dissolved silica, higher Na/Cl, Si/Ca, and lower Ca/Sr ratios than inland watersheds, indicating an increase in the relative proportion of silicate weathering and an increase in the extent of weathering toward the coast. More extensive weathering near the coast is also apparent in differences in the $^{87}$Sr/$^{86}$Sr ratios of stream water and bedload ($\Delta^{87}$Sr/$^{86}$Sr), which decreases from 0.017 inland to 0.005 at the coast, and in increased saturation states relative to amorphous SiO$_2$ and quartz. The steep weathering gradient from inland to coastal watersheds reflects enhancement of weathering over that expected from the 2 to 3 ky difference in exposure age caused by elevated coastal precipitation. The gradient of weathering with exposure age, water budget and distance from the ice sheet
indicates that oceanic and atmospheric fluxes will change as continental glaciers retreat, precipitation patterns across the deglacial region readjust, and the relative proportion of deglacial to proglacial runoff increases.

1. Introduction

Despite cool conditions, weathering rates, and thus solute fluxes, tend to be higher in glacial terrains than the global average (Sharp et al., 1995; White and Blum, 1995; Gaillardet et al., 1999; Nezat et al., 2001; Jacobson et al., 2003; Gislason et al., 2009) due to enhanced chemical weathering of comminuted bedrock (Petrovich, 1981; Gaillardet et al., 1999). Several studies have evaluated weathering fluxes from the proglacial watershed sourced directly from the Greenland Ice Sheet (GrIS; Wimpenny et al., 2010, 2011; Ryu and Jacobson, 2012; Hindshaw et al., 2014; Yde et al., 2014), but weathering rates in this environment may be distinct from rates in deglacial watersheds that only drain local precipitation and annual permafrost melt. Differences in weathering between proglacial and deglacial systems are likely to be related to differences in: 1) the residence time of the water and water/rock ratios, 2) the exposure age of the material that is weathering, and 3) climate conditions that are influenced by proximity to the ice sheet and the coast.

Most weathering studies in western Greenland focus on the proglacial environment of Akuliarusiarsuup Kuua (also known as the Watson River) (Wimpenny et al., 2010, 2011; Ryu and Jacobson, 2012; Hindshaw et al., 2014; Yde et al., 2014). In contrast, little work has evaluated weathering in deglacial watersheds, although they provide approximately 50% of the runoff for western Greenland (Helweg et al., 2004; Mernild et al., 2010). Weathering in both types of watersheds have the potential to impact several important environmental characteristics including drawdown of CO$_2$ associated with silicate weathering (Walker et al., 1981; Berner et
al., 1983; Sharp et al., 1995; Berner and Berner, 1997; Tranter, 2003; Ryu and Jacobson, 2012) as well as fluxes of solutes to the oceans, including nutrients, which impact primary productivity (Martin, 1990; Bhatia et al., 2013) and radiogenic isotopes, which reflect terrestrial weathering across glacial-interglacial transitions (Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010; Crocket et al., 2012, 2013). In addition to differences in the extents of weathering between deglacial and proglacial watersheds, variations in exposure ages and precipitation deglaciated watersheds should impact the magnitude and composition of elemental and isotopic fluxes to the oceans as the ice sheet retreats and, therefore, atmospheric drawdown of CO$_2$, fertilization of coastal zones, and records of retreat preserved in marine sediments.

Major element concentrations in alpine and GrIS proglacial streams illustrate that proglacial watersheds have typical patterns of cation concentrations with Ca > Mg > Na, and anion concentrations dominated by HCO$_3$ and/or SO$_4$ (Anderson et al., 1997; 2000; Jacobson et al., 2002; Wimpenny et al., 2010, 2011; Ryu and Jacobson, 2012). This solute chemistry has been attributed to preferential dissolution of select minerals (e.g., carbonates, biotite and sulfides) during early stages of weathering in the subglacial and proglacial environment (Anderson et al., 1997; Blum et al., 1998; Anderson et al., 2000; Jacobson et al., 2002; Wimpenny et al., 2010, 2011). Limited data from deglacial lakes in western Greenland (Anderson, et al., 2001; Ryu and Jacobson, 2012) and six deglacial streams near the GrIS (Wimpenny et al., 2010, 2011) indicate deglaciated watersheds have higher concentrations of total dissolved solids, higher mineral saturation states, more secondary mineral formation, and lower proportional concentrations of Ca, K, and SO$_4$ than the proglacial Watson River. Although differences between proglacial and deglacial watersheds are important, regional variations in weathering and geochemistry of
deglacial watersheds between the coast and the GrIS have not been studied and could have an important impact on atmospheric and oceanic fluxes.

In addition to major element chemistry, comparisons of radiogenic isotopic compositions of water and bedrock provide a technique for evaluating the extent of chemical weathering. Radiogenic Pb and Sr isotopes are enhanced relative to bedrock in weak-acid leaches during laboratory experiments of samples from alpine glacier systems (Sr: Blum and Erel, 1995, 1997, 2003 and Pb: Harlavan et al., 1998; Harlavan and Erel, 2002; Harlavan et al., 2009). These laboratory studies indicate radiogenic isotopes are preferentially leached during early stages of weathering as a result of dissolution of specific soluble mineral phases, a process we refer to here as incongruent weathering. More extensive leaching, representing more extensive weathering, decreases the offset between bedrock and solute. This concept has been exploited to study the extent of continental weathering in the past based on seawater isotopic values preserved in deep sea sediments (Christensen et al., 1997; von Blanckenburg and Nagler, 2001; Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010; Crocket et al., 2012, 2013; Basak and Martin, 2013). Due to the long residence time of Sr in seawater, these paleoceanographic studies focused on Pb isotopes; however, anthropogenic contamination of Pb in the modern environment precludes application of Pb isotopes to evaluate modern weathering processes.

In this study we evaluate variations in weathering intensity in the exposed portion of western Greenland across a ~125 km wide transect from the coast to approximately 25 km west of the edge of the GrIS, expanding the geographic distribution of data available. Specifically, we measure major element chemistry in four distinct deglacial watersheds that create a transect from Sisimiut (66.94° N, 53.67° W) on the coast to Kangerlussuaq (67.01° N, 50.69° W) near the ice sheet. We also analyzed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in water and bedload from two of those watersheds.
The major element data provide constraints on mineral saturation states and the Sr isotope ratios reflect extent of weathering. This transect includes gradients from a positive water balance and older moraine exposure ages near the coast, to desert-like conditions and younger moraines near the ice sheet. These data reveal how changes in climate across the deglacial watersheds and in the relative proportions of deglacial to proglacial watersheds may alter elemental and isotopic fluxes between the atmosphere, land, and ocean and impact interpretations of weathering intensity associated with records of ice sheet growth and decay preserved in marine sediments (Zachos et al., 1999; Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010; Crocket et al., 2012, 2013; Basak and Martin, 2013).

