

# Northumbria Research Link

Citation: Graly, Joseph, Licht, Kathy J., Bader, Nicole A. and Bish, David L. (2020) Chemical weathering signatures from Mt. Achernar Moraine, Central Transantarctic Mountains I: Subglacial sediments compared with underlying rock. *Geochimica et Cosmochimica Acta*, 283. pp. 149-166. ISSN 0016-7037

Published by: Elsevier

URL: <https://doi.org/10.1016/j.gca.2020.06.005>  
<<https://doi.org/10.1016/j.gca.2020.06.005>>

This version was downloaded from Northumbria Research Link:  
<http://nrl.northumbria.ac.uk/id/eprint/43775/>

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: <http://nrl.northumbria.ac.uk/policies.html>

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)

1 **Chemical weathering signatures from Mt. Achnar Moraine, Central Transantarctic Mountains I:**  
2 **Subglacial sediments compared with underlying rock**

3  
4 **Joseph A Graly<sup>1,2</sup>, Kathy J Licht<sup>2</sup>, Nicole A Bader<sup>2</sup>, David L Bish<sup>3</sup>**

5  
6 **1: Northumbria University, Geography and Environmental Sciences, Newcastle Upon Tyne, UK**

7 **2: Indiana University Purdue University Indianapolis, Earth Sciences, Indianapolis, IN, USA**

8 **3: Indiana University, Earth and Atmospheric Sciences, Bloomington, IN, USA**  
9

10 **Abstract**

11 In order to determine chemical weathering rates on the subglacial land surface of Antarctica, we  
12 compare the composition and mineralogy of freshly emerging fine sediments to that of the underlying  
13 bedrock, as represented by glacially derived cobble-sized clasts. Samples were collected from Mt.  
14 Achnar Moraine, a large blue ice moraine, where subglacial material naturally emerges through  
15 sublimation of the surrounding ice. Both rocks and sediments were analyzed for total elemental  
16 composition, mineral abundance by X-ray diffraction, and by sequential extractions targeting chemical  
17 weathering products. The fine sediment fraction is significantly enriched in chemical weathering  
18 products and depleted in primary minerals compared with the cobble clasts. The alteration pathways  
19 consist primarily of the development of smectite, kaolinite, carbonate minerals, and amorphous  
20 material. Extensive Fe oxidation is evidenced by a decline in magnetic susceptibility and by increases in  
21 extractable Fe. If we assume the only input into the subglacial system is the water and ice-trapped gas  
22 supplied by basal melt, the net chemical alteration is explained through oxidation of organic matter  
23 equal to ~0.7% of the bedrock mass and subsequent carbonation weathering. The underlying  
24 sedimentary rock is sufficiently rich in organic matter for this pathway to be plausible. For the O<sub>2</sub> that is  
25 oxidizing organic matter to be supplied by basal meltwater, water fluxes would need to be three orders  
26 of magnitude larger than sediment fluxes. Independent models of basal melt and sediment transport at  
27 our field site confirm that such a difference between water and sediment flux is likely at the study site.  
28 The rate of subglacial carbonation weathering inferred from the Mt. Achnar Moraine site may be

29 comparable to that found in high latitude subaerial environments. If Mt. Achnar Moraine is typical of  
30 other Antarctic sites, the subglacial land surface of Antarctica does play a role in global geochemical  
31 cycling.

32

### 33 **Introduction**

34 Chemical weathering is a process fundamental to the cycling of earth materials from the  
35 atmosphere to the land surface and from the land surface to the oceans. Contemporary fluxes from  
36 chemical weathering have been widely assessed from river chemistry (Gaillardet et al., 1999), and fluxes  
37 over geological time scales have been assessed through a variety of isotope systems (Kump et al., 2000).  
38 The glacial component of chemical weathering has been mostly assessed in alpine regions, where outlet  
39 streams integrate subglacial chemistry (Anderson et al., 1997; Hodson et al., 2000). Glacial discharge  
40 waters were once thought to play a relatively minor role in global geochemical cycling due to the  
41 predominance of highly reactive trace components in their chemistry (Tranter, 2003). However, work on  
42 Greenland and other large glaciohydraulic systems has shown substantially greater silicate weathering  
43 fluxes compared with alpine systems (Graly et al., 2014; Hawkings et al., 2017; Wadham et al., 2010),  
44 and new analyses have revised the geochemical impact of alpine systems upward (Graly et al., 2017;  
45 Torres et al., 2017). Because terrestrial proglacial fluvial discharge from Antarctic ice is extremely  
46 limited, Antarctic subglacial weathering has been excluded from chemical mass balance estimates that  
47 focus on riverine fluxes (i.e. Gaillardet et al., 1999).

48 Subglacial chemical fluxes within and from Antarctica's landscape have only been measured at a  
49 few locations (i.e. Michaud et al., 2016; Skidmore et al., 2010). As the subglacial environment of  
50 Antarctica accounts for ~10% of Earth's land surface, continent-wide assessment of its chemical fluxes is  
51 important to a global understanding of geochemical cycles. Most of the continent has liquid water at the  
52 glacier bed sourced from basal melt (Pattyn, 2010). This glacial meltwater contains atmospheric gases

53 trapped during initial ice formation, with O<sub>2</sub> capable of oxidizing organic matter and sulfides to form the  
54 acids driving chemical weathering (Graly et al., 2017). For the carbon cycle, this pathway potentially  
55 delivers a significant load from fossil carbon to the ocean atmosphere system (Petsch, 2014; Wadham et  
56 al., 2012). However, concentrations of dissolved solutes, which track chemical fluxes, are difficult to  
57 measure in Antarctica's subglacial environment. Inference to continent-wide rates of chemical alteration  
58 must presently rely on drilling access to subglacial water (e.g. Michaud et al., 2016) or on the rare and  
59 perhaps atypical cases where such water naturally emerges (e.g. Badgeley et al., 2017).

60         The alternative approach, explored here, is to analyze subglacial sediment rather than subglacial  
61 water. Glacial sediments originate from the comminution of rock underneath ice and once formed, such  
62 sediments can be chemically altered in the subglacial environment by subglacial meltwater and the  
63 atmospheric gases trapped therein (Crompton et al., 2015). The degree of chemical alteration is  
64 reflected by the mineralogical differences between rock and sediment. Where it is possible to compare  
65 subglacial sediment to underlying rock, the mass of the minerals newly formed within subglacial  
66 sediment is measured and compared to the mass loss of primary minerals. The total chemical  
67 weathering flux is inferred from this mineral mass balance. We consider minerals that are typically  
68 found in soil such as clays, oxyhydroxides, carbonates, and amorphous material to be like candidates for  
69 neof ormation within the subglacial environment. These minerals form in a wide range of soil settings  
70 the world over, however they may also be inherited from underlying rock (Wilson, 1999). Neof ormation  
71 or authigenesis is inferred where the mineral is significantly more abundant in subglacial sediment than  
72 in the underlying rock. It is further indicated where we see changes in mineral composition or layer  
73 stacking order within the crystal lattice between rock and sediment (Reynolds, 1989). These changes in  
74 sediment composition are translated into weathering rates where the rate of sediment delivery from  
75 the ice sheet can be observed or modeled.

76           We present a case study of a mineralogical method to assess subglacial chemical weathering  
77 fluxes at a site in the central Transantarctic Mountains where subglacial sediments emerge at the  
78 surface of a blue ice moraine. Blue ice moraines are formed where sublimation-driven ablation causes  
79 sediment from within the glacier to accumulate on the surface of the ice (Bintanja, 1999). Our study site,  
80 Mt Acheron Moraine (84.2° S, 161° E), is located near the head of Law Glacier, where the ice first  
81 crosses the Transantarctic Mountains. Studies here have characterized till composition and provenance  
82 (Bader et al., 2017), soil formation (Scarrow et al., 2014), and the timing of till accumulation (Graly et al.,  
83 2018b; Kaplan et al., 2017). Ground penetrating radar measurements at the site have shown that the  
84 sediment in the moraine sources from the glacier bed and accumulates laterally over time (Kassab et al.,  
85 2020). Stable isotopes of O and H in the moraine's ice suggest that sediment entrainment occurred in  
86 the presence of liquid subglacial water, upstream from the moraine, at the margin of the polar plateau  
87 (Graly et al., 2018c).

88           The exposed rocks of the central Transantarctic Mountains have been characterized at many  
89 locations (Faure and Mensing, 2010), however the bedrock geology under the ice is not directly known.  
90 The exposed rocks at Mt. Acheron belong to the spatially extensive Beacon Supergroup – a terrestrially  
91 deposited, alluvial sequence of sandstone, siltstone, and shale (Barrett et al., 1986). The lower  
92 formations of the Beacon Supergroup in this region derive from rocks associated with the Gondwana  
93 margin; sedimentary sources then shifted to a West Antarctic arc-derived volcanoclastic sediment  
94 source and finally to a mix of East and West Antarctic sources (Elliot et al., 2017). The Beacon is  
95 pervasively intruded by mafic sills of the Ferrar Dolerite, with local contact metamorphism to low  
96 temperature (200-300° C) hornfels facies. Burial diagenesis alongside fluids from the contact  
97 metamorphic event have caused widespread formation of illite, chlorite, and, in some cases, zeolite  
98 cements (Bernet and Gaupp, 2005). Locally, Mt. Acheron consists of Ferrar Dolerite interlayered with  
99 the lower Buckley Formation of the Beacon Supergroup (Isbell, 1990). Sedimentary rock clasts within the

100 moraine are dominantly from the lower formations of the Beacon Supergroup (i.e. Mackellar, Fairchild,  
101 and L. Buckley), the Ferrar Dolerite, and few erratics (Bader et al., 2017). Detrital zircon analyses confirm  
102 that only lower Beacon (i.e. East Antarctic source) material is supplied to the site (Bader et al., 2017).

103         At Mt. Achnar Moraine, fine sediment emerges together with rock clasts of a range of sizes,  
104 including pebbles, cobbles, and boulders. By analyzing both cobble size clasts, presumed to represent  
105 plucked bedrock from the catchment, and fine sediment (<63  $\mu\text{m}$ ), we assess the chemical alteration  
106 that occurs in the subglacial environment. Due to surface area effects, large rock clasts are minimally  
107 altered by the chemical processes of the subglacial environment compared with fine sediments such as  
108 silt and clay-sized particles (Graly et al., 2016). Chemical alteration is not visible in hand samples of  
109 freshly emerging cobble-sized clasts (Bader et al., 2017). The site has minimal potential for inherited  
110 preglacial or interglacial weathering within the emerging subglacial sediments. It is proximal to the polar  
111 plateau (El.  $\sim$ 1800 m), with little exposed rock upstream. The regional subglacial environment is high  
112 elevation (Jamieson et al., 2010) and Pliocene interglacial exposure in this area is not suggested by  
113 numerical models (Pollard and DeConto, 2009; Scherer et al., 2016). Similar sites occur at numerous  
114 locations around Antarctica where blue ice moraines form at the base of nunataks (Bintanja, 1999). This  
115 suggests that methods developed in this study could provide insights into subglacial weathering  
116 processes and fluxes for many regions around the continent.

117

## 118 **Methods**

119         During 2010 and 2015 field seasons, samples were collected from Mt. Achnar Moraine ranging  
120 from water-saturated sediment freshly emerging from melting ice to dry till with more than 500 ka of  
121 surface exposure. However, we limited our analysis here to ten samples where active ablation processes  
122 were ongoing and moisture from the ablating ice remained (Figure 1). Sediment samples were collected  
123 by shoveling sediment with an inert plastic scoop into plastic bags. Moisture was removed by freeze

124 drying. A grain size analysis was performed on the <1 mm fraction using a Malvern Mastersizer 2000  
125 (Table S1). At five sites, an adjoining pebble and cobble sample (~30-70 mm diameter clasts) was  
126 collected from a square meter surface area. The pebble count data and some of the grain size data were  
127 previously reported in Bader et al. (2017).

128 Twelve cobble samples representative of rock types common on the moraine surface were  
129 selected from the pebble and cobble samples. Igneous clasts that represent the ubiquitous Ferrar  
130 Dolerite sills represent 60% of the pebble and cobble clasts within the freshly emerging (<10 ka surface  
131 exposure) section of the moraine (Bader et al., 2017). The samples appeared relatively homogenous by  
132 visual inspection, and three dolerites were selected for detailed analyses. One dolerite (Rock 1) was  
133 striated and faceted and therefore had clear influence of transport in the subglacial environment. The  
134 other two samples contrast coarse-grained (Rock 2) and fine-grained (Rock 3) dolerite. We analyzed two  
135 sandstones (Rocks 4-5), two siltstones (Rocks 6-7), one striated and polished black argillite (Rock 8), one  
136 black argillite without signs of subglacial physical alteration (Rock 9), two shales (Rocks 10-11), and one  
137 white argillite (Rock 12). These samples were crushed and ground to <100  $\mu\text{m}$  grain size. The average of  
138 these 12 compositions was weighted to determine the total composition of the underlying rock.

139 We performed a series of analyses on the crushed rocks and glacial sediments in order to  
140 determine the abundance of chemical weathering products. Unless otherwise stated, results are  
141 reported from the whole crushed sample of the rocks and the <63  $\mu\text{m}$  fraction of the sediment, which  
142 was isolated from the bulk sample by dry sieving to preserve any water-soluble material in the sample.  
143 Major and trace elemental composition was analyzed by total dissolution of a fused sample, and  
144 inductively coupled plasma mass spectrometry by Actlabs. Eighteen standards, each appropriate to  
145 various ranges of elements, were included in the mass spectrometry analysis (Tables S2, S3). Magnetic  
146 susceptibility was analyzed on the crushed rock and on the 63-250  $\mu\text{m}$  fraction of the sediment,  
147 employing a Barrington MS2 meter. Values were converted to wt. % magnetite based on comparison

148 with a 1% magnetite standard. The abundance and speciation of salts and sulfates, carbonates,  
149 amorphous oxyhydroxides, and crystalline oxides were analyzed by a sequence of progressively stronger  
150 chemical extractions of the water-soluble, acetic acid-soluble, hydrochloric acid-soluble, and  
151 hydroxylamine hydrochloride-soluble fractions respectively on one-g aliquots of each sample (e.g.  
152 Wiederhold et al., 2007). The extraction sequence consisted of: 1) milli-Q water (H<sub>2</sub>O) for 2 hours; 2)  
153 0.11 M acetic acid (CH<sub>3</sub>COOH) for 16 hours; 3) 0.5 M hydrochloric acid (HCl) for 24 hours; 4) 1 M  
154 hydroxylamine hydrochloride (NH<sub>2</sub>OH-HCl) in 1 M HCl for 4 hours. For each step in the sequence, the 1-g  
155 sediment aliquot was mixed with 40 ml of extractant and agitated for a set time length. For the H<sub>2</sub>O,  
156 CH<sub>3</sub>COOH, and HCl extractions, samples were placed on a vibrating table at room temperature, set at a  
157 speed sufficient to keep material in suspension. During the NH<sub>2</sub>OH-HCl extraction, the samples were  
158 placed in a 70° C ultrasonic bath. The samples were removed every 10 minutes and manually agitated  
159 until all the material returned to suspension and were then returned to the bath. After each extraction  
160 step, the samples were centrifuged for 15 minutes at 3300 RPM. The supernatant was then decanted  
161 and stored for analysis. The sediment was mixed with 20 ml of milli-Q water and agitated for 20  
162 minutes. The sample was again centrifuged and the rinse water decanted and discarded. All extracts  
163 were measured in triplicate for major elements on a Perkin-Elmer Optima 7000 inductively coupled  
164 plasma – optical emission spectrometer (ICP-OES).

