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Identification and analysis of low molecular weight dissolved organic carbon in subglacial basal ice ecosystems by ion chromatography

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Abstract

Glacial runoff is an important source of dissolved organic carbon (DOC) for downstream heterotrophic activity, despite the low overall DOC concentrations. This is because of the abundance of bioavailable, low molecular weight (LMW) DOC species.

- However, the provenance and character of LMW-DOC is not fully understood. We investigated the abundance and composition of DOC in subglacial environments via a molecular level DOC analysis of basal ice, which forms by water/sediment freeze-on to the glacier sole. Spectrofluorometry and a novel ion chromatographic method, which has been little utilised in glacial science for LMW-DOC determinations, were employed
- to identify and quantify the major LMW fractions (free amino acids, carbohydrates and 10 carboxylic acids) in basal ice from four glaciers, each with a different basal debris type. Basal ice from Joyce Glacier (Antarctica) was unique in that 98 % of the LMW-DOC was derived from the extremely diverse FAA pool, comprising 14 FAAs. LMW-DOC concentrations in basal ice were dependent on the bioavailability of the overridden organic car-
- bon (OC), which in turn, was influenced by the type of overridden material. Mean LMW-15 DOC concentrations in basal ice from Russell Glacier (Greenland), Finsterwalderbreen (Svalbard) and Engabreen (Norway) were low (0-417 nM C), attributed to the relatively refractory nature of the OC in the overridden paleosols and bedrock. In contrast, mean LMW-DOC concentrations were an order of magnitude higher (4430 nM C) in basal ice
- from Joyce Glacier, a reflection of the high bioavailability of the overridden lacustrine 20 material (> 17% of the sediment OC comprised extractable carbohydrates, a proxy for bioavailable OC). We find that the overridden material may act as a direct (via abiotic leaching) and indirect (via microbial cycling) source of DOC to the subglacial environment and provides a range of LMW-DOC compounds that may stimulate microbial
- activity in wet sediments in current subglacial environments. 25





1 Introduction

Glacial runoff is a major freshwater input to coastal waters worldwide, including the high-latitude oceans (Neal et al., 2010). Recent work suggests that this runoff is rich in protein-like, low molecular weight dissolved organic carbon (LMW-DOC) (Singer et al., 2012; Stubbins et al., 2012; Lawson et al., 2014a, b; Hood et al., 2015) which,

- ⁵ et al., 2012; Stubbins et al., 2012; Lawson et al., 2014a, b; Hood et al., 2015) which, when exported downstream, is rapidly utilised by proglacial and near-coastal heterotrophic communities (Bardgett et al., 2007; Fellman et al., 2010). There are at least three different sources of bioavailable dissolved organic carbon (DOC) in glacial runoff. The first source is of ancient terrestrial origin, reflecting allochthonous DOC derived
- from overridden material at the bed (Hood et al., 2009). The second is derived from anthropogenic aerosol deposition on the glacier surface (Stubbins et al., 2012), while the third is from biological activity in both supraglacial (Anesio et al., 2009) and subglacial (Bhatia et al., 2013) environments. To date, there has been only limited examination of the potential for different bedrock types and overridden organic matter, such as pa-
- ¹⁵ leosols and lacustrine material (Wadham et al., 2008; Stibal et al., 2012), to act as a source of bioavailable DOC to subglacial meltwaters and runoff, either directly (via abiotic leaching) or indirectly (via microbial cycling). Thus, further knowledge is needed to accurately assess the source of LMW-DOC in glacial runoff, to quantitatively compare contributions from the surface and the bed, e.g. (Stubbins et al., 2012), and determine the abundance and composition of potentially bioavailable LMW-DOC in basal
- ice at the base of glaciers and ice sheets.

Basal ice is a mixture of refrozen glacial meltwater and sediment entrained from beneath the glacier. It hosts viable microbial communities that may play a significant role in the organic carbon (OC) turnover in glaciated regions (Sharp et al., 1999; Skidmore et al., 2000; Foght et al., 2004). OC cycling in the subglacial environment can be investigated by incubation experiments that monitor DOC decline and/or biogenic gas (CO₂ and CH₄) production (Montross et al., 2012; Stibal et al., 2012) and provide a direct measure of bioavailability. Analysis of marker compounds in the DOC, such as free





amino acids (Pautler et al., 2011), may provide an indirect assessment of bioavailability. These analyses may be complimented by fluorescence spectroscopy, where fluorescing components (fluorophores) are identified and associated with particular DOC compounds, e.g. protein-like and humic-like components. The protein-like compounds are more easily utilized by aquatic heterotrophs when compared with the more aromatic humic-like components (Fellman et al., 2008) and are indicative of recent microbial activity (Barker et al., 2006, 2010). More recently, glacial DOC has been characterised at the molecular level by electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS) (Grannas et al., 2006; Bhatia et al., 2010;
Lawson et al., 2014b), and by solution-state ¹H nuclear magnetic resonance (NMR) spectroscopy (Pautler et al., 2011, 2012). Both methods have provided unprecedented high resolution mass spectral information on DOC, but are not fully quantitative. Ion chromatography has been used to quantify a much smaller range of common LMW-

DOC compounds, including carboxylic acids in ice cores and snow from Greenland,
 ¹⁵ Antarctica, and alpine glaciers (Saigne et al., 1987; Maupetit and Delmas, 1994; Tison et al., 1998). These LMW-DOC compounds typically represent small fractions of the bulk DOC (Borch and Kirchmann, 1997), yet are believed to be highly bioavailable to microorganisms owing to their rapid turnover and uptake rates (Rich et al., 1997; Skoog and Benner, 1997). Ion chromatography has yet to be widely employed to

determine the molecular structure of glacial LMW-DOC due to the trace analyte concentrations. Recent advances in ion chromatography instrumentation and system optimisation (e.g. greater column sensitivities, low flow rates, multiple eluents and gradient elution) enabled this study to identify and quantify numerous LMW-DOC compounds at low (< 70 nMC) concentrations, and demonstrates a novel methodological approach to glacial LMW-DOC analysis.