2. Field Area Description

We divide the four sampled watersheds into two categories: coastal, including Sisimiut and Nerumaq and inland, including Qorlortoq and Lake Helen (Fig. 1, Tables S1-S4). The coastal watersheds experience slightly warmer mean annual temperatures (-3.9°C compared to -5.7°C) as well as more rainfall and less evapotranspiration than the inland watersheds (Cappelen et al., 2001; Aebly and Fritz, 2009; Leng et al., 2012). Sisimiut receives ~300 mm of precipitation and loses ~150 mm to evapotranspiration annually (Hasholt and Søgaard, 1978), while Kangerlussuaq receives ~150 mm of precipitation and loses ~300 mm annually through evapotranspiration (Hasholt and Søgaard, 1978; Aebly and Fritz, 2009). The boundary between positive and negative water balances is currently located at approximately 52°W (Anderson et al., 2001), between the Nerumaq and Qorlortoq watersheds (Fig. 1). Arid conditions inland result from distance from the coast and katabatic winds descending from the GrIS (Klein et al., 2001).
Exposure ages in the four deglacial watersheds studied here become progressively younger from the coast inland towards the GrIS. The GrIS extended to the continental shelf during the last glacial maximum (LGM) ~20 ka (Yokoyama et al., 2000; Simpson et al., 2009) and moved to its current position ~160 km inland through a series of retreats and advances. The Sisimiut watershed was deglaciated ~10.4 ka based on peat carbon dates (Kelly, 1979; Rinterknecht et al., 2009), a result supported by models of past GrIS retreat (Bennike and Björck, 2002; Simpson et al., 2009; Levy et al., 2012) (Fig. 1). Nerumaq is located ~30 km east of the Sisimiut watershed and separated from the Sisimiut watershed by a moraine dated 9.9 ka (van Tatenhove et al., 1996). Qorlortoq is ~60 km east and the Lake Helen watershed is ~80 km east of the Nerumaq watershed. Both the Qorlortoq and Lake Helen watersheds are located between 7.3 ka Umivit-Keglen moraines (van Tatenhove et al., 1996) and 8.5 ka Fjord moraines (Weidick, 1972; Levy et al., 2012). The trend of decreasing moraine and exposure ages from the coast to the ice sheet is well-defined, but the exact exposure age for each watershed is not. In general, the trend suggests that exposure age of the coastal watersheds is only ~2-3 ky greater than the inland watersheds.

The bedrock for the entire study area is part of the Nagssugtoqidian Mobile Belt (NMB), which is composed of Archean granodioritic to tonalitic orthogneisses deformed during the Paleoproterozoic (Escher and Watt, 1976; van Gool et al., 2002). The dominant rock-forming minerals of the NMB include feldspar and quartz with minor amounts of biotite, amphibole, pyroxene, apatite, and epidote (Mowatt, 1994). This bedrock lithology is relatively consistent across the region; however, the coastal region includes the Sisimiut charnockite, a calc-alkaline Paleoproterozoic plutonic magmatic complex (van Gool et al., 2002; Stendal and Garde, 2005).
3. Methods

3.1. Field Sampling

Water and sediment samples were collected from June 9 to July 23, 2013 using identical procedures at all sampling sites. Water was pumped from the center of stream channels through an overflow cup using tygon tubing attached to a Geotech II 12-V peristaltic pump located on stream banks. The overflow cup held a YSI Pro Plus multiparameter sonde that measured water temperature, pH, dissolved oxygen (DO), and SpC. The YSI was calibrated daily and showed little drift between calibrations. Water was filtered through a 0.45 µm trace metal grade canister filter and collected in sample-appropriate containers after triple rinsing with sample water.

Radiogenic isotope (125 or 250 mL) and cation/trace element (20 mL) samples were collected in acid washed HDPE bottles and acidified in the field to pH < 2 with optima grade HNO₃. Sixty ml of water were collected for measurements of total alkalinity and silica (Si). A 30 ml aliquot was titrated with 0.1 N HCl within 24 hrs using the Gran method. We consider the measured alkalinity to be carbonate alkalinity assuming only small concentrations of other weak acids (e.g., borate, bisulfide, organic anions etc.). Silica concentrations were measured within 30 days of collection from aliquots remaining from the alkalinity titrations using a Hach DR/890 Portable Colorimeter instrument and the Heteropoly Blue Method optimized for low concentrations (0 to 1.6 mg/L). Samples with concentrations > 1.6 mg/l were diluted and re-analyzed. All water samples were kept chilled in the field and refrigerated continuously in the laboratory prior to analysis. All samples were shipped chilled to the University of Florida (UF) by air within one month of field collection.

Stream bedload samples were collected using sterile plastic trowels or gloved hands and stored in Whirl-Pak bags. Care was taken to maintain original grain size distribution by
collecting large samples and minimizing disturbance during sampling. Sediments were stored at 4°C until processed.

### 3.2. Water Analyses

Major ion concentrations (Ca, K, Na, Mg, SO$_4$, and Cl) were analyzed on undiluted samples using a Dionex Model 500DX Ion Chromatograph and in-house multi-element standards. Precision was <5% based on an internal standard measured every five samples. All samples had charge balance errors <20% with 85% of the samples having <10% charge balance error; samples with large errors had low ionic strength. Minor elemental concentrations of Al, Mn, Fe, Sr, Ba, and Pb were measured using a Thermo Scientific Element 2 HR ICP-MS. Samples were diluted 1:1 with 5% HNO$_3$ spiked with 8 ppb rhenium and rhodium and analyzed using in-house standards. Long-term measurement reproducibility was checked against external Canadian river water standard SLRS4. Relative standard deviation between repeated measurements of SLRS4 remained under 8% for all elements.

