

## Accepted Manuscript

Influence of glaciation on mechanisms of mineral weathering in two high Arctic catchments

Ruth S. Hindshaw, Tim H.E. Heaton, Eric S. Boyd, Melody L. Lindsay, Edward T. Tipper

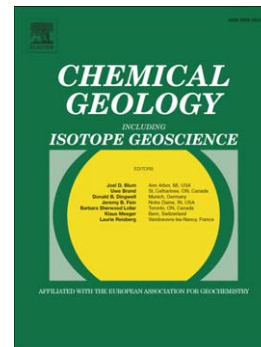
PII: S0009-2541(15)30096-6  
DOI: doi: [10.1016/j.chemgeo.2015.11.004](https://doi.org/10.1016/j.chemgeo.2015.11.004)  
Reference: CHEMGE 17758

To appear in: *Chemical Geology*

Received date: 22 June 2015  
Revised date: 26 October 2015  
Accepted date: 7 November 2015

Please cite this article as: Hindshaw, Ruth S., Heaton, Tim H.E., Boyd, Eric S., Lindsay, Melody L., Tipper, Edward T., Influence of glaciation on mechanisms of mineral weathering in two high Arctic catchments, *Chemical Geology* (2015), doi: [10.1016/j.chemgeo.2015.11.004](https://doi.org/10.1016/j.chemgeo.2015.11.004)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



## Influence of glaciation on mechanisms of mineral weathering in two high Arctic catchments

Ruth S. Hindshaw<sup>a,\*</sup>, Tim H. E. Heaton<sup>b</sup>, Eric S. Boyd<sup>c</sup>, Melody L. Lindsay<sup>c</sup>, Edward T. Tipper<sup>d</sup>

<sup>a</sup>Department of Earth and Environmental Sciences, University of St. Andrews, St. Andrews, UK

<sup>b</sup>NERC Isotope Geosciences Laboratory, Nottingham, UK

<sup>c</sup>Department of Microbiology and Immunology, Montana State University, Bozeman, Montana, USA

<sup>d</sup>Department of Earth Sciences, University of Cambridge, Cambridge, UK

---

### Abstract

In order to investigate the effect of glaciation on mineral weathering, the stream water chemistry and the bacterial community composition were analysed in two catchments containing nominally identical sedimentary formations but which differed in the extent of glaciation. The stream waters were analysed for major ions,  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and associated stream sediments were analysed by 16S rRNA gene tagged sequencing.

Sulfate comprised 72-86% and 35-45% of the summer anion budget (in meq) in the unglaciated and glaciated catchments respectively. This indicates that sulfuric acid generated from pyrite weathering is a significant weathering agent in both catchments. Based on the relative proportions of cations, sulfate and bicarbonate, the stream water chemistry of the unglaciated catchment was found to be consistent with a sulfide oxidation coupled to silicate dissolution weathering process whereas in the glaciated catchment both carbonates and silicates weathered via both sulfuric and carbonic acids.

Stable isotope measurements of sulfate, together with inferences of metabolic processes catalysed by resident microbial communities, revealed that the pyrite oxidation reaction differed between the two catchments. No  $\delta^{34}\text{S}$  fractionation relative to pyrite was observed in the unglaciated catchment and this was interpreted to reflect pyrite oxidation under oxic conditions. In contrast,  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  values were positively correlated in the glaciated catchment and were positively offset from pyrite. This was interpreted to reflect pyrite oxidation under anoxic conditions with loss of S intermediates.

This study suggests that glaciation may alter stream water chemistry and the mechanism of pyrite oxidation through an interplay of biological, physical and chemical factors.

### Keywords:

chemical weathering, pyrite, sulfur isotopes, bacteria, biogeochemical cycles

---

\*corresponding author

Email address: rh71@st-andrews.ac.uk (Ruth S. Hindshaw)

## 1. Introduction

The Arctic is currently experiencing a period of warming, resulting in the retreat of glaciers and an increase in the active layer depth of permafrost (Vaughan et al., 2013). Major emphasis has been placed on quantifying the effects of warming on nutrient fluxes, especially carbon (e.g. Schuur et al., 2009; Elberling et al., 2013), but major ion fluxes from both permafrost and glaciated areas (MacLean et al., 1999; Frey and McClelland, 2009; Pokrovsky et al., 2012; Nowak and Hodson, 2015) are also predicted to change with continued warming. Decreased permafrost cover is expected to increase overall fluxes of solutes as the active layer deepens (MacLean et al., 1999; Frey and McClelland, 2009). Likewise, solute fluxes from glaciers are predicted to increase by virtue of the increased discharge as a result of a longer melt season (Lafrenière and Sharp, 2005). However, it is unclear if, in addition to an increase in solute flux, the composition of this flux will change and what affect these changes will have on the carbon cycle and the microbial community which mediate many of the chemical reactions occurring in these environments (Skidmore et al., 2005; Boyd et al., 2011, 2014).

Chemical weathering, which is a key part of the biogeochemical cycles of many elements, is assumed to mainly occur by reaction with carbonic acid, formed by the dissolution of carbon dioxide (CO<sub>2</sub>) in water. However, where sulfide minerals e.g. pyrite (FeS<sub>2</sub>) exist, sulfuric acid may form through the oxidation of sulfide, which can also result in mineral dissolution (Holland, 1978). Understanding which agent is responsible for mineral dissolution is important for understanding inputs to the sulfur biogeochemical cycle and for quantifying the contribution of sulfuric acid weathering to global chemical weathering fluxes (Berner and Berner, 1996). Chemical weathering by sulfuric acid does not involve drawdown of atmospheric CO<sub>2</sub> and can even be a net source of CO<sub>2</sub> if carbonates are weathered. Therefore, if this reaction were significant on a global scale then the weathering-climate negative feedback would be weakened (Calmels et al., 2007; Li et al., 2008; Torres et al., 2014).

Sulfide oxidation coupled to carbonate dissolution (SOCD) is a key process determining stream water chemistry in the high physical erosion environment of glaciated catchments (Fairchild et al., 1999; Tranter et al., 2002; Sharp et al., 2002; Skidmore et al., 2005; Robinson et al., 2009; Wadham et al., 2010; Boyd et al., 2014). The high rates of physical erosion expose both the carbonate and pyrite grains allowing them to weather rapidly. In non-glaciated Arctic catchments, weathering is also strongly influenced by physical erosion processes such as frost shattering (Huh and Edmond, 1999; Hall et al., 2002) and where sulfide is present, sulfide oxidation is a key chemical weathering reaction (Elberling and Langdahl, 1998; Thorn et al., 2001; Calmels et al., 2007). Significant weathering by sulfuric acid is also observed in other high erosion settings such as Taiwan and the Himalayas (Wolff-Boenisch et al., 2009; Turchyn et al., 2013; Torres et al., 2014).

The stable isotopes of sulfate ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ) provide a useful tool with which to investigate the sources of sulfate and the reactions leading to sulfate formation (e.g. Mandernack et al., 2003; Calmels et al., 2007; Wadham et al., 2007; Turchyn et al., 2013). Based on stable isotope evidence, sulfate reduction was identified at Borup Glacier in Ellesmere Island, Canada due to supra-glacial sulfur springs (Grasby et al., 2003) and in a sub-glacial upwelling from

35 Finsterwalderbreen, Svalbard (Wadham et al., 2004) but not in the pro-glacial area of the same glacier (Wadham et al.,  
36 2007). However, bacterial sequencing data from other catchments has failed to detect sulfate reducing bacteria where  
37 water chemistry evidence suggested sulfate reduction was occurring (Skidmore et al., 2000, 2005). It is therefore not  
38 clear how widespread this reaction is in glaciated environments.

39 The chemical reactions involving sulfide oxidation and sulfate reduction are microbially mediated and it is only in  
40 the last 15 years that the diversity and functional importance of microorganisms in glacial landscapes has been recog-  
41 nised (e.g. Skidmore et al., 2000; Hodson et al., 2008). More recently, it has been shown that the microbial community  
42 composition is strongly influenced by bedrock composition and that the microbial community strongly influences so-  
43 lute chemistry (Larouche et al., 2012; Montross et al., 2013; Mitchell et al., 2013). In particular, the presence of  $\text{FeS}_2$   
44 was shown to be a dominant control on the composition of communities inhabiting the subglacial environment of  
45 Robertson Glacier, Canada (Mitchell et al., 2013), which likely reflects the utilisation of energy derived from mineral  
46 redox reactions to support primary productivity (Boyd et al., 2014). It is therefore probable that minerals which can  
47 serve as electron donors and acceptors play a key role in determining the composition of microbial communities, and  
48 by extension the chemical composition of solute fluxes, in other oligotrophic and obligately chemotrophic subglacial  
49 environments.

50 This study focusses on two adjacent catchments with nominally identical lithology: sedimentary rocks known to  
51 contain pyrite. One catchment was glaciated and the other was unglaciated and underlain by permafrost. We assume  
52 that the extent of glacial cover is the primary cause of differences in hydrology, biology and chemistry between the  
53 two catchments. The paired catchment approach provides clues to long-term changes in weathering processes induced  
54 by deglaciation. The aim of the study was to utilise the combination of stream water chemistry, S and O isotopes of  
55 sulfate, and molecular analyses of microbial community composition to investigate the formation of and the role of  
56 sulfuric acid weathering in the two catchments.

## 57 2. Description of field area

58 Svalbard is located in the Arctic Ocean. The archipelago has an arctic climate with a mean annual air temperature  
59 of  $-5\text{ }^\circ\text{C}$  and mean annual precipitation of 180 mm (measured at Longyearbyen airport, Humlum et al., 2003). Per-  
60 mafrost is continuous throughout the islands and can be up to 500 m thick (Humlum et al., 2003). The two studied  
61 catchments are situated next to each other (Fig. 1) in the Paleogene sedimentary Central Basin of Svalbard. The sedi-  
62 mentary formations exposed in the catchments are from the Van Mijenfjorden group which is Paleocene to Eocene in  
63 age (66 - 33.9 Ma) and contain sandstones, siltstones and shale (Fig. 2, Major et al., 2000).

64 Dryadbreen has been retreating since the end of the Little Ice Age (~1890, Ziaja, 2001). The thermal regime  
65 of the glacier is expected to be cold-based with temperate patches, based on similar sized glaciers in the same area  
66 (Etzelmüller et al., 2000; Etzelmüller and Hagen, 2005). Between 1936 and 2006 the area of the glacier decreased  
67 from 2.59 to 0.91  $\text{km}^2$  leaving large terminal and lateral ice-cored moraines and a sandur in front of the glacier (Ziaja

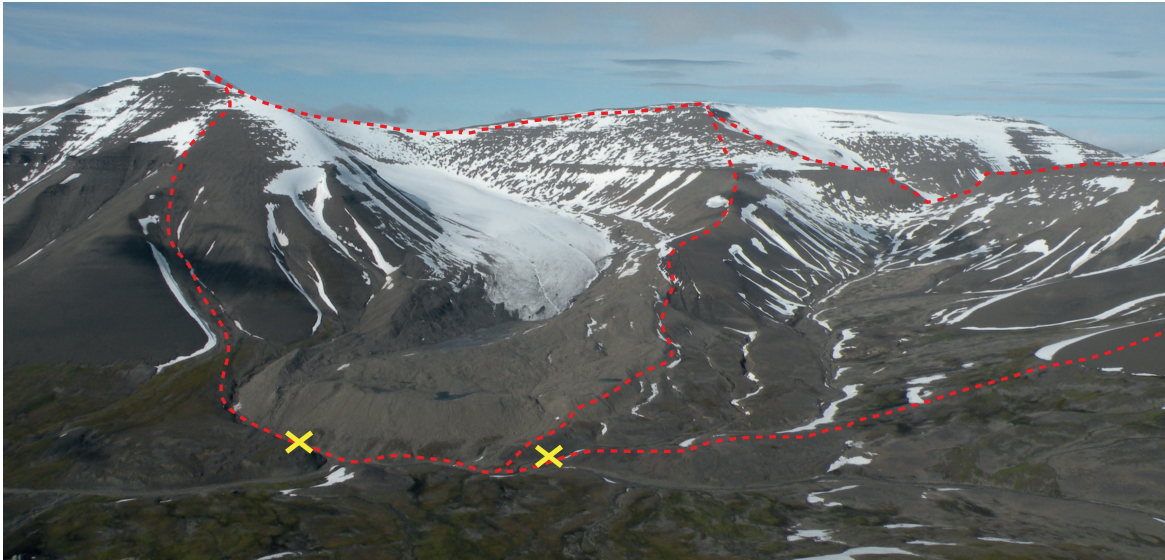


Figure 1: Panoramic view of the two study catchments. Dryadreen is on the left and Fardalen on the right. The red dashed line demarcates the catchment boundaries and the yellow crosses indicate the water sampling locations for each catchment. Note the large end moraine and sandur in the glaciated catchment. Photograph credit: Alix Guillot.

68 and Pipała, 2007). The sandur surface lowered 14 m between 2001 and 2006 due to the melting of dead ice (Ziaja and  
 69 Pipała, 2007). The uppermost part of the catchment faces north-north-east and the valley then curves around such that  
 70 at lower elevations (<500 m) the catchment faces south-east. The catchment area is 4.8 km<sup>2</sup> and ranges in elevation  
 71 from 250 - 1031 m.a.s.l. The river in the sandur plain is braided, but the braids merge such that one stream drains  
 72 the end moraine. This stream was sampled just before the confluence with the river in the main valley. In this paper  
 73 ‘Dryadreen’ will be used to refer to the whole catchment and not just the glacier.

74 Fardalen is a non-glaciated catchment at the head of a valley of the same name. In contrast to Dryadreen, the  
 75 whole catchment has a south-easterly aspect which contributes to the absence of present-day glaciation. The valley  
 76 is currently underlain by continuous permafrost and is likely to have been unglaciated for at least the last 10 kyr  
 77 (Svendsen and Mangerud, 1997). The catchment area is 3.4 km<sup>2</sup> and ranges in elevation from 250 - 1025 m.a.s.l. A  
 78 first-order stream drains the catchment and it was sampled just before the confluence with the river in the main valley.

### 79 3. Methods

#### 80 3.1. Hydrology

81 Water stand and water temperature were recorded every 10 minutes by a CS450 Campbell Scientific pressure  
 82 transducer connected to a Campbell CR200X data logger. In Dryadreen conductivity was recorded every 10 minutes  
 83 using a Ponsel CE4 meter. Water stand was converted to discharge using discharge measurements obtained by salt  
 84 tracing, which were performed using a point addition of 1-3 kg salt. The resulting change in conductivity ~70  
 85 m downstream was monitored by a Hobo U24 conductivity logger recording every second. The calibration of the

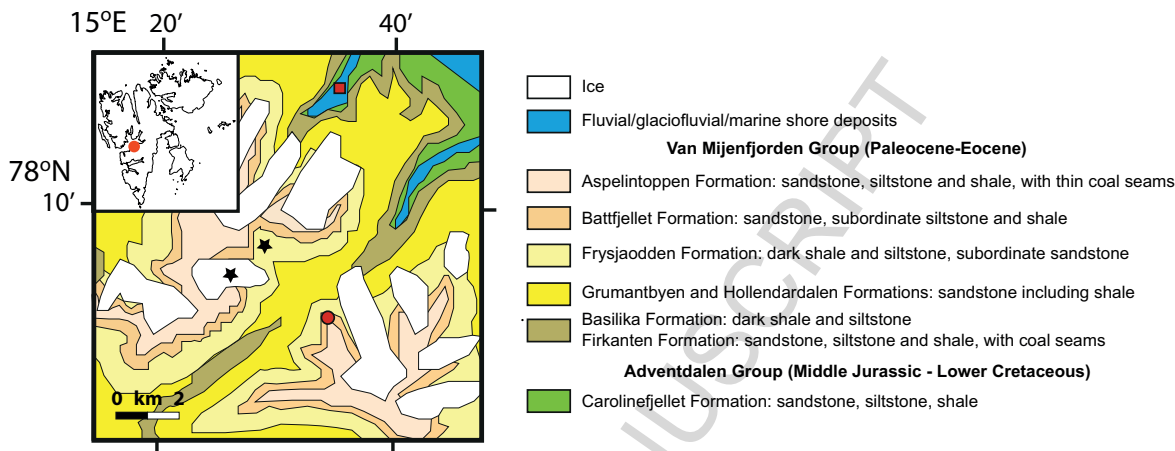


Figure 2: Geological map of the study area. The red dot in the inset shows the location of the study area in relation to the rest of Svalbard. The two stars indicate the location of the two catchments: Dryadbreen (glaciated) and Fardalen (unglaciated). The red square marks the location of Nybyen (part of the town of Longyearbyen) and the red circle shows from where the photograph in Figure 1 was taken. The map and the legend are from Major et al. (2000).