165 Mineral abundance was independently measured through powder X-ray diffraction and Rietveld  
166 refinement. Samples were mixed with a 20 wt. % corundum standard (1 μm) and pulverized in an agate  
167 mill. X-ray diffraction was performed on a Bruker D8 Discover instrument (Cu Kα), measuring from 2-70°  
168 2θ. The patterns were analyzed by Rietveld refinement (Bish and Post, 1989; Rietveld, 1969) with Topas  
169 (Bruker AXS, version 5) software to quantitatively determine mineral abundances, with uncertainties  
170 determined by the variance of the least squared fit. To further assess clay mineralogy, the <1 μm  
171 fraction was isolated by settling out larger material in water. The suspended sediment portion was



172 concentrated by centrifuging and dried onto a zero-background slide. These clay isolates were analyzed  
173 in the 2-30° 2θ range. Each slide was subsequently placed in an ethylene glycol chamber for 48 hours  
174 and was analyzed again to assess the prevalence of expandable clays.

175 X-ray diffraction cannot detect or characterize amorphous material and material with high layer  
176 stacking disorder. However, a Rietveld refinement method performed with a corundum standard  
177 quantifies the abundance of this unmodeled component of a sample, which represents the amorphous  
178 component along with trace phases that are below detection by X-ray diffraction (Bish and Post, 1989).  
179 We assess the composition of this unmodeled component from the residual of the bulk composition  
180 from total dissolution less the mineral composition and abundances from the Rietveld refinement. The  
181 sequential extractions are also designed to primarily target these phases. As a test of both the X-ray  
182 diffraction and sequential extraction methods, we compared the total extracted content of each major  
183 element to the residual of the bulk elemental composition less the mineral composition and abundances  
184 determined by X-ray diffraction and Rietveld refinement.

185

#### 186 *Average rock and sediment compositions*

187 For the analytical approaches employed, we assessed the magnitude and statistical significance  
188 of differences between the cobble-sized clasts and freshly emerging fine sediments. Because the cobble-  
189 sized clasts were chosen to represent the range of observed rock types, not their abundance, the  
190 arithmetic mean of the samples is not indicative of the actual average rock composition on the moraine.  
191 Thus, in order to more accurately explore the transformation between rock and fine sediment via  
192 geochemical modeling, we calculated an 'average' rock composition of the moraine using two different  
193 methods. For the 'pebble count' method, the composition of the cobble samples was weighted to their  
194 abundance among pebble and cobble sized clasts per square meter as described in Bader et al. (2017).  
195 The alternative is a 'mass balance' approach calculated by weighting the rock type abundances so that

196 generally immobile elements or minerals are conserved between the average rock composition and the  
197 average composition of the <63  $\mu\text{m}$  fraction. Unless otherwise noted, we treated difference between  
198 populations as statistically significant when they passed a two tailed t test with  $p \leq 0.05$ .

199 Both methods of assessing average rock composition have advantages and limitations. Pebble  
200 counts were performed to a high degree of precision ( $n > 1500$ ) (Bader et al. 2017). However, these  
201 abundances may not be representative of underlying rock contribution as a whole as sedimentary rocks  
202 with moderately weak cement are substantially less likely to be preserved in the pebble sized fraction  
203 than igneous dolerites (Lee and Rutter, 2004). The mass balance method also could be potentially  
204 unrepresentative, as certain elements will be selectively leached by subglacial chemical processes, and  
205 physical processes may selectively comminute certain elements into the fine sediment fraction (Graly et  
206 al., 2016).

207

#### 208 *Geochemical mass balance*

209 This study is focusing on the two end member products of the physical and chemical processes  
210 occurring beneath the ice: the cobble clasts that only have a thin surface subject to physical and  
211 chemical alteration, and the <63  $\mu\text{m}$  fraction which mixes detrital minerals that have been finely  
212 comminuted by physical processes with authigenic clays and other newly formed minerals. From these  
213 two end members we model the composition of the subglacial sediment and estimate the total loss and  
214 gain in the abundance of each mineral species. We treat the sample as a closed system, into which only  
215 water and air from ice melt can enter and only solutes can leave. Thus, any gain in a mineral's  
216 abundance is balanced with the loss of minerals from which its elemental components derive. Where  
217 loss on ignition is greater the <63  $\mu\text{m}$  fraction than the rock, we model derivation from meltwater via  
218 hydration and oxidation reactions. Where chemical elements are more abundant in the rock than the  
219 <63  $\mu\text{m}$  fraction, we model loss to solutes.

220 The mass balance methods described in this paper are new, but developed within the context of  
 221 mineral mass balance approaches that have been previously employed in a variety of settings (e.g.  
 222 Chadwick et al., 1990; Moulton et al., 2000). In order to model the total chemical alteration for the  
 223 entire sediment sample, we need to make assumptions about the composition of the sand, granule and  
 224 pebble fractions, whose compositions are not analyzed in this study. To do so, we assume that the  
 225 polymineralic fragments within the sand-pebble size fractions have the same composition as the cobble  
 226 clasts and that the single-mineral portion of the sand fraction has the same composition as the silt. Clay  
 227 minerals are assumed to be absent from the silt sized fraction, as the breakdown of minerals along grain  
 228 boundaries is assumed to be complete at silt size, leaving any detrital clays in the clay-sized fraction  
 229 (Haldorsen, 1981). These assumptions leave any chemical alteration that occurs within intermediate-  
 230 sized, multi-mineral grains unassessed in our analysis.

231 Mineral mass balance calculations between the cobble clasts and the disaggregated,  
 232 monomineralic fraction were performed by reweighting the abundance of each of the mineral species  
 233 analyzed in the <63  $\mu\text{m}$  fraction through the following:

$$234 \quad M_{Calc} = \left[ W_{clay} + \frac{m_{2-63} + m_{>63*}}{m_{2-63}} (1 - W_{clay}) \right] \frac{m_{<63}}{m_{<2} + m_{2-63} + m_{>63*}} M_{meas} \quad (1)$$

235 where  $M_{Calc}$  is the calculated mass of a mineral in the subglacial sediment as a whole,  $M_{Meas}$  is the  
 236 mass of that mineral measured within the <63  $\mu\text{m}$  fraction,  $m_{<2}$  is the percent weight of the bulk  
 237 sample that is <2  $\mu\text{m}$  (i.e. clay sized),  $m_{2-63}$  is the percent weight of the sample that is between 2 and  
 238 63  $\mu\text{m}$  (i.e. silt sized),  $m_{>63*}$  is the percent weight of the sample that is >63  $\mu\text{m}$  but not composed of  
 239 lithic fragments, and  $W_{clay}$  is the fraction of the measured mineral species that falls within the <2  $\mu\text{m}$   
 240 fraction.  $m_{<2}$  and  $m_{2-63}$  are determined from the particle size data.  $m_{>63*}$  can either be determined by  
 241 grain counting or by mass balance assuming conservation of a particular mineral or minerals. We used  
 242 mass balance, assuming illite conservation (i.e. that illite is not subglacially formed or chemically  
 243 weathered within the system) and verified the mass balance result by light microscope examination of

244 the sand sized fraction to determine the abundance of polymineralic in 5 samples. Particles greater than  
245 sand sized were assumed to be entirely lithic fragments. For clay minerals, we assumed a  $W_{clay}$  of 1. For  
246 quartz and zeolites, we estimate  $W_{clay}$  based on the quartz and zeolite abundance observed in the clay  
247 mount samples, as opposed to bulk powder diffraction samples. For products observed through the  
248 sequential extractions, we calculated a single  $W_{clay}$  that allows the clay mass observed from particle  
249 size analysis to equal the clay mass inferred from mineralogy. For all other minerals, we assumed  $W_{clay}$   
250 to be 0.

251 To compare the loss in rock-forming minerals with the gain in clays, we calculated the  
252 stoichiometric chemical weathering reactions that would govern the transformation. The crystal  
253 structures measured via Rietveld refinement of the powder X-ray diffraction pattern were used to  
254 calculate molar mass. From the individual element balances between reactants within rock and products  
255 within sediment, we estimated the scale and composition of the contribution of mineral derived cations  
256 to subglacial water. Anion composition is constrained by the sulfur and carbon content of the source  
257 rocks. This inferred fluid composition only includes elements weathered out of sampled tills.  
258 Groundwater could conceivably add elements of an unquantified composition (Gooch et al., 2016).

259 From our closed system mass balance assumptions, we can calculate the input of atmospheric  
260 gases necessary to perform the observed chemical weathering. The  $O_2$  input is calculated indirectly from  
261 the water composition under the assumption that the vast majority of the sulfate, bicarbonate, and  
262 carbonate either inferred as dissolved solutes or precipitated as newly formed minerals was oxidized  
263 from organic carbon and sulfite in the source rocks. This  $O_2$  estimate in turn allows for an estimate of  
264 meltwater input per g sediment from the known air content of ice (e.g. Gow and Williamson, 1975). The  
265 estimate of meltwater input also constrains aerosol salt input to the subglacial system, which is also  
266 known from ice cores (Legrand and Mayewski, 1997).

267 An erosion rate is required to convert the chemical mass changes and meltwater inputs per g  
268 sediment into fluxes. We employ a basal shear stress based model of subglacial sediment flux that  
269 includes Law Glacier (Golledge et al., 2013) and convert it to an erosion rate based on the surface area  
270 of the sediment supply catchment inferred from ice surface velocity (Rignot et al., 2011). We make an  
271 alternative flux estimate using long-term continent-wide denudation from the offshore record (Wilson  
272 et al., 2012). The former provides our estimate for our specific field site at Mt. Achernar Moraine. The  
273 latter provides an estimate for continent wide fluxes inasmuch as Mt. Achernar Moraine is  
274 representative of long-term continental averages.

275

## 276 **Results**

### 277 *Representative Rocks (Baseline rock geochemistry)*

278 The three igneous rock samples have broadly similar major and minor element abundances,  
279 with Rock 1 slightly more felsic and Rock 3 slightly more mafic (Figure 2a, Table S2). These differences  
280 are expressed by higher Ca and Mg, and lower Na and K in the more mafic rocks. Rock 1 is also enriched  
281 and Rock 3 depleted in the host of minor elements associated with felsic rocks (Table S3). The  
282 quantitative powder X-ray diffraction data show that all three samples are rich in plagioclase, with  
283 anorthite content varying from 62% in the most felsic sample to 70% in the most mafic sample (Table  
284 S4). The samples contain 21-37% clinopyroxene and 3-9% orthopyroxene. The more felsic samples are  
285 enriched in quartz and alkali feldspar; the more mafic samples are enriched in clinopyroxene. In the  
286 Rock 3, clinopyroxene is primarily pigeonite; in the others, clinopyroxene is primarily augite (Table S4).  
287 The most felsic sample (Rock 1) contains 4.4% smectite and 1% loss on ignition (LOI), reflecting the  
288 presence of secondary alteration products. Rock 2 has 3% smectite and 0.5% LOI (Figure 2d, Table S4).  
289 These abundances of secondary alteration products are also reflected in CH<sub>3</sub>COOH extracted Fe (which  
290 varies from 0.7 wt. % in Rock 1 to 0.3 wt. % in Rock 3) (Table S6). HCl extracted Fe, Al, and Ca are 1-2

291 orders of magnitude more abundant in Rock 1 than in the other two dolerites, suggesting formation of  
292 oxyhydroxides in this sample only (Figure 2c). Rock 1 was striated and faceted by subglacial processes,  
293 possibly indicating it sourced from a more chemically active environment. Magnetic susceptibility varies  
294 from 1.33 wt. % magnetite equivalent in Rock 1 to 0.51 wt. % in Rock 3 (Figure 2d).

295 The sedimentary and meta-sedimentary rocks have substantially greater ranges in bulk  
296 compositions, especially for Si, Fe and Al, reflecting large variability in the abundance of quartz, feldspar,  
297 and clay minerals (Figure 2). Compared with igneous rocks, the (meta)-sedimentary rocks have, on  
298 average, 14.2 wt. % more Si, 2.2 wt. % more K, and 1.8 wt. % more LOI, balanced by 8.9 wt. % less Ca,  
299 6.3 wt. % less Fe, and 4.5 wt. % less Mg (Table S2). Among minor elements, the sedimentary rocks are  
300 depleted in the period 4 transition metals compared to igneous rocks (lower values of Sc, Ti, V, Mn, Co,  
301 Ni, and Zn are statistically significant) (Table S3). The sedimentary rocks are enriched in most of the rest  
302 of the periodic table compared with the igneous rocks; enrichments in Ba, Sr, Zr, Ga, Rb, Nb, Cs, Hf, Ta,  
303 W, Tl, Pb, Th, U, and rare earth elements from La to Sm are statistically significant. Mineralogically, most  
304 of the sedimentary rocks contain some feldspar (mostly albite and K-feldspar), averaging 25% of the rock  
305 mass. Based on lack of separation within the  $\sim 23.6^\circ 2\theta$  (Cu) peak, we infer K-feldspar to be primarily  
306 orthoclase. Quartz ranges from 17-62% of the rock mass, with no discernable trend with respect to grain  
307 size (Figure 2). All samples except Rock 5 (sandstone) contained illite, with the highest clay abundances  
308 in the argillites and meta-sandstone (Figure 2). The two black argillites (Rocks 8 and 9) contained  
309 substantial chlorite (9 and 13% mass); 2-3% chlorite was found in four other samples (Figure 2d). The six  
310 chlorite-bearing rocks (Rocks 5-10) are also enriched in extractable Fe and Al ( $\text{CH}_3\text{COOH}$ , HCl, and  
311  $\text{NH}_2\text{OH-HCl}$  extracts); the black argillites (Rocks 8 and 9) have the highest abundances (Figure 2, Tables  
312 S6-S8). Magnetic susceptibility in the sedimentary rocks varies from 0.08 – 1.61 wt. % magnetite  
313 equivalent, with a weighted average of 0.57 %; half the average of the igneous rocks (Figure 2c).

314 Our confidence in the representativeness of this data is boosted by past studies of the  
315 mineralogy of the bedrock of the central Transantarctic Mountains which have found broadly similar  
316 results to our rock clast characterizations. Assessment of 203 sedimentary rock samples from the  
317 Beacon Supergroup shows a broad range of composition, with most samples in the feldspathic  
318 graywacke range, i.e. 10-50% feldspar composition (La Prade, 1972). Zeolite phase alteration in the  
319 Beacon Supergroup, associated with the intrusion of Jurassic dolerites, shows similar zeolites (i.e.  
320 laumontite, clinoptilolite) to the sedimentary rock samples we analyzed (Bernet and Gaupp, 2005;  
321 Vavra, 1989). Clays in Beacon Supergroup rocks were similarly shown to be primarily of illite and chlorite  
322 composition, though the illite was described as sericite in earlier literature (Vavra, 1989).

323 The Ferrar Dolerite at Mt. Achernar has been directly analyzed for major element composition,  
324 and shows results similar to the three detrital sample we analyzed (Faure and Mensing, 2010). Past  
325 analyses of the Ferrar Dolerite have shown similar composition along the length of the Transantarctic  
326 Mountains (Elliot et al., 1999), suggesting that subglacial Ferrar Dolerite should be broadly similar to the  
327 surface exposed rock. Detailed mineralogical analyses at various sites have shown plagioclase feldspar to  
328 range from 50%-90% anorthite with most samples falling in the 62-75% anorthite range that we observe  
329 both in our three representative cobble clasts (Elliot et al., 1995) (Table S4). Past studies have shown  
330 that orthopyroxenes range from 50-80% enstatite and that clinopyroxenes vary broadly within augite  
331 and pigeonite compositional space (Elliot et al., 1995), also mirroring our observations from cobble clasts  
332 (Table S4).