Here, we investigate the abundance and composition of LMW-DOC compounds (free amino acids, carbohydrates and carboxylic acids) in debris-rich basal ice. We investigate four different glaciers with distinct temperature regimes, overridden substrates, and hence, contrasting sources of allochthonous organic matter. These glaciers were



Joyce Glacier (Antarctica – lacustrine organic matter), Russell Glacier (Greenland Ice Sheet, GrIS – paleosols), Finsterwalderbreen (Svalbard – bedrock with high OC), and Engabreen (Norway – bedrock with low OC). We investigate whether LMW-DOC abundance in basal ice is influenced by the magnitude and bioreactivity of the OC in the overridden material.

2 Sample sites and basal ice sample collection

2.1 Joyce Glacier, Antarctica

Joyce Glacier (67°06′ S, 50°09′ W, 90 km²) is situated in the Garwood Valley, Antarctica (Elberling et al., 2006). A large proglacial lake, dammed by an ice sheet grounded in the McMurdo Sound > 23 000 ¹⁴C yr BP (Péwé, 1960; Hendy, 2000), is thought to have previously occupied the valley (Hendy, 2000). Joyce Glacier is cold-based, meaning that it is completely frozen to the underlying substrate. The bedrock lithology includes dolomite, granite and metamorphic rocks. Joyce Glacier recently advanced over lake sediment (Stuiver et al., 1981) and hence, the basal material is thought to contain labile OC and algal-derived organic matter of Holocene age.

2.2 Russell Glacier, GrIS

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Russell Glacier ($67^{\circ}03'$ N, $50^{\circ}10'$ W, > 600 km²), situated on the southwest margin of the GrIS, is polythermal-based. Warm ice, with a temperature at the pressure melting point, in the interior is surrounded by a frozen layer beneath the thinner ice of the margins. Surface melting delivers supraglacial meltwaters to the subglacial system from the onset of the spring thaw. The bedrock is predominantly Achaean gneiss (Knight

et al., 2002). Basal debris contains overridden Quaternary deposits (including paleosols) and relatively fresh organic matter (Knight et al., 2002) which was buried during the Holocene (Simpson et al., 2009).





2.3 Finsterwalderbreen, Svalbard

Finsterwalderbreen $(77^{\circ}28' \text{ N}, 15^{\circ}18' \text{ E}, 44 \text{ km}^2)$ is located on the southern side of Van Keulenfjorden, south Svalbard, and is polythermal-based. The glacier is currently retreating at a rate of $10-45 \text{ ma}^{-1}$ (Wadham et al., 2007). The bedrock consists of

⁵ Precambrian carbonates, sandstones, limestones and shales (Dallmann et al., 1990). Shales exposed to water may provide a steady source of DOC (Schillawski and Petsch, 2008). The shale beneath Finsterwalderbreen contains up to 2.3 % OC (Wadham et al., 2004).

2.4 Engabreen, Norway

Engabreen (66°41′ N, 13°46′ E, 40 km²) is warm-based and part of the western Svartisen ice cap, northern Norway. Engabreen bedrock consists mostly of schist and gneiss, with calcite filled cracks (Jansson et al., 1996), and contains relatively little OC. A combination of in-washed material from the glacier surface and overridden soils of Holocene age may be the principal OC sources (Stibal et al., 2012).

15 2.5 Sample collection

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Joyce Glacier basal ice samples were collected in the austral summer of 2010 from recently exposed, upthrust bands of frozen lacustrine sediment. Basal ice samples from Engabreen were collected in autumn 2009 from an underground tunnel system excavated through bedrock beneath 210 m of sliding ice (Cohen, 2000). Basal ice blocks from the Russell Glacier terminus were collected in spring 2008. Finsterwalderbreen was sampled in autumn 2008. Basal ice blocks were collected from the glacier terminus (referred to as basal ice, BI) and from surface outcrops of frozen subglacial material







to the very different mean debris concentrations (by weight); $86\pm6\%$ and $20\pm27\%$ for PR and BI, respectively.

Basal ice blocks (~ 40 cm³) were collected by chain-sawing. The outermost ~ 0.5 m of the ice surface was removed before the blocks were cut. The blocks were wrapped
⁵ in pre-combusted foil and stored at ≤ -20 °C, before being transported frozen to the University of Bristol and subsequently stored at ≤ -20 °C. We focus this study on "dirty basal ice" (hereafter referred to as basal ice) containing > 20 % sediment (by weight).