86 conductivity meter and conversion to discharge was done following the procedure outlined in Hudson and Fraser  
 87 (2005). The amount of snow in May 2012 prevented installation of the loggers that early in the season, therefore high  
 88 resolution hydrological data is only available for the period 25<sup>th</sup> July to 3<sup>rd</sup> August 2012. In mid-May there was no  
 89 surface water and no sub-surface water was found by digging. Three weeks later, the landscape was still dominated  
 90 by snow but both streams were flowing.

### 91 3.2. Collection of water samples

92 The Dryadbreen and Fardalen streams were sampled twice a day from 14<sup>th</sup> to 18<sup>th</sup> June 2012 and from 25<sup>th</sup> July  
 93 to 3<sup>rd</sup> August 2012. The number of days sampled corresponds to approximately 20% of the melt-season (Yde and  
 94 Knudsen, 2004). The two rivers were sampled just before they joined the main valley river. For Dryadbreen this  
 95 was approximately 1 km from the front of the glacier. Temperature and pH were measured in situ (Hanna HI 98160  
 96 pH meter). Water samples were filtered on the day of collection through 0.2  $\mu\text{m}$  nylon filters using a polycarbonate  
 97 vacuum filtration unit connected to a hand pump. A filtered water sample was titrated with 3.3 mM HCl within an  
 98 hour of collection and alkalinity was calculated from the titration curve using the Gran method (Stumm and Morgan,  
 99 1996). Assuming that alkalinity  $\approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  and using  $K_1$ ,  $K_2$ ,  $K_H$  values for 4 °C, then  $\text{HCO}_3^-$  comprises  
 100 more than 99.9% of alkalinity for all samples and we therefore assume that the measured alkalinity is equivalent to  
 101 the bicarbonate concentration. Filtered samples were stored in pre-cleaned HDPE bottles and those intended for the  
 102 analysis of cations were acidified to pH 2 with single-distilled concentrated  $\text{HNO}_3$ . Sulfate was pre-concentrated by  
 103 passing 3 L of filtered water through a column filled with 5 mL Dowex 1x8, 100-200 mesh chloride form resin. The  
 104 resin was pre-cleaned by rinsing with 60mL 3M HCl followed by 60 mL 18.2 M $\Omega$  water. Three snow samples were  
 105 taken by filling a bucket with snow and allowing it to melt at room temperature. Two rain samples were collected from

106 an HDPE bottle with a funnel. A supra-glacial stream sample was also collected. All of these samples were filtered  
107 as described for river water samples.

### 108 3.3. Analysis of water samples

109 For all water samples, major cations and Si were measured by inductively-coupled plasma optical emission spec-  
110 trometry (ICP-OES, Perkin Elmer Optima 5300 DV at the University of Edinburgh) and anions by ion chromatography  
111 (IC, Dionex DX 500 at Durham University). Measured cation concentrations of the water standards SLRS-5 (National  
112 Research Council Canada) and BATTLE-02 (Environment Canada) were within 8% of the certified values. Measured  
113 anion concentrations were within 5% of the certified values for LETHBRIDG-03 and BATTLE-02 (both Environment  
114 Canada). External reproducibility, as measured by the mean normalized difference of 9 pairs of replicate field samples,  
115 was <3% for cations and <5% for anions. Calculated charge balance errors (CBE) were <3% for the vast majority of  
116 samples, confirming the accuracy of the anion and cation measurements (Table 1).

117 The oxygen isotopic composition ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) of water samples was measured on 750  $\mu\text{L}$  samples of water which  
118 had been equilibrated with a mixture of 0.3%  $\text{CO}_2$  and He in septum capped vials. The  $\text{CO}_2/\text{He}$  mixture was measured  
119 using a Gas Bench II (Thermo Scientific) connected to an isotope ratio mass spectrometer (IRMS, Delta PLUS XP,  
120 Thermo Scientific at the University of St. Andrews). Measurements were calibrated with the international standards  
121 SLAP-2, GISP and VSMOW-2. The results are reported in the conventional delta notation with respect to VSMOW  
122 and sample standard deviation was less than 0.15‰ (2SD).

123 Sulfate from the anion resins was eluted with 2 M KCl, and the eluent acidified to pH 3 with HCl, heated to  
124 sub-boiling, and barium sulfate precipitated by addition of  $\text{BaCl}_2$ . The barium sulfate was then recovered by four  
125 cycles of centrifugation, discard of the supernatant, and washing in de-ionised water before oven drying at 80 °C. The  
126 sulfate blank for the process is less than 0.5 mg  $\text{BaSO}_4$  (limit of determination), which is less than 1% of the smallest  
127 sample.  $^{34}\text{S}/^{32}\text{S}$  ratios were determined by combustion to  $\text{SO}_2$  with  $\text{V}_2\text{O}_5$  in an EA-1120 elemental analyser on-line to  
128 an IRMS (Delta+XL, ThermoFinnigan at the NERC Isotope Geosciences Laboratory), with  $^{34}\text{S}/^{32}\text{S}$  ratios calculated  
129 as  $\delta^{34}\text{S}$  values versus CDT by comparison with standards IAEA SO6 and NBS-127. Analytical precision of replicates  
130 was typically  $\leq 0.2\text{‰}$  (1 SD).  $^{18}\text{O}/^{16}\text{O}$  ratios were determined by thermal conversion to CO in a TC/EA on-line to an  
131 IRMS (Delta+XL, ThermoFinnigan at the NERC Isotope Geosciences Laboratory), with  $^{18}\text{O}/^{16}\text{O}$  ratios calculated as  
132  $\delta^{18}\text{O}_{\text{SO}_4}$  values versus SMOW by comparison with standards IAEA SO5 and SO6. Analytical precision of replicates  
133 was typically  $< 0.5\text{‰}$  (1 SD).

### 134 3.4. Analysis of solid samples

135 Three rock samples were collected: R01 was collected from the Frysjaodden Formation (Fig. 2) in Fardalen,  
136 R02 was collected from the sandur in Dryadbreen and R04 was collected from the surface of the glacier. The rock  
137 samples, in addition to a sediment sample taken at the water sampling location in each catchment (O - Dryadbreen  
138 and L - Fardalen) were crushed and ground to fine powders. The rock samples were analysed by X-ray fluorescence

139 spectrometry (XRF, PANalytical Axios at the Norwegian Geological Survey) and all samples were analysed by X-  
140 ray diffraction (XRD). S contents of the rock samples were analysed by high temperature combustion followed by  
141 infrared detection (Leco SC-444 at the Norwegian Geological Survey). XRD analysis was performed on a PANalytical  
142 PW1050 X-ray diffractometer with a Hiltonbrooks DG2 X-ray generator (Co-K $\alpha$  radiation) at the University of St.  
143 Andrews. Data were collected between 5 and 70° 2 $\theta$  with a step size of 0.02° and a counting time of 3 s per step. Semi-  
144 quantitative mineralogical abundances were obtained using the Siroquant software. The typical error on abundances is  
145 estimated to be 5-10%. Carbon isotope analysis of calcite from R02 was performed by reaction of whole rock powder  
146 with anhydrous phosphoric acid overnight at 25 °C and subsequent analysis of the liberated CO<sub>2</sub> in a MAT 253 mass  
147 spectrometer (ThermoFinnigan at the NERC Isotope Geosciences Laboratory). <sup>13</sup>C/<sup>12</sup>C ratios were converted to  $\delta^{13}$ C  
148 values versus VPDB by comparison with a laboratory calcite standard calibrated against NBS-19 and NBS-18.

149 Pyrite was separated from two shale samples by using a solution of lithium heteropolytungstate (LST). The sep-  
150 arated fraction contained both pyrite and magnetite and the pyrite was separated from magnetite using a magnet and  
151 hand-picking. Pyrite separates were ground to a powder in an agate mortar and <sup>34</sup>S/<sup>32</sup>S ratios determined by com-  
152 bustion to SO<sub>2</sub> with V<sub>2</sub>O<sub>5</sub> in an EA-1120 elemental analyser on-line to an IRMS (Delta+XL, ThermoFinnigan at the  
153 NERC Isotope Geosciences Laboratory), with <sup>34</sup>S/<sup>32</sup>S ratios calculated as  $\delta^{34}$ S values versus CDT by comparison  
154 with standards IAEA S-1 and S-2. Analytical precision of replicates was  $\leq 0.4\%$  (1 SD).

155 Suspended sediment samples (>0.2 $\mu$ m, collected on nylon filter papers) were washed off the filter papers using  
156 deionized water and freeze-dried. Depending on the amount of sediment recovered, part or all of the sample was  
157 then reacted overnight with 1.5 M HCl to remove carbonates, washed free of acid, dried and homogenised. <sup>13</sup>C/<sup>12</sup>C  
158 ratios were determined by combustion to CO<sub>2</sub> in an EA-1120 elemental analyser on-line to an IRMS (Delta+XL,  
159 ThermoFinnigan at the NERC Isotope Geosciences Laboratory), with <sup>13</sup>C/<sup>12</sup>C ratios calculated as  $\delta^{13}$ C values versus  
160 VPDB by comparison with laboratory standards calibrated against NBS 19 and IAEA CH-7. Analytical reproducibil-  
161 ity was typically  $\leq 0.2\%$  (1 SD).



Table 1: Summary of water chemistry and isotopic data. These data have not been corrected for precipitation inputs.

Sample (YYYYMMDD)	Time (local)	Discharge (m <sup>3</sup> s <sup>-1</sup> )	pH	T °C	Cond. (µS/cm)	CBE <sup>1</sup> %	Ca µmol/L	Mg	Na	K	Si	Cl <sup>-</sup>	F <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	δ <sup>34</sup> S ‰	δ <sup>18</sup> O <sub>SO4</sub>	δ <sup>18</sup> O <sub>H2O</sub>
Dryadreen (glaciated) - spring																			
20120615D	11:26		6.91	0.1	56.9	-1	125	124	188	11	13	208	4	8	113	263	-0.57	-6.0	-15.28
20120616D	18:18		6.06	0.1	36.4	-1	92	92	137	10	11	137	4	3	85	212	+0.73	-5.4	-14.58
20120617D	10:20		5.94	0.3	61.2	0	96	93	160	14	12	190	4	6	75	195			-15.06
20120618D	09:40					-1	99	88	167	9	12	208	4	9	65	210			
Dryadreen (glaciated) - summer																			
20120725D	10:10	0.43	6.76	2.9	35.3	-3	108	100	85	14	8	40	4	2	94	315	-2.02	-7.7	-13.96
20120726D	08:11	0.38	7.10	2.3	39.0	-3	120	111	107	6	6	40	4	2	111	311	-2.28	-8.1	-13.82
20120727D	09:28	0.50	5.70	2.0	39.3	1	116	105	87	8	9	34	4	2	117	322	-2.31	-8.0	-13.49
20120728D	08:45	0.35	6.34	2.1	39.0	0	115	106	94	8	8	36	4	2	116	249	-2.31	-8.0	-13.54
20120730D	19:22	0.46	6.94	1.1	36.3	-2	117	108	87	8	8	37	4	2	111	307	-2.64	-9.7	-13.04
20120731D	08:37	0.25	6.91	2.6	52.6	0	144	135	111	11	13	44	4	1	141	349	-2.64	-9.7	-13.41
20120801D	16:17	0.39	6.86	3.6	33.5	7	109	98	80	9	8	37	4	1	90	212	-2.28	-8.5	-13.28
20120802D	08:50	0.36	6.89	1.6	46.1	5	137	125	131	17	11	53	4	1	124	299	-2.28	-8.5	-13.22
20120803D	19:10	0.38	6.70	2.0	49.4	0	142	130	95	12	9	37	4	1	132	346			-13.72
Fandalen (unglaciated) - spring																			
20120614F	10:26		7.37	0.1	129.1	-1	213	253	323	16	29	226	8	14	461	130	-3.56	-8.1	-15.76
20120615F	17:46		7.34	0.0	117.0	0	198	233	312	15	29	181	5	11	419	151	-3.66	-8.1	-15.43
20120616F	10:25		7.22	0.0	84.5	-1	147	176	255	11	21	174	4	10	313	116	-3.66	-8.1	-15.46
20120617F	16:28		5.70	0.1	66.0	-1	138	160	233	12	25	148	5	8	288	124	-3.40	-8.4	-15.17
20120618F	09:35		6.20	0.1	58.3	-2	136	156	230	11	27	153	5	7	287	134	-3.40	-8.4	-15.15
Fandalen (unglaciated) - summer																			
20120725F	18:31	0.24	7.12	2.8	82.5	0	172	191	167	12	28	30	5	4	323	225	-6.70	-9.7	-13.65
20120726F	09:32	0.27	6.50	2.3	108.3	2	216	245	207	13	23	40	8	6	423	249	-7.08	-9.5	-13.47
20120727F	09:05	0.14	5.82	3.3	119.7	2	236	267	211	14	33	43	8	6	459	219	-7.08	-9.5	-13.43
20120728F	09:05	0.18	5.82	3.5	135.9	4	257	292	238	15	34	43	9	6	529	135	-7.08	-9.5	-13.43
20120729F	19:19	0.38	6.27	3.2	99.6	1	200	224	182	12	29	31	5	4	374	239	-7.03	-9.7	-13.21
20120730F	09:30	0.26	6.70	2.3	112.9	1	216	248	206	13	30	38	8	4	438	201	-7.03	-9.7	-13.05
20120731F	18:10	0.38	6.82	5.0	126.2	1	252	283	205	15	37	47	8	5	475	259	-7.66	-10.1	-13.03
20120801F	08:35	0.23	7.15	5.3	162.2	1	298	344	282	18	37	47	9	7	640	223	-7.66	-10.1	-13.26
20120802F	19:35	0.14	6.85	3.2	150.3	-1	280	318	247	16	33	44	9	7	584	269	-7.12	-10.1	-13.17
20120803F	08:55	0.14	6.87	3.3	156.1	-2	283	323	253	15	34	46	9	7	602	265	-7.12	-10.1	-13.45
Supra-glacial sample																			
20120801SG	13:50						10	9	16	1	1	14	3		9				-13.98
Snow samples																			
20110713S							8	6	32	7	1	31			9				-12.87
20120527S							1	2	20	1	0	12			8				-17.01
20120614S							1	0	14	2	0	14			8				-20.24
Ice samples																			
20120729IX							16	5	19	9	1	19	3	4	13				-16.49
20120803IX							32	6	53	13	0	75	3	4	15				-14.56

<sup>1</sup>CBE = charge balance error = ((Σ<sup>+</sup> - Σ<sup>-</sup>)/(Σ<sup>+</sup> + Σ<sup>-</sup>)) \* 100 in meq

### 162 3.5. Sequencing of bacterial 16S rRNA genes

163 Four surface sediment samples were sequenced: two from Fardalen collected in spring at the water sampling  
164 location, L (river sediment) and M (sediment by the side of the river resting on snow) and two from Dryadreen  
165 collected in summer, A (sediment from a pool of water in the sandur, not connected to main river) and O (sediment  
166 adjacent to the river at water sampling location). Sediment samples were scooped directly into either sterile 300 mL  
167 PVC containers or sterile 50 mL centrifuge tubes. The samples were stored at ambient temperature (<4 °C) until they  
168 were transported to the lab where they were desiccated by drying at 40 °C (4 days). Desiccated samples were shipped  
169 internationally to the USA where they were subjected to molecular analyses.