333

#### 334 *Freshly Emerging Sediment Compared with Rock*

335 Some of the chemical differences between sediment and cobble clasts are large enough that  
336 they are robust regardless of which method is used to characterize average rock composition. Freshly  
337 emerging sediment is 9.2 wt. % LOI, compared with 1.3-2.4 wt. % in the rock (Figure 2a). Magnetic

338 susceptibility is only  $0.1 \pm 0.02$  wt. % magnetite equivalent, well below that found in either igneous or  
339 sedimentary rock averages (Figure 2c). There are also large changes in several of the minor elements  
340 across all three methods: Cr, Cu, Sb and Mo are substantially depleted in the sediment; Ti, Sr, Y, Zr, Ag,  
341 Cs, Hf and the rare earth elements are substantially enriched (Table S3). Some of these elements (i.e. Sb,  
342 Mo, Ag) are near detection limits and have variable reproducibility compared to reference standards  
343 (Table S3).

344 The pebble count method of comparison suggests that the  $<63 \mu\text{m}$  fraction contains more felsic  
345 minerals than the underlying rock. Major elements associated with mafic minerals (Fe, Ca, Mg) along  
346 with minor transition metals are significantly depleted; Si, Al and K and most other minor elements are  
347 significantly enriched (Figure 2a, Tables S2, S3). This pattern strongly suggests that the Ferrar Dolerite is  
348 preferentially preserved at the moraine surface and therefore enriched in the pebble counts. For this  
349 reason, the mass balance approach is a more accurate way to assess the average rock contribution to  
350 the  $<63 \mu\text{m}$  fraction in this setting.

351 The mass balance method assumes that an element is conserved in the system and that all rock  
352 types proportionately supply elements to the  $<63 \mu\text{m}$  fraction of the till. For rock abundance values to  
353 be positive, this requires that the element's abundance in the  $<63 \mu\text{m}$  fraction fall between that of  
354 igneous and sedimentary rocks. When normalized for the change in loss on ignition, Al, Ti, P, LOI, Sr, Y,  
355 Zr, Zn, Ga, Ge, Nb, Sn, Hf, Cs, Ta, Th, U, and the rare earth elements, are more abundant in the  $<63 \mu\text{m}$   
356 fraction than either the sedimentary rocks or the igneous rocks (Tables S2, S3). Fe, Na, Cr, Cu, Mo, and  
357 W are depleted in the  $<63 \mu\text{m}$  fraction compared with either rock type. This leaves 13 elements where a  
358 mass balance analysis weighing contributions from igneous and sedimentary rocks is possible: Si, Mn,  
359 Mg, Ca, K, Sc, V, Co, Ni, Ba, Rb, Tl, Pb. The central tendency among these elements implies a contribution  
360 between  $28 \pm 7\%$  igneous rock and  $72 \pm 7\%$  sedimentary or metasedimentary rock to the freshly  
361 emerging sediment (Table S2, S3). These ratios of igneous to sedimentary rock were employed to



362 reweight the relative clast abundance for each of the two rock types. Unsurprisingly, changes in the  
363 elements used to calibrate the mass balance are not statistically significant (Tables S2, S3). Gains in P  
364 and Ti and losses in Fe, Na remain statistically significant (Table S2), along with many of the differences  
365 in minor element abundance (Table S3).

366 Mineralogical differences between rocks and freshly emerging sediments assessed through  
367 powder X-ray diffraction show large losses in feldspar and pyroxene content paired with increases in  
368 smectite, illite, and kaolinite content (Figure 2d). X-ray diffraction patterns of the isolated clay fraction  
369 also indicate changes in clay mineralogy between rock and subglacial sediment. The <63  $\mu\text{m}$  fraction is  
370 dominated by smectites, which are only found in the igneous rocks (Figure 3). The smectite peaks in the  
371 sediments are also substantially broader than those of the igneous rocks, indicating greater disorder in  
372 layer stacking and/or multiple smectite fractions/compositions. The kaolinite peak shape in sediment  
373 approximately matches that found in igneous rock but at substantially greater abundance (Figures 2d,  
374 3). The shales and argillites are dominated by illite and chlorite, which are found in comparable  
375 abundance and degree of order in the subglacial sediments (Figure 3). The gains in clay abundance,  
376 particularly smectite and kaolinite, are significant regardless of which method is used to assess average  
377 rock composition. However, the loss of plagioclase and pyroxene is substantially larger when pebble  
378 count approach is used (Figure 2d).

379 The  $\text{H}_2\text{O}$  extractable fraction is very small for both rock and freshly emerging sediments,  
380 although there is a slight increase in extractable salts relative to rock for even the freshest sediments  
381 (Table S5). The  $\text{CH}_3\text{COOH}$  extraction is dominated by Ca, presumably from the dissolution of  $\text{CaCO}_3$ . The  
382 fine sediment samples are enriched by  $\sim 0.6$  wt. %  $\text{CH}_3\text{COOH}$  extractable Ca, compared with rock (Figure  
383 2c). Freshly emerging fine sediment samples are also enriched in  $\text{CH}_3\text{COOH}$  extractable Na, and P  
384 compared with crushed rock, but the change (although statistically significant) is trivial (Table S6).  
385  $\text{CH}_3\text{COOH}$  extractable K, Fe, and Al are depleted compared with rock. The HCl extraction was dominated

386 by Fe and Al, likely from dissolution of oxyhydroxides, as well as Ca, whose provenance is not  
387 determined. Compared with rock, sediment is enriched in HCl extracted Al by 0.13 wt. %, and in HCl  
388 extracted Ca by 0.22 wt. % (Figure 2c). HCl extracted Fe, P, Na, and K are less abundant in emerging <63  
389  $\mu\text{m}$  sediment than in rock by statistically significant values (Table S7). The  $\text{NH}_2\text{OH-HCl}$  extracted fraction  
390 was dominated by Fe and Al. Freshly emerging sediment has a 0.56 wt. % increase in  $\text{NH}_2\text{OH-HCl}$   
391 extracted Fe and a 0.2 wt. % increase in  $\text{NH}_2\text{OH-HCl}$  extracted Al (Figure 2, Table S8). Small losses in Na  
392 and Ca are statistically significant (Table S8). Magnetic susceptibility in the freshly emerging sediments is  
393 0.61 wt. % magnetite equivalent lower than the weighted rock average (Figure 2c). This value is  
394 comparable to the gain in  $\text{NH}_2\text{OH-HCl}$  extracted Fe.

395 In general, the compositional components isolated through sequential extractions align well  
396 with the composition of the amorphous component as determined by bulk composition minus minerals  
397 compositions and abundances identified through powder X-ray diffraction (Table S9). These two values  
398 approximately align for Mg, Ca, Na, and K and we assume that the sequential extractions primarily  
399 dissolved the amorphous components of the samples. For the <63  $\mu\text{m}$  samples, sequentially extracted  
400  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  exceeded the comparable components detected by X-ray diffraction by  $\sim 1$  wt. % each.  
401 For the rock samples, the opposite result is found, with the bulk weights of extracted Al and Fe being  
402 less than the amorphous component determined by X-ray diffraction by  $\sim 1$  wt. % each (Table S9). The  
403 cause of these discrepancies is not clear.

404 The bulk composition / X-ray diffraction analysis of the sediment also identifies Si within in the  
405 amorphous component and loss on ignition phases that were not analyzed by sequential extractions.  
406 Sediment contains 10.05 wt. % amorphous Si and 4.7 wt. % amorphous loss on ignition, contrasting with  
407 7.1 wt. % amorphous Si and 0.5 wt. % amorphous loss on ignition in the mass balance averaged rock  
408 (Figure 2c, Table S9).

409

#### 410 *Interpretation of Sequential Extraction Data*

411           The sequential extraction data provide quantitative data on elements soluble under specific  
412 extraction regimes. As an operationally defined procedure, the correspondence of these extractions to  
413 particular mineral phases is not fully resolvable (Tessier et al., 1979). The CH<sub>3</sub>COOH extraction targets  
414 carbonate phases, and where calcite is sufficiently abundant to appear in the X-ray diffraction patterns,  
415 calcite abundances correspond closely with CH<sub>3</sub>COOH extracted Ca (Tables S4, S6). However, most of the  
416 rock samples have large quantities of CH<sub>3</sub>COOH extracted Fe (Table S6) that does not appear in the  
417 sediment samples and is unlikely to be associated with carbonate phases; Fe-carbonates were not  
418 detected by X-ray diffraction. We think the most likely explanation for the CH<sub>3</sub>COOH extracted Fe is that  
419 the artificial comminution of the rock samples created new mineral surfaces with broken crystal surfaces  
420 ripe for chemical leaching. However, it's not clear the degree to which the artificial grinding caused the  
421 CH<sub>3</sub>COOH extracted Fe to come from pools of Fe that would have otherwise been extracted later in the  
422 sequence or whether it represents extraction of Fe that would have otherwise remained in crystalline  
423 phases. The increase in NH<sub>2</sub>OH-HCl extracted Fe in the sediment (Figure 2) would be entirely accounted  
424 for if the CH<sub>3</sub>COOH extracted Fe actually comes from amorphous phases (and is not an artifact of the  
425 grinding processes). We cannot rule out that other extractions from the rock samples were also subject  
426 to artificial comminution effects.

427           The HCl and NH<sub>2</sub>OH-HCl extractions are meant to target amorphous oxyhydroxides and  
428 poorly crystalline oxides respectively (Wiederhold et al., 2007), and are mostly expected to leach Fe and  
429 Al from those pools. However, substantial quantities of Ca are also leached in these phases, suggesting  
430 either further dissolution of carbonates or dissolution of silicates. A possible source for the HCl extracted  
431 Ca is zeolites whose abundance is below the XRD detection limits. Such zeolites are present in the clay  
432 mounts (Figure 3), but below detection in the whole rock samples. The molar abundances of the  
433 increases in HCl extracted Ca, extractable Al, and Si were measured at approximately a 1:2:4 molar ratio

434 (Table S10), similar to that of many zeolites. Such zeolites have been previously been documented as  
435 cement of Antarctic tills (Dickinson and Grapes, 1997). However, other amorphous species such as  
436 allophane, opal, etc., may also be newly formed in the subglacial environment. And, other explanations,  
437 including clay dissolution or cation exchange, cannot be ruled out.

438

#### 439 *Mineral Balance between Freshly Emerging Rock and Sediment*

440 The total mineral abundances in the disaggregated portion of the subglacial sediment (including  
441 monomineralic sand) is estimated via Equation 1 and compared with the average mineral abundance in  
442 rock (Figure 4). Mass balance assuming illite conservation, produces a sand fraction with 51%  
443 polymineralic, lithic fragments (Table S10). Light microscope examination of sand from 5 samples shows  
444 a sharp contrast at  $\sim 500 \mu\text{m}$ , with larger grains almost exclusively polymineralic, lithic grains and smaller  
445 grains predominately monomineralic. At first order, this is consistent with the mass balance estimate of  
446 the lithic fragment percentage. Employing the mass balance average for rock composition, per g  
447 sediment, the average sediment is short  $230 \pm 35 \mu\text{moles}$  of plagioclase feldspar,  $60 \pm 73 \mu\text{moles}$  of  
448 albite,  $113 \pm 10 \mu\text{moles}$  of orthoclase, and  $188 \pm 49 \mu\text{moles}$  of pyroxene compared with average rock.  
449 These losses are balanced by an increase of  $220 \pm 100 \mu\text{moles}$  of smectite and  $80 \pm 76 \mu\text{moles}$  of  
450 kaolinite (Figure 4, Table S10). Increases in HCl and  $\text{NH}_2\text{OH-HCl}$  extracted Al imply  $129 \pm 63 \mu\text{moles}$  of Al  
451 within amorphous or poorly crystalline material newly formed in the sediment.  $\text{CH}_3\text{COOH}$  extractable Ca  
452 represents  $154 \pm 58 \mu\text{moles}$ , assumed to speciate as calcite; HCl extractable Ca represents  $44 \pm 35$   
453  $\mu\text{moles}$ . The relative loss of pyroxene and feldspar suggests that 56% of the newly formed smectite is Al-  
454 bearing (i.e. beidellite or montmorillonite) and 44% is Fe- or Mg-bearing (e.g. saponite). Amorphous Si  
455 represents  $153 \pm 475 \mu\text{moles}$ . The total change in mineral balance requires gains in clays, carbonates,  
456 and other extractable compounds in the till (Figure 4).

457            Assuming the amorphous and extractable phases represent a pool of chemical weathering  
458 precipitates that are distinct from the clay minerals (Table S9), the loss of rock-forming minerals  
459 between cobble sized clasts and fine sediment requires  $929 \pm 156 \mu$  equivalents of cations released  
460 during mineral dissolution (i.e. Figure 4). Ca delivery to the  $\text{CH}_3\text{COOH}$  extractable and HCl extractable  
461 pools accounts for  $397 \pm 95 \mu$  equivalents. The cations in smectite interlayers represent  $84 \pm 44 \mu$   
462 equivalents. This leaves  $447 \pm 216 \mu$  equivalents per g of cation material lost to subglacial fluid. Based on  
463 the composition of the weathering material, the composition of this fluid per g of sediment includes  $100$   
464  $\pm 75 \mu\text{moles}$  of Na,  $112 \pm 10 \mu\text{moles}$  of K,  $35 \pm 81 \mu\text{moles}$  of Ca, and  $82 \pm 61 \mu\text{moles}$  of Mg (Table S10).  
465 Loss of Si and Fe to the dissolved fraction is also substantial (Figure 4, Table S10). Our assumptions of no  
466 weathering within lithic fragments, sand composition equal to silt, illite conservation between rock and  
467 sediment, and mass balance approach to average rock composition all introduce errors not expressed  
468 within the analytic uncertainties. Several of these assumptions (i.e. lithic fragments, mass balance  
469 approaches) minimize the total chemical weathering.

470            The total of  $447 \pm 216 \mu$  equivalents of cations lost to water in the weathering of rock minerals  
471 (Figure 4) requires a comparable release of anions by chemical weathering. Likewise, the  $\text{CH}_3\text{COOH}$   
472 extractable Ca requires a source of carbonate to form calcium carbonate as a product of carbonic acid  
473 weathering. Including carbonate precipitation,  $763 \mu$  equivalents of anions per gram sediment are  
474 needed. The plausible pathways for anion generation are the oxidation of Fe sulfides, producing sulfate  
475 as a product of sulfuric acid weathering, and the oxidation of organic carbon, producing bicarbonate or  
476 carbonate as a products of carbonic acid weathering. Carbon and sulfur wt. % values have been reported  
477 for rocks of the Ferrar Dolerite and Beacon Supergroup collected elsewhere. In the Permian sedimentary  
478 rocks that underly Mount Achnar Moraine, average organic matter content in unaltered rock samples  
479 ranges from 0.55 wt. % in the Mackellar Formation to 23 wt. % in the coal-bearing Buckley Formation  
480 (Horner, 1992). Through most of the sedimentary rock section, sulfur content is <200 ppm. However,

481 the Lower Buckley Formation has coal-rich lenses where sulfur values are as high as 2,500 ppm,  
482 concurrent with total organic matter content of >50% mass (Horner, 1992). At Tillite Glacier (~100  
483 kilometers down ice flow from our field site), Ferrar Dolerite sulfur contents range from 100 to 600 ppm  
484 (Faure and Mensing, 2010). These data suggest that taking igneous and sedimentary rock together, the  
485 sulfur content of the rock substrate of the Mt. Achnar moraine is unlikely to be more than 600 ppm,  
486 which when corrected for molar mass, would amount to <20 micromoles S per gram sediment. Even if  
487 this were fully oxidized to sulfuric acid, it would account only 40 out of 763  $\mu$ moles of the acid content  
488 needed to form the alteration product content observed in the glacial tills. If the remaining acid came  
489 entirely from carbonic acid, ~725 micromoles of carbonic acid derived alkalinity per g are needed to  
490 drive the observed alteration of rock-forming minerals.  $154 \pm 58$  micromoles of C are within the calcium  
491 carbonate precipitates found in the freshly emerging till (i.e. the  $\text{CH}_3\text{COOH}$  extraction – fig 2), providing  
492 ~300 micromoles of the necessary alkalinity. Assuming the non-precipitated carbon anions remained as  
493 aqueous bicarbonate, a total of  $575 \pm 224$  micromoles of carbon per gram sediment is implied. If this  
494 were predominately oxidized from organic carbon, the source rocks would need total organic carbon  
495 values of at least  $0.7 \pm 0.3$  wt. % mass. This value is within the range found in the Beacon Supergroup  
496 sedimentary rocks, even accounting for an ~30% input from Ferrar Dolerite.