Aliquots of water collected for radiogenic isotope analyses were transferred to clean Teflon beakers and dried in a class 1000 clean laboratory at UF. Optima grade aqua regia was added to each beaker to oxidize organic matter and then dried; this process was repeated until reactions ceased. Strontium was isolated using Eichrom Technologies Sr-spec resin (50-100 µm) according to standard column chemistry procedures (Pin and Bassin, 1992) for analyses of $^{87}$Sr/$^{86}$Sr. Separated Sr was loaded on degassed tungsten filaments and measured with a Micromass Sector 54 thermal ionization mass spectrometer (TIMS) in dynamic mode. Two hundred ratios were collected at an intensity of 1.5 V $^{88}$Sr and normalized to $^{86}$Sr/$^{88}$Sr = 0.1194. Repeat analyses of NBS-987 yielded a value of 0.71025 (+/- 0.00002, 2σ external reproducibility). Procedural blanks contained 20-250 pg Sr, which is four to five orders of magnitude lower than the Sr abundance (~5 µg) in water samples.
3.3. Sediment Analyses

Twenty-four bedload and moraine sediment samples were processed for measurements of major elements, 41 bedload samples were processed for Sr isotope analyses, and seven bedload samples were processed for carbonate mineral analyses. Processing was initiated by drying large aliquots of sediment in a 60°C oven and sieving to isolate the <2.0 mm size fraction. Sediment was ground to a fine powder with a clean mortar and pestle. For x-ray fluorescence (XRF) analyses, ~2.5 g of ground, oven-dried powder was heated to 1000°C for 1 hour to drive off organics, carbonate, and some mineral-bound water. Subsamples of 1.400±0.005 g of this volatile-free sediment were mixed with 5.600±0.005 g of lithium metaborate flux and fused into glass beads using a Katanax fusion instrument. These beads were analyzed for major element oxides (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MnO, MgO, CaO, Na$_2$O, K$_2$O, and P$_2$O$_5$) using a Rigaku “Supermini” model wavelength-dispersive XRF using a Majors/Str/Zr program. The precisions are ±1% for most element oxides and ±5% for Na$_2$O. Of the seven bedload samples measured for carbonate contents, two each came from Qorlortoq, Nerumaq, and Sisimiut, and one from Lake Helen. These samples were measured using a UIC (Coulometrics) 5011 CO$_2$ coulometer coupled with a UIC CM5240 TIC inorganic carbon preparation device. Analyses of six internal standards measured simultaneously with the samples yielded a relative standard deviation of 1%.

For Sr isotopic analyses, ~3 g of ground, oven-dried powder was heated to 550°C for 4 hours to drive off organics. Sr isotope ratios were measured on 50 mg subsamples of ground powders that were dissolved on a hotplate in capped Teflon beakers in a 3:1 solution of optima HF-HNO$_3$. The solutions were dried down and re-dissolved in optima HCl. This process was repeated until samples were completely dissolved, typically three times. Strontium was isolated using a two-step process. First, dissolved samples were passed through primary columns packed
with BioRad AG 50W-X12 cation exchange resin (volume ~3 ml) using 3.5 N trace metal grade
HCl as an eluent. The Sr cut from this column was evaporated to dryness, then Sr was further
isolated using the Sr Spec column chemistry described above. Isotope ratios were measured
using wet plasma on a Nu Plasma multiple-collector inductively-coupled-plasma mass
spectrometer (MC-ICP-MS) and a time-resolved analysis (TRA) method (Kamenov et al., 2008).
On-peak zero was determined prior to sample introduction to correct for isobaric interferences
caused by impurities of Kr in the Ar carrier gas. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were corrected for mass-bias
using $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$. $^{87}\text{Sr}$ was corrected for interference of $^{87}\text{Rb}$ by monitoring the intensity of
$^{85}\text{Rb}$, using $^{87}\text{Rb}/^{85}\text{Rb}=0.386$ and mass-bias correction factor determined from $^{86}\text{Sr}/^{88}\text{Sr}$. The
average $^{87}\text{Sr}/^{86}\text{Sr}$ value of TRA-measured NBS 987 is 0.71025 ($2\sigma = 0.00003$). Sr procedural
blanks of ~200 pg were ~ seven orders of magnitude smaller than Sr abundances in bed load
samples.

### 3.4. Saturation Indices

Saturation indices, $SI = \log(\text{IAp}/K_{eq})$, where IAP is the ion activity product and $K_{eq}$ is the
equilibrium product, were calculated for each stream water sample for a suite of minerals using
PHREEQc software and the PHREEQc database (Parkhurst and Appelo, 1999). Input parameters
included total alkalinity, pH, temperature, and concentrations of DO, Ca, K, Na, Mg, SO$_4$, Cl, Si,
Al, Mn, Fe, Sr, Ba, and Pb (Tables S1-S4).

### 4. Results

#### 4.1. Water Compositions

Water compositions (major and minor element concentrations) are presented in Tables
S1-S4 along with field measurements (pH, DO concentrations, temperature, and SpC). Waters
are more dilute in the coastal (Sisimiut and Nerumaq) than inland watersheds (Qorlortoq and
Lake Helen). Sisimiut has the lowest average SpC with an average value of 48.3 μS/cm (31.2-68.4 μS/cm). Qorlortoq exhibits the highest average SpC (300.9 μS/cm) and the greatest range (105.0-1632.0 μS/cm). Sismuit also has the lowest pH with an average value of 7.07 (6.45-7.31), while Qorlortoq has the highest average pH of 8.25 and the greatest range (6.86 – 8.09).

Major element chemistry is shown in ternary plots of relative proportions based on milliequivalent concentrations for major cations and anions and in molar proportions for Si and major cations (Fig. 2). Cations concentrations cluster among all watersheds, although the Sisimiut watershed has generally higher proportions of Na+K than other watersheds, where most samples plot toward the Ca apex (Fig. 2A). When Si is included in the ternary diagram, Lake Helen and Qorlortoq samples have <5% Si, while Sisimiut and Neramaq samples plot between 4 and 18% Si (Fig. 2B). Most anion charge is provided by HCO$_3$ and SO$_4$, with inland samples showing a general enrichment of HCO$_3$ and the coastal sites more enriched in SO$_4$ (Fig. 2C).

Sisimiut and two samples near a large lake (Tasersuaq) in Qorlortoq exhibit the highest anion proportion from Cl, but most samples have less than ~35% of the charge from Cl. Samples from Qorlortoq with elevated Cl concentrations also exhibit elevated Na+K concentrations (Fig. 2A).

