Stable isotope evidence for microbial sulphate reduction at the bed of a polythermal high Arctic glacier

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Abstract

Glacier beds may be host to a range of microbial communities, which drive oxic waters towards anoxia along certain hydrological flowpaths. Chemical and isotopic signatures in meltwaters from Finsterwalderbreen, a polythermal glacier on sedimentary bedrock in Svalbard, show clear evidence for anoxia at the glacier bed. Increases in $\delta^{34}S$ and $\delta^{18}O$ of sulphate indicate that microbial sulphate reduction has resulted in significant decreases in sulphate concentration. The $\delta^{13}C$ of the dissolved inorganic carbon (DIC) is isotopically light ($\delta^{13}C = -8\%$), which is consistent with the use of bedrock kerogen and/or the necromass of sulphide oxidising bacteria as organic substrates for the sulphate-reducing bacteria. Calculated rates of organic carbon mineralisation correspond to $\sim 10\%$ of the total annual DIC flux of the glacial meltwaters. This microbial ecosystem is chemoautotrophically based, ultimately being sustained by the kerogen and/or bacterial necromass and sulphides in the bedrock. This work suggests that glacier beds can be refugia for life when climatic and/or atmospheric conditions are otherwise inclement and also supports the contention that microbial life is present in subglacial Lake Vostok.
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1. Introduction

Recent work has established that glacier beds, although formerly thought to be abiological [1,2], provide suitable environments for microbial activity [3,4]. This has resulted in revision of subglacial geochemical weathering mechanisms [5], since microbial activity may drive certain sectors of the bed towards or into anoxia [6]. Significant populations of sulphate-reducing bacteria have been found in subglacial meltwaters from several glaciers [4]. Although this is consistent with there being sulphate reduction in subglacial environments, no geochemical evidence or measurements of this process have been presented to date. Here we report isotopic evidence for microbial sulphate reduction at the bed of a polythermal-based high Arctic glacier. The concentration of SO_4^{2-} relative to HCO_3^-, measured by the sulphate mass fraction

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(SMF; Eq. 1), is calculated for all meltwaters and used to support inferences made on the basis of isotope data [2]:

$$SMF = \frac{SO_4^{2-}}{(SO_4^{2-} + HCO_3^-)} \quad (1)$$

High SMF values (> 0.4) are typically observed in oxic subglacial environments, where carbonate hydrolysis, carbonate dissolution and sulphide oxidation are the dominant reactions [5]. Lower values (< 0.4) may be encountered in environments where sulphide minerals are in lesser abundance, e.g. supraglacial streams, or where anoxic conditions prevail and there is sulphate reduction [7,5]. Finally, we explore possible carbon sources for the sulphate-reducing bacteria and assess whether they have the capacity to utilise bedrock organic matter (kerogen) as an energy source. If this is the case, the sulphate produced from sulphide oxidation in more oxic parts of the hydroglacial system may be reduced in the more anoxic elements, and subglacial environments may act as isolated refugia for life on timescales of $> 10^6$ yr.

2. Field Site

Finsterwalderbreen (77°28′N, 15°18′E) is located on the southern side of Van Keulenfjorden, Spitzbergen (Fig. 1A). The active glacier is ~ 35 km^2 in area, ~ 11 km in length and is polythermal [7]. The lithology is mainly sedimentary, with the upper catchment and headwalls consisting of Precambrian carbonates, phyllite and quartzite, Permian sandstones, dolomite and limestones and the rest of the catchment comprising Triassic to Cretaceous siltstones, sandstones and shales [8]. About 70% of the glacier's meltwater drains via the western margin, by a subglacial upwelling (SGU) and an ice-marginal channel (IMC) (Fig. 1B). During the year of sampling (1997), the SGU accounted for $\sim 90\%$ of drainage at the western margin. This contrasts with earlier sampling seasons (1994 and 1995) when most melt on the western margin was routed via the IMC [7]. It indicates the capture of some lower glacier melt by the SGU, which was formerly routed to the IMC. These two outflows drain contrasting hydrological
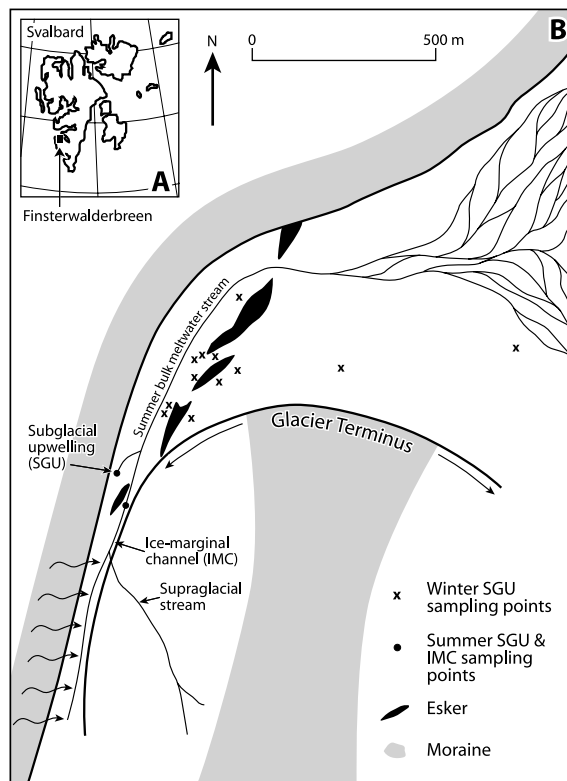

Fig. 1. (A) Map of Svalbard and field site location. (B) Sketch map of the glacier terminus and proglacial zone, denoting the location of sampling sites and meltwater streams.

environments [7]. The IMC, fed by lateral moraine porewaters and supraglacial icemelt from the lower glacier, is characterised by short residence times and is open to the atmosphere. Runoff from this outflow ceases in winter. The SGU is sourced by upper glacier snowmelt and supplemented by some icemelt from lower parts of the glacier via moulins and crevasses. It is characterised by prolonged residence times, low water:rock ratios and restricted access to the atmosphere in a subglacial environment. Melt continues to issue from the SGU during winter (< 0.5 m^3 s^{-1}), freezing to form proglacial fields of naled ice [9].