170 **Nucleic Acid Extraction and Quantification.** DNA extraction and purification were carried out with a Fast  
171 DNA Spin Kit for Soil (MP Biomedicals, Solon, OH). DNA was extracted in triplicate from three independent 250  
172 mg subsamples of sediment. Equal volumes of each replicate extract were pooled and the concentration of DNA  
173 was determined using a Qubit dsDNA HS Assay kit (Molecular Probes, Eugene, OR) and a Qubit 2.0 Fluorometer  
174 (Invitrogen, Carlsbad, CA).

175 **PCR Amplification of bacterial and archaeal 16S rRNA Genes from Genomic DNA.** Purified genomic DNA  
176 extracts were subjected to amplification of bacterial and archaeal 16S rDNA using primers  
177 344F (5'-ACGGGGYGCAGCAGGCGCGA-3') and 915R (5'-GTGCTCCCCGCAATTCCT-3') at an annealing  
178 temperature of 61°C or 1100F (5'-YAACGAGCGCAACCC-3') and 1492R (5'-GGTTACCTTGTTACGACTT-3') at  
179 an annealing temperature of 55 °C, respectively (Boyd et al., 2007). Approximately 1 ng of purified genomic DNA  
180 was subjected to PCR in triplicate using the following reaction conditions: initial denaturation at 94 °C (4 min),  
181 followed by 35 cycles denaturation at 94 °C (1 min), annealing at the optimal temperature for the primer pair (1 min),  
182 primer extension at 72 °C (1.5 min), followed by a final extension step at 72 °C for 20 min. Reactions contained 2 mM  
183 MgCl<sub>2</sub> (Invitrogen, Carlsbad, CA), 200 μM each deoxynucleotide triphosphate (Eppendorf, Hamburg, Germany), 0.5  
184 μM forward and reverse primer (Integrated DNA Technologies, Coralville, IA), 0.4 mg ml<sup>-1</sup> molecular-grade bovine  
185 serum albumin (Roche, Indianapolis, IN), and 0.25 units Taq DNA polymerase (Invitrogen, Carlsbad, CA) in a final  
186 reaction volume of 50 μL. Positive control reactions were performed using genomic DNA from *Azotobacter vinelandii*  
187 DJ and *Sulfolobus solfataricus* P2. Negative control reactions were performed in the absence of added genomic DNA.  
188 PCR amplicons were only obtained from extracts when bacterial primer sets were applied. Archaeal 16S rRNA gene  
189 amplicons were not recovered from any of the four sediment DNA extracts.

190 **Sequencing and analysis of bacterial 16S rRNA genes.** Bacterial 16S rDNA amplicons were sequenced by  
191 Molecular Research LC (Lubbock, TX). 16S rDNA from each site were barcoded and were sequenced using a 454  
192 Genome Sequencer FLX System. Post sequence processing was performed using the Mothur (ver. 1.33.3) sequence  
193 analysis platform (Schloss et al., 2009). Raw libraries were trimmed to a minimum length of 250 bases and were sub-  
194 jected to a filtering step using the quality scores file to remove sequences with anomalous base calls. Unique sequences  
195 were aligned using SILVA databases and sequences were trimmed using a defined start and end sites and a maximum  
196 length of 250 bases. The resulting unique sequences were pre-clustered to remove amplification and sequencing errors

197 and chimeras were identified and removed using UCHIME (Edgar et al., 2011). Operational taxonomic units (OTUs)  
 198 were assigned at a sequence similarity of 0.03 using the furthest-neighbour method. The remaining sequences were  
 199 randomly sub-sampled in order to normalize the total number of sequences in each library. Collectively, these steps  
 200 resulted in a normalized size of 1077 bacterial 16S rRNA gene sequences for each assemblage. Sequences were clas-  
 201 sified using the Bayesian classifier (Wang et al., 2007) and the RDP database, with manual verification using BLASTn  
 202 (Supp. Table 1). Sequences representing each OTU have been deposited in the NCBI SRA database under accession  
 203 number SRR1562043.

204 Sequences representing each unique OTU (defined at 0.03% sequence identities) were compiled for each domain.  
 205 ClustalX (ver. 2.0.9, Larkin et al., 2007) was used to align nucleic acid sequences using default parameters and the  
 206 alignment was subjected to evolutionary model prediction via jModeltest (ver. 2.1.1, Darriba et al., 2012), Maximum-  
 207 Likelihood phylogenetic reconstruction via PhyML (version 3.0, Guindon and Gascuel, 2003) specifying the general  
 208 time reversible model and gamma distributed rate variation with a proportion of invariable sites, and rate smoothing  
 209 using the multidimensional version of Rambaut's parameterization as implemented in PAUP (ver. 4.0, Swofford,  
 210 2001) as previously described (Meuser et al., 2013). Phylocom was used to calculate Rao's community phylogenetic  
 211 relatedness for the bacterial assemblages using relative sequence abundance weights and the rate-smoothed ultrameric  
 212 tree. PAST (ver. 1.72, Hammer et al., 2001) was used to generate cluster dendrograms specifying single linkage and  
 213 Euclidean distances. Bootstrap values correspond to the frequency that each node was observed in a given position  
 214 out of 1000 replicates.

### 215 3.6. Precipitation correction

216 Snow is the primary source of precipitation to the two studied catchments, but the chemical composition of the  
 217 water derived from melting snow varies temporally (e.g. Johannessen and Henriksen, 1978). Therefore instead of  
 218 using the snow samples collected for this study, which were collected relatively late in the season as a measure of  
 219 precipitation inputs, we compiled literature data on pre-melt Svalbard snow-pack chemistry (Hodgkins et al., 1997;  
 220 Wynn et al., 2006; Tye and Heaton, 2007; Yde et al., 2008). Pre-melt snow-pack samples are typically taken in  
 221 April and are assumed to represent "fresh" snow. From these data average X/Cl ratios were calculated, without any  
 222 weighting, where X is a major cation or anion. By assuming that chloride is conservative and only derived from  
 223 precipitation, the stream water data are corrected for snow inputs using the following formula:

$$X^* = X_{river} - (X/Cl)_{snow} \cdot Cl_{river} \quad (1)$$

224 where  $X^*$  and  $X_{river}$  denote precipitation-corrected and uncorrected concentrations respectively. The X/Cl ratios used  
 225 for the precipitation correction were ( $\pm 1SD$ ,  $n=8-10$ ): Ca/Cl  $0.11 \pm 0.10$ , Mg/Cl  $0.09 \pm 0.04$ , Na/Cl  $0.85 \pm 0.09$ , K/Cl  
 226  $0.02 \pm 0.01$  and  $SO_4/Cl$   $0.11 \pm 0.04$ . The propagated error on the precipitation corrected values in summer was less than  
 227 7% (RSD) for K and Na and less than 4% (RSD) for Ca, Mg and  $SO_4$ . In spring, the propagated error was higher

Table 2: Precipitation-corrected  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  values ( $\delta^{34}\text{S}^*$  and  $\delta^{18}\text{O}_{\text{SO}_4}^*$ ).

Sample (YYYYMMDD)	SO <sub>4</sub> in precipitation %	$\delta^{34}\text{S}$ ‰	$\delta^{34}\text{S}^*$ ‰	$\delta^{18}\text{O}_{\text{SO}_4}$ ‰	$\delta^{18}\text{O}_{\text{SO}_4}^*$ ‰
Dryadbreen (glaciated) - spring					
20120615D	21.3	-0.6	-4.5	-6.0	-10.2
20120617D	29.0	0.7	-4.7	-5.4	-11.5
Dryadbreen (glaciated) - summer					
20120725D	4.8	-2.0	-2.8	-7.7	-8.6
20120727D	3.5	-2.3	-2.9	-8.1	-8.7
20120729D	3.8	-2.3	-2.9	-8.0	-8.7
20120731D	3.6	-2.6	-3.2	-9.7	-10.4
20120802D	4.9	-2.3	-3.1	-8.5	-9.4
Fardalen (unglaciated) - spring					
20120614F	5.6	-3.6	-4.6	-8.1	-9.2
20120616F	6.4	-3.7	-4.9	-8.1	-9.2
20120618F	5.3	-3.4	-4.4	-8.4	-9.4
Fardalen (unglaciated) - summer					
20120726F	1.1	-6.7	-6.9	-9.7	-9.9
20120728F	0.9	-7.1	-7.3	-9.5	-9.7
20120730F	1.0	-7.0	-7.2	-9.7	-9.9
20120801F	0.8	-7.7	-7.8	-10.1	-10.2
20120803F	0.9	-7.1	-7.3	-10.1	-10.2

228 due to the greater amount of snow-melt and the error was consistently higher in Dryadbreen. Errors were less than  
 229 25% (RSD) except for Na in Dryadbreen which were closer to 50% (RSD). The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  values were also  
 230 corrected for snow inputs (Table 2). Reported values for the  $\delta^{34}\text{S}$  composition of snow in Svalbard vary from +11.5  
 231 to +18.0‰ (Tye and Heaton, 2007). To estimate a value of  $\delta^{34}\text{S}$  for the snow pack we took the percentage of SO<sub>4</sub>  
 232 derived from snow for the spring samples and extrapolated to a  $\delta^{34}\text{S}$  value at 100% SO<sub>4</sub> from snow (Fig. 3). The value  
 233 estimated for snow using this approach was +14‰ which is within the range previously reported (Tye and Heaton,  
 234 2007). Using this value,  $\delta^{34}\text{S}$  values were corrected using the following formula:

$$\delta^{34}\text{S}^* = (\delta^{34}\text{S}_{\text{river}} - f \cdot \delta^{34}\text{S}_{\text{snow}})/(1 - f) \quad (2)$$

235 where  $f$  is the fraction of SO<sub>4</sub> from snowmelt.  $\delta^{18}\text{O}_{\text{SO}_4}$  values were corrected in an identical manner to that described  
 236 above for  $\delta^{34}\text{S}$  using a snow value of +9.5‰ based on a fresh snow sample from Svalbard (Tye and Heaton, 2007).  
 237 Unless otherwise stated, precipitation-corrected values are used in all figures in this manuscript and are indicated by  
 238 an asterisk.

## 239 4. Results

### 240 4.1. Water chemistry and hydrology

241 The water samples taken in spring were dominated by snow-melt as evinced by the high proportion of Cl and  
 242 Na compared to the summer samples (Fig. 4, Table 1). The most abundant anion in Dryadbreen was HCO<sub>3</sub><sup>-</sup> which  
 243 comprised 48-58% of the major anions (in meq) in summer. This was in stark contrast to Fardalen where SO<sub>4</sub><sup>2-</sup> was  
 244 the major anion comprising 72-86% of the major anions (in meq) in summer (Fig. 4). The precipitation corrected

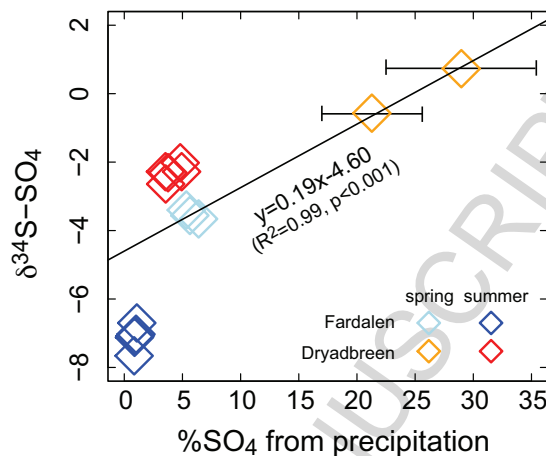


Figure 3: Stream water  $\delta^{34}\text{S}$  values against the calculated  $\% \text{SO}_4$  derived from precipitation. The regression line is derived from the spring samples only. The  $\delta^{34}\text{S}$  value when 100%  $\text{SO}_4$  is derived from precipitation is  $+14\text{‰}$  which is comparable with the  $+11.5$  to  $+18.0\text{‰}$  range reported for snow (fresh snow and snow-pack) from Svalbard by Tye and Heaton (2007). The  $\delta^{34}\text{S}$  value when 0%  $\text{SO}_4$  is derived from precipitation is  $-4.6 \pm 0.2\text{‰}$  and is assumed to represent sulfate derived from a pyrite weathering source. The summer samples do not lie on the mixing line between snow and a pyrite source which either indicates additional pyrite sources with different  $\delta^{34}\text{S}$  values or fractionation processes. Error bars smaller than symbol size are not depicted.

245 abundances of cations were similar in both catchments (Fig. 4). In Dryadbreen precipitation sources accounted for  
 246 34-48% of the cation abundance (in meq) in spring and 10% in summer. In Fardalen, the precipitation contribution  
 247 to the cation abundance was slightly less: 19-29% in spring and 4% in summer. The abundances of Ca and Mg were  
 248 very similar in both catchments but in Fardalen Mg was consistently more abundant compared to Dryadbreen where  
 249 Ca was most abundant. The total dissolved load of Fardalen ( $53 \pm 7 \text{ mgL}^{-1}$ , 1SD) was approximately double that of  
 250 Dryadbreen ( $25 \pm 4 \text{ mgL}^{-1}$ , 1SD).

251 The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of the stream water varied from around  $-15\text{‰}$  in spring to around  $-13\text{‰}$  in summer (Table 1),  
 252 reflecting the decrease in snow cover from spring to summer (Hindshaw et al., 2011). There is no significant differ-  
 253 ence in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values between the two catchments reflecting a common precipitation source. The sulfur isotopic  
 254 composition of sulfate ( $\delta^{34}\text{S}$ ) decreased from spring to summer: from  $+0.73$  to  $-2.64\text{‰}$  in Dryadbreen and from  $-3.40$   
 255 to  $-7.66\text{‰}$  in Fardalen (Table 1). Similar to  $\delta^{34}\text{S}$  values,  $\delta^{18}\text{O}_{\text{SO}_4}$  values exhibited a seasonal shift towards lower  
 256 values in summer with the lowest value ( $-10.1\text{‰}$ , Table 1) measured in Fardalen.

257 The discharge of both streams at the time of sampling is given in Table 1. Both streams exhibit diurnal cycles in  
 258 discharge and the range of discharge measured in both catchments was  $0-0.5 \text{ m}^3\text{s}^{-1}$  (not including periods of logger  
 259 malfunction), but the median discharge over the period of data collection for Dryadbreen ( $0.40 \text{ m}^3\text{s}^{-1}$ ) was greater  
 260 than for Fardalen ( $0.22 \text{ m}^3\text{s}^{-1}$ ).

Table 3: XRF data for rock samples.