Cross plots of some of major element concentrations reflect good correlations between some major elements, but limited or no correlations between others (Fig. 3). Sodium and Cl concentrations correlate well in all watersheds (Fig. 3A and B) and regression analyses indicate the Na/Cl ratio is similar to the seawater molar ratio of 0.86 for Qorlortoq and Lake Helen watersheds, but elevated relative to the seawater value for Sisimiut and Nerumaq watersheds (Table 1). Similarly, Ca correlates well with Sr concentrations for all four watersheds (Table 1), but the two coastal watersheds show enrichments of Ca relative to Sr compared to the two inland watersheds (Fig. 3C). Only Lake Helen watershed exhibits a significant correlation between SO$_4$
and Cl, with a value of 0.17, but all watersheds have SO$_4$ in excess of Cl relative to seawater (Fig. 3D). No correlation exists between Si and Ca in any watershed (Fig. 3E).

4.2 Bedload and Moraine Geochemistry

Similar to tightly clustered major element compositions observed in water samples, major element oxides for bedload and moraine samples cluster and show overlap between all four watersheds (Fig. 4). Calcium oxide contents of the sediment are similar among the watersheds, but the coastal watersheds have higher MgO contents and lower Na$_2$O+K$_2$O contents relative to the inland watersheds (Fig. 4A). The coastal watersheds tend to have higher Fe$_2$O$_3$ and lower Na$_2$O+K$_2$O contents relative to the inland watersheds (Fig. 4B). Most of the bedload and moraine samples contain >80% SiO$_2$, but a few of the samples from Sisimiut have 70-80% SiO$_2$.

The carbonate mineral contents, which are presumed to be disseminated calcite (e.g., Jacobson and Blum, 200), average 0.47 g/kg, with a range from 0.25-0.73 g/kg.

4.3. Saturation Indices

All watersheds have similar mineral-specific saturation states, although subtle differences in the magnitudes of over- or under-saturation exist between watersheds (Fig. 5). All water samples are 1) undersaturated with respect to feldspars, quartz, chlorite, and calcite, 2) supersaturated with respect to K-mica, gibbsite, kaolinite, and Fe oxides, and 3) near saturation with respect to illite. Water samples are closer to equilibrium with respect to quartz, amorphous SiO$_2$ and calcite in coastal than inland watersheds (Fig. 5 inset). The inland watersheds are also slightly more oversaturated than coastal watersheds with respect to various Fe-oxides.
4.4. Sr isotope ratios

Strontium isotope ratios from water samples are consistently more radiogenic than corresponding bedload sediment from both Nerumaq and Qorlortoq (Fig. 6). In Nerumaq, water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.708 to 0.719 (SD = 0.003) and bedload from 0.706 to 0.711 (SD = 0.001), while in Qorlortoq, water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.717 to 0.740 (SD = 0.003) and bedload ratios range from 0.710 to 0.717 (SD = 0.002). Although the ranges overlap, only one tributary at Qorlortoq (Q1-T3) has $^{87}\text{Sr}/^{86}\text{Sr}$ values for water that are similar to values observed at Nerumaq. On average, the difference between the $^{87}\text{Sr}/^{86}\text{Sr}$ value for the water and the bedload ($\Delta^{87}\text{Sr}/^{86}\text{Sr}$) is 0.017 in the Qorlortoq watershed, which is three times greater than the average $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ of 0.005 in the Nerumaq watershed. Differences between water and bedload at both sites as well as for the water and bedload between sites are statistically significant ($p < 0.0001$) based on Student’s t-tests.

5. Discussion

Understanding the causes of variations of water compositions within watersheds is complicated by variables that are unconstrained in this study, such as differences in vegetation, soil development, sediment grain size, channel conditions, and flow rates. Several samples were collected from lake outlets and likely have compositions altered by lake processes, such as concentrated loess weathering, elevation, evaporation, and elevated dissolved organic carbon concentrations (e.g., Anderson et al., 2001; 2007). Consequently, we focus here on larger, more consistent signals of weathering variations between the four sampled watersheds and interpret these trends in terms of bedrock chemistry and mineralogy, as well as gradients in exposure age and precipitation.
5.1 Coastal vs. Inland Deglacial Watersheds

The transect of watersheds show higher proportion of Si (Fig. 2B), higher Na/Cl and Si/Ca ratios, lower Ca/Sr ratios (Fig. 3), and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6) in the coastal than inland watersheds, despite similar major element chemistry of the bedrock (Fig. 4). The following discussion evaluates these variables to assess the relative extent of weathering between the coastal and inland watersheds.

5.1.1. Bedrock Geochemistry

We assume major element compositions of the bedload and moraine samples represent average bedrock compositions of each watershed due to homogenization of the rocks during transport processes (fluvial or glacial). The overlap of bedload element contents (Fig. 4) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 6) among the watersheds reflects similarity within the NMB of bedrock across the region. The slight enrichment of Fe$_2$O$_3$, MgO and CaO and depletion of SiO$_2$ proportions in the coastal watersheds are consistent with the presence of charnockite intrusions (e.g., van Gool et al., 2002; Stendal and Garder, 2005). This charnockite, which may be more susceptible to weathering than the granodiorite of the NMB, could affect weathering patterns observed in the elemental and isotopic compositions of water draining the different watersheds. However, the narrow range of cation concentrations in all watersheds (Fig. 2A) suggests preferential weathering of charnockite has little influence on geochemical differences in weathering between the coastal and inland watersheds. Weathering of different bedrock sources should also result in differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from coastal (Nerumaq) and inland (Qorlortoq). Although the ranges and averages of bedload $^{87}\text{Sr}/^{86}\text{Sr}$ for each site are distinct, there is overlap between these values (Fig. 6). The total range of bedload $^{87}\text{Sr}/^{86}\text{Sr}$ values across the study area (0.706 – 0.717) is small compared to the range of values observed in NMB stream...
sediments (0.707 – 0.731; Colville et al., 2011) and stream sediment silts (0.708 – 0.738; Reyes, et al., 2014), suggesting the Sisimiut charnockite may not greatly affect the bedload $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In addition, the $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ values should accurately reflect weathering extent because they do not depend on the isotopic ratio of the starting material. Thus, although heterogeneities exist in the bedload and moraine compositions between the coastal and inland watersheds, they are subtle and do not appear to account for trends in weathering based on differences in the water compositions we describe below.

5.1.2 Water chemistry and evidence for weathering patterns

In addition to inputs from weathered bedrock material (Meybeck, 1987; Clow et al., 1996), water compositions can be altered by seawater aerosols entrained in precipitation (Fitzgerald, 1991). This source of solutes is reflected in Na/Cl molar ratios similar to the seawater ratio in Qorlortoq and Lake Helen watersheds (Fig. 3A) and suggests both Na and Cl concentrations are conservative there. Higher concentrations of Na and Cl in inland than coastal watersheds are due to excess evaporation, consistent with higher SpC in these watersheds. The region contains no Cl-bearing minerals, suggesting that Cl is conservative and thus that Na/Cl ratios elevated above the seawater value in the coastal watersheds (Fig. 3B) reflect a source of Na from weathering reactions.