3 Methodology

3.1 Basal icemelt and sediment sample preparation

- Subsamples of the basal ice were prepared for analysis by chipping ~ 15 cm² chunks from the main block using a flame sterilised chisel. The outer ~ 10–30 mm of the chips was removed by rinsing with ultrapure (≥ 18.2 MΩ cm) deionized water (DI) (Millipore), and the remaining ice was transferred into a pre-combusted glass beaker covered with foil. The ice was allowed to melt inside a laminar flow cabinet (Telstar Mini-H) under ambient laboratory conditions, which allowed any sediment to settle out of suspension. The icemelt was then decanted into smaller pre-combusted beakers. Icemelt was filtered through Whatman polypropylene Puradisc™ 0.45 µm syringe filters. Water samples for subsequent OC analysis were stored in clean pre-combusted borosilicate glass bottles (thrice rinsed with the sample before storage) and those for major ion determinations were stored in clean, thrice-rinsed Nalgene bottles. Melting and filtration of
- 20 hattons were stored in clean, tince-finsed wagene bottles. Melting and hitration of snow, to be used to correct for the snowpack contribution to the basal ice major ion concentrations, followed the same protocol as described for basal ice. Five samples of filtered icemelt were taken from the ~ 15 cm² chunks cut out of the Joyce Glacier basal ice block, the Finsterwalderbreen BI ice block, and the Finsterwalderbreen PR ice block. Slightly larger volumes of icemelt permitted six samples of filtered icemelt to
- be collected from the Engabreen basal ice chunk, and seven from the Russell Glacier





chunk. DI procedural blanks were subject to identical processing as the samples from the filtration stage onwards to monitor for possible contamination during processing and storage. Sample concentrations were subsequently blank corrected (see Sect. 3.3.4).

Sub-samples from each ice block were also collected for free carboxylic acid (FCA)
determination. Ice was melted in an inert gas (O₂-free-N₂, OFN) atmosphere to limit potential contamination during the melting process (Saigne et al., 1987). The OFN gas first travelled through a hydrocarbon trap (HT200-4, Agilent) to remove any volatile OC compounds. Icemelt was filtered through Whatman polypropylene Puradisc[™] 0.45 µm syringe filters into 1.5 mL vials with PTFE caps (Chromacol). Samples were analysed
within 24 h of melting to minimise losses due to the volatile nature of the FCA compounds. Procedural blanks were collected in concert.

The subglacial sediment OC content was derived from analysis of the settled particles, which were transferred from the beakers with clean, ethanol-rinsed metal spatulas and stored in sterile 0.5 L Whirl-pak bags (Nasco). Every effort was made to collect as

- ¹⁵ much of the finer sediment as possible from the bottom and sides of the beakers. However, some fine sediment may have remained in the beaker and were thus excluded from the OC determinations. We were also unable to collect the fine particles that remained in suspension owing to the use of syringe filters to filter the icemelt. The total mass of this finer sediment was small compared to the mass of the settled
- sediment; therefore OC determinations were not unduly compromised. Sediment and filtered samples were stored in the dark at ≤ -20 °C until analytical processing.

3.1.1 Basal ice debris concentration

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Basal ice debris concentrations (% by weight) were determined by mass subtraction. First, the melted basal ice samples (sediment + icemelt) were weighed and the sediment extracted according to the procedure described above. The sediment was dried in a hot air oven (105 °C) for a minimum of 12 h and weighed. The basal ice debris concentration was expressed as a percentage on a weight (of sediment) to weight (total weight of ice and sediment) basis.



3.2 Basal sediment analysis

3.2.1 Elemental analysis

The subglacial sediments were first dried in a hot air oven (105 $^{\circ}$ C, 12 h) and then manually homogenized by grinding. Total carbon (TC) was measured on an EA1108

⁵ Elemental Analyser (EuroVector). Inorganic carbon (InC) was determined by a modified Coulomat 702 Analyser (Strohlein Instruments). Total OC was calculated as the difference between TC and InC. The precision of determinations was < 5%. Samples were calibrated using external reference standards at a detection limit of 0.1 mg g⁻¹ (or 0.01%).

10 3.2.2 Carbohydrate sediment extractions

Previous studies have estimated sediment OC bioavailability based on the concentration of extractable carbohydrates (Biersmith and Benner, 1998; Pusceddu et al., 2009). We employed this method to provide a conservative estimate and acknowledge that this is not a comprehensive assessment of bioavailable OC in the subglacial
¹⁵ material, as other compounds, such as enzymatically hydrolysable amino acids, were not quantified. Operationally-defined minimum estimates of extractable carbohydrate concentrations in basal sediment were quantified by ion chromatography following an acid-extraction protocol to convert any polysaccharides and sugar derivatives to lower molecular weight components (Jensen et al., 2005). We followed the protocol described

in (Stibal et al., 2010) and conducted each extraction procedure in triplicate. Monosaccharide losses occurred during hydrolysis, including the total loss of fructose, and were not compensated for (Borch and Kirchmann, 1997; Jensen et al., 2005). This methodological limitation means that some of the variability between samples will be due to procedural effects, rather than a true disparity between sediment carbohydrate con centrations.





3.2.3 Cell counts

Cell counts were conducted to quantify the microbial abundance in basal sediment and determine whether there is potential for subglacial microbial activity. We followed the protocol described in (Stibal et al., 2012). For Joyce Glacier samples, the method followed that of Porter and Feig (1980) (detailed in the Supplement).

3.3 Analysis of basal icemelt

3.3.1 Bulk DOC

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DOC was determined by high temperature combustion (680 °C) using a Shimadzu TOC-V_{CSN}/TNM-1 Analyzer equipped with a high sensitivity catalyst. Precision and accuracy of standard solutions (5–170 μ MC) of potassium hydrogen phthalate (C₈H₅KO₄) (Merck) were < ±6 %, and the limit of detection (LOD) was 5 μ MC.

3.3.2 Fluorescence spectroscopy

Fluorescence spectra were determined on a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer equipped with excitation and emission monochromators, a Xenon lamp
 (excitation source) and FluorEssence software. Synchronous scans were performed at 1 nm increments with a 0.1 s integration period, 10 nm bandwidth and an 18 nm offset between excitation and emission monochromators (Barker et al., 2006). The accuracy of the monochromators was ±0.5 nm. Synchronous scans of DI were run under identical scanning conditions and subtracted from all sample spectra to correct for Raman

scattering. All scans were dark corrected and internally corrected for inner filter effects and variations in lamp performance. Post-scan data correction followed the protocol described by (Barker et al., 2006). Fluorophore recognition was based on values reported in the literature (Miano and Senesi, 1992; Ferrari and Mingazzini, 1995; Coble, 1996; Yamashita and Tanoue, 2003) and all spectra were normalized to the sample fluorescence peak spectral maximum.