3. Methodology

Sampling was conducted during two weeks in

the summer of 1997 (2–14 July; days of year 184–195) and a short interval in late winter, 1999 (21–27 April; days of year 111–117). Meltwater samples were collected from the west IMC in summer, and from the SGU in both summer and in winter (Fig. 1B). IMC and SGU samples were collected twice daily (c. 10.00 h and 16.00 h) during summer 1997, in order to sample at approximate times of minimum and maximum flow. Stage in the IMC was also monitored at these times and is used as a proxy for IMC discharge. Winter SGU samples were collected two to four times daily from the naled ice fields, at variable distances downstream from the location of the SGU in summer. Air temperatures during winter sampling were between 0 and −5°C.

Meltwater samples were analysed for major ions and stable isotopes; $\delta^{13}C$ of dissolved inorganic carbon (DIC), $\delta^{18}O$ and $\delta^{34}S$ and $\delta^{18}O$-SO_4^{2-}. All IMC and SGU samples were vacuum filtered through 0.45 μM cellulose nitrate filters in the field. The major cations and anions were determined by ion chromatography [7,9]. Alkalinity (predominantly HCO_3) was determined by colorimetric titration in summer samples and from the negative charge deficit in winter samples [7,9].

Analysis of summer IMC and SGU meltwaters for DIC-$\delta^{13}C$ was impossible due the high turbidity of the water. DIC-$\delta^{13}C$ measurements were performed on winter SGU samples (standard = PDB), which contained trace quantities of sediment. These samples could not be filtered in the field due to air temperatures of $< 0°C$. Hence, the initial DIC-$\delta^{13}C$ of winter SGU samples included both the $\delta^{13}C$ of the DIC (precipitated as $SrCO_3$ [10]) and the $\delta^{13}C$ of the solid IC ($< 3\%$ in most cases). These initial DIC-$\delta^{13}C$ measurements have been corrected for the solid IC component by determining the $\delta^{13}C$ of the solid IC recovered from a duplicate sample filtered in the laboratory. Errors are calculated to be $< 0.4\permil$ on the DIC component. The $\delta^{18}O$ of SGU and IMC samples was determined by CO_2 equilibration [11] (standard = SMOW) and sulphate in these samples was recovered as $BaSO_4$ for analysis of $\delta^{34}S$ and $\delta^{18}O$-SO_4^{2-} [12,13] (standard = CDT and SMOW respectively). Isotopic analyses were made on a VG SIRA10 isotope ratio mass spectrometer at the University of Leeds. Raw data were corrected by standard procedures [14].

Representative rock samples (29) were collected from the proglacial moraine during the summer sampling season and analysed for their sulphide content and $\delta^{34}S$ isotopic composition [15,16]. The rock samples were also treated with phosphoric acid in vacuo to measure their IC content (by CO_2 yield) and carbonate $\delta^{13}C$. The residues were treated with 1 M HCl overnight before being analysed for their organic carbon content and $\delta^{13}C$ [17]. Organic carbon was analysed using a Carlo Erba 1106 Elemental Analyzer calibrated using pure organic compounds and a variety of commercial rock standards and corrected for weight loss on acid washing.

Table 1
Isotopic characteristics of catchment bedrock samples

Characteristic	No. of samples		Numerical mean	Mass-weighted mean
	Total	Sufficient yield for isotope analysis		
$\delta^{34}S$ sulphide (All samples)	29	12	−21.7‰ V-CDT	−20.4‰ V-CDT
$\delta^{13}C$ calcite (All samples)	29	28	+0.2‰ V-PDB	–
$\delta^{13}C$ dolomite (All samples)	4	4	−0.8‰ V-PDB	–
Kerogen content and isotope compositions			Kerogen carbon wt% (range)	Kerogen $\delta^{13}C$ Numerical mean
Shales	4	4	1.2–2.3	−25.4‰ V-PDB
Siltstones/sandstones	9	7	0.11–0.47	−22.0‰ V-PDB
Carbonates	12	8	< 0.05–0.27	−22.1‰ V-PDB

Table 2
Range of stable isotopic results shown by each group of samples

Sample type	$\delta^{13}C$ DIC (‰ V-PDB)	$\delta^{34}S$ SO$_4$ (‰ V-CDT)	$\delta^{18}O$ SO$_4$ (‰ V-SMOW)	$\delta^{18}O$ H$_2$O (‰ V-SMOW)	$\Delta^{18}O$ SO$_4$-H$_2$O (‰ V-SMOW)
IMC	–	−21.0 to −13.4	+8.4 to +23.2	−14.1 to −12.8	+21.8 to +37.3
Summer SGU	n/a	−18.3 to −5.8	+23.3 to +28.2	−15.3 to −12.9	+38.1 to +41.7
Winter SGU	−10.6 to −4.2	−8.9 to −12.0	+25.4 to +27.4	−16.0 to −13.3	+40.0 to +41.9

4. Results

A summary of all solid and aqueous isotope analyses is given in Tables 1 and 2 and Appendices A and B.

The SMF of IMC and summer/winter SGU waters is plotted against Cl$^-$ in Fig. 2A. The latter is derived entirely from snow and icemelt. Snowmelt typically has enhanced concentrations of Cl$^-$ relative to icemelt. The Cl$^-$ concentration can, therefore, be used to indicate the principle source of water in an IMC and SGU. Summer SGU and IMC samples have an SMF of ~ 0.3–0.4, while winter SGU values range from 0.35 to 0.7. The SMF of all samples increases with in-creasing Cl$^-$ concentration. The Cl$^-$ concentration of all SGU samples exceeds mean values observed in the snowpack (73 µeq l$^{-1[7]}$), whereas the IMC is relatively depleted in Cl$^-$.