This Na source is likely weathering of plagioclase, which would also contribute Ca, considering its common occurrence in the region (Kalsbeek et al., 1987; Mowatt and Naidu, 1994). Plagioclase weathers according to

$$\text{Ca}_{x}\text{Na}_{(1-x)}\text{Al}_{(1+x)}\text{Si}_{(3-x)}\text{O}_8+(1+x)\text{CO}_2+(2+2x)\text{H}_2\text{O} \rightarrow \text{xCa}+(1-x)\text{Na}+(3-x)\text{SiO}_2+(1+x)\text{HCO}_3+{(1+x)}\text{Al(OH)}_3$$  \hspace{1cm} (1)
where $x$ represents the molar concentration of Ca in plagioclase, and Al is assumed to be conserved as Al hydroxide (White et al., 2005). Water compositions controlled solely by reaction 1 should have Si/Ca ratios that vary from 2 for dissolution of anorthite (i.e., $x = 1$) to 3 for dissolution of albite (i.e., $x = 0$). Additional contributions from weathering of alkali feldspar, which lacks Ca but contains Na, would increase the Si/Ca ratio and Na/Cl ratio. The Si/Ca ratio would decrease with calcite weathering, which would contribute Ca but no Si to the water (e.g., Blum et al., 1998). This contribution could be important, since calcite weathers more rapidly than plagioclase minerals (Jacobson et al., 2003; Li et al., 2014) even though calcite contents averages only 0.47 g/kg in the bedload and moraine material. Multiple sources of Si and Ca can account for their lack of correlation (Table 1); however, Si concentrations are elevated over Ca concentrations in coastal compared to inland watersheds (Fig. 3E), suggesting weathering shifts between relatively more feldspar weathering in the coastal watersheds and relatively more carbonate weathering in the inland sites.

Preferential carbonate weathering in Greenland is supported by previous observations of elemental and isotopic compositions of dissolved solutions. For example, carbonate weathering is reflected in light Mg isotope measurements observed in deglacial watersheds near our inland deglacial watersheds (Wimpenny et al., 2011). Furthermore, major cation and anion concentrations measured in water samples collected from deglacial watersheds and which have been interpreted to reflect carbonate mineral weathering (Wimpenny et al., 2010; Ryu and Jacobson, 2014) plot near our data from Lake Helen and Qorlortoq (Fig. 2).

The relative importance of carbonate vs. silicate weathering can be evaluated by Ca/Sr ratios, as illustrated by variations in these ratios in variously aged glacial deposits in the Raikhot region of the Himalayas in Pakistan, a region underlain by high-grade quartzo-feldspathic biotite
gneiss (Jacobson et al., 2002). Although two different sources of calicite with different compositions occur in the Raikhot watershed, Ca/Sr ratios of bedload sediments range from 1.35 mmol/µmol for acetic leaches, which are presumed to represent a carbonate mineral end member, to ~0.20 mmol/µmol for carbonate-free whole sample digestions, presumed to represent the silicate end member (Blum et al., 1998; Jacobson et al., 2002). The Ca/Sr ratios we measure for water from the inland watersheds of Greenland are around 0.85 mmol/µmol for the inland watershed, consistent with dissolution of carbonate minerals with elevated Ca/Sr ratios relative to silicate minerals (Table 1). In contrast, the coastal watersheds have Ca/Sr ratios of 0.06 to 0.17, which although lower than the silicate end-member found by Blum et al. (1998) in the Raikhot region, suggests weathering in the coastal watersheds is dominated by Sr-rich silicate minerals. The lower Ca/Sr ratios observed in the coastal Greenland water relative to the Raikhot bedload silicate mineral leaches from Blum et al. (1998) may reflect differences in the composition of the rocks.

The distributions of SO$_4$/Cl ratios also reflect a shift in minerals being weathering between the coastal and inland watersheds. The elevated SO$_4$/Cl ratios at all four watersheds relative to the seawater SO$_4$/Cl ratios (Fig. 3D) reflect a source of SO$_4$ to the water, which is likely oxidative dissolution of sulfide minerals (e.g., Anderson et al., 2000; Tranter, 2003) as no gypsum is present at the surface in these areas. Sulfide dissolution throughout the deglaciated watersheds and in the proglacial Watson River contrasts with the occurrence of SO$_4$-free sub-glacial water collected up to 45 km inland from the edge of the GrIS (Graley et al., 2014). This lack of SO$_4$ was interpreted to reflect complete oxidation of sulfide minerals from the bedrock underlying the GrIS, but elevated SO$_4$/Cl ratios in our exposed watersheds suggest sub-glacial sulfide minerals are preserved until they are exposed to atmospheric oxygen in the periglacial
environment. This preservation could result from reducing conditions below the GrIS. Elevated
SO$_4$/Cl ratios in the coastal relative to the inland watersheds suggest more sulfide oxidation
occurs in coastal watersheds. This oxidation is important because it contributes to the lower pH
values found in the coastal watersheds (Table S1-S4), which in turn could contribute to increased
dissolution of silicate minerals and indicates limited buffering capacity compared to the inland
watersheds. The water compositions thus reflect a shift from predominately carbonate mineral
weathering to predominately silicate and sulfide mineral weathering from inland to the coast.