Sample	Class <sup>1</sup>	Fm. <sup>2</sup>	SiO <sub>2</sub> wt%	Al <sub>2</sub> O <sub>3</sub> wt%	Fe <sub>2</sub> O <sub>3</sub> wt%	TiO <sub>2</sub> wt%	MgO wt%	CaO wt%	Na <sub>2</sub> O wt%	K <sub>2</sub> O wt%	MnO wt%	P <sub>2</sub> O <sub>5</sub> wt%	LOI <sup>3</sup> wt%	Total wt%
R01	Shale	Fry.	63.2	16.3	7.1	0.8	1.4	0.3	1.0	2.6	0.1	0.3	7.5	101.0
R02	Wacke	Batt.	65.4	13.0	7.9	0.6	1.5	0.6	0.7	2.2	0.1	0.3	7.2	99.5
R04	Shale	Fry.	57.1	19.1	3.5	0.9	1.3	0.2	0.6	3.6	0.0	0.1	12.9	99.3

<sup>1</sup> Classification using SandClass for terrigenous sands and shales (Herron, 1988).

<sup>2</sup> Formation assignment based on Schlegel et al. (2013). Fry. = Frysjaodden Formation and Batt. = Battfjellet Formation.

<sup>3</sup> LOI = Loss on Ignition.

#### 261 4.2. Solid samples

262 Based on the SandClass system for terrigenous sand and shale samples (Herron, 1988), R01 and R04 were clas-  
 263 sified as shales and R02 as a wacke (Table 3). Schlegel et al. (2013) have previously classified rock core samples  
 264 from the Frysjaodden Formation as shales and those from the Battfjellet and Aspelintoppen formations as wackes and  
 265 litharenites respectively. We therefore assume that R01 and R04 originated from the Frysjaodden Formation and R02  
 266 from the Battfjellet Formation (Fig. 2). The main minerals in the bulk rock and sediment samples analysed by XRD  
 267 were quartz, plagioclase, chlorite, kaolinite, illite/mica and illite/smectite (Table 4). Clay minerals accounted for 44%  
 268 (sediment O) to 65% (R04) of the total composition. Calcite abundance was below 1% in all samples analysed. How-  
 269 ever, calcite was detected in XRD analysis of orientated clay fractions from river sediments collected in the glaciated  
 270 catchment (Dryadbreen) but not in sediments collected from the unglaciated catchment (Fardalen). The low calcite  
 271 abundance is in agreement with previous studies which report <1-2% carbonate in core samples from these formations  
 272 (Dypvik et al., 2011; Schlegel et al., 2013). Calcite in rock sample R02 had a  $\delta^{13}\text{C}$  value of  $-1.7\text{‰}$  (Table 5). The  
 273  $\delta^{13}\text{C}$  values of suspended sediments show neither temporal nor spatial variation and the average value of  $-26\text{‰}$  (Table  
 274 5) reflects carbon fixed by the Calvin-Benson-Bassham cycle (C3) which may be of plant (Kendall and Doctor, 2003)  
 275 or microbial origin (Havig et al., 2011).

276 Pyrite was detected in the bulk phase XRD analysis of R02 (Table 4) and was separated from both R01 and R02.  
 277 No gypsum was detected by XRD analysis and none was detected in thin sections from these same formations (Dypvik  
 278 et al., 2011; Schlegel et al., 2013). The S content of R01 and R02 was 0.02 and 0.90 wt% respectively. Assuming  
 279 that all the S is from pyrite with a formula  $\text{FeS}_2$ , then this corresponds to 0.04 and 1.69 wt% pyrite in the two rocks  
 280 samples, in agreement with the XRD data (Table 4). It is therefore highly likely that pyrite is the main S-bearing  
 281 mineral phase in these rock samples. The  $\delta^{34}\text{S}$  values of pyrite mineral separates from samples R01 and R02 were  
 282  $-5.4 \pm 0.4\text{‰}$  and  $-7.6 \pm 0.2\text{‰}$  (1SD) respectively (Table 5). The difference in values is likely due to the two samples  
 283 being derived from different formations (Table 3).

#### 284 4.3. Bacterial community composition

285 The phylogenetic affiliation of the 16S rRNA genes recovered from the sediment samples, as determined by  
 286 BLASTn analysis, are depicted in Fig. 5.

Table 4: Semi-quantitative mineral abundances (% total) in rock and sediment samples.

Mineral	Sample				
	R01	R02	R04	O <sup>1</sup>	L <sup>1</sup>
Quartz	38	46	31	51	40
Plagioclase	7	3	3	5	6
K-Feldspar	<1	<1	1	<1	<1
Chlorite	9	8	11	12	5
Illite/Mica	26	24	28	17	32
Illite/Smectite	8	7	9	<3	<3
Kaolinite	12	9	17	15	17
Pyrite	<1	1	<1	<1	<1
Siderite	<1	3	<1	<1	<1
Calcite	<1	<1	<1	<1	<1

<sup>1</sup>O = Dryadbreen sediment, L = Fardalen sediment

Table 5: Summary of C contents and C and S isotope data of solid samples.

Sample	C wt%	1SD*	$\delta^{13}\text{C}$ ‰	1SD*	$\delta^{34}\text{S}$ ‰	1SD*
<b>&gt;0.2<math>\mu\text{m}</math> suspended sediments</b>						
<i>Dryadbreen (glaciated)</i>						
20120615D#	4.07		-26.1			
20120617D#	2.88		-26.3			
20120725D	2.17		-25.6			
20120725D#	2.33	0.10	-26.2	0.1		
20120727D#	2.17		-26.2			
20120729D	2.60		-25.7			
20120729D#	2.64	0.25	-26.2	0.0		
20120731D	2.46		-25.6			
20120731D#	2.30	0.10	-26.2	0.1		
20120802D#	2.54		-26.4			
<i>Fardalen (unglaciated)</i>						
20120616F#	2.43		-26.4			
20120618F#	2.02		-26.6			
20120726F#	2.59		-26.8			
20120728F#	2.63		-26.0			
20120730F#	2.49		-26.5			
<b>Pyrite mineral separates</b>						
R01					-5.4	0.4
R02					-7.6	0.2
<b>Calcite mineral separate</b>						
R02			-1.7			

\*Errors reported where there was enough sample material for repeat measurements.

# Denotes that sample was treated with 5% HCl to remove carbonates.

287 Clear differences were observed in the composition of sediment associated bacterial communities that were sub-  
 288 merged in the stream versus those that were collected on the banks of the stream. For example, samples M (Fardalen,  
 289 sediment on snow adjacent to river) and O (Dryadbreen, sediment adjacent to river) both comprised large numbers  
 290 of firmicutes, whereas the two samples collected under water (A and L) contained very low abundances of these lin-  
 291 eages (Fig. 5b). A (Dryadbreen) and L (Fardalen) were dominated by sequences affiliated with Proteobacteria (48  
 292 and 65% of the total bacterial community, respectively) with those affiliated with Betaproteobacteria representing the  
 293 most abundant proteobacterial class (21% and 31% respectively). Sequencing studies from glaciated environments  
 294 have found that Betaproteobacteria are the dominant phylogenetic group in subglacial and proglacial sediments where  
 295 they are likely to be involved in S and Fe cycling under oxic conditions (Foght et al., 2004; Skidmore et al., 2005;

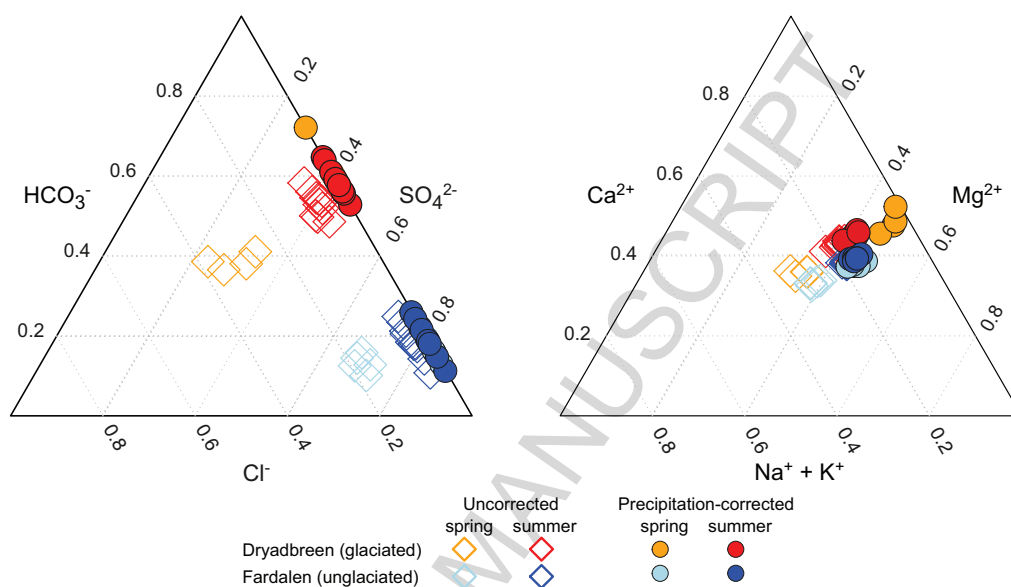


Figure 4: Major ion water chemistry (in meq) shown in ternary diagrams. Uncorrected data are shown as open diamonds and precipitation corrected data are shown as filled-in circles. The data are further divided into samples collected in spring and those collected in summer. The striking difference between the two catchments is in their relative anion abundances with Dryadbreen (glaciated) dominated by  $\text{HCO}_3^-$  and Fardalen (unglaciated) dominated by  $\text{SO}_4^{2-}$ . Error bars are smaller than the symbols.

296 Mitchell et al., 2013).

297 Differences in the composition of the bacterial communities associated with sediments sampled from the two sub-  
 298 merged sites A (Dryadbreen) and L (Fardalen) were also apparent. For example, sequences affiliated with the anaero-  
 299 bic phylum Bacteroidetes represented the most abundant phylum (24%) in the community sampled from Dryadbreen  
 300 (A), whereas Bacteroidetes represented only a minor fraction of the community (3%) from Fardalen (L). This may  
 301 indicate a shift toward more anaerobic metabolisms in the proglacial sediment bacterial communities at Dryadbreen.

302 In the discussion we will focus on sediment samples A and L as representative of each catchment since they  
 303 were collected under water and therefore are most likely to be adapted to or responsible for the differences in water  
 304 chemistry observed between the two catchments.

## 305 5. Discussion

### 306 5.1. Overall weathering reactions

307 The most obvious difference between the two streams is in the anion composition: Dryadbreen is dominated by  
 308  $\text{HCO}_3^-$ , whereas Fardalen is dominated by  $\text{SO}_4^{2-}$ . This indicates that different weathering reactions are occurring  
 309 in the two catchments despite nominally identical lithology. A first indication of which weathering reactions are  
 310 important for each catchment can be gained by looking at element ratios since the reactions of carbonates and silicates



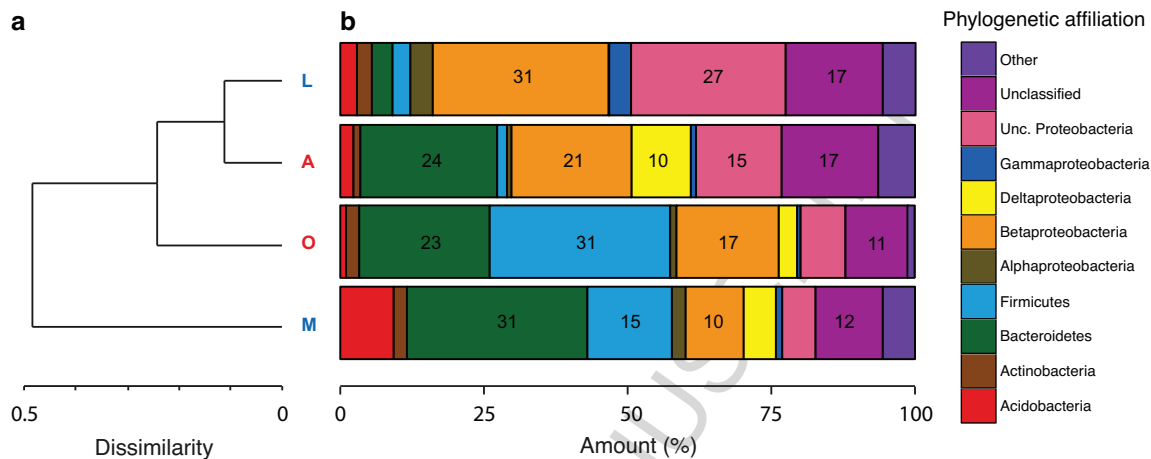
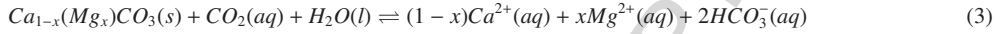


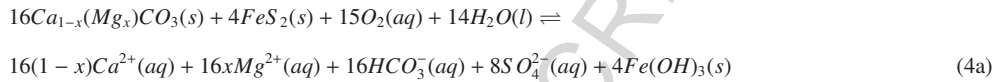
Figure 5: (a) Dendrogram based on the Rao phylogenetic diversity index (Rao, 1982) which depicts the degree of phylogenetic dissimilarity between the bacterial communities associated with the different sediment samples. Samples A and O were collected in Dryadbreen (red letters) and L and M were collected in Fardalen (blue letters). Samples A and L were collected under water and form a cluster, indicating they are more similar in their bacterial phylogenetic composition as compared to samples O and M. Sample O was collected adjacent to the river and sample M was collected adjacent to the river but on top of snow. (b) Relative abundance of bacterial phyla or classes (Proteobacteria only) based on percent identities to their closest cultivated sequence, as determined by BLASTn analysis. The phyla Armatimonadetes, Chlamydiae, Gemmatimonadetes, Nitrospinae, Nitrospira, Nitrospirales, Planctomycetes, TM7, Verrucomicrobia and WS3 are grouped together in 'Other'.

311 with either carbonic or sulfuric acids will give distinct ratios of cations versus  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  (Fairchild et al.,  
 312 1994; Tranter et al., 2002; Wadham et al., 2010). Example reactions and their corresponding slopes in units of  
 313 equivalents (eq) are presented below (Eqns. 3-6) and in Table 6. Feldspars are the primary silicate minerals in these  
 314 rocks and although feldspars are a compositional solid solution between  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ,  $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$ , the  
 315 variation in composition does not affect the ratio (in equivalents) of the product cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) to either the  
 316  $\text{HCO}_3^-$  or the  $\text{SO}_4^{2-}$  produced (cf. Eqns 5a, 5b, 6a and 6b). Analogous equations can be written for the main Mg-  
 317 bearing silicate phases: illite ( $(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}\text{OH}_2$ ) and chlorite ( $(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}$ ) (Table 4). In addition  
 318 to mineral weathering, the oxidation of organic matter will produce  $\text{HCO}_3^-$ , and this reaction, which is expected to  
 319 occur in these permafrost-dominated catchments, is represented by equation 7.