The saturation of index with respect to gypsum (SI$_{Gyp}$) and calcite (SI$_{Cal}$) has been calculated for all samples using the chemical speciation pro-gramme PHREEQ [18]. Summer SGU and IMC samples were all undersaturated with respect to both minerals. Winter SGU samples were close to saturation with respect to calcite, but under-saturated with respect to gypsum (Table 3). These samples also had a partial pressure of CO$_2$ (PCO$_2$) higher than atmospheric (i.e. $> 10^{-3.5}$ atm) (Table 3).
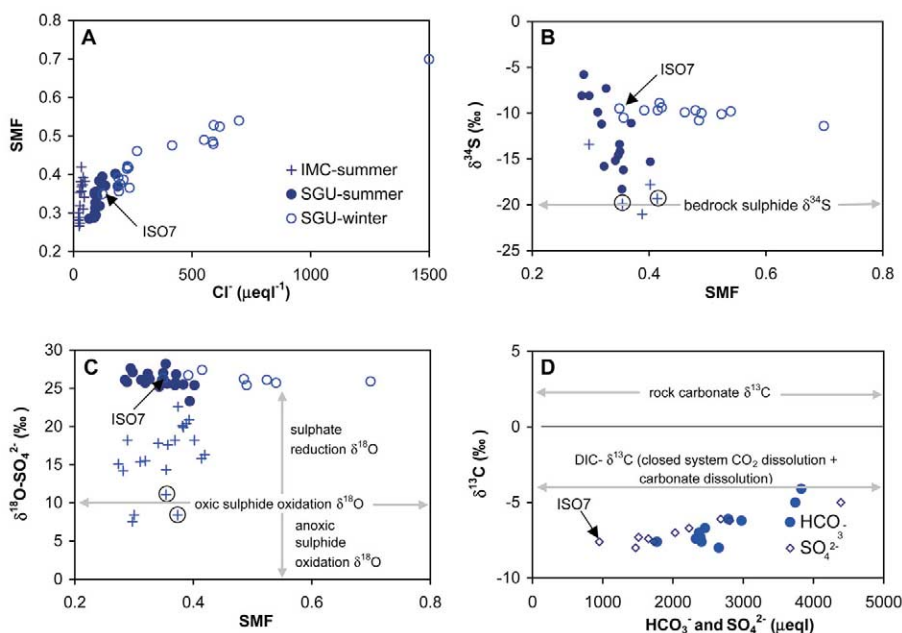

Fig. 2. Isotope and ion data for meltwater samples: (A) SMF vs Cl$^-$ concentration, (B) sulphate $\delta^{34}S$ vs SMF; (C) sulphate $\delta^{18}O$-SO$_4^{2-}$ vs SMF; (D) SO$_4^{2-}$ and HCO$_3^-$ vs $\delta^{13}C$ DIC (there are no $\delta^{13}C$-DIC data for the summer SGU or IMC samples).

Table 3
Summary statistics of the SI_{Gyp}, SI_{Ca} and PCO_2 of winter SGU samples

	SI_{Gyp}	SI_{Ca}	PCO_2
Mean	−1.8	−0.12	−3.0
S.D.	0.17	0.14	0.12
Max	0.24	−1.5	−2.7
Min	−0.36	−2.2	−3.2
n	16	16	16

Fig. 2B shows a scatter plot of $\delta^{34}S$ versus SO_4^{2-}. The IMC and summer SGU samples form a steep array, with $\delta^{34}S$ inverse to SMF. The lower end of the $\delta^{34}S$ range, containing most IMC samples, corresponds to values of typical bedrock sulphide at $\sim -20‰$ (Table 1). The winter SGU samples have a $\delta^{34}S$ similar to the more ^{34}S-enriched summer SGU samples. There is no significant variation in $\delta^{34}S$ of winter SGU samples with SMF. The consistency of winter SGU-$\delta^{34}S$ reflects the fact that these waters, and the SO_4^{2-}, derive from a single and relatively invariant source during late winter.

The $\delta^{18}O$-SO_4^{2-} in winter and summer SGU waters ranges from +25 to +27‰ (Fig. 2C). This, together with the similar $\delta^{34}S$ (Fig. 2B), confirms that the sulphate in the winter and summer

SGU has a common origin. There is considerable variation in the $\delta^{18}O$-SO_4^{2-} of IMC samples, but all values are isotopically lighter than SGU waters. A time series of IMC $\delta^{18}O$-SO_4^{2-} is plotted alongside concentrations of Cl^- and the IMC stage in Fig. 3. Two periods can be identified. Between days 184 and 187, $\delta^{18}O$-SO_4^{2-} co-varied with stage and high concentrations of Cl^- were observed. After day 187, channel stage rose and both $\delta^{18}O$-SO_4^{2-} and Cl^- decreased. Although the overall trend in the latter period was one of Cl^- and $\delta^{18}O$-SO_4^{2-} decrease, both these variables varied positively with stage on a diurnal basis. There was a significant positive relationship between $\delta^{18}O$-SO_4^{2-} and Cl^- concentration throughout the latter part of the study period, i.e. days 188–195 ($P < 0.01$).

Fig. 2D shows that winter SGU waters all have a negative $\delta^{13}C$-DIC. The $\delta^{13}C$-DIC also trends towards less negative values as the HCO_3^- and SO_4^{2-} concentrations increase.

5. Discussion

5.1. Hydrochemistry

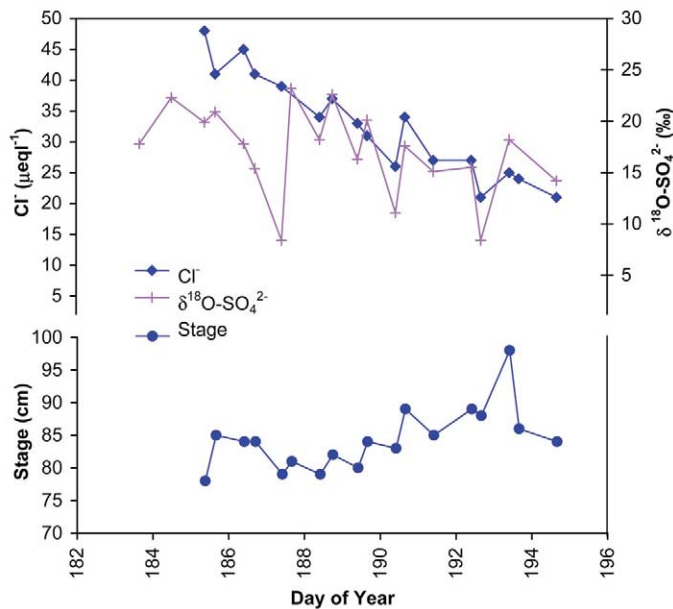Data presented in Fig. 2A confirm the existence