5.1.3 Extent of Chemical Weathering

Our observations of the predominance of carbonate weathering at the inland watershed
and predominance of silicate and sulfide weathering at the coastal watersheds suggest the coastal
area has experienced a greater extent of weathering than the inland watersheds, because
carbonates weather more easily and rapidly than silicate and sulfide minerals (e.g., Anderson et
al., 1997; Jacobson et al., 2003). The extent of weathering can be further evaluated by
comparing $^{87}$Sr/$^{86}$Sr ratios of the bedload and dissolved solutes. Elevated $\Delta$$^{87}$Sr/$^{86}$Sr are likely
to reflect incongruent leaching of radiogenic Sr due to preferential biotite (e.g., Blum and Erel,
1995, 1997) and possibly K-feldspar (e.g., Bullen et al., 1997) dissolution. Although this
evaluation could be complicated by differences in the $^{87}$Sr/$^{86}$Sr ratios of the solid phases (Fig. 6),
except for one tributary, all Qorlortoq water and bedload sample pairs have a larger $\Delta$$^{87}$Sr/$^{86}$Sr
value than Nerumaq sample pairs (Fig. 6A). The average $\Delta$$^{87}$Sr/$^{86}$Sr at Qorlortoq is 0.017
compared to 0.005 at Nerumaq. The low values at Nerumaq may reflect more extensive
weathering since this watershed was exposed; a hypothesis we evaluate below.
Mineral saturation states also support differences in the extent of weathering at coastal and inland watersheds (Fig. 5). Ongoing carbonate mineral dissolution shifts water compositions closer to calcite saturation in inland than coastal watersheds. The greater undersaturation with respect to calcite in the coastal watersheds in part results from lower pH values in coastal watersheds (Tables S1-S4) from combined greater rainfall, sulfide oxidation, and less buffering through calcite dissolution. Undersaturation of silicate minerals, such as albite, anorthite, K-feldspar, amorphous silica, quartz, and chlorite indicates these minerals should dissolve within all four watersheds. Amorphous SiO$_2$ and quartz are slightly closer to saturation in the coastal than the inland watersheds, as expected given the greater proportion of silicate weathering. In all watersheds, feldspar minerals appear to weather to clay minerals based on undersaturation of albite, anorthite and K-feldspar and supersaturation of gibbsite and kaolinite, which would result in the observed low Si concentrations (Fig. 2B). According to Wimpenny et al. (2010), most Fe occurs as colloids, but concentrations are high enough that all streams are supersaturated with respect to Fe-oxide minerals. Precipitation of Fe-oxides could limit iron fluxes to the ocean from deglacial watersheds, unlike proglacial systems, which appear to be a major source to the oceans of bioavailable iron (Bhatia et al., 2013).

**5.2. Controls on the Extent of Weathering**

Assuming the shift from predominantly carbonate to silicate weathering, and thus an increased extent of weathering from the inland to coastal watersheds is not a function of subtle differences in bedrock geochemistry, other environmental factors must be responsible. Since all watersheds have similar elevations, latitudes, and temperature ranges, two likely variables include gradients in exposure ages of the sediment being weathered and the water balance across the transect; we discuss below evidence for the potential influences of these variables on
weathering. Because our data represent the first regional observations of weathering in deglacial river systems of an actively retreating continental ice sheet, we compare our observations to published records of weathering in alpine deglacial and proglacial systems.

5.2.1 Exposure Age as a Control on Weathering

A transition from carbonate to silicate weathering with increased exposure age has been documented in glacial watersheds around the world, including the Bench River, Alaska (Anderson et al., 2000) and glacial deposits in the Wind River Mountains, Wyoming (Blum and Erel, 1997). A similar pattern emerges at the Raikhot watershed in the Himalaya of Pakistan, although this pattern is complicated by supply of fresh carbonate material in wind-blown dust (Blum et al., 1998; Jacobson et al., 2002). A decrease in carbonate dissolution with time has also been corroborated in leaching experiments with granitoid rocks (White et al., 1999). The pattern of decreasing carbonate weathering in the observed natural systems develop across exposure ages that range from as short as about 50 yrs to as long as 55 ky, although this range does not occur in all watersheds. In contrast to the large range observed elsewhere, the range of exposure ages in Greenland watersheds is small, on the order of 2 to 3 ky.

The shifts in minerals being weathered both at Bench River and Raikhot watershed result in systematic changes in the Ca/Sr ratios (Fig. 7A). Specifically, water draining the terminus of moraine at Bench River that was exposed after 1950 has Ca/Sr ratios of around 1.13 and this value drops to 0.35 as the Bench River flows through deposits from the LGM (Anderson et al., 2000). The Ca/Sr ratios in ammonium acetate and acetic acid leaches of sediments from the Raikhot watershed, which represent exchangeable and carbonate fractions, respectively, and should simulate values in water draining the watersheds, decrease from around 1.0 - 2.0 in moraines that are < 1 ky old, to around 0.3 - 0.6 in moraines that are 5-8 ky old, to 0.2 in
moraines that are ~0.2 ky old (Jacobson et al., 2002). The rate of decrease in Ca/Sr ratios from our inland watersheds (7-8 ky; 0.37 to 0.65 mmol/µmol) to coastal sites (~10 ky; 0.14 to 0.26 mmol/µmol) is more rapid than the decrease observed at Bench Glacier. The Ca/Sr ratios for the inland watersheds in Greenland are similar to ratios found in moraines with similar ages (5 to 8 ky) in the Raikhot watershed, but the Ca/Sr ratios of our coastal sites are smaller than values found there in older, 55 ky old moraines (Jacobson et al., 2002). This comparison also reflects a more rapid rate change in Ca/Sr ratios with exposure age in the Greenland watersheds than at the Raikhot watershed.

Differences in bedload and water $^{87}$Sr/$^{86}$Sr isotopes ($\Delta^{87}$Sr/$^{86}$Sr) from the Bench River, Wyoming and Greenland also illustrate interesting trends with the extent of weathering (Fig. 7B). Bench River $\Delta^{87}$Sr/$^{86}$Sr values in moraines exposed ~50 yrs are 0.002 compared to a value of 0.0002 in LGM moraines (Anderson et al., 2000). The $\Delta^{87}$Sr/$^{86}$Sr values for ammonium acetate extracts compared to whole soil digests from Wyoming show a decrease from around 0.055 for 300 yr old moraines, to 0.008 for 2000 year old moraines, to 0.004 for 20 ky old moraines (Blum and Erel, 1997). In comparison, average $\Delta^{87}$Sr/$^{86}$Sr ratios of ~0.017 at Qorlortoq (an inland site) and of ~0.005 at Nerumaq (a coastal site) are higher than the 0.002 to 0.0002 values observed by Anderson et al. (2000) across the ~14 ky exposure age range at the Bench River (Fig. 7B) and the $\Delta^{87}$Sr/$^{86}$Sr value from Nerumaq is similar to values found in 12 and 20 ky old moraines in Wyoming (Blum et al., 1998). Because the difference in exposure age in the Greenland watersheds is only about 2 – 3 ky, the differences in both Ca/Sr ratios and $\Delta^{87}$Sr/$^{86}$Sr values between these watershed represent a steeper gradient in weathering with exposure age than other glacial deposits with similar data.
The rapid variations in Ca/Sr and $\Delta^{87}$Sr/$^{86}$Sr values across the Greenland transect could be attributed to the presence of the Sisimiut charnockite in the coastal watersheds; however, the overlap in major bedload cation compositions (Fig. 4) suggests that environmental factors, such as exposure age and precipitation may be more important to the observed variations. Comparisons between Greenland watersheds and other glacial deposits could also reflect differences in bedrock geology; however, trends in ratios of elements and isotopes rather than absolute values have been interpreted to reflect weathering extents, rather than initial compositions, and thus should be comparable across the watersheds. Since both the Ca/Sr ratios and $\Delta^{87}$Sr/$^{86}$Sr values indicate a steeper weathering gradient with exposure age in western Greenland than other locations, we suggest that factors in addition to exposure age control this weathering gradient. Specifically, as discussed below, we propose that the precipitation gradient from the coast to the GrIS plays an important role.