3.3.3 OC compound determination by ion chromatography

Free amino acid (FAA), carbohydrate (FCHO) and carboxylic acid (FCA) determinations were performed by an ICS-3000 dual-analysis reagent-free ion chromatography system, employing electrolytic NaOH eluent generation (Dionex[™], part of Thermo

- ⁵ Fisher Scientific). Precision and accuracy were monitored by periodically running certified external standards (Dionex[™]), and internal standards during each sample run, at concentrations within the range of sample concentrations (10–2000 nMC). The limit of quantification (LOQ) was defined as the concentration of the lowest standard that could be significantly differentiated from the next highest.
- FAA: were separated via gradient anion exchange on an AminoPac PA10 column (2 mm × 250 mm) after passing through an AminoPac PA10 guard column (2 mm × 50 mm). Pulsed electrochemical detection with an Au electrode was employed. A gradient mix of 0.25 M NaOH, 1.0 M Na-acetate (NaOAC) and DI was used to elute 14 FAAs (lysine, alanine, threonine, glycine, valine, serine/proline, isoleucine, leucine, methio-
- ¹⁵ nine, phenylalanine, cysteine, aspartic acid, glutamic acid and tyrosine) at a flow rate of 0.25 mLmin⁻¹. Serine and proline were reported together due to co-elution. Precision was typically c. ±5% for lysine, alanine, threonine, glycine, valine, serine/proline, isoleucine, leucine, methionine, and cysteine, and c. ±10% for phenylalanine, aspartic acid, glutamic acid and tyrosine. Accuracy was < ±7% for all analytes (certified exter-
 ²⁰ nal standard, Fluka Analytical). The LOQ ranged from 10–60 nMC.

FCHO: fucose, rhamnose, arabinose, galactose, glucose, xylose/mannose, fructose/sucrose, ribose and lactose were separated isocratically at a flow rate of 0.35 mLmin⁻¹ on a CarboPac PA20 column (3mm × 150 mm) after passing through a CarboPac PA20 guard column (3mm × 30 mm). Xylose and mannose, and fructose and sucrose, were reported together due to co-elution. Precision for fucose, rhamnose, arabinose, glucose and xylose/mannose was generally c. ±5%, and c. ±10% for galactose, fructose/sucrose, ribose and lactose. Accuracy of a certified external standard (Dionex[™]) was < ±7% for all analytes. The LOQ ranged from 10–80 nMC.





FCA: acetate, formate, propionate and butyrate were separated via gradient anion exchange on an IonPac Hydroxide-Selective Anion Exchange AS11-HC column (2mm × 250 mm) with an AS11-HC guard column (2mm × 50 mm) and Anion Self-Regenerating Suppressor (ASRS). Electrolytic eluent generation was employed to al Iow analyte separation along a NaOH gradient during the 30 min run at a flow rate of 0.5 mL min⁻¹. Precision and accuracy of the four FCAs in a certified reference standard (Supelco Analytics) was 5–8% (precision) and 3–4% (accuracy). The LOQ ranged from 90–130 nMC.

3.3.4 Blank corrections

¹⁰ Preparation of DI blanks is described in Sect. 3.1. Blank corrections were not required for Cl⁻ and FAAs due to the negligible blank concentrations. Minimal corrections were required for all major ions ($\leq 0.3 \,\mu \, \text{eq} \, \text{L}^{-1}$) and FCHOs (1.3 nMC), but larger corrections were required for DOC (5.85 μ MC) and FCAs (23.06 nMC).

4 Results

15 4.1 Basal sediment characteristics

Basal ice debris concentrations (by weight) differed between glaciers. Finsterwalderbreen pressure ridge (FPR) and Russell Glacier basal ice contained the highest concentration of debris (86 ± 7 and 55 ± 25 %, Table 1), which are similar to percentages in GrIS banded ice (46-57 %), solid ice (61 %) (Yde et al., 2010) and debris bands (71 %)

- ²⁰ (Sugden et al., 1987). Debris concentrations in basal ice from Engabreen $(37 \pm 21\%)$, Joyce Glacier $(21 \pm 6\%)$, and Finsterwalderbreen basal ice (FBI) $(20 \pm 27\%)$ were lower than percentages in GrIS and FPR ice. The sediment OC content was low (< 0.6%) in all basal ice samples (Table 2). Minor fractions of extractable carbohydrate (< 0.5% of the sediment OC) were measured in Engabreen, Russell Glacier and Finsterwalder-
- $_{25}$ breen sediments. A higher carbohydrate fraction (17 % of the sediment OC) was mea-









sured at Joyce Glacier (Table 2). Microbial cell abundance was comparable in all samples $(1-7 \times 10^5 \text{ cells g}^{-1}, \text{ Table 2})$.

4.2 Subglacial DOC quantity and complexity

DOC abundance and composition varied between the four glaciers. The highest mean DOC concentrations were observed in basal ice from Joyce Glacier $(272 \pm 99 \,\mu\text{MC})$ and Engabreen $(114\pm106\,\mu\text{MC})$, with lower concentrations in Russell Glacier basal ice $(53\pm29\,\mu\text{MC})$, FBI $(15\pm10\,\mu\text{MC})$ and FPR $(33\pm33\,\mu\text{MC})$ (Table 1). The relatively large standard deviations show that subglacial DOC concentrations are highly variable, even in basal ice from the same glacier. Between 5 and 7 replicate samples were taken from each of the ~ $15 \,\text{cm}^2$ chunks cut out of the main ice blocks from each glacier (detailed in Sect. 3.1). The variability in the DOC concentrations suggests that there is significant spatial heterogeneity even at the level of the ~ $15 \,\text{cm}^2$ basal ice chunks analysed from each glacier.