Fig. 3. Temporal variation in IMC stage, Cl^- and SO_4^{2-} concentration and $\delta^{18}O$-SO_4^{2-}.

of two contrasting systems draining the glacier via the IMC and SGU [7]. Relatively high Cl^- concentrations in the SGU are consistent with the partial sourcing of this outflow by concentrated snowmelt within the upper part of the catchment. An SMF of < 0.4 (Fig. 2A) and relatively high SO_4^{2-} concentrations [7] in this closed system indicate sulphide oxidation in a subglacial environment that may be also undergoing sulphate reduction [7]. During winter, carbonate and other salts are precipitated from the SGU waters as they freeze-concentrate. The frozen meltwater forms large fields of 'naled ice' or 'aufeis' in the proglacial zone of the glacier [9]. During warmer periods in winter SGU water flows through this icing and re-dissolves precipitates and entrains brine inclusions. This process accounts for the large range of solute concentrations encountered in winter SGU samples. Only one sample (ISO 7, Fig. 2C) is thought to be pristine SGU water, displaying Cl^- concentrations and an SMF in line with those of end of summer SGU water [7]. Virtually all winter SGU samples were undersaturated with respect to calcite and gypsum and hence able to acquire further solute (Table 3).

Relatively low Cl^- concentrations (< 50 μeq l^{-1}) in the IMC (Fig. 2A) confirm that this outflow is supplied predominantly by Cl^--depleted icemelt from supraglacial streams on the lower glacier [7]. The Cl^- and SO_4^{2-} present in IMC waters reflect the drainage of small volumes of solute rich porewaters, held in lateral and medial moraines [19], into the channel.

In the following discussion, we employ isotope data presented in Fig. 2C,D to identify whether or not anoxia and the associated processes of bacterial sulphate reduction and organic carbon decomposition prevail within the two contrasting hydrological systems.

5.2. Evidence for anoxic conditions within the subglacial and ice-marginal hydrological systems

Oxidation of sulphide within an oxygenated weathering environment should produce $\delta^{34}S$ values that lie close to that of sulphide in bedrock ($\sim -20\%o$, Table 1) and a $\delta^{18}O\text{-}SO_4^{2-}$ of $\sim +10\%o$, derived from a mixture of 3.5 of 4 oxygen atoms from O_2 (+23.7‰) and 0.5 from water molecules (-13 to $-16\%o$; Table 2) [20–25] (Eq. 2):

$$FeS_2 + 3.5O_2 + H_2O \Leftrightarrow 2SO_4^{2-} + 2Fe^{2+} + 2H^+ \qquad (2)$$

Just two samples (circled in Fig. 2B,C), both from the IMC, display such an isotopic signature. Relative enrichment of the majority of the remaining samples in $\delta^{18}O\text{-}SO_4^{2-}$ and $\delta^{34}S$ can only be explained by one of two processes. Either (a) there is a supply of ^{34}S- and ^{18}O-enriched sulphate to these waters, for example, from evaporites or marine-derived sulphate aerosol, or (b) anoxic conditions and associated bacterial sulphate reduction prevail to some extent in both the SGU and IMC. Most SO_4^{2-} in sampled waters is too depleted in ^{34}S and enriched in ^{18}O to have an evaporitic or marine origin (estimated $\delta^{18}O$ and $\delta^{34}S$ of evaporites for the age range of catchment rocks $= +10–+18\%o$ and $+12–+22\%o$ respectively [25]. Moreover, there are no sulphate-containing evaporites, such as gypsum, present in the catchment lithology [8]. This leads us to favour bacterial sulphate reduction in an anoxic environment as the explanation for the enrichment of ^{34}S and ^{18}O in the sulphate.

Bacterial sulphate reduction (Eq. 3) reduces the SMF, because of both the decrease in sulphate and the increase in bicarbonate concentrations. The residual sulphate is enriched in ^{34}S and ^{18}O, since the lighter ^{32}S isotope is preferentially incorporated into the H_2S reaction product and equilibration processes concentrate ^{18}O in the residual sulphate [26–28]:

$$SO_4^{2-} + 2CH_2O \Leftrightarrow H_2S + 2HCO_3^- \qquad (3)$$
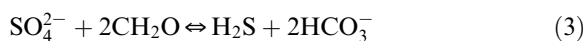
The trend of the SGU samples to less negative $\delta^{34}S$ with decreasing SMF is consistent with the removal of variable amounts of sulphate from these waters by bacterial reduction. The smaller number of IMC samples analysed for $\delta^{34}S$ means that no such trend is evident for this outflow, although these data points do align with the SGU trend.

The enrichment of all SGU and most IMC sulphate in $\delta^{18}O$ relative to sulphate produced by

sulphide oxidation under oxic (δ^{18}O $\sim 10\%$) or anoxic conditions (δ^{18}O adopts a value close to the composition of environmental water, -13 to -15% in this case [6]) is also consistent with there being sulphate reduction in the subglacial and ice-marginal drainage systems. Bacterially mediated reduction of sulphate is accompanied by isotope exchange between the water and sulphate, brought about by the formation of sulphate–enzyme complexes as intermediary reaction products [29,27]. This will ultimately lead to a constant equilibrium isotopic difference between the residual sulphate and water, which is dependent on temperature [27]. The consistency of SGU δ^{18}O-SO$_4^{2-}$ values at $+25$–27% reflects this process, and indicates that bacterial sulphate reduction in the SGU has attained isotopic equilibrium, which equates to a difference of $\sim 38.5\%$ between the water (here, ~ -13 to -15%; see Table 2) and the residual sulphate at 0°C [29].