5.2.2. Precipitation as a Control on Weathering

Water drives most chemical weathering reactions (e.g., White and Blum, 1995) supporting the idea that the rapid shift in weathering extent from coastal to inland watersheds results from the precipitation gradient, although the slight increase in exposure age at the coast complicates the interpretation of the relative importance of each factor. Precipitation has been found to be important to weathering reactions in New Zealand watersheds that include glacial deposits, but weathering there is also enhanced by increased uplift rate, thus confounding direct comparisons with the Greenland watersheds (Jacobson et al., 2003). Interestingly, the Ca/Sr ratios and $\Delta^{87}$Sr/$^{86}$Sr values from the Bench River are consistently smaller than these values in Greenland (Fig. 7), which suggests a larger extent of weathering in Alaska than Greenland. Although the precipitation in the Bench River watershed is not known precisely, estimates
suggest it is ~2000 mm per year (Anderson et al., 2000), or approximately an order of magnitude
greater than in the Greenland watersheds. This high rainfall could account for elevated
weathering in Alaska as expressed by low Ca/Sr ratios and $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ values.

Precipitation is similar in the Greenland watershed to Pinedale, Wyoming, about 5 km
east of sites sampled by Blum and Erel (1997), but the temperature is about 5 to 7º C warmer in
Pinedale than Greenland. This warmer temperature could account for more rapid weathering and
thus lower $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ values of the 21.7 ka moraine in Wyoming relative to the Greenland
watersheds (Fig. 7B). Variations in precipitation could also complicate weathering rates and
Ca/Sr ratios and $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ values in the Raikhot watershed. Although not well known, annual
precipitation in this region appears to range from around 100 to 1000 mm/yr depending on the
elevation, which ranges over ~3000 m (Jacobson et al., 2002). The temperature is also likely to
decrease with elevation and may result in variations in weathering across this watershed. Thus,
changes in precipitation and temperature combined with exposure age could affect the observed
pattern of weathering at the Raikhot watershed.

5.3 Implications

The controlling factors and magnitude of weathering extents are important to evaluate
fluxes between the atmosphere, land and oceans. The shift from a negative water balance near
the GrIS to a positive water balance at the coast is likely a feature of dry katabatic winds from
the ice sheet and elevated humidity near the coast. This feature indicates the boundary between
negative and positive water balance should move inland with retreat of the GrIS, and thus
increase the area of elevated precipitation and associated intense weathering relative to the area
of aridity. Consequently, the chemical and isotopic fluxes of solutes from the deglacial
watersheds to the oceans will reflect an increasing component of silicate weathering products.
and radiogenic isotopes associated with more extensive weathering as the ice sheet retreats.

Elevated precipitation at the coastal watersheds dilutes solute concentrations. Nonetheless, coastal discharge and therefore solute fluxes may be greater than inland, but discharge data needed for this evaluation are currently unavailable. In addition, the proportion of deglacial relative to proglacial watersheds will increase. This cumulative increase in area of watersheds characterized by a higher proportion of silicate relative to carbonate weathering could increase atmospheric drawdown of CO$_2$, contributing to global carbon cycling associated with silicate weathering in proglacial watersheds near ice sheets (e.g., Ryu and Jacobson, 2012).

Variations in seawater Pb isotopes preserved in authigenic marine sediments from the North Atlantic record an evolution of continental weathering intensity consistent with our data from deglacial watersheds. Several studies illustrate an increase in Pb isotope ratios from the LGM into the Holocene; the magnitude of change and the isotopic ratios themselves increase with proximity to Northern Hemisphere ice sheets (Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010; Crocket et al., 2012). Foster and Vance (2006) suggested this increase was due to preferential release of radiogenic Pb during rapid chemical weathering of fresh soils exposed by retreating ice sheets (e.g., Harlavan et al., 1998), similar to the processes documented by Sr isotopes in the inland watersheds. Following the Holocene Climatic Optimum (~7.5 ka), seawater Pb isotopes start to decrease (Gutjahr et al., 2009; Kurzweil et al., 2010; Crocket et al., 2012, 2013) possibly in response to both increased exposure age and cooler temperatures. Our data suggest changes in weathering extent caused by the growth of deglacial watersheds and related to both exposure age and rainfall patterns contributed to this decrease and that understanding the weathering regimes across these deglaciated regions may enhance our interpretations of these long term records of continental weathering.
This study provides an assessment of weathering in a transect of deglaciated watersheds in western Greenland that were exposed as the continental ice sheet retreated during the Holocene. Despite the dominant regional silicate mineralogy, geochemical analyses of major element concentrations, mineral saturation states, and Sr isotope ratios indicate both carbonate and silicate weathering reactions occur across the transect, although carbonate weathering decreases and silicate and sulfide weathering increase from inland to the coast. This shift indicates that coastal watersheds experience a greater extent of weathering than inland watersheds, although exposure ages between the two areas differ by only 2 to 3 ky.

The gradient in weathering intensity with exposure age is greater between the deglacial inland and coastal watersheds of western Greenland than previously observed in alpine watersheds, although variations in dissolved ions and isotopes are similar. The steeper gradient corresponds to the precipitation gradient from inland to the coast, which would compound the control on weathering associated with exposure age. Although exposure age may modulate weathering reactions over thousands to tens of thousands of years, abrupt changes in precipitation over small areas, such as the transect from high precipitation near the coast to high aridity associated with katabatic winds from the GrIS, have the potential to significantly impact the timescale of weathering. This gradient is likely to move inland as the GrIS retreat continues.