497

#### 498 *Erosion Rate and Total Chemical Flux*

499 In order to convert chemical weathering per g sediment into a chemical drawdown rate, we  
500 need to estimate the erosion rate at the site. Golledge and others' (2013) model of sediment flux as a  
501 function of basal shear stress suggest that down-glacier sediment flux across Law Glacier at Mt.  
502 Achnar moraine is on the order of  $1 \text{ m}^3$  sediment per glacier cross-section m per year (Figure 5). Ice  
503 surface velocities indicative of basal shear capable of sediment transport begin ~100 km up glacier from

504 Mt. Achnernar Moraine (Rignot et al., 2011), suggesting a sediment catchment area on the order of  
505  $\sim 4000 \text{ km}^2$  (Figure 5).

506 Using a  $1 \text{ m}^3 \cdot \text{m}^{-1} \cdot \text{yr}^{-1}$  sediment flux rate through the 25 km width of Law Glacier, a subglacial till  
507 density of  $2 \text{ g} \cdot \text{cm}^{-3}$ , and a  $4000 \text{ km}^2$  sediment catchment area (i.e. Figure 5), we infer an approximate  
508 erosion rate for the sediment catchment of Mt. Achnernar Moraine of  $12.5 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ . This model result is  
509 highly comparable to the sediment accumulation rate inferred at Mt. Achnernar moraine, which  
510 accumulates  $12.4 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  if surface till density is assumed at  $1.8 \text{ g} \cdot \text{cm}^{-3}$  (Graly et al., 2018b). If the  
511 density of the underlying rock is  $2.7 \text{ g} \cdot \text{cm}^{-3}$ , this is equivalent to a time-averaged denudation rate of  $4.6$   
512  $\text{m} \cdot \text{Ma}^{-1}$ . Based on our calculated carbon oxidation mass per g sediment of  $0.7 \pm 0.3\%$ , this erosion rate  
513 gives a  $\text{CO}_2$  drawdown rate of  $0.33 \pm 0.14 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  for the Mt. Achnernar basin. This erosion rate is  
514 consistent with the relatively small ice flux through the Law Glacier outlet. If we alternatively use  
515 modeled erosion rates averaged for the entire East Antarctic Ice Sheet from the Oligocene to the  
516 present, which are on the order of  $15\text{-}25 \text{ m} \cdot \text{Ma}^{-1}$  (Wilson et al., 2012),  $1.40 \pm 0.35 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  of  $\text{CO}_2$   
517 drawdown is inferred.

518

#### 519 *Inferred Water Flux and Sediment Residence Time*

520 To oxidize the estimated levels of carbon and sulfur into carbonic and sulfuric acid,  $\sim 600$   
521 micromoles of  $\text{O}_2$  are needed per g sediment. Although, in principle, some of the oxidation could occur  
522 through the reduction of a multi-valent metal, there is no evidence of such oxidation-reduction coupling  
523 in the data we present. In particular, the decline in magnetism between the rock and subglacial  
524 sediment and the commensurate increase in  $\text{NH}_2\text{OH}\text{-HCl}$  extracted Fe (Figure 2) strongly suggest that Fe  
525 is also being oxidized in the system. None of the other redox capable metals (e.g. Mn, Co, Cu, etc.) occur  
526 at anywhere near the abundance necessary to be a substantial source of  $\text{O}_2$  (Table S3). During  
527 formation, Antarctic ice traps  $\sim 12 \text{ cm}^3$  of air per 100 g of ice (Gow and Williamson, 1975). Given the

528 density of air and ice and partial pressure of oxygen, this is equivalent to  $\sim 1$  micromole  $O_2$  per  $cm^3$  of ice.  
529 Thus, in a subglacial system closed to contact with the atmosphere,  $\sim 600 cm^3$  of ice per g sediment  
530 would have to be delivered as basal melt to produce the chemical alterations we infer. Analyses of  
531 Antarctic subglacial tills elsewhere give densities of  $\sim 2 g \cdot cm^{-3}$  and porosities of  $\sim 0.4$  (Tulaczyk, 1999),  
532 suggesting  $\sim 0.2$  ml  $H_2O$  per g sediment. Using these values and correcting for the density of ice, the  
533 meltwater required to supply the inferred level of  $O_2$  would fill the pore space around the sediment  
534  $\sim 2700$  times, or  $543 \pm 201$  ml meltwater per g sediment (Figure 6, Table S10). This would require water  
535 to be cycled through the system more than three orders of magnitude faster than sediment, even as  
536 basal melt delivers water to the system at rates of less than 1 cm per year (Pattyn, 2010).

537

## 538 **Discussion**

### 539 *Subglacial Alteration Processes*

540 Three processes can affect bulk chemical and mineralogical differences when comparing  
541 subglacial fine sediment with the underlying bedrock: 1) Physical processes can preferentially grind one  
542 mineral or rock type into fine sediment (Sharp and Gomez, 1986); 2) Chemical processes can dissolve  
543 minerals, producing weathering products such as solutes, clays, oxides and oxyhydroxides (Graly et al.,  
544 2016; Tranter et al., 2002); and 3) Subglacial water can preferentially transport sediment of a certain  
545 grain size within the subglacial system (Alley et al., 1997). Each of the elements and mineral species  
546 enriched in the fine sediment must be formed or concentrated by one of these processes. Because we  
547 measured the  $<63 \mu m$  fraction in contrast to cobble clasts, we assume that preferential comminution (1)  
548 plays a large role in the chemical and mineralogical differences we observe. And we normalize the data  
549 with illite conservation (Eq.1, Figure 4) to minimize newly formed clay minerals and thereby maximize  
550 the role of comminution in our model. However, the following changes are far too large to be explained  
551 by these grain size sorting processes: the 15-fold increase in smectite clay, the 7-fold increase in



552 kaolinite clay, and the 6-fold increase in calcite as CH<sub>3</sub>COOH extractable Ca (Figure 4; Tables S4, S6).  
553 Comparably, the 50% decline in abundance for feldspar and pyroxene in the <63 μm fraction cannot be  
554 explained by a preference of these minerals for larger grain sizes, especially when quartz, which is a less  
555 friable mineral (Sharp and Gomez, 1986), shows a smaller decline. We must either infer selective  
556 transport of clay and calcite into the subglacial environment supplying sediment to Mt. Achernar  
557 moraine (3) or conclude that the clay minerals and calcite formed *in situ* (2) from the weathering of the  
558 pyroxene and feldspar and the saturation precipitation of carbonate minerals (i.e. Figure 4). The  
559 glaciology at the Mt. Achernar site suggests insufficient water in the subglacial system to mobilize  
560 subglacial sediment or cause grain size sorting. We therefore consider the mass conservative, chemical  
561 weathering approach employed in our analysis to best explain the data presented.

562         Within a mass conservative system, chemical differences between rock and the <63 μm fraction  
563 of the sediment must either be explained by preferential comminution of certain minerals into the <63  
564 μm fraction, preferential precipitation of elements from those minerals into newly formed minerals  
565 within the <63 μm fraction, or preferential leaching of those elements into out-fluxing water. For a wide  
566 range of rare earth and trace elements, the increase in their abundance in <63 μm sediment compared  
567 with rock is too large to be explained by mass loss to the solute fraction alone (Figure 2b, Table S3).  
568 Either small initial crystal sizes that disaggregate into the fine fraction or preferential comminution of  
569 minerals bearing these elements is the most likely explanation. Al is the only major element associated  
570 with primary rock-forming minerals that is enriched in the <63 μm fraction. This likely reflects  
571 disaggregated and newly precipitated Al-rich clays found only in the <63 μm fraction. Our mineral  
572 balance suggests that Si, Fe, Mg, Ca, Na, and K are chemically leached from the system (Figure 4, Table  
573 S10). Of these, only Na and Fe are depleted in the <63 μm fraction (Figure 2). For Na, this is likely  
574 because it is largely excluded from clay interlayers, carbonates, and zeolites, which precipitate in the  
575 fine fraction. The depletion of Fe in the <63 μm fraction is more difficult to explain. Physical preference

576 against comminution of Fe-rich minerals would also affect Ca and Mg, for which such effects are not  
577 observed (Figure 2). Fe is no more chemically leached than any other major element. The sedimentary  
578 rocks included in this analysis have highly variable Fe abundances (Figure 2), due to high amorphous Fe  
579 oxide and oxyhydroxide content in some of the shales and argillites. It is possible that our calculation of  
580 Fe abundance in the sedimentary rocks is therefore skewed by outlier samples. With the entire range of  
581 elements and minerals considered, we have strong evidence of both preferential comminution of  
582 minerals into the <63  $\mu\text{m}$  fraction and chemical leaching at the Mt. Achernar site.

583         The fundamental hydrology of the East Antarctic subglacial environment does not favor physical  
584 sorting of grains by subglacial water. Subglacial water under the East Antarctic Ice Sheet has been  
585 observed and modeled to occur in lakes and as groundwater between lakes (Siegert et al., 2018; Wright  
586 and Siegert, 2012). The catchment of Law Glacier, together with several other outlet glaciers of the  
587 Transantarctic Mountains, has small lakes (i.e. <0.1  $\text{km}^3$ ) in the subglacial environment (Smith et al.,  
588 2009). The steep surface slopes or seasonal fluctuations that support sediment transport via large flow  
589 through subglacial conduits (Alley et al., 1997) do not exist in this setting. Rapid subglacial lake drainage  
590 events have been observed in some settings and would cause flows capable of mobilizing subglacial  
591 sediment (Wingham et al., 2006), but with limited spatial and temporal extent.

592         Physical transport of clays in the subglacial environment is a highly unlikely explanation for clay  
593 enrichment at our site. During the rare lake drainage event, flowing water would primarily winnow away  
594 fine particles. For clay minerals to be enriched at Mt. Achernar Moraine by physical means, clay-sized  
595 particles winnowed elsewhere would have to be preferentially deposited in the subglacial environment  
596 delivering sediment to Mt. Achernar moraine. No evidence of such sorting exists in the emerging till.  
597 Clay- to car-sized boulders emerge in the same debris bands, indicating a lack of sorted sediment in the  
598 subglacial environment. The isotopic signature of the ice entraining the debris is consistent with a  
599 regelation enrichment process occurring at the glacier bed (Graly et al., 2018c), which provides a

600 mechanism for sediment entrainment into a till bed without grain size discrimination (Iverson and  
601 Semmens, 1995; Rempel, 2008). Finally, the enrichment in clay mineral content with respect to rock is  
602 fairly uniform along the length of the moraine, with samples up to 12 km apart showing comparable clay  
603 content (Figures 1, 2d). In contrast, the deposition of clays winnowed from elsewhere depends on very  
604 low flow conditions and is likely to be a heterogeneous process. In sum, we find our mass conservative  
605 assumptions robust against considerations of grain-size selective transport within the regional subglacial  
606 system.

607

#### 608 *Ice Melt Budget for the Subglacial Environment*

609 The erosion rate for the Law Glacier catchment inferred from Golledge and others' (2013) model  
610 balances very closely with the estimated input of O<sub>2</sub> inferred by our closed system assumptions. If we  
611 assume steady and uniform loss of sediment from the catchment, 7400 cm<sup>3</sup>·m<sup>-2</sup>·a<sup>-1</sup> of ice would have to  
612 melt to obtain the oxidation balance implied by the rate of chemical weathering, creating a basal melt  
613 rate 7.4 mm per year (Figure 6, Table S10). Modeling suggests basal melting on the order of 5-10 mm·yr<sup>-1</sup>  
614 in the region of the Law Glacier catchment area (Figure 5) (Pattyn, 2010). Thus, independent models of  
615 basal melt (Pattyn, 2010) and sediment generation (Golledge et al., 2013) suggest three orders of  
616 magnitude greater rates of water cycling than sediment cycling in the catchment of Mt. Achnar  
617 Moraine, consistent with the budget of oxygen and carbon that we infer by comparing rock composition  
618 with freshly emerging subglacial sediments. If we knew the thickness of the actively weathering  
619 subglacial sediment, we could extrapolate from a basal melt rate to a sediment residence time. For  
620 instance, a basal melt rate of 7.5 mm per year and an active subglacial sediment thickness of 1 m would  
621 give a sediment residence time of 160,000 years, whereas saturated porewater under these conditions  
622 would have a residence time of only ~60 years.

623           Despite the support of model results for these rates of chemical cycling, there are alternative  
624 explanations for the balance of weathering products that would lead to substantially different  
625 interpretations of water and O<sub>2</sub> cycling. A substantial component of the CO<sub>2</sub> that forms carbonic acid  
626 could source from fermentation of organic matter, which produces CO<sub>2</sub> and CH<sub>4</sub> in an anoxic  
627 environment (Wadham et al., 2012). This requires twice as much organic matter consumption but still  
628 could be within the range of organic carbon concentrations found in Beacon Supergroup rocks. If this is  
629 the case, then the same observed level of chemical weathering per g sediment could occur with  
630 substantially lower basal melt rates, limited only by the abundance of organic matter in the system.

631           We also presently cannot rule out an inherited weathering signal from a preglacial (e.g.  
632 Miocene) or Pliocene period of surface exposure, which would imply a portion of the chemical  
633 weathering occurred when the material was in direct contact with the atmosphere. Smectite and  
634 kaolinite minerals are observed in regions of Antarctica that have never been covered by ice (Vennum  
635 and Nejedly, 1990). However, at least under present environmental conditions, these remain at very low  
636 abundances (<1 wt. %). Furthermore, the smectite clays are described as highly ordered (Vennum and  
637 Nejedly, 1990), resembling what we observe in samples of underlying rock and not the subglacial  
638 sediments (Figure 3). If soil minerals are inherited from pre-glacial exposure, it represents a time in the  
639 Antarctica's deep past, where thick, clay-rich saprolite formed under environmental conditions very  
640 different from present. We find it unlikely that such material would have survived the intervening tens  
641 of millions of years of erosive forces.

642

#### 643 *Implications for the Offshore Record*

644           Analyses of the clay minerals in Antarctic offshore cores have long been interpreted as recording  
645 climatic information. The preglacial clay mineral assemblages from the Eocene have >90% smectite (and,  
646 in some cases, kaolinite), consistent with intensively weathered material being delivered to the marine

647 environment (Ehrmann et al., 1992), although some of the smectite may have formed authigenically in  
648 the marine environment (Ehrmann et al., 2005). The onset of glaciation in the Oligocene is concurrent  
649 with a rapid rise of offshore illite and chlorite; typical glacial-era assemblages contain ~50% illite, ~30%  
650 smectite, ~10% chlorite, and ~10% kaolinite (Ehrmann et al., 1992). These glacial-era assemblages  
651 closely match the relative clay mineral abundances that we observe in the freshly emerging fine  
652 sediment of Mt. Achernar Moraine. Detailed analyses of the degree of layer stacking order and  
653 composition of the offshore clay minerals show that glacial-era smectite is more disordered (i.e. broader  
654 X-ray diffraction peaks) and is more Al-rich (less Fe/Mg rich) than preglacial clays (Ehrmann, 2001;  
655 Ehrmann et al., 2005; Setti et al., 2004). The morphology of poorly ordered smectite, as seen in SEM  
656 images, is consistent with a non-authigenic origin and attributed to non-glacial volcanic input (Ehrmann  
657 et al., 2005). However, our recognition of smectite formed in the subglacial environment, which could  
658 then be detrital in the offshore environment, presents an alternative source of these offshore clays. The  
659 offshore smectites and the smectites analyzed here are similar in degree of order (i.e. Figure 3) and  
660 similarly Al-rich (i.e. Table S10). We therefore suspect that subglacially formed smectite subsequently  
661 transported to the marine environment could be a major component of offshore smectite during glacial  
662 periods.