The large variation ($\sim 15\%$) in the δ^{18}O-SO$_4^{2-}$ of IMC waters (Fig. 2C) indicates that, here, sulphate oxygen isotopes approached but did not attain equilibrium during sulphate reduction. The trend in IMC δ^{18}O-SO$_4^{2-}$ from values of $\sim +10\%$ towards the equilibrium value of $\sim +25\%$ suggests that the ICM may receive sulphate from oxic and anoxic environments in varying proportions at different stages of the sampling season. The moraine porewaters that drain into the IMC tend to be anoxic (Wadham, unpublished data). We suggest, therefore, that enrichment of IMC samples in δ^{18}O-SO$_4^{2-}$ reflects the inflow of these porewaters from moraines, where there is active bacterial sulphate reduction. The significant relationship between IMC δ^{18}O-SO$_4^{2-}$ and Cl$^-$, also present in high concentrations in moraine porewaters [19], is consistent with this hypothesis. The rising IMC stage and decrease in Cl$^-$ concentrations over the course of the sampling season reflects an increasing influx of supraglacial icemelt to the IMC as glacier surface melt rates rise (Fig. 3). The ice-cored lateral moraines would undergo progressive thaw during this period. A quasi-continuous flow of oxygenated icemelt through these sediments might explain the decrease in IMC δ^{18}O-SO$_4^{2-}$ to values of 10% over this period as sulphide oxidation takes place

under more oxic conditions. The diurnal in-phase variation of both δ^{18}O-SO$_4^{2-}$ and Cl$^-$ with stage after day 187 suggests that ice-marginal porewaters make their greatest contribution to IMC discharge at daily maximum flow (~ 16.00 h). At night, when melt rates are reduced, lower Cl$^-$ and lighter δ^{18}O-SO$_4^{2-}$ in the IMC suggest that moraine porewater inflow to the channel decreases and sulphate is acquired by oxic sulphide oxidation within the channel and medial moraines. Although not presented, there is a significant direct relationship between IMC SO$_4^{2-}$ and Cl$^-$ concentrations, which is consistent with there being increased moraine porewater influx to the IMC at high IMC stage. The explanation for the jump in IMC δ^{18}O-SO$_4^{2-}$ on day 187 is less easily explained with the given dataset, but may reflect hydrological reorganisation in the moraines and associated changes of SO$_4^{2-}$ sources following the minimum flow conditions recorded on day 187.

5.3. Quantification of sulphate reduction and organic carbon oxidation

Sulphate stable isotope compositions of the SGU and IMC show clear evidence for the activity of sulphate-reducing bacteria at the glacier bed and margins respectively. The amount of sulphate reduced in these environments can be calculated using the sulphate and isotopic composition of the summer SGU waters. Fig. 4 shows an inverse relationship between SGU SO$_4^{2-}$ concentration and δ^{34}S, that is significant ($P = 0.01$) once two outliers are removed. Some of the decrease in SO$_4^{2-}$ with increasing δ^{34}S is due to sulphate reduction and some to dilution of the subglacial water with supraglacial icemelt. Simple isotope mass balance can be used to discriminate between these two processes. The maximum change in SO$_4^{2-}$ in the SGU is ~ 162 μeq l^{-1}, assuming maximum sulphate values of 358 μeq l^{-1} (produced when δ^{34}S $= -20\%$, equivalent to the composition of bedrock sulphide) and measured minimum values of 196 μeq l^{-1} (Fig. 4). According to isotope mass balance calculations presented in Appendix C, some 98 μeq l^{-1} ($\pm 10\%$) of this must be a consequence of sulphate reduction in order to pro-
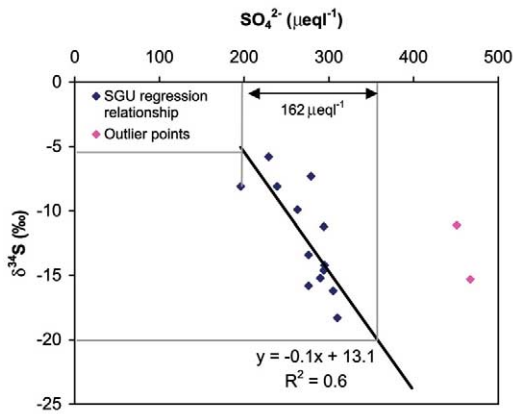
Fig. 4. Association between sulphate $\delta^{34}S$ and SO_4^{2-} concentration in summer SGU samples (the maximum change in $\delta^{34}S$ and SO_4^{2-} is denoted).

duce the associated $\sim 15\permil$ shift in $\delta^{34}S$ (Fig. 4). This equates to a reduction of ~ 6.5 µeq l^{-1} SO_4^{2-} per $\permil$ increase in $\delta^{34}S$.

It is notable that for each µeq of sulphate reduced in the subglacial environment, an equivalent amount of HCO_3^- is generated from organic carbon (Eq. 3). Thus bacterial sulphate reduction both decreases the SO_4^{2-} flux and increases the DIC flux from the glacier. These flux alterations can be quantified for the summer and winter seasons and over an annual cycle as follows.

The mean summer, winter and annual rates of sulphate reduction are derived as follows:

$$SO_4^{2-}\,RED = |(\delta^{34}S_{MEAN}^{ROCK} - \delta^{34}S_{MEAN}^{SGU})$$

$$(\partial SO_{4\,SGU}^{2-}/\partial\delta^{34}S_{SGU})(Q_{MEAN}^{SGU}t)| \qquad (4)$$

where, $SO_4^{2-}\,RED$ is the amount of SO_4^{2-} (in

µmol) reduced in summer or winter, $\delta^{34}S_{MEAN}^{ROCK}$ ($-20\permil$) and $\delta^{34}S_{MEAN}^{SGU}$ ($-12\permil$ for summer and $-10\permil$ for winter) are the mean bedrock sulphide and mean SGU $\delta^{34}S$ respectively, $(\partial SO_{4\,SGU}^{2-}/\partial\delta^{34}S_{SGU})$ is the calculated decrease in SO_4^{2-} per $\permil$ increase in $\delta^{34}S$ (6.5 µeq l^{-1} per increase in $\delta^{34}S$) and Q_{MEAN}^{SGU} is the mean discharge from the SGU (in $l\ s^{-1}$). Values of 5000 $l\ s^{-1}$ and 10 $l\ s^{-1}$ are used for Q_{MEAN}^{SGU} during summer and winter respectively [7]. The flux is integrated over time, t, equal to the approximate duration of the summer and winter seasons (in s). The summer and winter seasons run approximately from 1st June–30th September (122 days) and 1st October–31st May respectively (243 days).