In response, fluxes of solutes and radiogenic isotopes from deglacial watersheds should shift toward a regional signal of more extensive weathering that includes a greater contribution from silicate weathering and a more congruent weathering signature in Sr isotopes. Improved understanding of the evolution of weathering reactions in deglacial watersheds will improve our understanding of how changing weathering environments affect ocean chemistry, nutrient fluxes
to the ocean, and the global carbon budget in the past. This information could also improve interpretations of variations in the past and predictions of future changes in oceanic and atmospheric fluxes with continued retreat of continental glaciers.

Acknowledgements: We thank G. Kamenov and A. Heatherington for their technical support on the Nu-Plasma MC-ICP-MS, Element 2 ICP-MS, and Micromass Sector 54 TIMS. J Curtis aided in the coulometric measurements of granitic carbonate content. We thank the Kangerlussuaq International Science Support facility and staff, as well as CH2MHILL Polar Services, for help in planning and implementing field logistics. M. Davlantes, and A. Portier were members of the field collection team. We thank A.D. Jacobson, J. Wimpenny and an anonymous reviewer for constructive comments that substantial improved the manuscript. This research was funded by NSF grant ARC-1203773 (JBM and EEM) and National Geographic grants 9076-12 (JBM) and 9121-12 (KMD).
References Cited


Table 1. Summary of regression analyses.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Regression</th>
<th>Na/Cl (mM/mM)</th>
<th>Ca/Sr (mM/µM)</th>
<th>SO₄/Cl (mM/mM)</th>
<th>^{87}Sr/^{86}Sr:Ca/Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>1.25</td>
<td>0.062</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.70</td>
<td>0.64</td>
<td>N.S.</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>p-value</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sisimiut</td>
<td>Slope</td>
<td>1.9</td>
<td>0.16</td>
<td>3.79</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.83</td>
<td>0.82</td>
<td>0.41</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>p-value</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.0007</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Nerumaq</td>
<td>Slope</td>
<td>0.84</td>
<td>0.56</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.98</td>
<td>0.91</td>
<td>N.S.</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>p-value</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td></td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Qorlortoq</td>
<td>Slope</td>
<td>0.85</td>
<td>0.49</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>r²</td>
<td>0.99</td>
<td>0.99</td>
<td>0.95</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>p-value</td>
<td>&lt;0.0001</td>
<td>0.005</td>
<td>0.005</td>
<td></td>
</tr>
</tbody>
</table>

N.S. indicates regressions are not significant and are not plotted in figures. Site Q2-M2 is excluded from regressions as a statistical outlier. N.A. = Not analyzed.
Figure 1. Sample Locations. A. Map of Greenland showing location of sampling transect. B. Locations of the Sisimiut, Nerumaq, Qorlortoq and Lake Helen watersheds and sample sites in western Greenland. Blue dashed lines represent contours of the ages and locations of mapped moraines compiled by Levy et al. (2012). The dotted orange line represents the boundary between the region with positive water balance (west) and negative water balance (east) from Anderson et al. (2001). C. Sample locations for Sisimiut watershed (n=17), D. Nerumaq watershed (n=22), E. Qorlortoq watershed (n=19), and F. Lake Helen watershed (n=5). See appendices for additional information about sample designations and locations.
Figure 2. Major ion ternary plots showing ion proportions in all watersheds. A. Major cation proportions in % milliequivalents. B. Relative K+Na, Ca+Mg, and silica proportions in % millimoles. C. Major anion proportions in % milliequivalents. Black ‘X’ represents nonglacial watersheds from Ryu and Jacobson (2014) and ‘+’ represents nonglacial watersheds from Wimpenny et al (2010). Grey triangle is average world river values from Meybeck (1987).
Figure 3. Comparisons of solute concentrations. A) Na versus Cl concentrations at all location. Dotted line is seawater molar ratio of 0.86 (Keene et al., 1986). B) Expanded view of Sisimiut and Nerumaq data from box in A including seawater ratio. C) Ca versus Sr concentrations. Ca and Sr trends for silicate (dashed line) and carbonate (dotted lines) fractions of sediments in the Raikhot watershed (Blum et al., 1998; Jacobson et al., 2002). D) SO$_4$ versus Cl concentrations. Dotted line is seawater molar ratio of
0.14 (Morris and Riley, 1966). E) Si versus Ca concentrations. Dotted line is the ion ratio expected from anorthite dissolution (Reaction 1). Solid lines with colors for each watershed are linear regressions through data with statistically significant slope values (p<0.005; Table 1).
Figure 4. Relative proportions of weight percent oxides for bedload and moraine material. A. Relative MgO, CaO and Na₂O+K₂O proportions, B. Relative SiO₂, CaO+MgO and Na₂O+K₂O proportions, C. Relative Fe₂O₃, MgO and Na₂O+K₂O proportions.
Figure 5. Saturation indices of selected minerals plotted by watershed. The data points represent the average mineral saturation index of all of the samples from each watershed and error bars represent ±1 standard deviation of the data within each watershed. Inset shows expanded scale of y-axis for SiO$_2$(a) and quartz.
Figure 6. $^{87}\text{Sr}/^{86}\text{Sr}$ data for Nerumaq (filled circles) and Qorlortoq (filled diamonds) samples. A. Difference between water and bedload $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Average $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ is 0.005 for Nerumaq and 0.017 for Qorlortoq. B. $^{87}\text{Sr}/^{86}\text{Sr}$ values for water (colored symbols) and bedload (black symbols) for Nerumaq and Qorlortoq watersheds. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Nerumaq bedload is 0.708 and water is 0.713. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Qorlortoq bedload is 0.713 and water is 0.731. $^{87}\text{Sr}/^{86}\text{Sr}$ errors are smaller than data points.
Figure 7. A. Ca/Sr ratios for samples from Bench Glacier, Alaska (filled squares; Anderson et al., 2000), Raikhot watershed, Pakistan (open diamonds; Jacobson et al., 2002) and the inland (orange circles) and coastal (blue circles) watersheds in Greenland (this study). Note the x-axis is plotted on a log scale to account for the large age spread. B. $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ ratios for samples from Bench Glacier, Alaska (filled squares; Anderson et al., 2000), Wind River Mountains, Wyoming (open triangles; Blum and Erel, 1997), and inland (orange circles) and coastal (blue circles) watersheds in Greenland (this study). The dashed line highlights 0 offset. The total range of values for the inland and coastal watersheds in Greenland is depicted by vertical bars in both panels. The data point at ~14 ky for Bench Glacier is from a sample described as Last Glacial Maximum in age. The horizontal bar in both panels illustrates the range of possible ages encompassed by that designation.