663

#### 664 *Solute Composition and Flux Compared with Existing Measurements*

665 The subglacial water composition inferred from the mineral mass balance can be compared with  
666 measurements of subglacial water compositions collected elsewhere on the Antarctic continent, thereby  
667 putting our observations into the context of direct chemical weathering observations. Subglacial water  
668 samples have been collected at Subglacial Lake Whillans (Christner et al., 2014; Michaud et al., 2016)  
669 and in the till porewaters beneath the Kamb and Bindschadler ice streams (Skidmore et al., 2010). A  
670 jökullhaup event near Casey Station, East Antarctica in 1985 and 1986 allowed for sampling of what had

671 likely been stored subglacial water (Goodwin, 1988). As a permanently ice-covered proglacial lake, Lake  
672 Untersee, Dronning Maud Land, has a chemical composition primarily influenced by input of subglacial  
673 water into the lake (Wand et al., 1997). The lake is chemically stratified with a thin (<20 m) surface-  
674 water layer containing most of Lake Utersee's sulfate. Upwelling subglacial brines at land terminal  
675 margins have been characterized at Lewis Cliff Ice Tongue (Fitzpatrick et al., 1990; Liu et al., 2014; Sun et  
676 al., 2015) and Blood Falls (Badgeley et al., 2017; Mikucki et al., 2004).

677         The major ions measured at these diverse Antarctic sites span a very wide compositional range,  
678 especially for anions (Figure 7). Unless there is a source of sulfate or chlorine (e.g. from groundwater) in  
679 the system that we have not identified, the sulfur and carbon abundances in the underlying rock suggest  
680 bicarbonate is the dominant anion in the system at Mt. Achernar Moraine, resembling the bottom  
681 waters of Lake Untersee more than any other site. The cation composition is also comparable to the  
682 bottom waters of Lake Untersee, but is within the range of values from the ice stream porewaters as  
683 well as Blood Falls. The largest difference between the inferred Mt. Achernar Moraine and most  
684 observed Antarctic water compositions is the input of brine or seawater at other sites. Geology probably  
685 exerts some control on these compositions, as the pyroxene and plagioclase feldspar that dominate the  
686 loss to chemical weathering at Mt. Achenar (Figure 2) may not be present at every site. Likewise, the  
687 underlying presence of sulfide or organic carbon for oxidation would control the anion composition.  
688 Water and sediment residence times likely also play a role (Graly et al., 2018a). The similarity to Lake  
689 Untersee suggests commonality between Mt. Achernar Moraine with other Antarctic sites where brine  
690 formation is minimal.

691         The CO<sub>2</sub> drawdown rate inferred at Mt. Achernar moraine is the first such calculation for the  
692 Antarctic subglacial environment and can be compared to data sets from elsewhere on Earth (Figure 8).  
693 Data from the world's major river basins and volcanic islands suggest a value of 4.3 g·m<sup>-2</sup>·yr<sup>-1</sup> as the  
694 global average CO<sub>2</sub> drawdown through silicate weathering in the world's riverine landscapes more than

695 order of magnitude larger than the  $0.33 \pm 0.14 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  we estimate for Mt Acheron Moraine  
696 (Gaillardet et al., 1999). The Mt. Acheron Moraine CO<sub>2</sub> drawdown value is equivalent to those found in  
697 arid regions of cratonic land masses, which represent the low end of silicate weathering CO<sub>2</sub> drawdown  
698 rates in the Gaillard et dataset (Figure 8). However, if we employ the long term average denudation rate  
699 for the East Antarctic Ice Sheet to calibrate CO<sub>2</sub> drawdown, our value of  $1.40 \pm 0.35 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$  is  
700 equivalent to silicate weathering CO<sub>2</sub> drawdown rates found in the highest latitude river basins in the  
701 Gaillardet dataset (Figure 8).

702 Other ice flow catchments of Antarctic outlet glaciers have substantially larger sediment fluxes  
703 than Law Glacier (Golledge et al., 2013), potentially suggesting far larger rates of chemical cycling in the  
704 continent's largest ice streams. However, we would only expect chemical weathering rates to scale to  
705 sediment flux if chemical weathering under Antarctica is sediment supply limited. Inasmuch as the  
706 primary factor limiting chemical weathering in the Antarctic subglacial system is basal melt and the  
707 consequent supply of O<sub>2</sub> to meltwater, Law Glacier, with a basal melt rate around that of the continent  
708 average (Pattyn, 2010), may be a fairly representative study site. Furthermore, it is likely that most of  
709 the CO<sub>2</sub> drawn down under Antarctic ice originates as organic carbon, whereas the bicarbonate in rivers  
710 that sources from silicate weathering reactions primarily contains CO<sub>2</sub> of atmospheric origin (Petsch,  
711 2014). Further work is needed to determine the representativeness of our field site and confirm the  
712 inferred rates of water and sediment cycling.

713

## 714 **Conclusions**

715 Subglacial sediments freshly emerging at Mt. Acheron moraine are chemically weathered  
716 compared with cobble clasts representative of underlying bedrock. This is evidenced by large increases  
717 in the smectite and kaolinite content of the subglacial sediment relative to rock. Although smectite  
718 exists in the underlying rock, rock-bound smectite has greater layer stacking order and occurs in far

719 lower abundance than what is found in freshly emerging subglacial sediments. Carbonates, zeolites, and  
720 amorphous or poorly crystalline oxides detected by acid-leachable Ca, Fe, and Al also have higher  
721 abundance in glacial sediments. The total balance of mineral species between rock and sediment  
722 suggests that observed sediment chemical weathering products could have formed entirely from  
723 mineral material found in rock, without need for selective addition or removal of mass from the  
724 subglacial system by physical means. Independent models of basal melt and sediment flux at the site  
725 suggest that the gases released from melting basal ice over the sediment residence time would supply  
726 sufficient oxygen to form the carbonic and sulfuric acid necessary to perform the weathering reactions  
727 indicated by the mineralogical changes. These data, together with a growing body of evidence collected  
728 elsewhere on the Antarctic continent, suggest that chemical alteration in Antarctica's subglacial  
729 environment occurs on a scale that is likely to be significant for global geochemical cycles.

730

### 731 **Acknowledgements**

732 This paper was edited by A. Dosseto and thoughtfully reviewed by R. Rudnick and two  
733 anonymous reviewers. This work was supported by National Science Foundation Antarctic grants PLR-  
734 1443433, PLR-1443213, ANT-0944578 and ANT-0944475, by an Indiana University Collaborative  
735 Research Grant, and by funding from the IUPUI Office of the Vice Chancellor for Research. The US  
736 Antarctic Program, Kenn Borek Air, Ltd., and field team members from the 2010 and 2015 seasons are  
737 gratefully acknowledged for their support, particularly M. Kaplan. T. Kennedy assisted with magnetic  
738 susceptibility analyses. H. Johnston assisted with particle size analyses. S. Cox and S. Olund assisted with  
739 the sequential extraction analyses. We would like to acknowledge the Integrated Nanosystems  
740 Development Institute (INDI) for use of their Bruker D8 Discover X-ray diffraction instrument, which was  
741 awarded through NSF grant MRI-1429241.



742 **Figure Captions**

743

744 Figure 1: Sampling locations for freshly emerging sediment on Mt. Achernar Moraine, Central -  
745 Transantarctic Mountains. Approximate flowlines on Law Glacier are illustrated both down glacier and  
746 into the moraine (Kassab et al., 2020). Digital Globe imagery (©2014) provided by the Polar Geospatial  
747 Center (St. Paul, Minnesota, USA)

748

749 Figure 2: Abundance of selected elements, minerals, and amorphous phases in rock compared with the  
750 fine fraction of emerging subglacial sediments. For each element or phase, the first column shows  
751 igneous rocks (n=3), the second column shows sedimentary and metasedimentary rocks (n=9), and the  
752 third column shows freshly emerging sediments (black triangles) compared with two methods of  
753 averaging rocks (red and yellow stars). The clast-count average uses the raw abundance of each rock  
754 type on the freshly emerging moraine surface, where mafic igneous rocks (Ferrar dolerite) make up 62%  
755 of the rock clasts, and (meta) sedimentary rocks comprise 38% (Beacon Supergroup). The mass balance  
756 average reweights these abundances so that igneous rock accounts for 28% and (meta) sedimentary  
757 rock accounts for 72% of the underlying material.

758

759 Figure 2 continued

760

761 Figure 3: Selected peaks and patterns from X-ray diffraction patterns of clay mineral isolates, rescaled  
762 for peak comparison. A) Patterns for air-dried and ethylene glycol-saturated for clays isolated from <63  
763  $\mu\text{m}$  sample 1A; patterns from other <63  $\mu\text{m}$  sediment samples are nearly identical. B) Smectite peaks  
764 from <63  $\mu\text{m}$  air-dried sediment (1A) compared with those found in the igneous rock (Rock 1); note that  
765 the smectite peak is far broader in the sediment sample than in the rock sample. C) Ethylene glycol-  
766 saturated samples of the same. D) Illite and zeolite peaks in <63  $\mu\text{m}$  sediment (1A) compared with  
767 typical sedimentary rocks. The peak shape found in the Rock 4 clay sample is also found in the clay  
768 mounts from rocks 7, 9, 10, and 12; the peak shape from rock 6 is also found in rock 11. Rock 5 is the  
769 only clay mount from rock with a detectable laumontite peak; laumontite is detected in all <63  $\mu\text{m}$   
770 sediment samples. The clinoptilolite peak observed at  $9.6^\circ$  in the <63  $\mu\text{m}$  sediment samples is not  
771 present in any of the analyzed rocks. E) Kaolinite and chlorite peaks from <63  $\mu\text{m}$  sediment compared  
772 with a chlorite peak from sedimentary rock (Rock 9 – other rocks similar) and a kaolinite peak from  
773 igneous rock (Rock 1); the glacial sediment peak integrates the two.

774

775 Figure 4: The balance of mineral content between subglacial sediment and the underlying rock  
776 highlighting the subglacial transformation. A) The proportion of the rock minerals that alter to form the  
777 new secondary products in sediment are indicated by the flow of material into the box labeled  
778 authigenic contribution. The glacial sediment is significantly enriched in smectite and kaolinite, calcite,  
779 and amorphous products, which are labeled as products of the authigenic contribution. Water and  
780 oxygen from ice melt also add mass to the authigenic contribution and mass is lost into dissolved solids.  
781 B) The authigenic contribution is broken down by element. Height scales to mass in weight % of each  
782 element dissolved or precipitated into each fraction.

783

784 Figure 5: Estimate of the approximate Mt. Achernar moraine sediment catchment area imposed on  
785 models of A) surface velocity (Rignot et al., 2011), B) basal melt (Pattyn, 2010), and C) sediment flux  
786 (Golledge et al., 2013). The catchment for Law Glacier above the Mt. Achernar moraine is delineated  
787 with a dashed line in A and B. The moraine is marked with a star in C.

788  
789 Figure 6: Conceptual sketch illustrating fluxes relevant to the subglacial system at Mt. Achernar Moraine.  
790 The ice column values are from ice core studies (Gow and Williamson, 1975; Legrand and Mayewski,  
791 1997). The sediment flux reflects results from a model of down glacier sediment shear as a function of  
792 surface velocity (Golledge et al., 2013) as well as the sediment accumulation rate for Mt. Achernar  
793 moraine (Graly et al., 2018b). The total O<sub>2</sub> load in the sediment is from our mass balance calculations  
794 (Figure 4, Table S10). The melt rate value reflects model results (Pattyn, 2010) as well as balance  
795 between the O<sub>2</sub> load and the sediment flux. All values are approximate.

796  
797 Figure 7: A Piper diagram comparing geochemical results for Antarctic emerging and subglacial waters  
798 with the inferred subglacial water composition at Mt. Achernar Moraine based on the mineral balance  
799 between rock and <63 μm sediment. The chemical weathering regime in the source regions for Mt.  
800 Achernar Moraine appears similar to that observed at Lake Untersee.

801 Figure 8. Rate of alteration of CO<sub>2</sub> into calcite or bicarbonate at Mt. Achernar moraine compared with  
802 the CO<sub>2</sub> drawdown caused by silicate weathering in representative large river basins (Gaillardet et al.,  
803 1999). The two Mt. Achernar values were derived using the erosion rate implied from sediment flux  
804 estimates past Mt. Achernar moraine and an estimated catchment size (Fig. 5) (Local Catchment) and  
805 from an estimate for average Quaternary erosion rate for the entire East Antarctic Ice Sheet (Wilson et  
806 al., 2012) (Continent Average). These are compared with the five highest latitude rivers in the Gaillardet  
807 dataset, their global average estimate, and the minimum value from the Gaillardet dataset, which was  
808 obtained from the Zambese River.

809 **Table Titles**

810

811 Table S1. Sample location, descriptions, and analyses performed

812

813 Table S2. Major element concentrations in bulk sediment and rock samples

814

815 Table S3. Trace element concentrations in bulk sediment and rock samples

816

817 Table S4. Powder X-ray diffraction and Rietveld refinement results.

818

819 Table S5. Water extraction results

820

821 Table S6. Acetic acid extraction results.

822

823 Table S7. HCl extraction results.

824

825 Table S8. Hydroxylamine HCl extraction results.

826

827 Table S9. Amorphous compositions from bulk composition and X-ray diffraction

828

829 Table S10. Mineral Balance between rock and sediment

830

831 **References Cited**

832

833 Alley, R. B., Cuffey, K. M., Evenson, E. B., Strasser, J. C., Lawson, D. E., and Larson, G. J., 1997, How  
834 glaciers entrain and transport basal sediment: physical constraints: *Quaternary Science*  
835 *Reviews*, v. 16, p. 1017-1038.

836 Anderson, S. P., Drever, J. I., and Humphrey, N. F., 1997, Chemical weathering in glacial environments:  
837 *Geology*, v. 25, no. 5, p. 399-402.

838 Bader, N. A., Licht, K. J., Kaplan, M. R., Kassab, C., and Winckler, G., 2017, East Antarctic ice sheet  
839 stability recorded in a high-elevation ice-cored moraine: *Quaternary Science Reviews*, v. 159, p.  
840 88-102.

841 Badgeley, J. A., Pettit, E. C., Carr, C. G., Tulaczyk, S., Mikucki, J. A., and Lyons, W. B., 2017, An englacial  
842 hydrologic system of brine within a cold glacier: Blood Falls, McMurdo Dry Valleys, Antarctica:  
843 *Journal of Glaciology*, v. 63, no. 239, p. 387-400.

844 Barrett, P. J., Elliot, D. H., and Lindsay, J. F., 1986, The Beacon Supergroup (Devonian-Triassic) and Ferrar  
845 Group (Jurassic) in the Beardmore Glacier Area, Antarctica: *Geology of the central Transantarctic*  
846 *Mountains*, v. 36, p. 339-428.

847 Bernet, M., and Gaupp, R., 2005, Diagenetic history of Triassic sandstone from the Beacon Supergroup in  
848 central Victoria Land, Antarctica: *New Zealand Journal of Geology & Geophysics*, v. 48, p. 447-  
849 458.