The contribution of sulphate reduction to the summer, winter and annual DIC flux (Eq. 4) from the glacier bed can be calculated from the amount of SO_4^{2-} reduced, according to the stoichiometry of Eq. 3, where 1 mol of sulphate gives 2 mol of DIC. Calculated amounts of SO_4^{2-} reduced and DIC generated microbially are presented in Table 4. These amounts are also expressed as a proportion of the total DIC/SO_4^{2-} fluxes from the SGU, calculated as the product of mean winter/summer DIC/SO_4^{2-} concentrations and the winter/summer water flux. Annual rates of sulphate reduction and DIC production (in mol m^{-2} yr^{-1}) are also presented. These calculations indicate that sulphate reduction removes 14% of the sulphate generated beneath the glacier by sulphide oxidation and delivers $\sim 10\%$ of the total DIC flux from this glacier [30]. It is notable that the removal of sulphate and microbially produced DIC decreases by two to three orders of magnitude from summer

Table 4
Comparison of the quantity of SO_4^{2-} removed and DIC added by microbial sulphate reduction with total sulphate and DIC loads

	Winter load (mmol)	Summer load (mmol)	Annual load (mmol)	Annual rate (mmol m^{-2} yr^{-1})
SO_4^{2-} removed (reduction)	6.8×10^6	1.3×10^9	1.3×10^9	38
SO_4^{2-} produced (oxidation)	1.1×10^8	9.2×10^9	9.3×10^9	266
SO_4^{2-} reduced/total SO_4^{2-} (%)	6	14	14	14
Microbial DIC production	1.4×10^7	2.6×10^9	2.7×10^9	76
Total DIC production	3.7×10^8	2.6×10^{10}	2.6×10^{10}	760
Microbial DIC/total DIC (%)	4	10	10	10

Maximum errors of 20% are estimated in summer load calculations and 50% in winter load calculations.

to winter. This may indicate that the size of the active bacterial population at the glacier bed also decreases between the two seasons and that there must be a significant die off or dormancy of bacterial cells moving into the winter period. It may also indicate, however, changes in hydrological conditions between summer and winter.

5.4. Sources of carbon to sulphate-reducing bacteria

Evidence for a microbial contribution to the DIC flux is provided by the δ^{13}C-DIC of winter SGU (Fig. 2D). Potential carbon sources to the DIC in winter SGU water are dissolved atmospheric CO_2, dissolved carbonate and CO_2 from bacterial respiration. The upwelling waters are derived from flow paths with restricted access to the atmosphere, so closed system conditions are more likely to describe their chemical evolution. Under these conditions, DIC from atmospheric CO_2 dissolution will have a δ^{13}C close to the atmospheric value of $-8\permil$. Each mole of CO_2 dissolved will be capable of dissolving an equal amount of rock carbonate. We assume that the δ^{13}C of rock carbonate is $+0.2\permil$ (see Table 1), and thus the DIC in these waters will have a δ^{13}C around $-4\permil$ (Fig. 2D). This assumption is invalid for dilute solutions that arise during the initial stages of wetting carbonates, since hydrolysis produces DIC enriched in ^{12}C [41]. It is valid for more concentrated solutions, such as the SGU waters, which arise as a consequence of sulphide oxidation and carbonate dissolution, since a greater proportion of the carbonate lattice is dissolved (Skidmore et al., in preparation). Any degree of air equilibration will produce a more positive δ^{13}C-DIC than the $-4\permil$ estimate, since, isotopic fractionation produces DIC that is $\sim 11\permil$ heavier than the atmospheric CO_2 at 0°C [31]. Both carbonate hydrolysis and carbonate dissolution coupled to sulphide oxidation will produce a more positive δ^{13}C-DIC. All SGU samples are significantly depleted in δ^{13}C relative to the $-4\permil$ minimum estimate (Fig. 2D), indicating the addition of DIC from a light carbon source. This is consistent with there being microbial oxidation of organic carbon at the glacier bed.

The large range in the δ^{13}C (δ^{13}C-DIC = -4 to $-10\permil$) of SGU samples reflects the re-dissolution of calcite precipitates in the naled ice as the meltwaters flow through the proglacial zone. Only samples with a δ^{13}C of $-8\permil$ are believed to be the emergent upwelling waters, since they have concentrations of Cl^- that are similar to those in end of summer runoff (see earlier). All other samples have higher Cl^- concentrations and have undergone solute acquisition from the naled ice. The trend towards a heavier isotopic carbon composition with increasing HCO_3^- concentration suggests that the $CaCO_3$ precipitates dissolved are relatively enriched in δ^{13}C relative to the emergent SGU waters. Assuming the HCO_3^- concentration increase arises purely from $CaCO_3$ re-dissolution, the bulk isotopic composition of the salts can be estimated by isotope mass balance as follows:

$$\lfloor (HCO_{3\,Final}^-) \times DIC_{Final} - \delta C^{13} \rfloor =$$
$$[(HCO_{3\,Initial}^-) \times DIC_{Initial} - \delta C^{13}] \times$$
$$[((HCO_{3\,Final}^-) - (HCO_{3\,Initial}^-)) \times$$
$$DIC_{CaCO_3} - \delta C^{13}] \qquad (5)$$

where, $(HCO_{3\,Final}^-)$ and $(HCO_{3\,Initial}^-)$ are the concentrations of HCO_3^- in the SGU waters before and after calcite re-dissolution respectively (taken as minimum and maximum winter SGU HCO_3^- concentrations respectively; see Appendix D), $DIC_{Final} - \delta C^{13}$, $DIC_{Initial} - \delta C^{13}$ and $DIC_{CaCO_3} - \delta C^{13}$ are the δ^{13}C compositions of the DIC in the SGU water before and after re-dissolution (taken as the δ^{13}C of SGU samples with minimum and maximum HCO_3^- concentrations respectively; see Appendix D) and of the $CaCO_3$ precipitated respectively.

The solution of Eq. 5 for $DIC_{CaCO_3} - \delta C^{13}$ gives a value of $-0.5\permil$. Calculations using the chemical speciation programme PHREEQ indicate that only ~ 70 µeq l^{-1} of HCO_3^- and Ca^{2+} would be lost from SGU waters by precipitation during degassing in the proglacial zone. This compares with actual losses of ~ 2000 µeq l^{-1}, estimated by subtracting $(HCO_{3\,Final}^-)$ from $(HCO_{3\,Initial}^3)$ (Appendix D). Hence, most calcite precipitation takes place
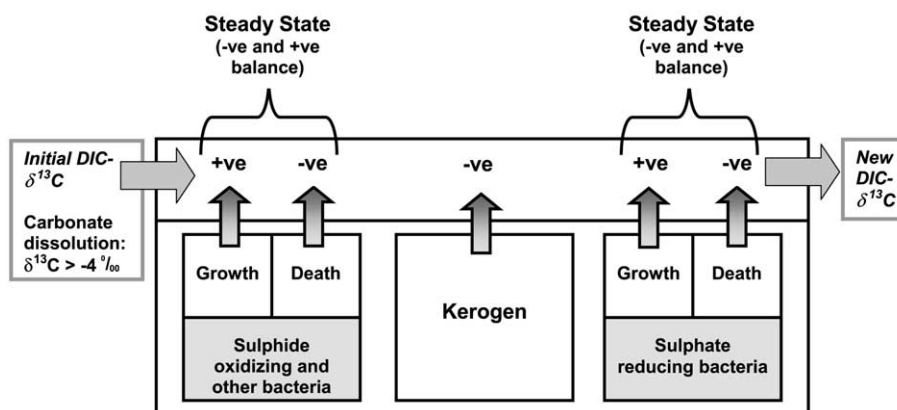
Fig. 5. Potential influences of bacterial activity at the glacier bed on SGU δ^{13}C-DIC.

following freeze concentration of these waters. If SGU waters attained and maintained equilibriation with the atmosphere during freezing, carbonate precipitated would have a δ^{13}C of +4‰ (assuming an initial air equilibrated δ^{13}C-DIC of +3‰ [31], and a 1‰ fractionation of δ^{13}C-DIC to δ^{13}C-CaCO$_3$ at 0°C [32]). Non-equilibriation with the atmosphere would produce calcite with a δ^{13}C of −7‰ (assuming an initial δ^{13}C-DIC of −8‰ and a 1‰ fractionation of δ^{13}C-DIC to δ^{13}C-CaCO$_3$ at 0°C [32]). The value of −0.5‰ falls some way between these two end member values, suggesting that precipitation of the carbonate took place within a partially air-equilibriated solution. This seems reasonable given that SGU waters tend to freeze and develop a surface ice crust soon after they leave the glacier and may only partially air equilibrate before bring closed off from the atmosphere. We note that these inferences are purely speculative since they rely on equilibrium arguments, and there is some evidence to suggest that carbonate precipitates may form under non-equilibrium conditions in micro-environments, e.g. next to gas bubbles [33].

There are two potential sources of organic carbon for the sulphate-reducing bacteria in the subglacial and ice-marginal drainage systems. One is kerogen in the catchment bedrock and moraine, which has concentrations of up to 2.3 wt% in shale (Table 1). Another is the necromass of sulphide oxidising and other bacteria. Both forms of

organic carbon are isotopically light. Kerogen in the Finsterwalderbreen bedrock has a δ^{13}C of ∼ −22 to −25‰ (Table 1). Chemoautotrophs, such as sulphide oxidisers, fix DIC as organic carbon [34]. Significant carbon isotope fractionation takes place during this process, such that the microbial mat may be ∼ 25‰ depleted in δ^{13}C relative to the DIC [35,36]. Heterotrophic bacterial activity should have no effect on the δ^{13}C of the DIC.

It is not possible to determine conclusively from the δ^{13}C-DIC of the SGU which of these two organic carbon forms is being used as the substrate for sulphate-reducing bacteria. A summary of the possible microbial influences on the winter SGU δ^{13}C-DIC is presented in Fig. 5. This illustrates that where microbial populations of sulphate reducers and other microbes are in steady state (i.e. rate of cell growth = rate of cell decay), a δ^{13}C-DIC of < −4‰ must indicate the utilisation of kerogen and/or its derivative organic compounds by sulphate reducers. For a non-steady state system where cell death > cell growth, a δ^{13}C-DIC of < −4‰ could be generated by oxidation of microbial necromass alone. The several order of magnitude decrease in rates of sulphide oxidation, sulphate reduction and organic carbon moving from summer to winter indicates that the SGU microbial population is not at steady state throughout an annual cycle. This seems reasonable given the variable water fluxes, meltwater sources and hence nutrient supplies to the subgla-

cial environment through the year that will result in periods of microbial population growth and decline. The most likely period of cell growth is in early summer when there is renewed water and nutrient supply to the subglacial system. By the mid to late summer, microbial populations should have attained steady state as the subglacial drainage system stabilises and water and nutrient supplies become more consistent. In early winter, the closure of the subglacial system off from the atmosphere and cessation of water supply to the glacier bed will result in a progressive decline in water and nutrient supply and shrinkage of the active subglacial drainage system. Die off of bacteria would be expected during this period. After 9 months of closure from the atmosphere, steady state conditions should be resumed. Winter SGU samples were collected during this latter period. If this model of conditions within the subglacial drainage system is correct, a δ^{13}C-DIC of $< -4‰$ indicates the utilisation of kerogen in bedrock as a substrate for sulphate-reducing bacteria.

6. Conclusions

These data show that elements of both the glacier bed and margins become anoxic due to microbial activity given suitable conditions, here a ready supply of sulphides and kerogen from shale and hydroglacial flowpaths that prohibit free exchange with the atmosphere. Isotopic evidence of sulphate reduction in subglacial and ice-marginal meltwaters suggests that bacteria are able to exploit these conditions of increasing anoxia. The extent of sulphate reduction is greatest at the glacier bed. These subglacial sulphate-reducing bacteria augment the annual DIC flux from the glacier by 10% and reduce the sulphate flux by 14%.

Rates of sulphide oxidation, sulphate reduction and organic carbon oxidation are considerably greater during summer than winter, implying significant die off or dormancy of bacterial populations during the winter period. Ice-marginal environments are characterised by variable conditions of anoxia and hence of sulphate reduction, controlled by the intensity of flushing by oxygenated icemelt and rainfall. It is highly probable that kerogen is being used an energy source for these sulphate-reducing bacteria, at least during periods with population steady state. The ability of subglacial microbes to utilise kerogen in a range of bedrock substrates suggests that certain glacier beds may be refugia for life given catastrophic climatic variations, for example on a Snowball Earth [37], following the catastrophic impact of large meteorites [38] and the onset of a nuclear winter [39]. The prerequisites for life in these refugia include the presence of biologically utilisable sulphides and organic carbon and/or kerogen, oxidising agents from icemelt and the persistence of subglacial water. Such conditions are found in subglacial Lake Vostok, lying at the centre of the Antarctic Ice Sheet beneath $\sim$4km of ice [40]. Hence, this work is consistent with the view that there is microbial life in Lake Vostok.

Appendix A
Stable isotopic analyses of IMC aqueous samples

IMC sample I.D.	δ^{13}C-DIC[a] (‰ V-PDB)	δ^{34}S-SO$_4$ (‰ V-CDT)	δ^{18}O-SO$_4$ (‰ V-SMOW)	δ^{18}O-H$_2$O (‰ V-SMOW)
CON2		−19.6	+17.8	−13.9
CON3			+22.3	−13.0
CON4A		−21.0	+19.9	−13.7
CON4P			+20.9	−12.7
CON5A			+17.8	
CON5P			+15.4	
CON6A		−19.3	+8.4	−13.8
CON6P			+23.2	−14.1
CON7A			+18.2	−13.5
CON7P			+22.6	−12.7
CON8A		−17.8	+16.3	
CON8P			+20.1	−19.9
CON9A			+11.1	
CON9P			+17.6	−14.1
CON10A		−13.4	+15.1	−13.2
CON10P			+15.5	
CON11A			+8.4	−13.4
CON12A			+18.2	
CON12P				
CON13A			+14.2	−12.8

} indicates a value from two pooled samples.
[a] Since δ^{13}C analyses are calculated from a difference between two samples, in many cases the uncertainty was too great to provide a reliable analysis. In such cases where the calculated error is > 0.4‰ no value is quoted.

Appendix B
Stable isotopic analyses of SGU aqueous samples

Sample I.D.	δ^{13}C-DIC[a] (‰ V-PDB)	δ^{34}S-SO$_4$ (‰ V-CDT)	δ^{18}O-SO$_4$ (‰ V-SMOW)	δ^{18}O-H$_2$O (‰ V-SMOW)
Summer SGU samples				
U2A		−11.1	+25.4	−15.2
U3P		−15.3	+25.4	−15.3
U4A			+26.8	−15.1
U4P			+23.3	−14.8
U5A			+25.7	
U5P			+25.5	
U6A		−14.6	+26.1	−14.0
U6P		−16.2	+25.6	−14.3
U7A		−13.4	+27.0	−14.7
U7P		−15.8	+26.9	−14.6
U8A		−15.2	+25.2	
U8P		−18.3	+28.2	
U9A		−11.2	+25.7	
U9P		−14.2	+26.2	−13.0
U10A		−7.3	+26.2	−13.8
U11A		−5.8	+25.8	−12.9
U11P		−8.1	+27.1	
U12A			+27.6	
U12P		−9.9	+26.1	
U13A		−8.1	+26.1	−15.0

Appendix B (*Continued*).

Sample I.D.	$\delta^{13}C$-DIC[a] (‰ V-PDB)	$\delta^{34}S$-SO$_4$ (‰ V-CDT)	$\delta^{18}O$-SO$_4$ (‰ V-SMOW)	$\delta^{18}O$-H$_2$O (‰ V-SMOW)
Winter SGU samples				
ISO 1	−7.6			−13.4
ISO 2		−10.1, −10.7	+26.1	−14.3
ISO 3	−5.1	−9.8, −10.3	+25.7	−14.8
ISO 4				
ISO 5	−10.6	−9.7, −10.4		−15.8
ISO 6		−9.7, −10.1	+26.7	−13.3
ISO 7	−8.0	−9.5, −9.9	+26.3	−13.8
ISO 8	−7.9	−8.9, −9.3		−13.6
ISO 9	−6.3	−10.0, −10.7	+25.4	−15.8
ISO 10	−4.2	−11.4, −12.0	+25.9	−16.0
ISO 11	−8.2	−10.5, −10.9		−13.3
ISO 12	−7.0			−15.2
ISO 13	−7.3	−9.9, −10.3		−13.9
ISO 14	−6.4	−10.8, −11.5	+26.2	−15.7
ISO 15	−7.7	−9.7, −10.1	+27.4	−13.7
ISO 16		−9.4, −9.8		−13.6

} indicates a value from two pooled samples.

[a] Since $\delta^{13}C$ analyses are calculated from a difference between two samples, in many cases the uncertainty was too great to provide a reliable analysis. In such cases where the calculated error is > 0.4‰ no value is quoted.

Appendix C

Isotope mass balance equations used to calculate the amount of SO_4^{2-} reduced in winter SGU waters:

$$(INITSO_4^{2-} \times INIT\delta^{34}S - SO_4^{2-}) =$$

$$(FINSO_4^{2-} \times FIN\delta^{34}S - SO_4^{2-}) +$$

$$(H_2S \times \delta^{34}S - H_2S)$$

Where $INITSO_4^{2-}$ and $INIT\delta^{34}S - SO_4^{2-}$ are the initial SO_4^{2-} concentration (= 358 µeq l^{-1}) and $\delta^{34}S$-SO$_4$ (= −20‰) in winter SGU waters, $FINSO_4^{2-}$ and $FIN\delta^{34}S - SO_4^{2-}$ are the SO_4^{2-} concentration and $\delta^{34}S$-SO$_4$ (= −5‰) in SGU waters after sulphate reduction, and H_2S and $\delta^{34}S$-H$_2S$ are the concentration and $\delta^{34}S$ (~ −60‰) of the H$_2$S produced.

Appendix D

Solution of carbon isotope mass balance (Eq. 5)

(HCO$_3^-$ Final) (µeq l^{-1})	(HCO$_3^-$ Initial) (µeq l^{-1})	DIC$_{Final}$−δC^{13} (‰)	DIC$_{Initial}$−δC^{13} (‰)
3828	1775	−4	−8

The maximum and minimum HCO$_3^-$ concentrations in winter SGU waters are used as (HCO$_3^-$ Final) and (HCO$_3^-$ Initial)

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