The composition of the subglacial DOC was investigated by spectrofluorescence and
 ion chromatography. The synchronous fluorescence spectra of all basal ice samples illustrated the dominance of three key fluorophores of a marine humic-like/fulvic acid type, at c. 340, 385 and 440 nm (Fig. 1, Table 3), and several unresolved fluorophores at longer excitation wavelengths. Protein-like peaks (~ 279 nm), indicative of tyrosine-like compounds (Ferrari and Mingazzini, 1995; Yamashita and Tanoue, 2003), were only
 evident in Joyce Glacier and FPR basal ice (Table 3). Ion chromatographic analyses provided a greater level of detail on the molecular composition of the DOC. LMW-DOC compounds, with concentrations > LOQ, accounted for < 3% of the DOC in all basal ice samples. Mean LMW-DOC concentrations in Engabreen, Finsterwalderbreen and Russell Glacier basal ice were < 420 nMC (Table 1). Mean LMW-DOC concentrations

concentrations, the variability in the LMW-DOC compound concentrations suggests high spatial heterogeneity within the basal ice.

LMW-DOC was typically dominated by FCAs (Table 1), except in Joyce Glacier samples which are subsequently discussed. Overall, acetate was the most common analyte (Fig. 2), being present in 60 % of the samples that contained FCAs at concentrations > LOQ. Basal ice FCHO concentrations were typically < LOQ (< 4 % of the LMW-DOC, Table 1) and only detected in Joyce Glacier samples, comprising glucose (16–49 nMC) and ribose (16–19 nMC, data not shown). Joyce Glacier basal ice DOC was unique in that most (98 %) of the LMW-DOC was derived from the extremely diverse FAA pool (Fig. 3). Mean FAA concentration in Joyce Glacier basal ice (4353 ± 2643 nMC) was an order of magnitude higher than mean FAA concentrations in Engabreen, Finsterwalderbreen and Russell Glacier basal ice (0–51 nMC, Table 1). Some 14 FAAs were detected in Joyce Glacier basal ice, including methionine, glutamic acid, aspartic acid and cysteine, which were not observed in the other basal ice sam-

acid, aspartic acid and cysteine, which were not observed in the other basal ice samples. Serine/proline, alanine and valine dominated the Joyce Glacier FAA pool. FAAs accounted for 59% of the LMW-DOC in Russell Glacier basal and FPR ice, primarily in the form of alanine and valine, respectively.

4.3 Debris concentrations

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We investigated the relationships between DOC (and LMW-DOC) and debris concentrations. We hypothesize that if the DOC was largely terrestrially derived and leached from sediments, there should also be a positive correlation between DOC and the debris content of the basal ice. Significant positive associations between debris concentration and DOC were only evident in Joyce Glacier ($R^2 = 0.71$, p = 0.05) and Russell Glacier ($R^2 = 0.72$, p = 0.05) basal ice (Fig. 4a). No significant associations between LMW-DOC and debris concentrations were observed (Fig. 4b, $R^2 < 0.1$, p = 0.05).



5 Discussion

The application of a novel methodological approach (within the field of glacial science) using ion chromatography has allowed the identification and quantification of a range of LMW-DOC compounds in debris-rich basal ice, including FCAs, FCHOs and FAAs, at

⁵ unprecedented low concentrations (< 70 nMC). This represents one of the first studies to quantify LMW-DOC in basal ice from a range of glaciers and ice sheets. We demonstrate that ion chromatographic systems that have been optimised for the detection of trace level LMW-DOC concentrations, e.g. by using multiple eluents, low flow rates and gradient elution, can be utilised as an additional quantitative technique to supplement
 ¹⁰ characterisations of glacial LMW-DOC by ESI FT-ICR MS (Grannas et al., 2006; Bhatia et al., 2010; Lawson et al., 2014b) and solution-state ¹H NMR spectroscopy (Pautler et al., 2011, 2012).

5.1 The influence of debris type on sediment OC and basal ice DOC concentrations

- ¹⁵ We find little evidence that the type of overridden material and the mean sediment OC content has a significant influence on the DOC content in basal ice. Indeed, the mean basal ice DOC concentrations (< 280 µMC) and mean sediment OC content (< 0.6%) were comparable in all basal ice samples despite the differences in the types of overridden material. Furthermore, the fact that the highest mean DOC concentration was</p>
- observed in Joyce Glacier basal ice (272 μMC) yet the corresponding sediment OC % was the lowest (0.01 %) of all four sites demonstrates the lack of a relationship between sediment OC % and basal ice DOC. This may be due to the particular section of basal sediment that was sampled as, in the case of Joyce Glacier, higher OC content has previously been observed in other Antarctic lacustrine samples, such as subglacial sediment beneath Lower Wright Glacier (0.7 % OC) (Stibal et al., 2012), and Antarctic
- Dry Valley lacustrine sediments containing microbial mats (~ 9 % OC) (Squyres et al., 1991). This suggests a more diverse basal sediment matrix comprising algal mats and





organic lacustrine material that mixed with sand and/or other low-OC, mineral-based material during basal ice formation beneath Joyce Glacier. However, we acknowledge that some of the difference in sediment OC (and extractable carbohydrate concentrations) may be due to the different analytical methods employed in this and previous

⁵ studies. The concentrations that we present may also be conservative as our methodological approach meant that fine sediment fractions, which may be OC-rich, remained in suspension and were not included in the OC determinations.