850 Bintanja, R., 1999, On the glaciological, meteorological, and climatological significance of Antarctic blue  
851 ice areas: *Reviews of Geophysics*, v. 37, no. 3, p. 337-359.

852 Bish, D. L., and Post, J. E., 1989, Modern Powder Diffraction, *Mineralogical Society of America Reviews in*  
853 *Mineralogy*, Volume 20, p. 369.

854 Chadwick, O. A., Brimhall, G. H., and Hendricks, D. M., 1990, From a black to a gray box—a mass balance  
855 interpretation of pedogenesis: *Geomorphology*, v. 3, no. 3-4, p. 369-390.

856 Christner, B. C., Priscu, J. C., Achberger, A. M., Barbante, C., Carter, S. P., Christianson, K., Michaud, A. B.,  
857 Mikucki, J. A., Mitchell, A. C., Skidmore, M. L., Vick-Majors, T. J., and WISSARD, S. T., 2014, A  
858 microbial ecosystem beneath the West Antarctic ice sheet: *Nature*, v. 512, p. 310-313.

859 Crompton, J. W., Flowers, G. E., Kirste, D., Hagedorn, B., and Sharp, M. J., 2015, Clay mineral  
860 precipitation and low silica in glacier meltwaters explored through reaction-path modelling:  
861 *Journal of Glaciology*, v. 61, no. 230, p. 1-18.

862 Dickinson, W. W., and Grapes, R. H., 1997, Authigenic chabazite and implications for weathering in Sirius  
863 Group diamictite, Table Mountain, dry valleys, Antarctica: *Journal of Sedimentary Research*, v.  
864 67, no. 5, p. 815-820.

865 Ehrmann, W., 2001, Variation in smectite content and crystallinity in sediments from CRP-3, Victoria  
866 Land Basin, Antarctica: *Terra Antarctica*, v. 8, no. 4, p. 533-542.

867 Ehrmann, W., Setti, M., and Marinoni, L., 2005, Clay minerals in Cenozoic sediments off Cape Roberts  
868 (McMurdo Sound, Antarctica) reveal palaeoclimatic history: *Palaeogeography,*  
869 *Palaeoclimatology, Palaeoecology*, v. 229, p. 187-211.

870 Ehrmann, W. U., Melles, M., Kuhn, G., and Grobe, H., 1992, Significance of clay mineral assemblages in  
871 the Antarctic Ocean: *Marine Geology*, v. 107, no. 4, p. 249-273.

872 Elliot, D. H., Fanning, C. M., Isbell, J. L., and Hulett, S. R. W., 2017, The Permo-Triassic Gondwana  
873 sequence, central Transantarctic Mountains, Antarctica: zircon geochronology, provenance, and  
874 basin evolution: *Geosphere*, v. 13, no. 1, p. 155-178.

875 Elliot, D. H., Fleming, T. H., Haban, M. A., and Siders, M. A., 1995, Petrology and mineralogy of the Kirkpatrick  
876 Basalt and Ferrar Dolerite, Mesa Range Region, North Victoria Land, Antarctica, *in* Elliot, D. H.,  
877 and Blaisdell, G. L., eds., *Contributions to Antarctic Research IV*, p. 103-141.

878 Elliot, D. H., Fleming, T. H., Kyle, P. R., and Foland, K. A., 1999, Long-distance transport of magmas in the  
879 Jurassic Ferrar Large Igneous Province, Antarctica: *Earth and Planetary Science Letters*, v. 167, p.  
880 89-104.

881 Faure, G., and Mensing, T. M., 2010, *The Transantarctic Mountains: Rocks, ice, meteorites and water*,  
882 Springer Science & Business Media.

883 Fitzpatrick, J. J., Muhs, D. R., and Jull, A. J. T., 1990, Saline minerals in the Lewis Cliff Ice Tongue,  
884 Antarctic Research Series, Volume Contributions to Antarctic Research I, p. 57-69.

885 Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C. J., 1999, Global silicate weathering and CO<sub>2</sub>  
886 consumption rates deduced from the chemistry of large rivers: *Chemical Geology*, v. 159, p. 3-  
887 30.

888 Golledge, N. R., Levy, R. H., McKay, R. M., Fogwill, C. J., White, D. A., Graham, A. G. C., Smith, J. A.,  
889 Hillenbrand, C.-D., Licht, K. J., Denton, G. H., Ackert, R. P., Maas, S. M., and Hall, B. L., 2013,  
890 Glaciology and geological signature of the Last Glacial Maximum Antarctic ice sheet: *Quaternary*  
891 *Science Reviews*, v. 78, p. 225-247.

892 Gooch, B. T., Young, D. A., and Blankenship, D. D., 2016, Potential groundwater and heterogeneous heat  
893 source contributions to ice sheet dynamics in critical submarine basins of East Antarctica:  
894 *Geochemistry, Geophysics, Geosystems*, v. 17, no. 2, p. 395-409.

895 Goodwin, I., 1988, The nature and origin of a jökulhlaup near Casey Station, Antarctica: *Journal of*  
896 *Glaciology*, v. 34, no. 116, p. 95-101.

897 Gow, A. J., and Williamson, T., 1975, Gas inclusions in the Antarctic ice sheet and their glaciological  
898 significance: *Journal of Geophysical Research*, v. 80, no. 36, p. 5101-5108.

899 Graly, J. A., Drever, J. I., and Humphrey, N. F., 2017, Calculating the balance between atmospheric CO<sub>2</sub>  
900 drawdown and organic carbon oxidation in subglacial hydrochemical systems: *Global*  
901 *Biogeochemical Cycles*, v. 31, no. 4, p. 709-727.

902 Graly, J. A., Humphrey, N. F., and Harper, J. T., 2016, Chemical depletion of sediment under the  
903 Greenland Ice Sheet: *Earth Surface Processes and Landforms*, v. 41, no. 13, p. 1922-1936.

904 Graly, J. A., Humphrey, N. F., Landowski, C. M., and Harper, J. T., 2014, Chemical weathering under the  
905 Greenland Ice Sheet: *Geology*, v. 42, p. 551-554.

906 Graly, J. A., Humphrey, N. F., and Licht, K. J., 2018a, Two Metrics Describing the Causes of Seasonal and  
907 Spatial Changes in Subglacial Aqueous Chemistry: *Frontiers in Earth Science*, v. 6, no. 195.

908 Graly, J. A., Licht, K. J., Drushel, G. K., and Kaplan, M. R., 2018b, Polar desert chronologies through  
909 quantitative measurements of salt accumulation: *Geology*, v. 46, p. 351-354.

910 Graly, J. A., Licht, K. J., Kassab, C. M., Bird, B. W., and Kaplan, M. R., 2018c, Warm-based basal sediment  
911 entrainment and far-field Pleistocene origin evidenced in central Transantarctic blue ice through  
912 stable isotopes and internal structures: *Journal of Glaciology*, v. 64, p. 185-196.

913 Haldorsen, S., 1981, Grain-size distribution of subglacial till and its relation to glacial crushing and  
914 abrasion: *Boreas*, v. 10, no. 1, p. 91-105.

915 Hawkings, J. R., Wadham, J. L., Benning, L. G., Hendry, K. R., Tranter, M., Tedstone, A., Nienow, P., and  
916 Raiswell, R., 2017, Ice sheets as a missing source of silica to the polar oceans: *Nature*  
917 *communications*, v. 8, p. 14198.

918 Hodson, A., Tranter, M., and Vatne, G., 2000, Contemporary rate of chemical denudation and  
919 atmospheric CO<sub>2</sub> sequestration in glacier basins: An arctic perspective: *Earth Surface Processes*  
920 *and Landforms*, v. 25, p. 1447-1471.

921 Horner, T. C., 1992, Sedimentological, mineralogical, and geochemical evaluation of the provenance and  
922 paleoclimatic record of Permian mudrocks from the Beardmore Glacier area, Antarctica [Ph.D.:  
923 The Ohio State University.

924 Isbell, J. L., 1990, Fluvial sedimentology and basin analyses of the Permian Fairchild and Buckley  
925 Formations, Beardmore Glacier region, and the Weller Coal Measures, Southern Victoria Land,  
926 Antarctica: The Ohio State University.

927 Iverson, N. R., and Semmens, D. J., 1995, Intrusion of ice porous media by regelation: A mechanism of  
928 sediment entrainment by glaciers: *Journal of Geophysical Research*, v. 100, no. B7, p. 10219-  
929 10230.

930 Jamieson, S. S. R., Sugden, D. E., and Hulton, R. J., 2010, The evolution of the subglacial landscape of  
931 Antarctica: *Earth and Planetary Science Letters*, v. 293, p. 1-27.

932 Kaplan, M. R., Licht, K. J., Winckler, G., Schaefer, J. M., Bader, N., Mathieson, C., Roberts, M., Kassab, C.  
933 M., Schwartz, R., and Graly, J. A., 2017, Mid-Late Pleistocene stability of the central East  
934 Antarctic Ice Sheet at the head of Law Glacier: *Geology*, v. 45, no. 11, p. 963-966.

935 Kassab, C. M., Licht, K. J., Petersson, R., Lindbäck, K., Graly, J. A., and Kaplan, M. R., 2020, Formation and  
936 evolution of an extensive blue ice moraine in central Transantarctic Mountains, Antarctica:  
937 *Journal of Glaciology*, v. 66, p. 49-60.

938 Kump, L. R., Brantley, S. L., and Arthur, M. A., 2000, Chemical weathering, atmospheric CO<sub>2</sub> and climate:  
939 *Annual Review of Earth and Planetary Sciences*, v. 28, p. 611-667.

940 La Prade, K. E., 1972, Petrology and petrography of the Beacon Supergroup, Shackleton Glacier area,  
941 Queen Maud Range, Transantarctic Mountains, Antarctica, *Proceedings of the third symposium*  
942 *on Antarctic geology and geophysics: Madison, Wisconsin, USA, The University of Wisconsin*  
943 *Press*, p. 581-590.

944 Lee, A., and Rutter, E., 2004, Experimental rock-on-rock frictional wear: Application to subglacial  
945 abrasion: *Journal of Geophysical Research: Solid Earth*, v. 109, no. B9.

946 Legrand, M., and Mayewski, P., 1997, Glaciochemistry of polar ice cores: A review: *Reviews of*  
947 *Geophysics*, v. 35, no. 3, p. 219-243.

948 Liu, T., Bish, D. L., Socki, R. A., Harvey, R. P., and Tonui, E., 2014, Mineralogy and formation of evaporite  
949 deposits from the Lewis Cliff ice tongue, Antarctica: *Antarctic Science*, v. 27, no. 1, p. 73-84.

950 Michaud, A. B., Skidmore, M. L., Mitchell, A. C., Vick-Majors, T. J., Barbante, C., Turetta, C., vanGelder,  
951 W., and Priscu, J. C., 2016, Solute sources and geochemical processes in Subglacial Lake  
952 Whillans, West Antarctica: *Geology*, v. 44, no. 5, p. 347-350.

953 Mikucki, J. A., Foreman, C. M., Sattler, B., Lyons, W. B., and Priscu, J. C., 2004, Geomicrobiology of Blood  
954 Falls: an iron-rich saline discharge at the terminus of the Taylor Glacier, Antarctica: *Aquatic*  
955 *Geochemistry*, v. 10, no. 3-4, p. 199-220.

956 Moulton, K. L., West, J., and Berner, R. A., 2000, Solute flux and mineral mass balance approaches to the  
957 quantification of plant effects on silicate weathering: *American Journal of Science*, v. 300, no. 7,  
958 p. 539-570.

959 Pattyn, F., 2010, Antarctic subglacial conditions inferred from a hybrid ice sheet/ice stream model: *Earth*  
960 *and Planetary Science Letters*, v. 295, p. 451-461.

961 Petsch, S. T., 2014, Weathering of organic carbon: *Treatise on Geochemistry (Elsevier, ed. 2)*, v. 12, p.  
962 217-238.

963 Pollard, D., and DeConto, R. M., 2009, Modelling West Antarctic ice sheet growth and collapse through  
964 the past five million years: *Nature*, v. 458, no. 7236, p. 329.

965 Rempel, A. W., 2008, A theory for ice-till interactions and sediment entrainment beneath glaciers:  
966 *Journal of Geophysical Research*, v. 113, p. F01013.

967 Reynolds, R., 1989, Diffraction by small and disordered crystals, *in* Bish, D. L., and Post, J. E., eds.,  
968 *Modern Powder Diffraction, Volume 20*, p. 145-182.

969 Rietveld, H. M., 1969, A profile refinement method for nuclear and magnetic structures: *Journal of*  
970 *applied Crystallography*, v. 2, no. 2, p. 65-71.

971 Rignot, E., Mouginot, J., and Scheuchl, B., 2011, Ice flow of the Antarctic Ice Sheet: *Science*, v. 333, p.  
972 1427-1430.

973 Scarrow, J. W., Balks, M. R., and Almond, P. C., 2014, Three soil chronosequences in recessional glacial  
974 deposits near the polar plateau, in the Central Transantarctic Mountains, *Antarctica: Antarctic*  
975 *Science*, v. 26, no. 5, p. 573-583.

976 Scherer, R. P., DeConto, R. M., Pollard, D., and Alley, R. B., 2016, Windblown Pliocene diatoms and East  
977 antarctic ice sheet retreat: *Nature communications*, v. 7, p. 12957.

978 Setti, M., Marinoni, L., and Lopez-Galindo, A., 2004, Mineralogical and geochemical characteristics  
979 (major, minor, trace elements and REE) of detrital and authigenic clay minerals in a Cenozoic  
980 sequence from Ross Sea, *Antarctica*, De Gruyter.

981 Sharp, M., and Gomez, B., 1986, Processes of debris comminution in the glacial environment and  
982 implications for quartz sand-grain morphology: *Sedimentary Geology*, v. 46, p. 33-47.

983 Siegert, M. J., Kulesa, B., Bougamont, M., Christoffersen, P., Key, K., Andersen, K. R., Booth, A. D., and  
984 Smith, A. M., 2018, Antarctic subglacial groundwater: a concept paper on its measurement and  
985 potential influence on ice flow: *Geological Society, London, Special Publications*, v. 461, no. 1, p.  
986 197-213.

987 Skidmore, M., Tranter, M., Tulaczyk, S., and Lanoil, B., 2010, Hydrochemistry of ice stream beds -  
988 evaporitic or microbial effects?: *Hydrological Processes*, v. 24, p. 517-523.

989 Smith, B. E., Fricker, H. A., Joughin, I. R., and Tulaczyk, S., 2009, An inventory of active subglacial lakes in  
990 Antarctica detected by ICESat (2003–2008): *Journal of Glaciology*, v. 55, no. 192, p. 573-595.

991 Sun, T., Socki, R. A., Bish, D. L., Harvey, R. P., Bao, H., Niles, P. B., Cavicchioli, R., and Tonui, E., 2015, Lost  
992 cold Antarctic deserts inferred from unusual sulfate formation and isotope signatures: *Nature*  
993 *Communications*.

994 Tessier, A., Campbell, P. G. C., and Bisson, M., 1979, Sequential extraction procedure for the speciation  
995 of particulate trace metals: *Analytical Chemistry*, v. 51, no. 7, p. 844-851.

996 Torres, M. A., Moosdorf, N., Hartmann, J., Adkins, J. F., and West, A. J., 2017, Glacial weathering, sulfide  
997 oxidation, and global carbon cycle feedbacks: *Proceedings of the National Academy of Sciences*,  
998 v. 114, no. 33, p. 8716-8721.

999 Tranter, M., 2003, *Geochemical weathering in glacial and proglacial environments: Treatise on*  
1000 *geochemistry*, v. 5, p. 189-205.