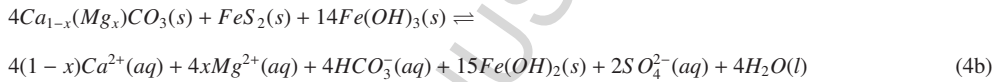
Carbonate dissolution with carbonic acid (CDC)



Aerobic sulfide oxidation coupled to carbonate dissolution (SOCD)



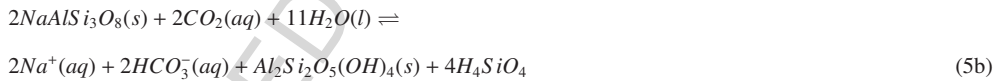
Anaerobic sulfide oxidation coupled to carbonate dissolution (SOCD)



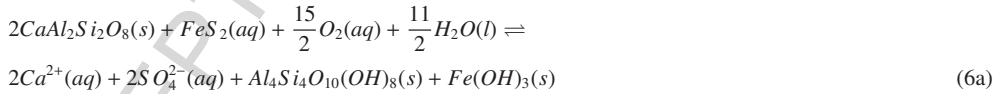
Silicate dissolution with carbonic acid, divalent cation (SDC)



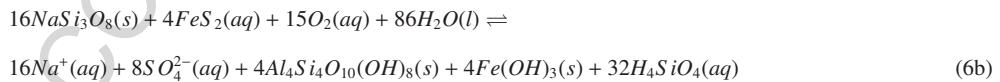
Silicate dissolution with carbonic acid, monovalent cation (SDC)



Sulfide oxidation coupled to silicate dissolution, divalent cation (SOSD)



Sulfide oxidation coupled to silicate dissolution, monovalent cation (SOSD)



Organic matter oxidation (OMO)



320 In the unglaciated catchment, Fardalen, the slope of the data in a plot of total cations versus  $SO_4^{2-}$  (Fig. 6a) is  
 321  $1.04 \pm 0.04$  which is the same as the slope which would be expected by sulfide oxidation coupled to silicate weathering  
 322 (SOSD, Eqn. 6). The intercept of this line is not zero which suggests that a portion of the cations are being produced  
 323 by other weathering reactions such as silicate dissolution by carbonic acid (SDC, Eqn. 5). In Figs. 6b and 6d, the  
 324 slopes greater than 1 (carbonic acid weathering of silicates and carbonates, Table 6), together with the greater scatter  
 325 of the Fardalen points support the notion that sulfuric acid is the main weathering agent in this catchment. In summary,  
 326 although it is not possible to quantify the relative importance of each of the reactions represented by equations 3 -

Table 6: Predicted and observed slopes of Ca+Mg and total cations versus either  $\text{SO}_4^{2-}$  or  $\text{HCO}_3^-$ .

Reaction	Predicted slope (in eq)			
	$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{SO}_4^{2-}$	$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{HCO}_3^-$	Total Cations vs $\text{SO}_4^{2-}$	Total Cations vs $\text{HCO}_3^-$
Carbonate + $\text{H}_2\text{CO}_3$ (Eqn. 3)	$\infty$	1	-	-
Carbonate + $\text{H}_2\text{SO}_4$ (Eqn. 4a,b)	2	2	-	-
Silicate + $\text{H}_2\text{CO}_3$ (Eqn. 5a,b)	-	-	$\infty$	1
Silicate + $\text{H}_2\text{SO}_4$ (Eqn. 6a,b)	-	-	1	$\infty$
	Observed slope			
Dryadbreen	$1.54 \pm 0.14$	$1.48 \pm 0.29$	$1.84 \pm 0.18$	$2.04 \pm 0.42$
Fardalen	$0.88 \pm 0.04$	$6.68 \pm 2.10$	$1.04 \pm 0.04$	$7.92 \pm 2.50$

327 7, the data from Fardalen is consistent with weathering mainly by a sulfide oxidation coupled to silicate dissolution  
328 process.

329 If only silicate minerals were weathering in the glaciated catchment (Dryadbreen) then the slopes of the data in  
330 Figs. 6a and 6b, which lie intermediate between SOSD (Eqn. 6) and SDC (Eqn. 5), would suggest that silicates  
331 are weathered by both carbonic and sulfuric acid. However, if it were assumed that all the Ca and Mg came from  
332 carbonates then the data points would also be consistent with carbonate weathering by sulfuric and carbonic acids  
333 (Figs. 6c and 6d). In summary, the data from Dryadbreen suggests that all four reactions are occurring i.e. weathering  
334 of both silicates and carbonates by both carbonic and sulfuric acid and further data from, for example,  $\delta^{13}\text{C-DIC}$  and  
335  $^{87}\text{Sr}/^{86}\text{Sr}$ , would be needed to constrain the relative proportions of the different reactions.

336 The high proportion of silicate weathering in the unglaciated catchment is likely due to the presence of the active  
337 layer (the seasonally thawed top layer of soil above permafrost). If, over a long enough period, the active layer has  
338 remained at a constant depth, this would mean that despite frost-shattering exposing fresh mineral surfaces, the vast  
339 majority of carbonate phases will have already been leached, leaving behind the silicate minerals to weather. This  
340 is in agreement with the lack of carbonate detected by XRD in the orientated clay fractions of solid samples from  
341 Fardalen (Section 4.2). However, if the active layer deepens through a warming climate then fresh carbonates could  
342 become exposed (Keller et al., 2010). In contrast, high rates of physical erosion still occur in the glaciated catchment  
343 exposing carbonates to chemical weathering.

344 The nature of the weathering reactions in the glaciated catchment is in agreement with the conclusions of Tranter  
345 et al. (2002) who identified sulfide oxidation and Fe(III) reduction as key reactions in subglacial environments. The  
346 importance of sulfide oxidation reactions is also apparent in high-latitude unglaciated, permafrost dominated catch-  
347 ments (Fig. 6). This is in contrast to low-latitude, unglaciated catchments where weathering reactions are mainly  
348 driven by reaction with  $\text{CO}_2$  either from respiration or from the atmosphere (Tranter et al., 2002).

349 Although the information in Fig. 6 provides an overview of the weathering reactions occurring in each catch-  
350 ment, further processes may modify these broad interpretations. Firstly, it is assumed that reactions have idealised  
351 stoichiometry and secondly, reactions removing solutes are not considered. The latter point is especially critical in  
352 subglacial environments where carbonate precipitation and sulfate reduction can occur (Wadham et al., 2004). Car-  
353 bonate precipitation would decrease  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , whereas sulfate reduction would decrease  $\text{SO}_4^{2-}$ . All water

354 samples were undersaturated with respect to calcite and we therefore assume that carbonate precipitation did not have  
 355 a significant impact on the stream water chemistry. In the following section we utilise the fact that the isotopes of sul-  
 356 fate ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ) are fractionated during reduction and can therefore be used to assess whether sulfate reduction  
 357 is occurring and under what conditions.

## 358 5.2. Oxic or anoxic weathering conditions?

359 Sulfate reduction only occurs under anoxic conditions and previous studies have distinguished between aerobic  
 360 and anaerobic environments based on the source of O atoms in sulfate (e.g. Bottrell and Tranter, 2002; Wadham et al.,  
 361 2004). There are two main sources of oxygen: atmospheric  $\text{O}_2$  and aqueous oxygen ( $\text{H}_2\text{O}$ ) and each has a distinct  
 362 isotopic composition.

363 During the oxidation of sulfide to sulfate the exchange of oxygen atoms in the intermediate molecules is very  
 364 rapid but once sulfate has formed then exchange is negligible (Lloyd, 1968). Previously it has been assumed that if  
 365 more than 75% of the O atoms in sulfate derive from water then the pyrite was oxidised under anoxic conditions and  
 366 less than 75% implied oxidation under oxic conditions (Taylor et al., 1984; van Everdingen and Krouse, 1985). The  
 367 fraction of O atoms in sulfate derived from atmospheric  $\text{O}_2$  or water can be calculated as follows (Balci et al., 2007):

$$\delta^{18}\text{O} * \text{SO}_4 = x(\delta^{18}\text{O}_{\text{H}_2\text{O}} + \varepsilon^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}) + (1 - x)(\delta^{18}\text{O}_{\text{O}_2} + \varepsilon^{18}\text{O}_{\text{SO}_4\text{-O}_2}) \quad (8)$$

368 where  $x$  is the fraction of O atoms derived from  $\text{H}_2\text{O}$  and  $\varepsilon$  are the fractionation factors. When this principle was  
 369 applied to glaciated catchments it was found that  $\text{FeS}_2$  oxidation in subglacial environments proceeded primarily  
 370 under anoxic conditions (Bottrell and Tranter, 2002; Wadham et al., 2004; Wynn et al., 2006; Wadham et al., 2007).  
 371 However, recent studies have questioned the utility of  $\delta^{18}\text{O}_{\text{SO}_4}$  isotopes in distinguishing between oxic and anoxic  
 372 conditions. These studies (Usher et al., 2004, 2005; Chandra and Gerson, 2011) found that even in solutions containing  
 373 dissolved  $\text{O}_2$  the vast majority of the oxygen atoms in sulfate derive from water because water outcompetes  $\text{O}_2$  for  
 374 adsorption sites. The percentage of oxygen atoms derived from water can therefore not be used to assess whether  
 375 anoxic conditions are present or not during the oxidation of sulfide.

376 The bacterial sequencing data can, however, be used to gain a rough idea of the redox status of the two catchments.  
 377 The samples from Dryadreen were collected in summer whilst those from Fardalen were collected in spring and  
 378 therefore may not be directly comparable as a result of seasonal variation in the microbial community composition  
 379 (Crump et al., 2009; Schostag et al., 2015). However, a study on seasonal variations in the microbial community  
 380 composition in soils found that the relative abundance of most phyla was constant over a year (Schostag et al., 2015).  
 381 In addition, Arctic stream microbial community compositions were found to be strongly correlated with inorganic  
 382 stream water chemistry (Crump et al., 2009) and given that there is more variation in relative ion proportions between  
 383 the catchments than between the seasons (Fig. 6), we assume limited seasonal variability in the microbial community  
 384 compositions for the purposes of this discussion.

Table 7: Abundance (%) of bacteria associated with Fe and S cycling. Sites A and O are from Dryadbreen and site L and M are from Fardalen.

Phylum/Class	Order	Genera	A	O	L	M
<i>Reduces Fe(III)</i>						
Acidobacteria	Holophagales	Geothrix	1.9	0.4	0.5	7.9
Betaproteobacteria	Burkholderiales	Albidiferax	0.6	1.1	0.2	1.3
Betaproteobacteria	Burkholderiales	Rhodiferax ferrireducens	2.9	4.1	0.4	1.3
Deltaproteobacteria	Desulfuromonadales	Geobacter	8.1	1.8	0.0	3.9
<i>Oxidizes Fe(II)</i>						
Betaproteobacteria	Feritrophicales	Feritrophicum radicicola	0.5	0.0	0.0	0.0
Betaproteobacteria	Gallionellales	Sideroxydans lithotrophicus	0.6	1.1	3.4	0.1
Betaproteobacteria	Hydrogenophilales	Thiobacillus	5.9	0.1	2.9	0.8
<i>Oxidizes reduced S compounds</i>						
Betaproteobacteria	Burkholderiales	Thiobacter subterraneus	0.0	0.1	0.8	0.0
Betaproteobacteria	Hydrogenophilales	Sulfuricella	0.9	0.0	0.8	0.4
Betaproteobacteria	Hydrogenophilales	Thiobacillus	5.9	0.1	2.9	0.8
Gammaproteobacteria	Chromatiales	Halothiobacillus neapolitanus	0.0	0.0	0.5	0.0
Gammaproteobacteria	Chromatiales	Thioalkalivibrio versutus	0.0	0.0	0.1	0.0
Gammaproteobacteria	Chromatiales	Thiocapsa machilipatnamensis	0.0	0.0	0.5	0.0
<i>Reduces sulfate</i>						
Deltaproteobacteria	Desulfobacterales	Desulfatferula	0.0	0.1	0.0	0.0
Deltaproteobacteria	Desulfobacterales	Desulfobulbus	0.0	0.0	0.0	0.1
Deltaproteobacteria	Desulfobacterales	unclassified	0.1	0.4	0.0	0.4
Firmicutes	Clostridiales	Desulfosporosinus	0.3	0.6	0.0	5.2

Some bacteria only live in anaerobic environments and therefore their presence can be used as an indication that anoxic conditions are present. In both catchments, we found evidence for both anaerobic and aerobic bacteria in the under-water sites (A and L) suggesting that anoxic micro-niches exist in the aqueous system. Sequences affiliated with *Thiobacillus*, a facultative aerobe capable of oxidizing iron and sulfur compounds was represented in both catchments (Table 7). It is likely that *Thiobacillus* is involved in the aerobic oxidation of pyrite and as a result may help establish anoxic conditions. However, the Deltaproteobacteria class of bacteria, which consists of numerous lithotrophic anaerobes (Kuever et al., 2005), was strongly represented in Dryadbreen (glaciated, Site A, 10.3%) but was nearly absent in Fardalen (unglaciated, Site L, 0.1%) (Fig. 5), suggesting that anoxic conditions may be more prevalent in the glaciated catchment and that iron reduction may be an important process. In support of this notion, a number of genera capable of reducing iron compounds were identified (Table 7). For example, 8.1% and 2.9% of the sequences from Dryadbreen (A) were closely affiliated with *Geobacter* (obligate anaerobe, Lovley, 2000) and *Rhodiferax* (facultative anaerobe, Finneran et al., 2003) respectively (Table 7). Anoxia may be more prevalent in the glaciated catchment due to the sandur, which is a large wet area covered by fine glacial flour, conditions which would favour pyrite oxidation and the development of anoxia, analogous to marine sediments (e.g. Burdige, 1993). Additionally, the sandur is underlain by ice (Ziaja and Pipała, 2007) which could be hydraulically linked to the subglacial drainage system providing a pathway for anoxic subglacial meltwater to enter the stream downstream of the apparent glacier front (Irvine-Fynn et al., 2011). In the unglaciated catchment, the aforementioned processes are not relevant. Although the deeper permafrost areas will be anoxic, they may not have a strong hydraulic connection to the stream, resulting in a stream which is dominantly oxic.

### 404 5.3. Sulfur isotope fractionation: oxidation or reduction?

405 Sulfate reduction only occurs in anaerobic environments and in low-temperature natural systems it is biologically  
 406 mediated (Seal II, 2006). During sulfate reduction both  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  values in the remaining  $\text{SO}_4$  will increase  
 407 as the light isotope is the preferred reactant. A positive correlation between  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  has therefore been  
 408 proposed as diagnostic of sulfate reduction (e.g. Mandernack et al., 2003).

409 The spring  $\delta^{34}\text{S}$  values from both catchments have similar  $\delta^{34}\text{S}$  values that are within error of one of the measured  
 410 pyrite mineral separates suggesting that no sulfate reduction has occurred (Fig. 7). The summer  $\delta^{34}\text{S}$  values from  
 411 Fardalen are about 3‰ lighter in  $\delta^{34}\text{S}$  compared to the spring points but have the same isotopic composition as one  
 412 of the measured pyrite mineral separates, again suggesting the absence of sulfate reduction. The apparent shift in the  
 413 inferred source pyrite  $\delta^{34}\text{S}$  value could be due to differences in pyrite  $\delta^{34}\text{S}$  values between the different formations  
 414 (Table 5): waters in spring could predominantly drain the Frysjaodden Formation whereas waters in summer could  
 415 access formations higher up in the catchment (e.g. Battfjellet) as the snow pack retreats. However, the summer  
 416  $\delta^{34}\text{S}$  values from Dryadbreen are heavier in  $\delta^{34}\text{S}$  compared to both measured and inferred pyrite compositions and,  
 417 additionally, there is also a significant positive correlation between  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  and  $\delta^{34}\text{S}$  ( $R^2=0.99$ ,  $p<0.001$ ,  $m=6\pm 1$ )  
 418 which is suggestive of sulfate reduction (Mandernack et al., 2003; Turchyn et al., 2013).  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  is used instead  
 419 of  $\delta^{18}\text{O}_{\text{SO}_4}$  in order to remove the effect on  $\delta^{18}\text{O}_{\text{SO}_4}$  of the temporal variation in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ . The gradient of the slope  
 420 between  $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta^{34}\text{S}$  is thought to give information on reaction pathways. Oxygen isotope variations during  
 421 reduction are thought to be controlled by a combination of intra-cellular isotope exchange between intermediate sulfur  
 422 compounds and ambient water (Brunner et al., 2005; Farquhar et al., 2008) and kinetic fractionation at the cell level  
 423 (Aharon and Fu, 2000; Mandernack et al., 2003). The balance between exchange and kinetic isotope fractionation  
 424 is dependent on the overall reaction rate. Thus, the exact slope of  $\delta^{18}\text{O}_{\text{SO}_4}$  versus  $\delta^{34}\text{S}$  depends on which microbial  
 425 species mediate the reaction and the forward and backward reaction rates (Aharon and Fu, 2000; Mandernack et al.,  
 426 2003; Kleikemper et al., 2004; Turchyn et al., 2010; Wankel et al., 2014). The slope of  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  versus  $\delta^{34}\text{S}$  from  
 427 Fig. 7 is 6 which would indicate a slow reaction rate (Brunner et al., 2005).

428 However, if significant sulfate reduction was occurring in Dryadbreen then appreciable amounts of sulfate reducing  
 429 bacteria would have been expected to be detected using molecular analysis. In the sediment sample (A), only 0.4% of  
 430 the bacteria were inferred to have the capacity to reduce sulfate. In addition, attempts to amplify the gene encoding a  
 431 fragment of the alpha and beta subunit of the bisulphate reductase (*dsrAB*, a biomarker for sulfate reduction, Wagner  
 432 et al., 1998) were not successful in any of the four sediment samples despite 40 cycles of PCR (data not shown). This  
 433 supports the notion that the observed sulfur isotope fractionation was not due to sulfate reduction.

434 It is generally assumed that negligible sulfur isotope fractionation occurs during pyrite oxidation, however frac-  
 435 tionation can occur under certain conditions. Several biotic and abiotic experiments under anoxic and oxic conditions  
 436 have observed  $\epsilon_{\text{SO}_4\text{-pyrite}}$  with values between -1.3 and +3.5‰ (Balci et al., 2007; Pisapia et al., 2007; Brunner et al.,  
 437 2008). The difference between pyrite and sulfate in the Dryadbreen summer samples is  $\Delta^{34}\text{S}_{\text{SO}_4\text{-sulfide}} = +2.2$  to  
 438 +4.8‰, depending on which value for  $\delta^{34}\text{S}_{\text{sulfide}}$  is used (Table 5). Positive values, of similar magnitude ( $\epsilon_{\text{SO}_4\text{-sulfide}}$

439 = +3.5 and +0.4) have previously been reported for the initial, non-stoichiometric stages of pyrite oxidation (Pisapia  
440 et al., 2007; Brunner et al., 2008). Non-stoichiometric reactions are expected to occur in areas of significant physical  
441 erosion e.g. glaciated catchments, as material is removed before reactions are completed (kinetic limitation, Stallard  
442 and Edmond, 1983). Positive values of  $\epsilon_{SO_4-sulfide}$  have been attributed to heightened loss of  $SO_2$  in the early stages  
443 of the reaction and the breaking of thiosulfate S-S covalent bonds (Pisapia et al., 2007; Brunner et al., 2008). De-  
444 gassing of  $SO_2$  is likely under acidic conditions, but the pH of this river is around 6.5 (Table 1), suggesting that this  
445 mechanism of fractionation is likely to be minor. Similarly, the fractionation of O isotopes in sulfate can occur when  
446 sulfite species are present, allowing oxygen isotope exchange with water, enriching sulfite, and ultimately sulfate,  
447 with  $^{18}O$  (Brunner et al., 2008). The  $\Delta^{18}O_{SO_4-water}$  values from Dryadbreen summer samples (+3.0 to +5.4‰) are  
448 in agreement with  $\epsilon^{18}O_{SO_4-water}$  data from pyrite oxidation experiments (+2.8 to +16‰, Balci et al., 2007; Pisapia  
449 et al., 2007; Brunner et al., 2008). In conclusion, sulfate enriched in both  $^{34}S$  and  $^{18}O$ , as observed in Dryadbreen,  
450 does not necessarily imply sulfate reduction and can be adequately explained as a result of non-stoichiometric reaction  
451 pathways during the oxidation of pyrite.

452 In Dryadbreen (site A) 21.7% of the bacteria (collected in summer) are inferred to be involved in Fe and S cycling  
453 reactions and 13.5% are inferred to have the ability to reduce Fe(III) e.g. *Geobacter* and *Rhodoferrax* (Table 7).  
454 Given that pyrite is likely the main source of iron in the system, the obligate anaerobic nature of *Geobacter* and  
455 the facultative anaerobic nature of *Rhodoferrax*, are suggestive of the presence and potential importance of anoxic  
456 portions of the catchment where the ‘anoxic’ pyrite oxidation pathway may occur (Eqn 4b, note that this pathway can  
457 also occur where oxygen is present e.g. Balci et al. (2007)). The pH of the water is circumneutral, likely due to the  
458 buffering capacity of calcite dissolution, and at this pH Fe can be cyclically oxidised and reduced (Moses and Herman,  
459 1991) accounting for the presence of bacteria associated with both Fe reduction and Fe oxidation. It is also possible  
460 for other compounds to act as the electron acceptor in pyrite reduction such as  $NO_3^-$  and  $MnO_2$ , and it is likely that all  
461 will be involved in pyrite oxidation to some extent if they are available in the system (e.g. Burdige and Neelson, 1986;  
462 Jørgensen et al., 2009). Indeed, an abundant component of the microbial community identified at Site A (Dryadbreen)  
463 is *Thiobacillus* (Table 7) which can couple  $FeS_2$  oxidation with  $NO_3^-$  reduction (Bosch et al., 2012). Therefore,  
464 the presence of the above-mentioned bacteria indicates that the non-stoichiometric reaction pathway, identified as  
465 being responsible for the observed change in  $\delta^{34}S$  and  $\delta^{18}O_{SO_4}$  values, most likely occurs under anoxic conditions  
466 and involves the reduction of Fe. In Fardalen (site L) the bacteria involved in Fe and S cycling are associated with  
467 oxidation of Fe and reduced S compounds, with a much lower fraction (~ 1%) inferred to be involved in Fe reduction.  
468 This corroborates the inference of pyrite oxidation under oxic conditions and isotopic fractionation of S and O in  
469 sulfate is not observed due to the complete conversion of sulfide to sulfate (Seal II, 2006).

## 470 6. Wider implications

471 The isotopic and concentration data suggest that in the unglaciated catchment, mineral dissolution occurs mainly  
472 by reaction with sulfuric acid. In the glaciated catchment the balance between sulfuric acid and carbonic acid is  
473 more even, but due to the non-stoichiometric conversion of pyrite to sulfate (loss of intermediate S compounds) as  
474 indicated by the stable isotope data, weathering by sulfuric acid may be underestimated. This indicates that sulfuric  
475 acid weathering is not only important in glaciated catchments (e.g. Wadham et al., 2010) but also in permafrost  
476 dominated catchments (Nowak and Hodson, 2015) and could therefore be a widespread phenomenon throughout the  
477 permafrost zone where shale exists (approximately 46% of the land draining into the Arctic ocean, Amiotte Suchet  
478 et al., 2003). Indeed, data from the Mackenzie river, the fourth largest Arctic river by discharge and with extensive  
479 shale and permafrost areas, demonstrates the significant contribution of sulfuric acid weathering (Calmels et al., 2007).  
480 Quantification of the contribution of sulfuric acid weathering on a global scale is necessary because, if significant,  
481 it weakens the climate-weathering negative feedback because it allows cations to be released without accompanying  
482 bicarbonate in the case of silicates and the release of bicarbonate without uptake of atmospheric CO<sub>2</sub> in the case of  
483 carbonates (Calmels et al., 2007; Li et al., 2008; Torres et al., 2014).

## 484 7. Conclusions

485 The presence of a glacier appeared to alter both the bacterial community composition and chemical weathering re-  
486 actions in a sedimentary catchment containing pyrite in Svalbard, compared to a neighbouring unglaciated catchment.  
487 The dominant anion in the unglaciated catchment was SO<sub>4</sub><sup>2-</sup> whereas in the glaciated catchment the dominant anion  
488 was HCO<sub>3</sub><sup>-</sup>. The difference in major anion composition was attributed to differences in the chemical weathering re-  
489 actions occurring in both catchments: silicate weathering by sulfuric acid in the unglaciated catchment and carbonate  
490 and silicate weathering by carbonic and sulfuric acids in the glaciated catchment. We speculate that the high erosion  
491 rates in the glaciated catchment continually expose carbonate minerals whereas carbonate has already been leached  
492 from the permafrost active layer in the unglaciated catchment.

493 Sulfide oxidation was a key process generating acidity in both catchments but this reaction appeared to occur by  
494 different mechanisms in each catchment. In the unglaciated catchment,  $\delta^{34}\text{S}$  values of stream water were identical to  
495 those measured in pyrite and, together with the bacterial community composition, this suggested that pyrite oxidation  
496 occurred under oxic conditions. A seasonal shift in the absolute  $\delta^{34}\text{S}$  value of stream water was attributed to the  
497 draining of different sedimentary formations. In the glaciated catchment, the summer  $\delta^{34}\text{S}$  values were positively  
498 correlated to  $\delta^{18}\text{O}_{\text{SO}_4}$ , suggesting sulfate reduction. However, this process is microbially mediated and a biomarker for  
499 sulfate reduction (*dsrAB* genes) was not detected in stream sediments. Instead, the bacterial composition is consistent  
500 with fractionation due to sulfide oxidation under anoxic conditions with loss of sulfur intermediates, inducing isotopic  
501 fractionation in S between sulfide and sulfate. The presence of bacteria associated with iron redox cycling suggests  
502 the involvement of Fe<sup>3+</sup> as an electron acceptor in this environment.



503 As the local environment changes due to deglaciation and permafrost thaw, the bacterial community is expected  
504 to change in response. As a result, microbial mediated reactions, such as those involving sulfur compounds, will be  
505 affected. Thus, changes in the solute composition of streams can be expected as a result of continued warming in the  
506 Arctic.

## 507 8. Acknowledgments

508 This project was funded by a Swiss National Science Foundation fellowship for prospective researchers PBEZP2-  
509 137335 and a Marie Curie Intra-European Fellowship (PIEF-GA-2012-331501) to RSH. Fieldwork was supported by  
510 an Arctic Field Grant 219165/E10 (The Research Council of Norway) to RSH. ESB acknowledges support for this  
511 work from NASA (NNA15BB02A and NNA13AA94A). We wish to thank the late Kjell Mork for generously helping  
512 with this project by loaning his hunting cabin, thereby saving us from polar bear watch every night; Samuel Faucherre  
513 and Liam Harrap for taking in food and equipment by snowmobile; Spitsbergen Travel bringing the samples back  
514 from the field and posting them on; Alix Guillot, Adrian Flynn, Marita Danielsen, Andrea Viseth, Kjetil Halvorsen  
515 and Thorstein Viseth for help and company in the field, Wiesław Ziaja for insights into the glacial history of Dryad-  
516 breen and Angus Calder for help with the pyrite mineral separation, XRD analysis and processing the XRD data for  
517 mineral abundances. We thank the four reviewers for their comments which have helped to considerably improve this  
518 manuscript.

## 519 9. References

- 520 Aharon, P., Fu, B., 2000. Microbial sulfate reduction rates and sulfur and oxygen isotope fractionations at oil and gas seeps in deepwater Gulf of  
521 Mexico. *Geochim. Cosmochim. Acta* 64, 233–246.
- 522 Amiotte Suchet, P., Probst, J. L., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil  
523 CO<sub>2</sub> uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochem. Cycles* 17, 1038.
- 524 Balci, N., Shanks III, W. C., Mayer, B., Mandernack, K. W., 2007. Oxygen and sulfur isotope systematics of sulfate produced by bacterial and  
525 abiotic oxidation of pyrite. *Geochim. Cosmochim. Acta* 71, 3796–3811.
- 526 Berner, K. E., Berner, R. A., 1996. *Global environment: Water, air and geochemical cycles*. Prentice-Hall, Upper Saddle River, N.J.
- 527 Bosch, J., Lee, K. Y., Jordan, G., Kim, K. W., Meckenstock, R. U., 2012. Anaerobic, nitrate-dependent oxidation of pyrite nanoparticles by  
528 *thiobacillus denitrificans*. *Environ. Sci. Technol.* 46, 2095–2101.
- 529 Bottrell, S. H., Tranter, M., 2002. Sulphide oxidation under partially anoxic conditions at the bed of the Haut Glacier d’Arolla, Switzerland. *Hydrol.*  
530 *Process.* 16, 2363–2368.
- 531 Boyd, E. S., Hamilton, T. L., Havig, J. R., Skidmore, M. L., Shock, E. L., 2014. Chemolithotrophic primary production in a subglacial ecosystem.  
532 *Appl. Environ. Microbiol.* 80, 6146–6153.
- 533 Boyd, E. S., Jackson, R. A., Encarnacion, G., Zahn, J. A., Beard, T., Leavitt, W. D., Pi, Y., Zhang, C. L., Pearson, A., Geesey, G. G., 2007. Geother-  
534 mal springs in yellowstone acid-sulfate-chloride-containing sulfur-respiring crenarchaea inhabiting isolation, characterization, and ecology of  
535 sulfur-respiring *Crenarchaea* inhabiting acid-sulfate-chloride-containing geothermal springs in Yellowstone National Park. *Appl. Environ. Mi-*  
536 *crobiol.* 73, 6669–6677.

- 537 Boyd, E. S., Lange, R. K., Mitchell, A. C., Havig, J. R., Hamilton, T. L., Lafrenière, M. J., Shock, E. L., Peters, J. W., Skidmore, M., 2011.  
538 Diversity, abundance, and potential activity of nitrifying and nitrate-reducing microbial assemblages in a subglacial ecosystem. *Appl. Environ.*  
539 *Microbiol.* 77, 4778–4787.
- 540 Brunner, B., Bernasconi, S. M., Kleikemper, J., Schroth, M. H., 2005. A model for oxygen and sulfur isotope fractionation in sulfate during  
541 bacterial sulfate reduction processes. *Geochim. Cosmochim. Acta* 69, 4773–4785.
- 542 Brunner, B., Yu, J. Y., Mielke, R. E., MacAskill, J. A., Madzunkov, S. and McGenity, T. J., Coleman, M., 2008. Different isotope and chemical  
543 patterns of pyrite oxidation related to lag and exponential growth phases of *Acidithiobacillus ferrooxidans* reveal a microbial growth strategy.  
544 *Earth Planet. Sci. Lett.* 270, 63–72.
- 545 Burdige, D. J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. *Earth Sci. Rev.* 35, 249–284.
- 546 Burdige, D. J., Neelson, K. H., 1986. Chemical and microbiological studies of sulfide-mediated manganese reduction. *Geomicrobiol. J.* 4, 361–387.
- 547 Calmels, D., Gaillardet, J., France-Lanord, C., 2007. Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin:  
548 Climatic perspectives. *Geology* 35, 1003–1006.
- 549 Chandra, A. P., Gerson, A. R., 2011. Pyrite (FeS<sub>2</sub>) oxidation: A sub-micron synchrotron investigation of the initial steps. *Geochim. Cosmochim.*  
550 *Acta* 75, 6239–6254.
- 551 Crump, B. C., Peterson, B. J., Raymond, P. A., Amon, R. M. W., Rinehart, A., McClelland, J. W., Holmes, R. M., 2009. Circumpolar synchrony in  
552 big river bacterioplankton. *P. Natl. Acad. Sci.* 106, 21208–21212.
- 553 Darriba, D., Taboada, G. L., Doalla, R., Posada, D., 2012. jModelTest 2: more models, new heuristics and parallel computing. *Nat. Meth.* 9, 772.
- 554 Dypvik, H., Riber, L., Burca, F., Rütger, D., Jargvoll, D., Nagy, J., Jochmann, M., 2011. The Paleocene-Eocene thermal maximum (PETM) in  
555 Svalbard - clay mineral and geochemical signals. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 302, 156–169.
- 556 Edgar, R. C., Haas, B. J., Clemente, J. C., Quince, C., Knight, R., 2011. UCHIME improves sensitivity and speed of chimera detection. *Bioinform-*  
557 *atics* 27, 2194–2200.
- 558 Elberling, B., Langdahl, B. R., 1998. Natural heavy-metal release by sulphide oxidation in the High Arctic. *Can. Geotech. J.* 35, 895–901.
- 559 Elberling, B., Michelsen, A., Schädel, C., Schuur, E. A. G., Christiansen, H. H., Berg, L., Tamstorf, M. P., Sigsgaard, C., 2013. Long-term CO<sub>2</sub>  
560 production following permafrost thaw. *Nat. Clim. Change* 3, 890–894.
- 561 Etzelmüller, B., Hagen, J. O., 2005. Glacier-permafrost interaction in Arctic and alpine mountain environments with examples from southern  
562 Norway and Svalbard. In: Harris, C., Murton, J. B. (Eds.), *Cryospheric systems: Glaciers and Permafrost*. Vol. 242 of Special Publications.  
563 Geological Society, London, pp. 11–27.
- 564 Etzelmüller, B., Ødegård, R. S., Vatne, G., Mysterud, R. S., Tønning, T., Sollid, J. L., 2000. Glacier characteristics and sediment transfer system of  
565 Longyearbreen and Larsbreen, western Spitsbergen. *Norsk Geografisk Tidsskrift* 54, 157–168.
- 566 Fairchild, I. J., Bradby, L., Sharp, M., Tison, J.-L., 1994. Hydrochemistry of carbonate terrains in alpine glacial settings. *Earth Surf. Process.*  
567 *Landforms* 19, 33–54.
- 568 Fairchild, I. J., Killawee, J. A., Hubbard, B., Dreybrodt, W., 1999. Interactions of calcareous suspended sediment with glacial meltwater: a field  
569 test of dissolution behaviour. *Chem. Geol.* 155, 243–263.
- 570 Farquhar, J., Canfield, D. E., Masterson, A., Bao, H., Johnston, D., 2008. Sulfur and oxygen isotope study of sulfate reduction in experiments with  
571 natural populations from Fællestrand, Denmark. *Geochim. Cosmochim. Acta* 72, 2805–2821.
- 572 Finneran, K. T., Johnson, C. V., Lovley, D. R., 2003. *Rhodoferrax ferrireducens* sp. nov., a psychrotolerant, facultatively anaerobic bacterium that  
573 oxidises acetate with the reduction of Fe(III). *Int. J. Syst. Evol. Microbiol.* 53, 669–673.
- 574 Foght, J., Aislabie, J., Turner, S., Brown, C. E., Ryburn, J., Saul, D. J., Lawson, W., 2004. Culturable bacteria in subglacial sediments and ice from  
575 two southern hemisphere glaciers. *Microbial Ecology* 47, 329–340.
- 576 Frey, K. E., McClelland, J. W., 2009. Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrol. Process.* 23, 169–182.
- 577 Grasby, S. E., Allen, C. C., Longazo, T. G., Lisle, J. T., Griffin, D. W., Beauchamp, B., 2003. Supraglacial sulfur springs and associated biological  
578 activity in the Canadian High Arctic - signs of life beneath the ice. *Astrobiology* 3, 583–596.
- 579 Guindon, S., Gascuel, O., 2003. A simple, fast, and accurate algorithm to estimate large phylogenies by maximum likelihood. *Syst. Biol.* 52,

- 580 696–704.
- 581 Hall, K., Thorn, C. E., Matsuoka, N., Prick, A., 2002. Weathering in cold regions: some thought and perspectives. *Prog. Phys. Geog.* 26, 577–602.
- 582 Hammer, Ø., Harper, D. A. T., Ryan, P. D., 2001. PAST: Paleontological statistics software package for education and data analysis. *Palaeontol.*  
583 *Electronica* 4, 1–9.
- 584 Havig, J. R., Raymond, J., Meyer-Dombard, D. R., Zolotova, N., Shock, E. L., 2011. Merging isotopes and community genomics in a siliceous  
585 sinter-depositing hot spring. *J. Geophys. Res.* 116, G01005.
- 586 Herron, M. M., 1988. Geochemical classification of terrigenous sands and shales from core or log data. *J. Sediment. Petrol.* 58, 820–829.
- 587 Hindshaw, R. S., Tipper, E. T., Reynolds, B. C., Lemarchand, E., Wiederhold, J. G., Magnusson, J., Bernasconi, S. M., Kretzschmar, R., Bourdon,  
588 B., 2011. Hydrological control of stream water chemistry in a glacial catchment (Damma Glacier, Switzerland). *Chem. Geol.* 285, 215–230.
- 589 Hodgkins, R., Tranter, M., Dowdeswell, J. A., 1997. Solute provenance, transport and denudation in a high arctic glacierized catchment. *Hydrol.*  
590 *Process.* 11, 1813–1832.
- 591 Hodson, A., Anesio, A. M., Tranter, M., Fountain, A., Osborn, M., Priscu, J., Laybourn-Parry, J., Sattler, B., 2008. Glacial ecosystems. *Ecol.*  
592 *Monogr.* 78, 41–67.
- 593 Holland, H. D., 1978. *The chemistry of the atmosphere and oceans.* Wiley-Interscience, New York.
- 594 Hudson, R., Fraser, J., 2005. Introduction to salt dilution gauging for streamflow measurement Part IV: The mass balance (or dry injection) method.  
595 *Streamline Watershed Management Bulletin* 9, 6–12.
- 596 Huh, Y., Edmond, J. M., 1999. The fluvial geochemistry of the rivers of Eastern Siberia: III. Tributaries of the Lena and Anabar draining the  
597 basement terrain of the Siberian Craton and the Trans-Baikal Highlands. *Geochim. Cosmochim. Acta* 63, 967–987.
- 598 Humlum, O., Instanes, A., Sollid, J. L., 2003. Permafrost in Svalbard: a review of research history, climatic background and engineering challenges.  
599 *Polar Res.* 22, 191–215.
- 600 Irvine-Fynn, T. D. L., Hodson, A. J., Moorman, B. J., Vatne, G., Hubbard, A. L., 2011. Polythermal glacier hydrology: a review. *Reviews of*  
601 *Geophysics* 49, 1–37.
- 602 Johannessen, M., Henriksen, A., 1978. Chemistry of snow meltwater: changes in concentration during melting. *Water Resour. Res.* 14, 615–619.
- 603 Jørgensen, C. J., Jacobsen, O. S., Elberling, B., Aamand, J., 2009. Microbial oxidation of pyrite coupled to nitrate reduction in anoxic groundwater  
604 sediment. *Environ. Sci. Technol.* 43, 4851–4857.
- 605 Keller, K., Blum, J. D., Kling, G. W., 2010. Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem.*  
606 *Geol.* 273, 76–81.
- 607 Kendall, C., Doctor, D. H., 2003. Stable isotope applications in hydrologic studies. In: Holland, H. D., Turekian, K. K. (Eds.), *Treatise on*  
608 *Geochemistry.* Vol. 5. Surface and groundwater, weathering, and soils. Elsevier, pp. 319–364.
- 609 Kleikemper, J., Schroth, M. H., Bernasconi, S. M., Brunner, B., Zeyer, J., 2004. Sulfur isotope fractionation during growth of sulfate-reducing  
610 bacteria on various carbon sources. *Geochim. Cosmochim. Acta* 68, 4891–4904.
- 611 Kuever, J., Rainey, F. A., Widdel, F., 2005. Class IV. Deltaproteobacteria class nov. In: Garrity, G., Brenner, D. J., Krieg, N. R., Staley, J. T. (Eds.),  
612 *Bergey's Manual® of Systematic Bacteriology.* Vol. 2: The Proteobacteria (Part C). Springer Verlag, pp. 922–1144.
- 613 Lafrenière, M. J., Sharp, M. J., 2005. A comparison of solute fluxes and sources from glacial and non-glacial catchments over contrasting melt  
614 seasons. *Hydrol. Process.* 19, 2991–3012.
- 615 Larkin, M. A., Blackshields, G., Brown, N. P., Chenna, R., McGettigan, P. A., McWilliam, H., Valentin, F., Wallace, I. M., Wilm, A., Lopez, R.,  
616 Thompson, J. D., Gibson, T. J., Higgins, D. G., 2007. Clustal W and Clustal X version 2.0. *Bioinformatics* 23, 2947–2948.
- 617 Larouche, J. R., Bowden, W. B., Giordano, R., Flinn, M. B., Crump, B. C., 2012. Microbial biogeography of arctic streams: exploring influences  
618 of lithology and habitat. *Front. Microbiol.* 3, 309.
- 619 Li, S. L., Calmels, D., Han, G., Gaillardet, J., Liu, C. Q., 2008. Sulfuric acid as an agent of carbonate weathering constrained by  $\delta^{13}\text{C}_{\text{DIC}}$ : Examples  
620 from Southwest China. *Earth Planet. Sci. Lett.* 270, 189–199.
- 621 Lloyd, R. M., 1968. Oxygen isotope behavior in the sulfate-water system. *J. Geophys. Res.* 73, 6099–6110.
- 622 Lovley, D. R., 2000. Dissimilatory Fe(III)- and Mn(IV)-reducing prokaryotes. In: Dworkin, M., Falkow, S., Rosenberg, E., Stackebrandt, E. (Eds.),

- 623 The Prokaryotes. Springer, New York.
- 624 MacLean, R., Oswood, M. W., Irons III, J. G., McDowell, W. H., 1999. The effect of permafrost on stream biogeochemistry: A case study of two  
625 streams in the Alaskan (U.S.A.) taiga. *Biogeochemistry* 47, 239–267.
- 626 Major, H., Haremo, P., Dallmann, W. K., Andresen, A., 2000. Geological map of Svalbard 1:100 000, sheet C9G Adventdalen, Temakart nr. 31.  
627 Norsk Polarinstittutt, Tromsø, Norway.
- 628 Mandernack, K. W., Krouse, H. R., Skei, J. M., 2003. A stable sulfur and oxygen isotopic investigation of sulfur cycling in an anoxic marine basin,  
629 Framvaren Fjord, Norway. *Chem. Geol.* 195, 181–200.
- 630 Meuser, J. E., Baxter, B. K., Spear, J. R., Peters, J. W., Posewitz, M. C., Boyd, E. S., 2013. Contrasting patterns of community assembly in the  
631 stratified water column of Great Salt Lake, Utah. *Microb. Ecol.* 66, 268–280.
- 632 Mitchell, A. C., Lafrenière, M. J., Skidmore, M. L., Boyd, E. S., 2013. Influence of bedrock mineral composition on microbial diversity in a  
633 subglacial environment. *Geology* 41, 855–858.
- 634 Montross, S. N., Skidmore, M., Tranter, M., Kivimäki, A. L., Parkes, R. J., 2013. A microbial driver of chemical weathering in glaciated systems.  
635 *Geology* 41, 215–218.
- 636 Moses, C. O., Herman, J. S., 1991. Pyrite oxidation at circumneutral pH. *Geochim. Cosmochim. Acta* 55, 471–482.
- 637 Nowak, A., Hodson, A., 2015. On the biogeochemical response of a glacierized High Arctic watershed to climate change: revealing patterns,  
638 processes and heterogeneity among micro-catchments. *Hydrol. Process.* 29, 1588–1603.
- 639 Pisapia, C., Chaussidon, M., Mustin, C., Humbert, B., 2007. O and S isotopic composition of dissolved and attached oxidation products of pyrite  
640 by *Acidithiobacillus ferrooxidans*: Comparison with abiotic oxidations. *Geochim. Cosmochim. Acta* 71, 2474–2490.
- 641 Pokrovsky, O. S., Viers, J., Dupré, B., Chabaux, F., Gaillardet, J., Audry, S., Prokushkin, A. S., Shirokova, L. S., Kirpotin, S. N., Lapitsky, S. A.,  
642 Shevchenko, V. P., 2012. Biogeochemistry of carbon, major and trace elements in watersheds of northern Eurasia drained to the Arctic Ocean:  
643 The change of fluxes, sources and mechanisms under the climate warming prospective. *C. R. Geosci.* 344, 663–677.
- 644 Rao, C. R., 1982. Diversity and dissimilarity coefficients: A unified approach. *Theor. Popul. Biol.* 21, 24–43.
- 645 Robinson, Z. P., Fairchild, I. J., Spiro, B., 2009. The sulphur isotope and hydrochemical characteristics of Skeiðarársandur, Iceland: identification  
646 of solute sources and implications for weathering processes. *Hydrol. Process.* 23, 2212–2224.
- 647 Schlegel, A., Lisker, F., Dörr, N., Jochmann, M., Schubert, K., Spiegel, C., 2013. Petrography and geochemistry of siliclastic rocks from the Central  
648 Tertiary Basin of Svalbard - implications for provenance, tectonic setting and climate. *Z. Dt. Ges. Geowiss.* 164, 173–186.
- 649 Schloss, P. D., Westcott, S. L., Ryabin, T., Hall, J. R., Hartmann, M., Hollister, E. B., Lesniewski, R. A., Oakley, B. B., Parks, D. H., Robinson,  
650 C. P., Sahl, J. W., Stres, B., Thallinger, G. G., Van Horn, D. J., Weber, C. F., 2009. Introducing mothur: open-source, platform-independent,  
651 community-supported software for describing and comparing microbial communities. *Appl. Environ. Microbiol.* 75, 7537–7541.
- 652 Schostag, M., Stibal, M., Jacobsen, C. S., Bælum, J., Taş, N., Elberling, B., Jansson, J. K., Semenchuk, P., Priemé, A., 2015. Distinct summer and  
653 winter bacterial communities in the active layer of Svalbard permafrost revealed by DNA- and RNA-based analyses. *Front. Microbiol.* 6, 399.
- 654 Schuur, E. A. G., Vogel, J. G., Crummer, K. G., Lee, H., Sickman, J. O., Osterkamp, T. E., 2009. The effect of permafrost thaw on old carbon  
655 release and net carbon exchange from tundra. *Nature* 459, 556–559.
- 656 Seal II, R. R., 2006. Sulfur isotope geochemistry of sulfide minerals. In: Vaughan, D. J. (Ed.), *Sulfide mineralogy and geochemistry*. Vol. 61 of  
657 *Reviews in Mineralogy and Geochemistry*. Mineralogical Society of America, pp. 633–677.
- 658 Sharp, M., Creaser, R. A., Skidmore, M., 2002. Strontium isotope composition of runoff from a glaciated carbonate terrain. *Geochim. Cosmochim.*  
659 *Acta* 66, 595–614.
- 660 Skidmore, M., Anderson, S. P., Sharp, M., Foght, J., Lanoil, B. D., 2005. Comparison of microbial community compositions of two subglacial  
661 environments reveals a possible role for microbes in chemical weathering processes. *Appl. Environ. Microb.* 71, 6986–6997.
- 662 Skidmore, M. L., Foght, J. M., Sharp, M. J., 2000. Microbial life beneath a High Arctic glacier. *Appl. Environ. Microb.* 66, 3214–3220.
- 663 Stallard, R. F., Edmond, J. M., 1983. *Geochemistry of the Amazon 2. The influence of geology and weathering environment on the dissolved load.*  
664 *J. Geophys. Res.* 88, 9671–9688.
- 665 Stumm, W., Morgan, J. J., 1996. *Aquatic Chemistry: chemical equilibria and rates in natural waters*, 3rd Edition. Wiley.

- 666 Svendsen, J. I., Mangerud, J., 1997. Holocene glacial and climatic variations on Spitsbergen, Svalbard. *Holocene* 7, 45–57.
- 667 Swofford, D. L., 2001. PAUP: Phylogenetic analysis using parsimony (and other methods). Sinauer Associate: Sunderland, MA, USA, 4.0b10 Edn.
- 668 Taylor, B. E., Wheeler, M. C., Nordstrom, D. K., 1984. Isotope composition of sulphate in acid mine drainage as measure of bacterial oxidation.  
669 *Nature* 308, 538–541.
- 670 Thorn, C. E., Darmody, R. G., Dixon, J. C., Schlyter, P., 2001. The chemical weathering regime of Kärkevagge, arctic-alpine Sweden. *Geomorphology* 41, 37–52.
- 671
- 672 Torres, M. A., West, A. J., Li, G., 2014. Sulphide oxidation and carbonate dissolution as a source of CO<sub>2</sub> over geological timescales. *Nature*.
- 673 Tranter, M., Sharp, M. J., Lamb, H. R., Brown, G. H., Hubbard, B. P., Willis, I. C., 2002. Geochemical weathering at the bed of Haut Glacier  
674 d’Arolla, Switzerland - a new model. *Hydrol. Process.* 16, 959–993.
- 675 Turczyn, A. V., Brüchert, V., Lyons, W. B., Engel, G. S., Balci, N., Schrag, D. P., Brunner, B., 2010. Kinetic oxygen isotope effects during  
676 dissimilatory sulfate reduction: A combined theoretical and experimental approach. *Geochim. Cosmochim. Acta* 74, 2011–2024.
- 677 Turczyn, A. V., Tipper, E. T., Galy, A., Lo, J. K., Bickle, M. J., 2013. Isotope evidence for secondary sulfide precipitation along the Marsyandi  
678 River, Nepal, Himalayas. *Earth Planet. Sci. Lett.* 374, 36–46.
- 679 Tye, A. M., Heaton, T. H. E., 2007. Chemical and isotopic characteristics of weathering and nitrogen release in non-glacial drainage waters on  
680 Arctic tundra. *Geochim. Cosmochim. Acta* 71, 4188–4205.
- 681 Usher, C. R., Cleveland, C. A., Strongin, D. R., Schoonen, M. A., 2004. Origin of oxygen in sulfate during pyrite oxidation with water and dissolved  
682 oxygen: an in-situ horizontal attenuated total reflectance infrared spectroscopy isotope study. *Environ. Sci. Technol.* 38, 5604–5606.
- 683 Usher, C. R., Paul, K. W., Narayansamy, J., Kubicki, J. D., Sparks, D. L., Schoonen, M. A., Strongin, D. R., 2005. Mechanistic aspects of pyrite  
684 oxidation in an oxidizing gaseous environment: an in situ HATR-IR isotope study. *Environ. Sci. Technol.* 39, 7576–7584.
- 685 van Everdingen, R. O., Krouse, R. O., 1985. Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature* 315,  
686 395–396.
- 687 Vaughan, D. G., Comiso, J. C., Allison, I., Carrasco, J., Kaser, G., Kwok, R., Mote, P., Murray, T., Paul, F., Ren, J., Rignot, E., Solomina, O.,  
688 Steffen, K., Zhang, T., 2013. Observations: Cryosphere. In: Stocker, T. F., Qin, D., Plattner, M., Tignor, M., Allen, S. K., Boschung, J., Nauels,  
689 A., Xia, Y., Bex, V., Midgley, P. M. (Eds.), *Climate change 2013: The physical science basis. Contribution of Working Group I to the fifth*  
690 *assessment report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New  
691 York, NY, USA.
- 692 Wadham, J. L., Bottrell, S. H., Tranter, M., Raiswell, R., 2004. Stable isotope evidence for microbial sulphate reduction at the bed of a polythermal  
693 high Arctic glacier. *Earth Planet. Sci. Lett.* 219, 341–355.
- 694 Wadham, J. L., Cooper, R. J., Tranter, M., Bottrell, S., 2007. Evidence for widespread anoxia in the proglacial zone of an arctic glacier. *Chem.*  
695 *Geol.* 243, 1–15.
- 696 Wadham, J. L., Tranter, M., Skidmore, M., Hodson, A. J., Prisco, J., Lyons, W. B., Sharp, M., Wynn, P., Jackson, M., 2010. Biogeochemical  
697 weathering under ice: size matters. *Global Biogeochem. Cycles* 24, GB3025.
- 698 Wagner, M., Roger, A. J., Flax, J. L., Brusseau, G. A., Stahl, D. A., 1998. Phylogeny of dissimilatory sulfite reductases supports an early origin of  
699 sulfate respiration. *J. Bacteriology* 180, 2975–2982.
- 700 Wang, Q., Garrity, G. M., Tiedje, J. M., Cole, J. R., 2007. Naïve Bayesian classifier for rapid assignment of rRNA sequences into the new bacterial  
701 taxonomy. *Appl. Environ. Microbiol.* 73, 5261–5267.
- 702 Wankel, S. D., Bradley, A. S., Eldridge, D. L., Johnston, D. T., 2014. Determination and application of the equilibrium oxygen isotope effect  
703 between water and sulfite. *Geochim. Cosmochim. Acta* 125, 694–711.
- 704 Wolff-Boenisch, D., Gabet, E. J., Burbank, D. W., Langner, H., Putkonen, J., 2009. Spatial variations in chemical weathering and CO<sub>2</sub> consumption  
705 in Nepalese High Himalayan catchments during the monsoon season. *Geochim. Cosmochim. Acta* 73, 3148–3170.
- 706 Wynn, P. M., Hodson, A., Heaton, T., 2006. Chemical and isotopic switching within the subglacial environment of a High Arctic glacier. *Biogeo-*  
707 *chemistry* 78, 173–193.
- 708 Yde, J. C., Knudsen, N. T., 2004. The importance of oxygen isotope provenance in relation to solute content of bulk meltwaters at Imersuaq Glacier,

- 709 West Greenland. *Hydrol. Process.* 18, 125–139.
- 710 Yde, J. C., Riger-Kusk, M., Christiansen, H., Knudsen, N. T., Humlum, O., 2008. Hydrochemical characteristics of bulk meltwater from an entire  
711 ablation season, Longyearbreen, Svalbard. *J. Glaciol.* 54, 259–272.
- 712 Ziaja, W., 2001. Glacial recession in Sørkappland and central Nordenskiöldbreen, Spitsbergen, Svalbard, during the 20th century. *Arct. Antarct.*  
713 *Alp. Res.* 33, 36–41.
- 714 Ziaja, W., Pipała, 2007. Glacial recession 2001-2006 and its landscape effects in the Lindströmfjellet-Håbergnuten mountain ridge, Nordenskiöld  
715 Land, Spitsbergen. *Pol. Polar Res.* 28, 237–247.

ACCEPTED MANUSCRIPT

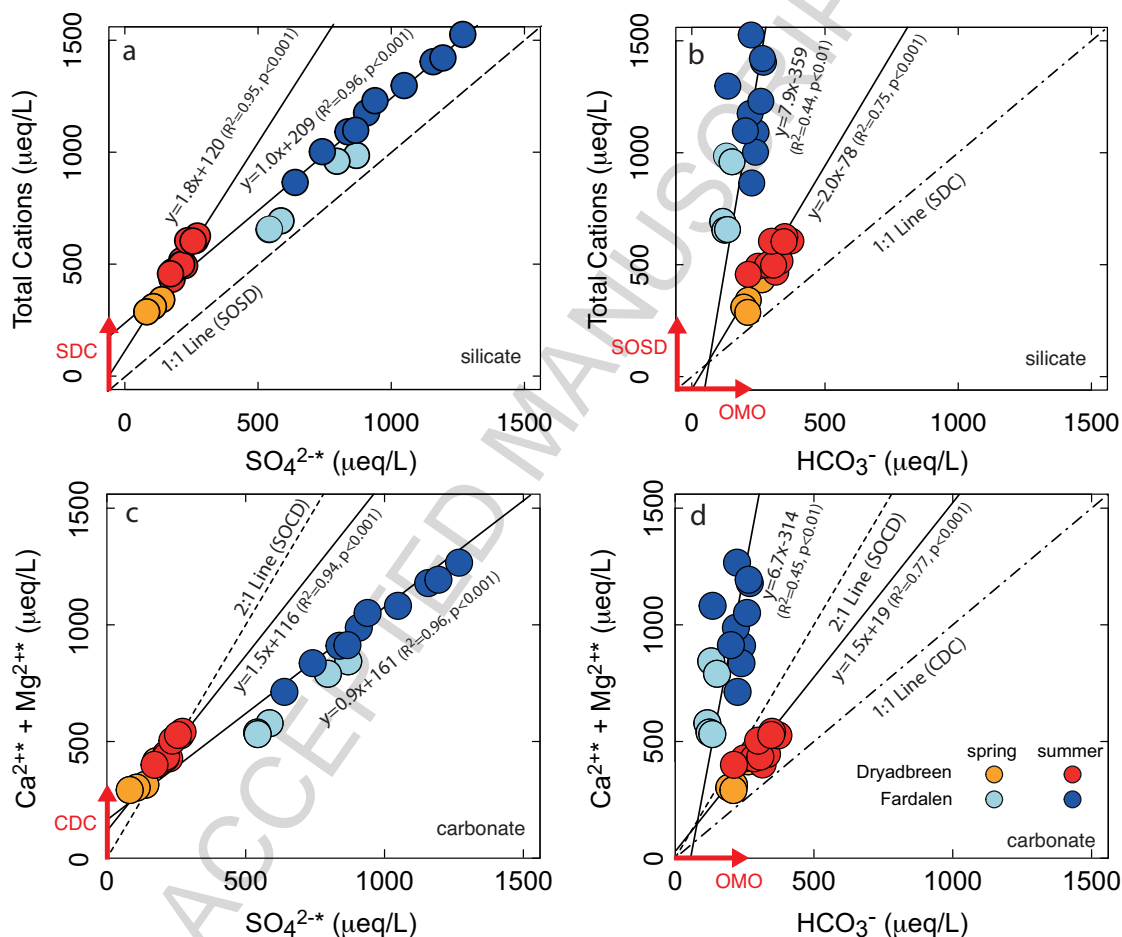


Figure 6: Plots of total cations ( $\text{Ca}+\text{Mg}+\text{Na}+\text{K}$ ) versus  $\text{SO}_4^{2-}$  (a) and  $\text{HCO}_3^-$  (b) together with  $\text{Ca}^{2+}+\text{Mg}^{2+}$  versus  $\text{SO}_4^{2-}$  (c) and  $\text{HCO}_3^-$  (d). Concentrations have been corrected for precipitation inputs apart from  $\text{HCO}_3^-$  for which the correction is negligible. Orthogonal distance regression lines (solid) for each catchment (summer and spring points combined) together with the theoretical slopes (dashed and red arrows) describing idealised reactions are shown. Figures (a) and (b) depict idealised silicate weathering reactions assuming all the cations are from silicates. The 1:1 line in (a) (long dash) arises from sulfide oxidation coupled to silicate dissolution (SOSD, Eqn. 6). The 1:1 line in (b) (dot-dash) arises from carbonation of silicate (SDC, Eqn. 5). The vertical arrows in (a) and (b) indicate SDC (Eqn. 5) and SOSD (Eqn. 6) respectively i.e. cations are produced without  $\text{SO}_4^{2-}$  (SDC, Eqn. 5) or  $\text{HCO}_3^-$  (SOSD, Eqn. 6). Figures (c) and (d) depict idealised carbonate weathering reactions assuming Ca and Mg derive from carbonate only. The 2:1 line (short dash) in both figures represents the expected slope if the only weathering reaction occurring was sulfide oxidation coupled to carbonate dissolution (SOCD, Eqn. 4). This reaction can occur aerobically (Eqn. 4a) and anaerobically (Eqn. 4b). It is not possible to distinguish between the aerobic (Eqn. 4a) or anaerobic (Eqn. 4b) reaction based on reaction stoichiometry alone (Table 6). Note that depending of the exact formula of the reactant and product Fe species (e.g.  $\text{Fe}^{3+}$  vs  $\text{Fe}(\text{OH})_3$ ), slopes in  $\text{Ca}^{2+}+\text{Mg}^{2+}$  vs  $\text{SO}_4^{2-}$  space greater than 2 are possible for the anaerobic reaction without changing the slope in  $\text{Ca}^{2+}+\text{Mg}^{2+}$  vs  $\text{HCO}_3^-$  space (Tranter et al., 2002). The 1:1 line in (c) (dot-dash) arises from carbonation of carbonate (CDC, Eqn. 3). The vertical arrow in (c) indicates CDC (Eqn. 3) i.e.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are produced without  $\text{HCO}_3^-$ . The horizontal arrows in (b) and (d) indicate the production of  $\text{HCO}_3^-$  without cation release from organic matter oxidation (Eqn. 7). Theoretical and observed slopes are summarised in Table 6. Error bars are smaller than the symbols.

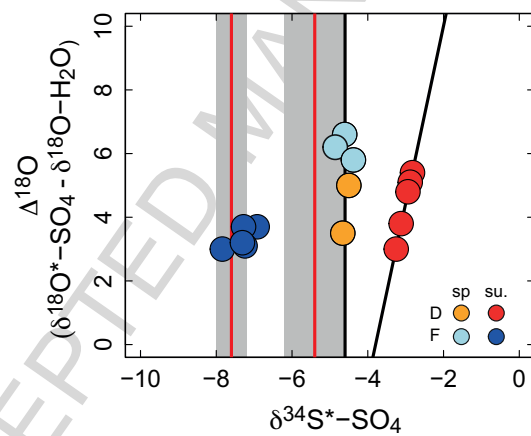


Figure 7: Plot of  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  versus  $\delta^{34}\text{S}^*_{\text{SO}_4}$ . In order to remove the effect of temporal variations in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ,  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  is used. In the key sp. is spring su. is summer, D is Dryadreen and F is Fardalen. The vertical red lines indicate the  $\delta^{34}\text{S}$  values of measured pyrite mineral separates (Table 5) and the grey shading indicates the analytical error (2 SD) on those measurements. The vertical black line is an inferred  $\delta^{34}\text{S}$  value of  $\text{SO}_4$  derived from pyrite oxidation (Fig. 3). The correlation ( $R^2=0.99$ ,  $p<0.001$ ) between  $\Delta^{18}\text{O}_{\text{SO}_4\text{-H}_2\text{O}}$  and  $\delta^{34}\text{S}$  for Dryadreen in summer (red points) suggests sulphate reduction and therefore an anoxic environment, however the magnitude of S isotope fractionation is not as great as would be expected for sulfate reduction (Seal II, 2006). Error bars are smaller than the symbols.



## Highlights

Comparison of weathering processes in a glaciated and an unglaciated catchment  
Combination of major elements,  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}\text{-SO}_4$ ,  $\delta^{18}\text{O}\text{-H}_2\text{O}$  and 16S-RNA  
Mechanism of pyrite oxidation differed between the two catchments  
No evidence for sulfate reduction

ACCEPTED MANUSCRIPT