Key differences were, however, observed in the proportions of extractable carbohydrates (a proxy for bioavailable compounds in the basal sediment) and LMW-DOC

- ¹⁰ concentrations in basal ice from the four sites. The LMW-DOC concentrations in Joyce Glacier basal ice, which were an order of magnitude higher than LMW-DOC concentrations in samples from the other three sites and predominantly due to high FAA concentrations, may have derived from the relatively large pool of potentially-bioreactive extractable carbohydrates in Joyce Glacier basal sediment (17% of the sediment
- OC, compared with < 0.5% of the sediment OC in samples from Russell Glacier, Engabreen and Finsterwalderbreen). The bioreactive OC pool in Joyce Glacier basal sediment may have been enhanced by the assimilation of proglacial algal mats into overridden material during glacial advance, which likely enriched the basal ice with lacustrine material and associated algal necromass (Pautler et al., 2012), which may
- include autochthonous material produced by microorganisms prior to basal ice formation. Indeed, lacustrine material is generally acknowledged as a source of reactive OC to microorganisms (Meyers and Ishiwatari, 1993). The lower extractable carbohydrate concentrations in basal sediment from Russell Glacier, Engabreen and Finsterwalderbreen (compared with Joyce Glacier) are thought to reflect the more refractory nature of
- the overridden material. OC in subglacial material beneath the GrIS is thought to derive from a soil origin, based on relatively high concentrations of *n* alkanoic acids, steroids, and other soil-derived functional compounds identified in Russell Glacier ice (Stibal et al., 2012). Due to this, and the relatively young age of Russell Glacier sediment OC (< 1900¹⁴C yr BP), we expected the total and bioreactive OC concentrations to be





higher than 0.44 and 0.47 % of the OC, respectively. For instance, OC content in Greenland soils range from 0.1–44.8 % in C horizons and peat soils (Horwath Burnham and Slettern, 2010). The low OC and extractable carbohydrate concentrations in Russell Glacier basal ice, collected from the GrIS margin, may reflect a heterogeneous sedi-

- 5 ment matrix that incorporates a lower proportion of paleosols mixed with other low-OC, mineral-based material. However, as discussed earlier, these differences in sediment OC concentrations may be due to the conservative nature of our methodological approach that may have excluded the potentially OC-rich fine sediment fractions. The low extractable carbohydrate concentration (0.04 % of the OC) in Finsterwalderbreen basal
- sediment is likely influenced by the predominance of OC from kerogen in the overridden shale bedrock (Wadham et al., 2004) that has been incorporated into the basal ice matrix. Kerogen is ancient carbon comprising stable carbon macromolecules (Petsch et al., 2001) and has limited bioreactivity. Similarly, low bioreactive OC in Engabreen basal sediment (0.17 % of the OC comprised extractable carbohydrates) is influenced
- ¹⁵ by the subglacial substrate comprising overridden continental shield rock depleted in reactive OC, the limited opportunity for material from supraglacial environments to be in-washed, and the limited input of overridden paleosols (Stibal et al., 2012). A lack of organic biomarkers (derived from algal and higher plant inputs) in Engabreen basal ice further suggests that incorporation of organic material is probably limited (Stibal et al., 2012).
 2012).

In summary, our data suggests that where glaciers and ice sheets override lakes, there is an injection of particulate and dissolved bioavailable compounds into the basal ice at the bed, which is less evident where the glacier overrode paleosols or bedrock. This has implications for subglacial LMW-DOC cycling as this abiotic input of LMW-

²⁵ DOC (via leaching) has the potential to stimulate microbial activity in wet sediments in the subglacial environment. We go on to investigate the DOC and LMW-DOC signatures in basal ice from these contrasting subglacial environments.





5.2 Basal ice LMW-DOC signatures and provenance

The presence of LMW-DOC compounds and the similarities in the types of compounds detected in basal ice samples from the four sites may reflect common sources and pathways of transformation of DOC in subglacial environments beneath glaciers

- ⁵ and ice sheets. The potential for interactions between basal sediment and subglacial icemelt suggest that allochthonous inputs from the overridden subglacial material may represent a key contribution to basal ice DOC. The chemical composition of basal ice, including DOC compounds, should reflect characteristics of the parent water prior to being frozen (Knight, 1997), where this water might be either flowing at the base of
- the glacier or held in porewaters in overridden water-saturated sediment. Both water sources have extensive contact with the subglacial material and so have the potential to acquire dissolved compounds via biogeochemical interactions. DOC and LMW-DOC components in basal ice may also be acquired by in situ abiotic processes, e.g. by reactions, such as dissolution, in water films around debris and in liquid water veins
- (Mader et al., 2006). It is likely that certain organic compounds will remain associated with the debris and others will dissociate to become DOC. We hypothesized that if the DOC was largely terrestrially derived and leached from sediments, there should also be a positive correlation between DOC and the debris content of the basal ice. We find that, in general, for sites where there is a bioavailable OC source in sediments
- (Joyce Glacier) or the sediment contains relatively young OC (i.e. < 1900¹⁴C yr BP) (Russell Glacier), there are significant relationships between DOC and debris content (Fig. 4a). This suggests that, at these sites, meltwater contact with the sediments is likely a major control on DOC acquisition. We find several additional lines of evidence to support the leaching of DOC from subglacial sediments, including the presence of
- fulvic acids that have previously been associated with terrestrial material (> 440 nm fluorescence wavelengths) in all basal ice samples (McKnight et al., 2001). The basal ice LMW-DOC compounds may also be a leached relic of the overridden material that has been preserved in the ice when frozen. However, the lack of significant associa-





tion between LMW-DOC and debris content (Fig. 4b) is reflective of additional sources and sinks of these compounds in the basal ice layer and/or in the parent water body from which basal ice formed. The LMW-DOC signature in basal ice may also be influenced by in situ microbial production and consumption, as illustrated in earlier work

- that has proposed a range of microbial processes to be active in the subglacial environment, including in situ chemoautotrophic production (Bhatia et al., 2006, 2013), chemoheterotrophic oxidation of OC substrates to protein-like LMW-DOC compounds (Bhatia et al., 2010) and release of LMW-DOC from decaying cells. It is probable that subglacial microbial activity cycles LMW-DOC both before and after the formation of
- ¹⁰ basal ice. For instance, microorganisms in subglacial sediment porewaters and basal meltwaters flowing at the rock:water interface may actively utilise OC substrates and energy sources derived from the overridden material. Via this activity, they may also go on to produce simple LMW-DOC compounds which may subsequently be incorporated into basal ice. The protein-like peaks that were observed in the spectrofluorescence
- spectra in Joyce Glacier and FPR ice (Table 3) tentatively suggests that some of the LMW-DOC is derived from a microbial provenance. Protein-like fluorescence is linked with recent biological activity (De Souza Sierra et al., 1994) and is associated with active FAA production during microbial metabolism (Yamashita and Tanoue, 2003).

In this study, we were not able to categorically separate LMW-DOC derived from bi-

- otic and abiotic processes as, at a molecular level, many LMW-DOC compounds are non-specific biomarkers due to their pervasive occurrence in plants and microorganisms (Biersmith and Benner, 1998). For example, valine, a common FAA in most basal ice samples, can be synthesized in plants via several steps starting from pyruvic acid (e.g. described in Singh, 1999). Valine can also be microbially-synthesized from pyru-
- vate (Blombach et al., 2007) and produced by aerobic gram-positive microbes (Valle et al., 2008). Similarly, glucose can be produced by photosynthesis (Kirchman et al., 2001) and chemoautotrophic bacterial activity (Jansen et al., 1982). The key point is that the presence of numerous LMW-DOC compounds in basal ice from all four glacial sites provides evidence that viable substrates for microbial growth, whether derived





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from an allochthonous or autochthonous source, are available in subglacial environments. These LMW-DOC compounds may help support microbial communities within the present-day basal ice, e.g. beneath Russell Glacier, where recent work has shown that the basal ice may be microbially-active in the current frozen state (Yde et al., 2010).

The microbial cell counts observed in all basal ice samples in this study (10⁵ cells g⁻¹, Table 2) are comparable to microbial populations (10⁵ – 10⁸ cells g⁻¹) reported in other subglacial sediments that have been proven to be microbially-active (Sharp et al., 1999; Foght et al., 2004; Kastovska et al., 2007; Yde et al., 2010; Montross et al., 2012).

5.3 Implications for LMW-DOC cycling beneath glaciers with bioreactive subglacial sediment

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The margin of Joyce Glacier rests upon ancient lake sediments and hence, represents a case where a very labile organic matter source is overridden. This situation may have been common in past periods of glaciation, when, for example, the Pleistocene ice sheets advanced over regions with a high density of lakes, such as in northern
 ¹⁵ Canada and Scandinavia (Wadham et al., 2008). Hence, the potential for LMW-DOC incorporation in Joyce Glacier basal ice and sediment may be applicable to these other types of lacustrine-based subglacial ecosystems. In addition, the abundance of LMW-DOC in Joyce Glacier suggests that overridden lacustrine material can be sequestered even if the glacier is cold-based. In the case of cold-based glaciers, a change in the

- melt regime would be needed to release the DOC to downstream ecosystems, which may not be that unlikely in a warming climate. If the glacier was warm-based then the DOC could be flushed out during the summer melt seasons and contribute to the net export of bioavailable DOC to downstream environments. The dramatic difference in the DOC composition beneath glaciers resting on different OC substrates that our data
- have highlighted may have implications for the rate and degree to which this overridden OC can be cycled to biogenic gases in current subglacial environments, which in turn, has relevance for global carbon cycles (Wadham et al., 2008; Stibal et al., 2012). While the DOC and LMW-DOC signatures of basal ice may arise from several confounding



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factors which are difficult to disentangle, identifying the abundance and composition of DOC in basal ice is an important first step to understanding LMW-DOC cycling in subglacial environments.

6 Conclusion

- ⁵ We employ spectrofluorometry and an ion chromatographic methodological approach to produce the first identification and quantification, at trace level concentrations, of major LMW-DOC fractions (free amino acids, carbohydrates and carboxylic acids) in debris-rich basal ice. We demonstrate that ion chromatographic systems that are optimised for trace level LMW-DOC analyte detection can supplement traditional methods of LMW-DOC characterisation as a quantitative technique. Our work adds to the
- ¹⁰ ods of LMW-DOC characterisation as a quantitative technique. Our work adds to the growing body of research addressing sources and reactivity of DOC in subglacial ecosystems and provides a characterisation of LMW-DOC in basal ice from four different glacial environments with distinctive basal debris type including lacustrine material (Joyce Glacier), overridden soils and tundra (Russell Glacier), kerogen in bedrock
- (Finsterwalderbreen) and bedrock/soils (Engabreen). We infer that allochthonous inputs from the overridden subglacial material represent a key contribution to basal ice DOC. Our data show that LMW-DOC concentrations in basal ice are dependent on the bioavailability of the overridden OC, which in turn, is influenced by the type of overridden material. We find that where glaciers and ice sheets override lakes, such as at
- Joyce Glacier, there is an injection of particulate and dissolved bioavailable compounds into the basal ice at the bed of the ice, which is less evident where glaciers overrode paleosols or bedrock. There is also potential for the overridden substrate to also act as an indirect (via microbial cycling) source of DOC, as the leached LMW-DOC compounds may stimulate microbial activity in wet sediments in the subglacial environment. This
- has implications for the cycling of overridden OC to biogenic gases in subglacial environments and concurs with recent findings that accelerated melting of glaciers and ice sheets could constitute a significant source of DOC and other, potentially-bioavailable





dissolved organic matter, to glacially-fed ecosystems. The abundance of LMW-DOC in Joyce Glacier basal ice suggests that overridden material may be sequestered even if the glacier is cold-based. A change in the melt regime could release this bioavailable DOC to downstream ecosystems, which has relevance for local carbon cycles and wider ecosystem processes.

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A. E. Pickard, and M. Stibal undertook the lab analysis. P. Dewsbury, G. P. Lis and E. C. Lawson assisted with the Dionex[™] ICS-3000 ion chromatography system optimisation and method development. E. C. Lawson, J. L. Wadham and M. Tranter wrote the paper with additional comments from the co-authors.

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Table 1. Biogeochemical data for basal ice from Engabreen (E), Finsterwalderbreen (F), Russell Glacier (R) and Joyce Glacier (J). B = basal and PR = pressure ridge ice. Values given are the mean concentrations for each analyte and the standard deviation is given in parentheses. LMW-DOC = free carbohydrates (FCHOs) + free amino acids (FAAs) + free carboxylic acids (FCAs). Only values > LOQ have been included.

Sample	% debris (by weight)	DOC (µMC)	LMW-DOC (nM C)	FCHOs (nM C)	FAAs (nM C)	FCAs (nM C)
E (<i>n</i> = 6)	36.83 (20.96)	113.56 (106.60)	417.70 (213.07)	0.00	22.41 (24.24)	442.19 (164.00)
FB (<i>n</i> = 5)	20.22 (26.74)	14.85 (9.91)	169.67 (183.90)	0.00	0.00	169.67 (183.90)
FPR (<i>n</i> = 5)	86.47 (6.58)	33.38 (33.30)	312.67 (502.64)	0.00	46.47 (48.99)	274.91 (549.83)
R (<i>n</i> = 7)	54.89 (24.51)	53.31 (28.89)	343.72 (689.83)	0.00	50.59 (62.97)	365.62 (817.56)
J (<i>n</i> = 5)	21.22 (6.41)	272.09 (99.38)	4429.83 (2625.95)	28.29 (15.83)	4353.30 (2643.59)	0.00





Table 2. Mean sediment characteristics.

Sample	¹⁴ C age (years, BP) ^a	% OC	% InC	Extractable carbohydrates (µgg ⁻¹)	Carbohydrate fraction (% of OC)	Cell abundance (cell g ⁻¹)
E (<i>n</i> = 5)	ND	0.19 (0.08)	0.24 (0.18)	3.26	0.17	6.80 × 10 ⁵
F (<i>n</i> = 5)	3750 (150)	0.57 (0.12)	1.80 (0.25)	2.34	0.04	1.68 × 10 ⁵
R (<i>n</i> = 5)	1830 (50)	0.44 (0.09)	0.01 (0.00)	20.83	0.47	2.26 × 10 ⁵
J (<i>n</i> = 5)	ND	0.01 (0.02)	0.28 (0.05)	23.95	17.11	1.16×10^{5}

^a Sediment OC age from Stibal et al. (2012), method described in the online supporting information. ND = not determined. E = Engabreen, F = Finsterwalderbreen, R = Russell Glacier, J = Joyce Glacier. Standard deviation is given in parentheses.

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Table 3. Summary of the dominant fluorophores in basal ice from four contrasting glacial environments. The dominant fluorophores (denoted by *) have been identified according to previous characterisation of spectral compounds (see Barker et al., 2009 and references therein). BI = basal ice, PR = pressure ridge ice.

Sample	Fluorophore (peak wavelength, nm)	Dominant fluorophore identification	n
Engabreen	342, 386 [*] , 440, 483	Fulvic acid, marine humic-like	6
Finsterwalderbreen Bl	342, 389 [*] , 440	Fulvic acid, marine humic-like	5
Finsterwalderbreen PR	276, 336, 389 [*] , 440	Fulvic acid, marine humic-like	5
Russell Glacier	335*, 385, 440, 483	Protein-like/marine humic-like	7
Joyce Glacier	279, 342, 386*, 440, 460, 551	Fulvic acid, marine humic-like	5













Figure 2. FCA compositions in basal ice samples. E = Engabreen, F = Finsterwalderbreen, R = Russell Glacier, BI = basal ice, PR = pressure ridge ice. Samples with zero concentrations have been excluded from the plot and only values > LOQ have been included.







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Lysine Alanine

Threonine

Valine I S/P Isoleucine

> Methionine Phenylalanine

Glutamic acid

Aspartic acid Cysteine

Tyrosine

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(F), Russell Glacier (R) and Joyce Glacier (J), (b) FAAs in Joyce Glacier basal ice, plotted separately due to an order of magnitude increase in concentrations. Samples with zero concentrations have been excluded from the plot and only values > LOQ have been included. S/P = serine and proline, reported together due to co-elution. PR = pressure ridge.



Figure 4. Associations between (a) DOC and debris concentration, and (b) LMW-DOC and debris concentration. Engabreen samples are given in black, Finsterwalderbreen in red (FBI as triangles and FPR as circles), Russell Glacier in blue and Joyce Glacier in green. p = 0.05 for all regression equations, only significant correlations are shown.