1001 Tranter, M., Sharp, M. J., Lamb, H. R., Brown, G. H., Hubbard, B. P., and Willis, I. C., 2002, Geochemical  
1002 weathering at the bed of the Haut Glacier d'Arolla, Switzerland - a new model: *Hydrological*  
1003 *Processes*, v. 16, p. 959-993.

1004 Tulaczyk, S. M., 1999, *Basal mechanics and geologic record of ice streaming, West Antarctica: California*  
1005 *Institute of Technology*.

1006 Vavra, C. L., 1989, Mineral reactions and controls on zeolite facies alteration in sandstone of the Central  
1007 Transantarctic Mountains, *Antarctica: Journal of Sedimentary Petrology*, v. 59, no. 5, p. 688-703.

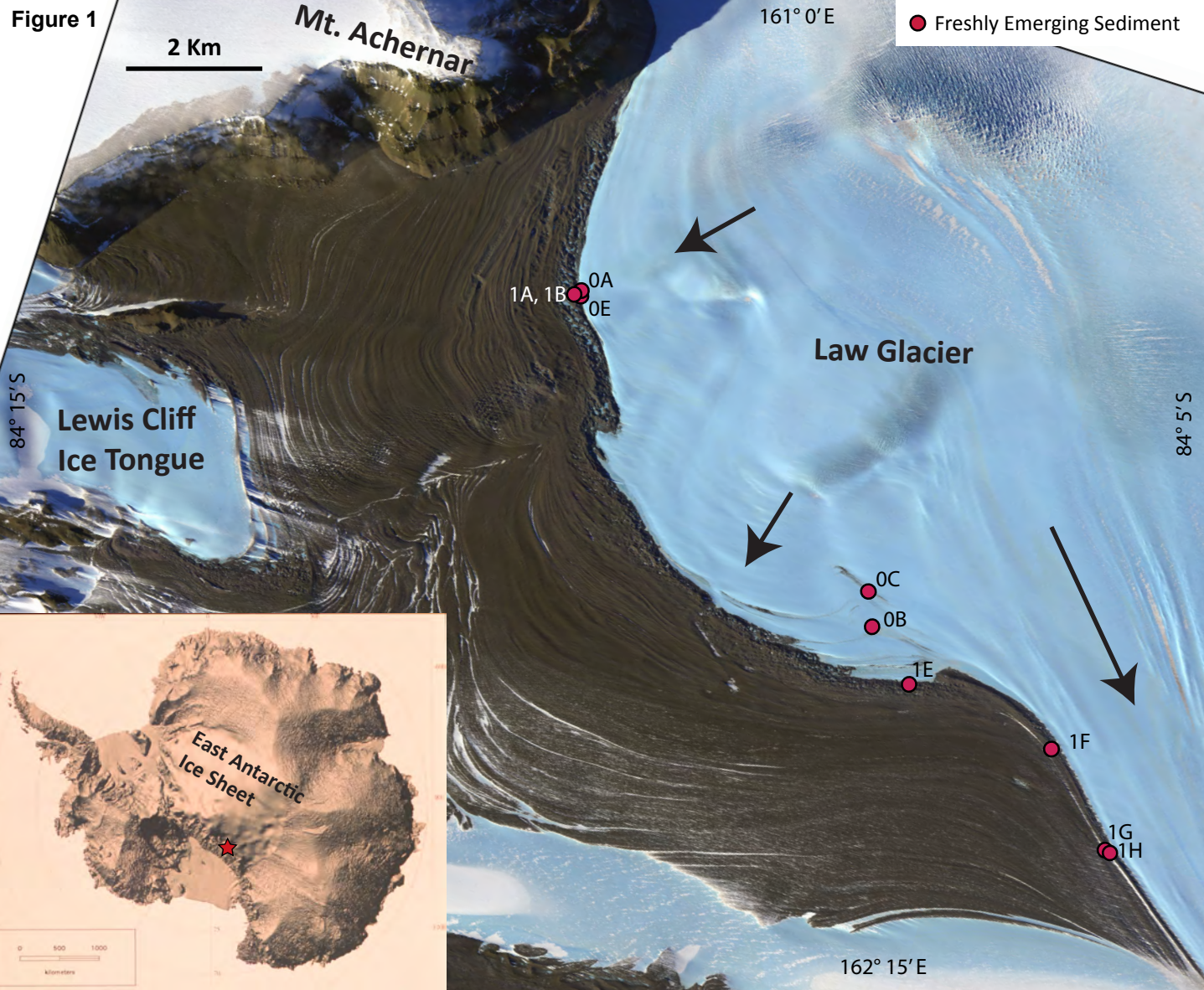
1008 Vennum, W. R., and Nejedly, J. W., 1990, Clay mineralogy of soils developed on weathered igneous  
1009 rocks, West Antarctica: *New Zealand Journal of Geology and Geophysics*, v. 33, no. 4, p. 579-  
1010 584.

1011 Wadham, J. L., Arndt, S., Tulaczyk, S., Stibal, M., Tranter, M., Telling, J., Lis, G. P., Lawson, E., Ridgwell, A.,  
1012 Dubnick, A., Sharp, M. J., Anesio, A. M., and Butler, C. E. H., 2012, Potential methane reservoirs  
1013 beneath Antarctica: *Nature*, v. 488, p. 633-637.

1014 Wadham, J. L., Tranter, M., Skidmore, M., Hodson, A. J., Priscu, J., Lyons, W. B., Sharp, M., Wynn, P., and  
1015 Jackson, M., 2010, Biogeochemical weathering under ice: Size matters: *Global Biogeochemical*  
1016 *Cycles*, v. 24, p. GB3025.

- 1017 Wand, U., Schwarz, G., Brüggemann, E., and Bräuer, K., 1997, Evidence for physical and chemical  
1018 stratification in Lake Untersee (central Dronning Maud Land, East Antarctica): *Antarctic Science*,  
1019 v. 9, no. 1, p. 43-45.
- 1020 Wiederhold, J. G., Teutsch, N., Kraemer, S. M., Halliday, A. N., and Kretzschmar, R., 2007, Iron isotope  
1021 fractionation in oxic soils by mineral weathering and podzolization: *Geochimica et*  
1022 *Cosmochimica Acta*, v. 71, p. 5821-5833.
- 1023 Wilson, D. S., Jamieson, S. S. R., Barrett, P. J., Leitchenkov, G., Gohl, K., and Larter, R. D., 2012, Antarctic  
1024 topography at the Eocene–Oligocene boundary: *Palaeogeography, Palaeoclimatology,*  
1025 *Palaeoecology*, v. 335-336, p. 24-34.
- 1026 Wilson, M. J., 1999, The origin and formation of clay minerals in soils: past, present and future  
1027 perspectives: *Clay Minerals*, v. 34, p. 7-25.
- 1028 Wingham, D. J., Siegert, M. J., Shepherd, A., and Muir, A. S., 2006, Rapid discharge connects Antarctic  
1029 subglacial lakes: *Nature*, v. 440, no. 7087, p. 1033.
- 1030 Wright, A., and Siegert, M., 2012, A fourth inventory of Antarctic subglacial lakes: *Antarctic Science*, v.  
1031 24, no. 6, p. 659-664.
- 1032





**Figure 2**

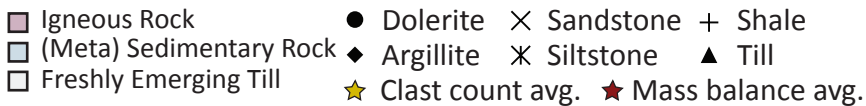
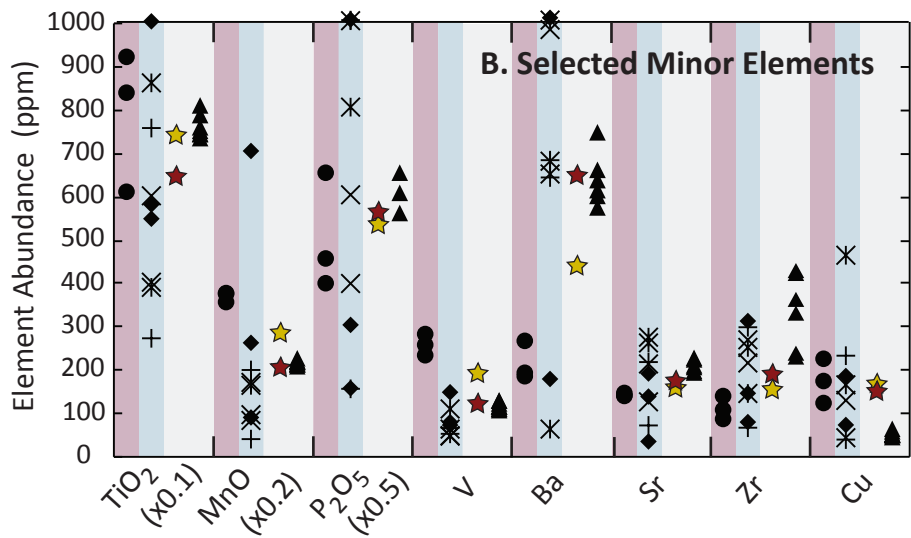
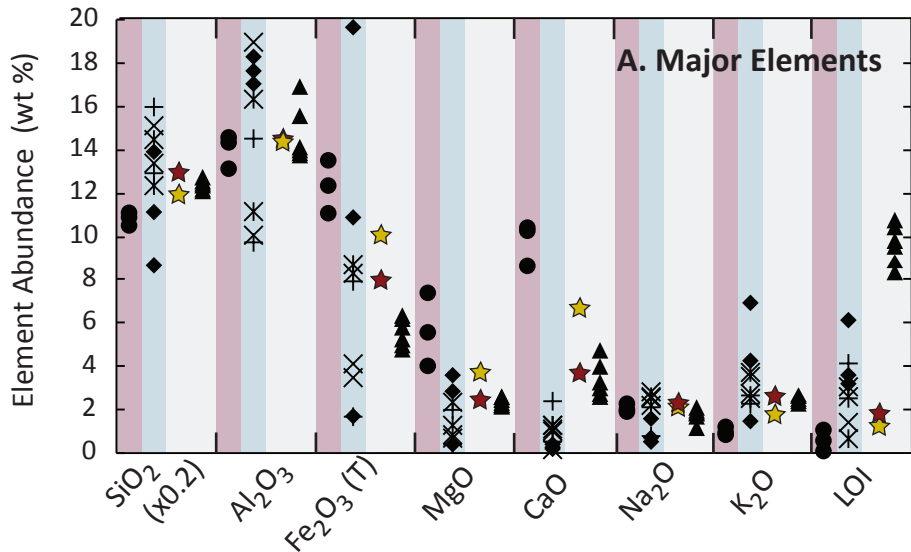
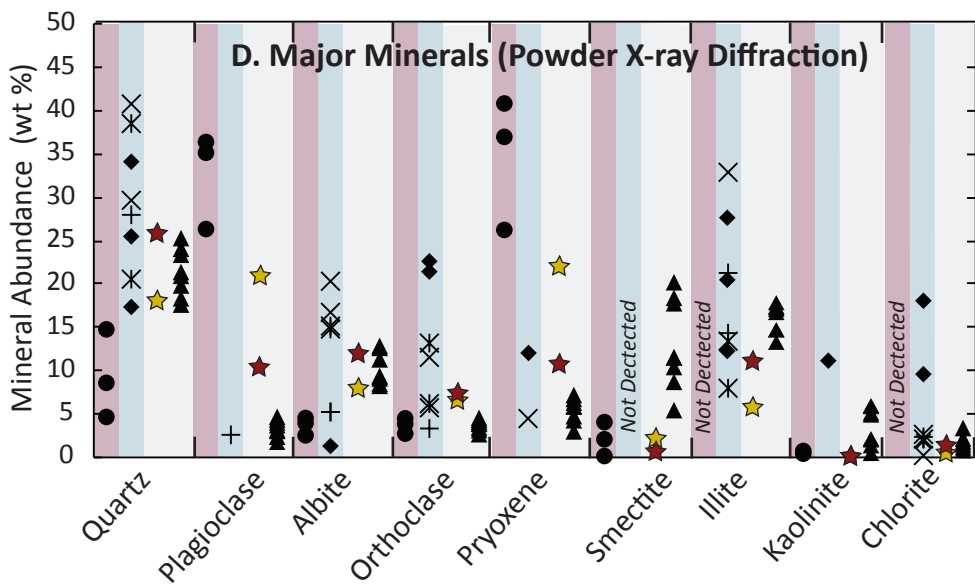
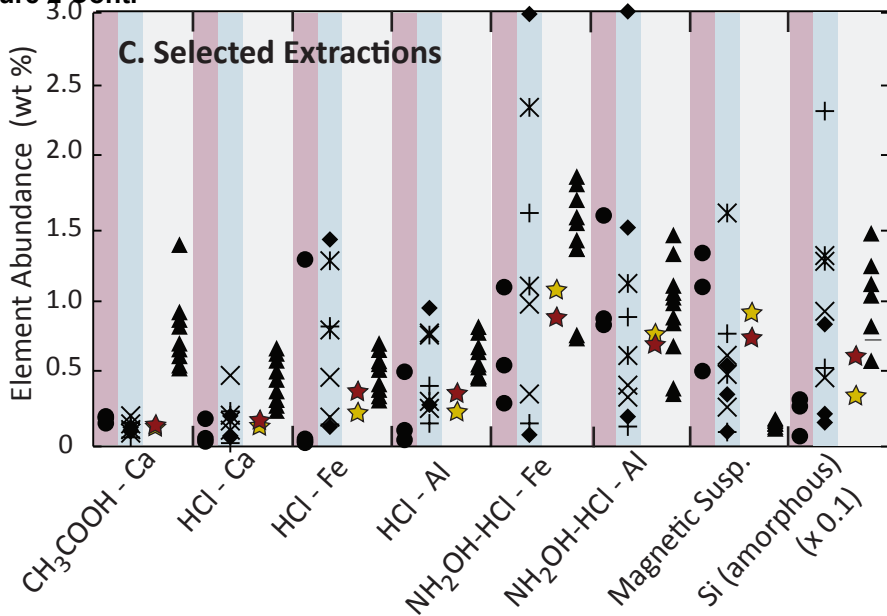


Figure 2 Cont.



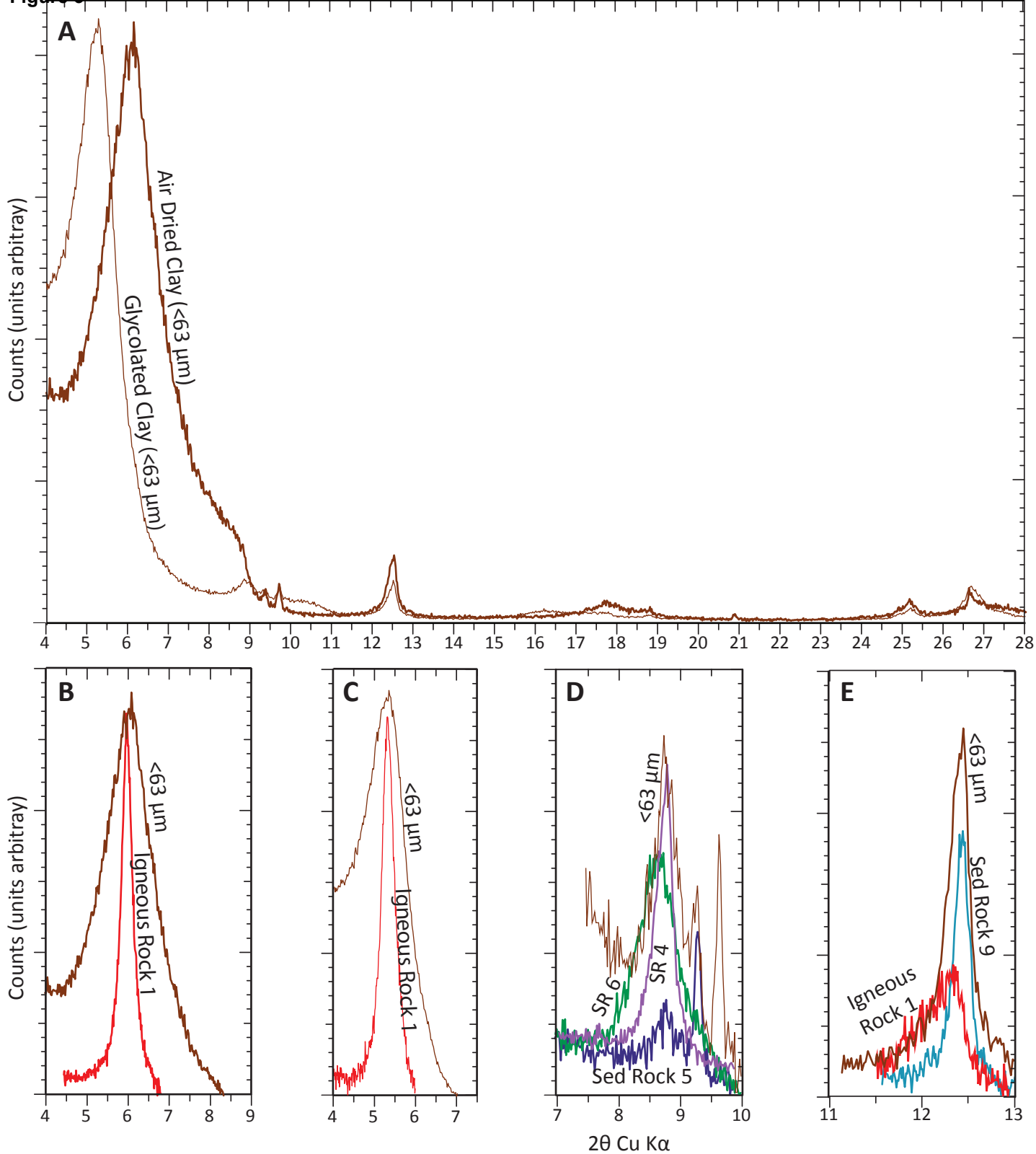
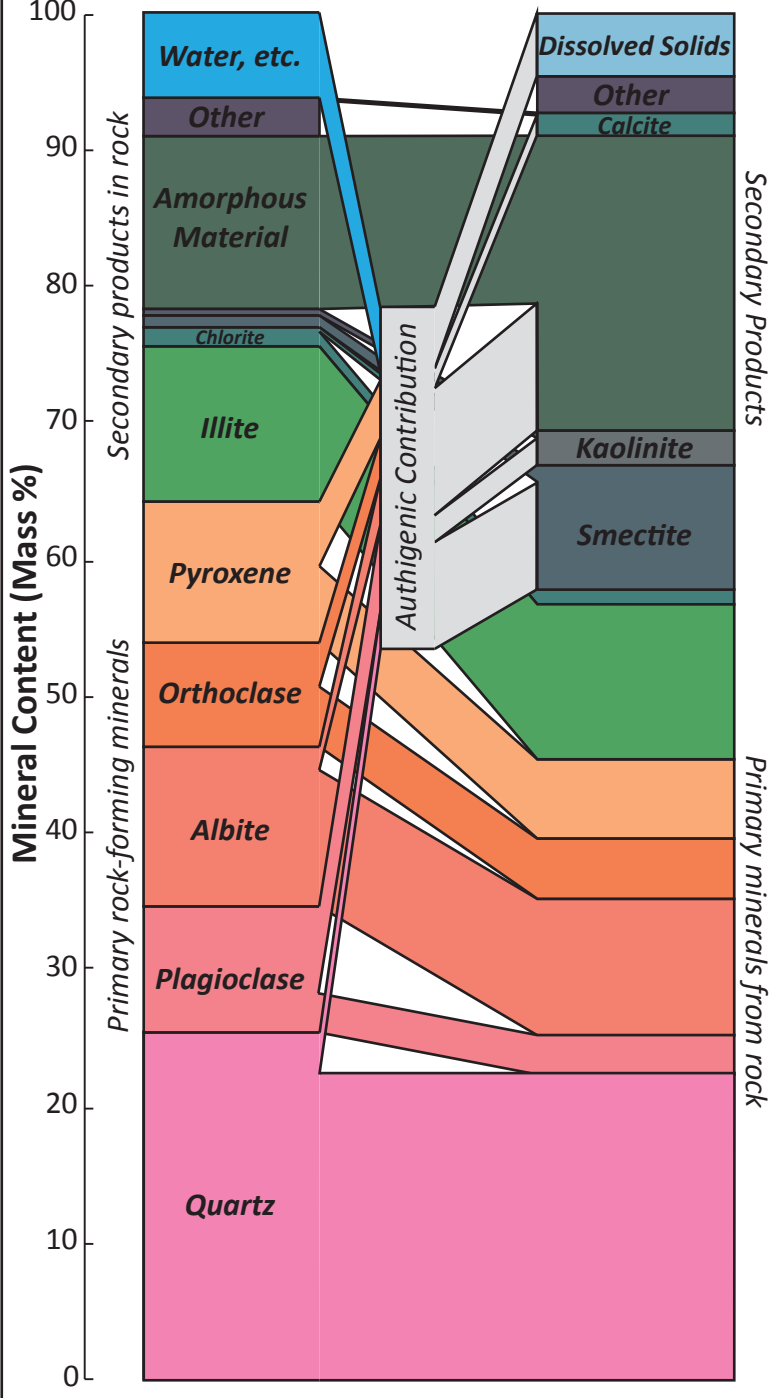
**Figure 3**

Figure 4

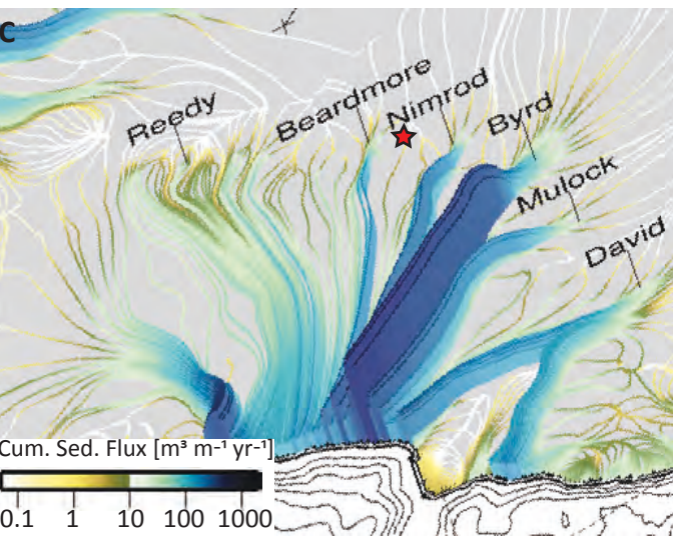
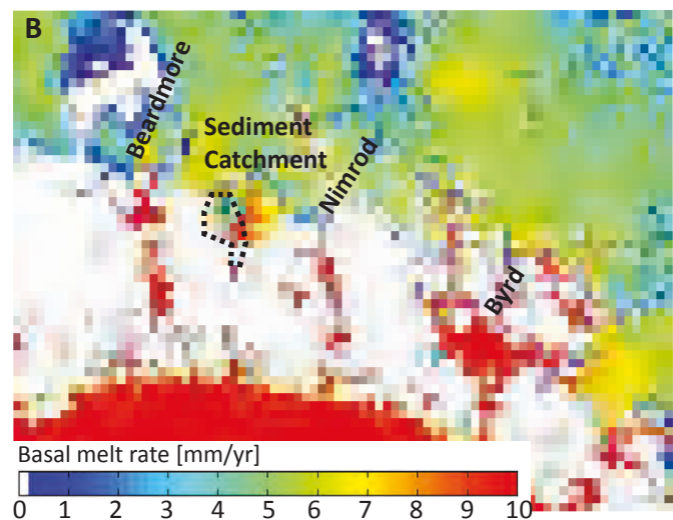
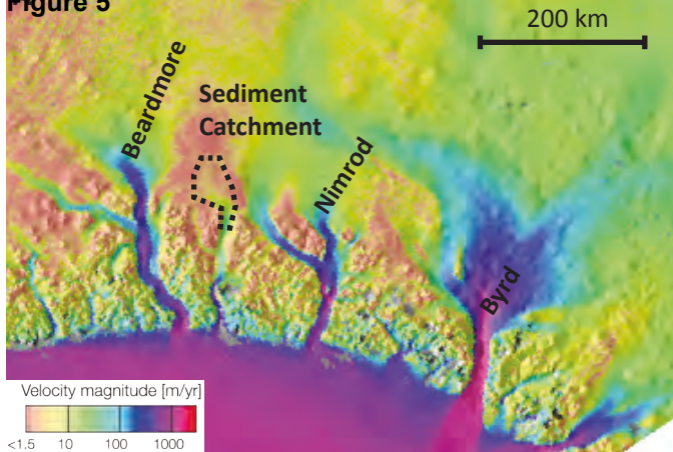
**A: Mineral Balance**



**B: By Element**



**Figure 5**



**Figure 6**

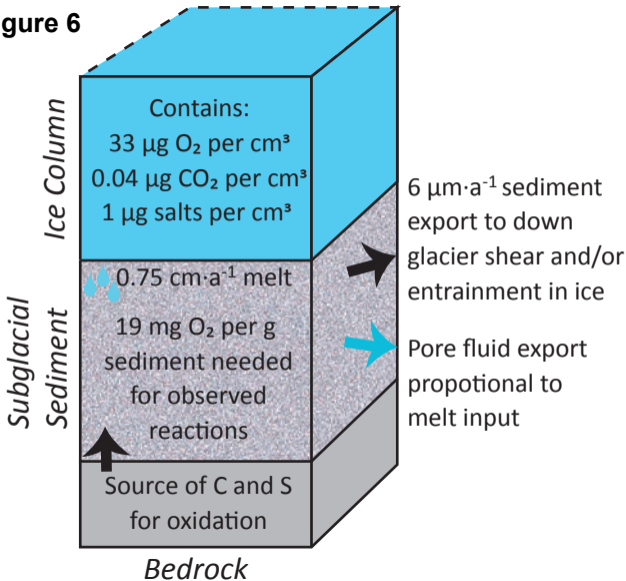
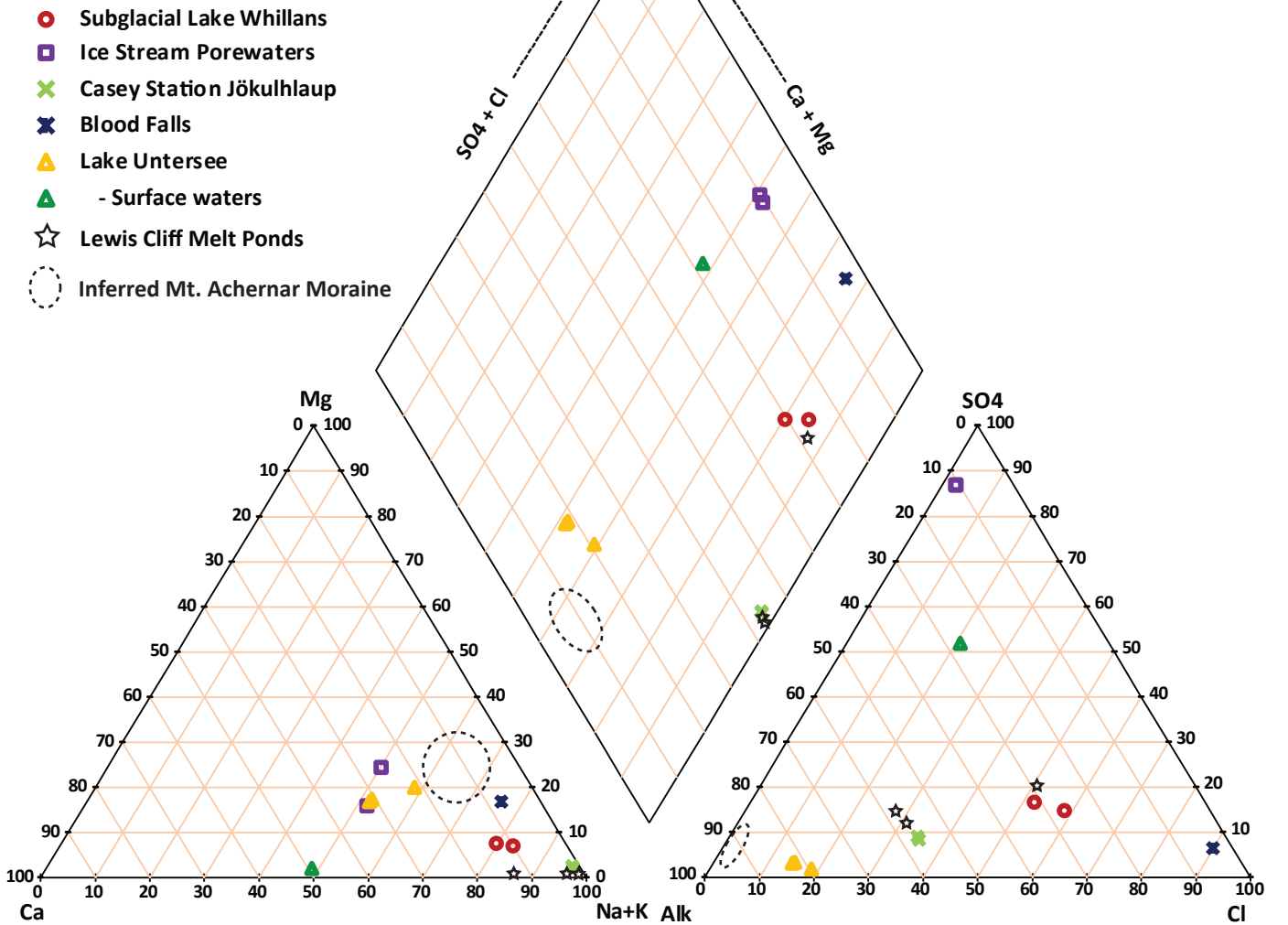
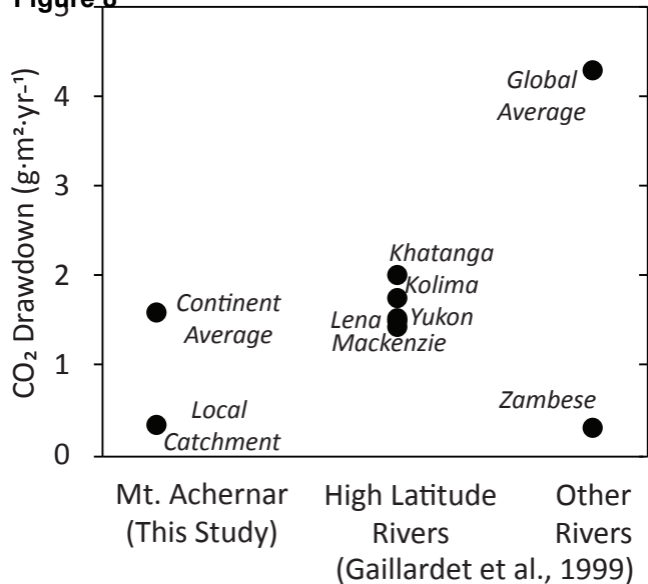


Figure 7





**Figure 8**



**Electronic Annex**

[Click here to download Electronic Annex: Gralyetal\\_Supplemental.xlsx](#)

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: