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# Do Cryoconite Holes Have the Potential to be Significant Sources of C, N, and P to Downstream Depauperate Ecosystems of Taylor Valley, Antarctica?

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## Abstract

Nutrient recycling occurs in hydrologically isolated cryoconite holes on the glaciers of the McMurdo Dry Valleys, Antarctica. Biogeochemical processes enrich the cryoconite holes with solute and nutrients compared to the source sediment and glacier ice. The position of the glacier within the landscape affects the physical and biogeochemical character of the cryoconite holes, with those found in more biologically productive areas of the valley having higher concentrations of C, N, and P and higher pH. Comprehensive assessment of the quality and quantity of bioavailable C, N, and P shows that the cryoconite holes represent a significant store of nutrient in this depauperate landscape, since the total mass of C and N is similar to that found in the ephemeral streams. The dissolved nutrients within the holes, and a significant proportion of the particulate store, are released to the valley ecosystem via the network of ephemeral streams and perennially ice-covered lakes as a result of hydrological connection with the supraglacial drainage system. In most cases, cryoconite holes are flushed every several years, but during warm periods which occur with near decadal frequency, all holes connect and flush their contents off the glaciers. Simple mass balance modeling shows that an increase in primary productivity observed in Lake Fryxell that followed such a melt event in 2001/2002 can be explained by an influx of nutrients (specifically N) generated in the cryoconite holes. These features are hence an integral part of the Dry Valley ecosystem and should be considered in models of downstream biological processes.

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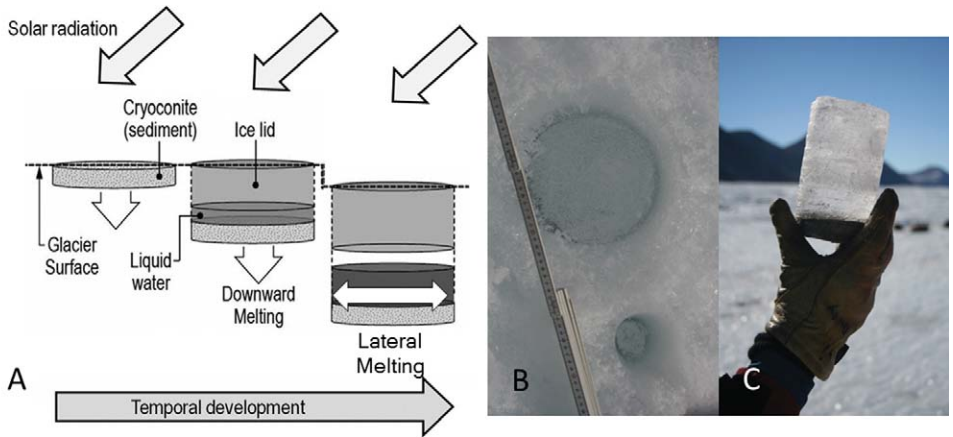
## Introduction

The McMurdo Dry Valleys (MCMDV) of Antarctica are among the coldest and driest environments on Earth (Doran et al., 2002) and are analogs for cold, dry, and dusty environments on Mars (Wentworth et al., 2005; Tranter et al., 2010). Microbial life thrives throughout the landscape of the MCMDV, despite the extreme climate, in ice-covered lakes, stream channels, poorly developed soils, small supraglacial lakes (cryolakes), and cryoconite holes (Priscu, 1999), all of which are critically dependent on glacier melt for supply of liquid water (Fountain et al., 1999). The ecosystem is also limited by the availability of organic matter and nutrients (Barrett et al., 2007), and potential sources of bioavailable nutrient may have significant impacts on the system as a whole. Glacial meltwaters flow for a few weeks per year within a drainage system located a few centimeters below the ice surface, even when surface air temperatures are below freezing (Fountain et al., 2004; Hoffman et al., 2008). This arises from solar heating of patches of debris on the ice surface, which melt down and form pools of water called cryoconite holes (Gribbon, 1979). These features are an important element in how the glaciers melt (Fountain et al., 2004; Hoffman et al., 2008). Although cryoconite holes are ubiquitous on exposed ice (versus snow) zones of glaciers everywhere that melting occurs, the holes found in the Antarctic are unique because they form an ice lid that isolates the entombed waters from the atmosphere and the supraglacial hydrologic system (Fig. 1) (Tranter et al., 2004; Brandt et al., 2009; Hodson et al., 2013). Once formed, the holes

freeze completely in winter and in summer melt from within, under the surface, maintaining the ice lid (Fountain et al., 2004, 2008). They may remain isolated over multiple melt seasons (Fountain et al., 2004), although up to 50% become hydrologically connected each summer (Bagshaw et al., 2007) via subsurface connections whose origins are unclear, or by melting of the ice lid and exchange with surface water during extreme melt events.

Cryoconite holes provide habitats for a range of microbial life in an otherwise hostile supraglacial environment (Wharton et al., 1981; Tranter et al., 2004; Hodson et al., 2008). The ‘‘sediment’’ that forms the holes is termed *cryoconite* (Leslie, 1879), is derived from a variety of local sources (Porazinska et al., 2004; Foreman et al., 2007), and is generally composed of rock fragments, flakes of algal material, and microorganisms that are transported onto the glacier surfaces by prevailing winds (Nylen et al., 2004; Nkem et al., 2006). The holes are inhabited by a range of organisms, including cyanobacteria, rotifers, tardigrades, and ciliates (Wharton et al., 1981; Porazinska et al., 2004). Phylogenetic studies have suggested that they are derived from the surrounding aquatic ecosystems (Christner et al., 2003). Hydrological isolation promotes recycling of nutrients via autotrophic and heterotrophic organisms (Bagshaw et al., 2007; Hodson et al., 2010), and understanding these processes can improve our comprehension of how life operates at the limits of survival (Cowan and Tow, 2004) and may act as a model for life in extra-terrestrial environments (Tranter et al., 2004, 2010).

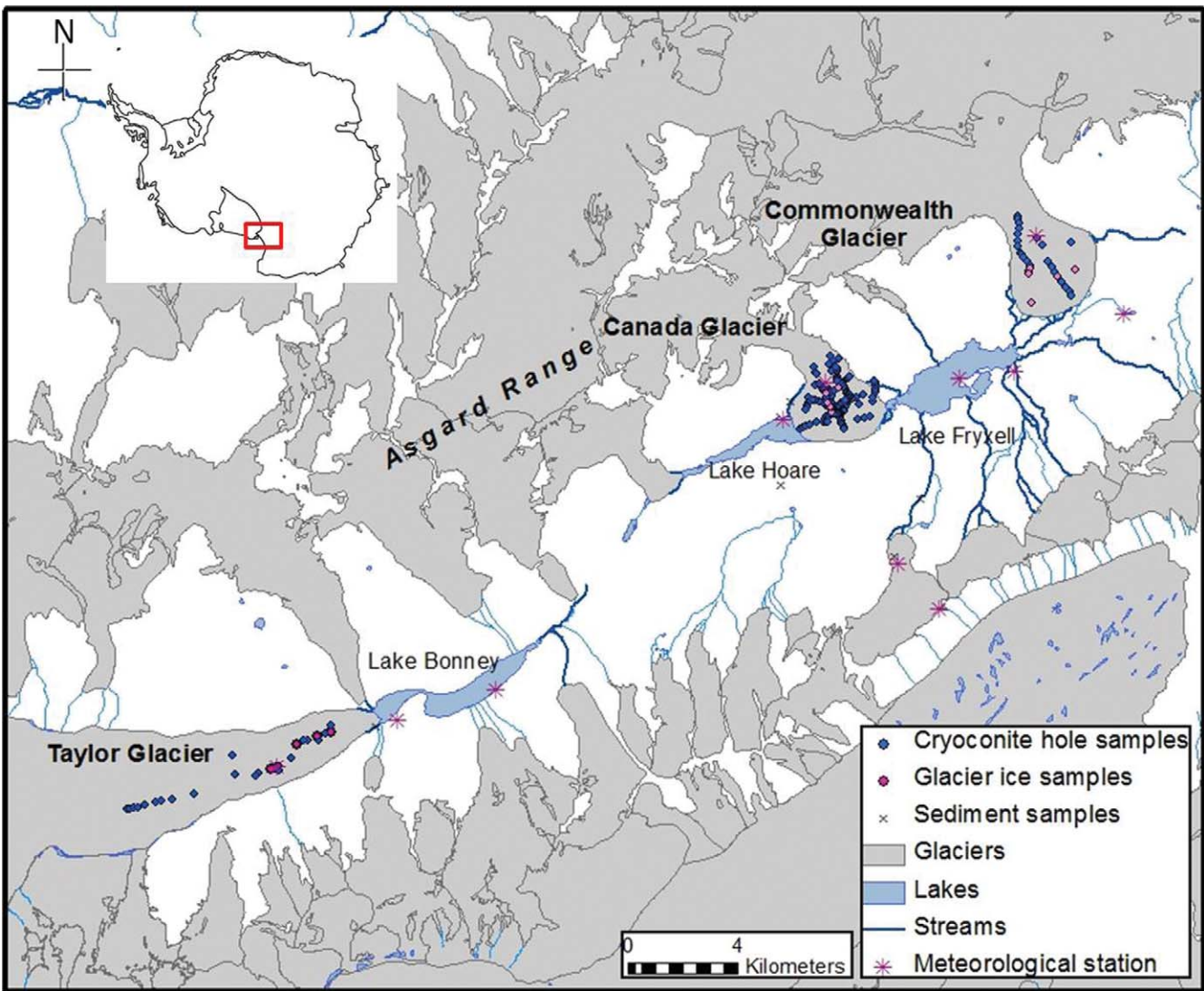
Solar heating of the sediment in the holes not only melts the surrounding ice but also results in a series of biogeochemical reac-



**FIGURE 1.** (A) Development and (B) examples of ice-lidded cryoconite holes on the surface of Canada Glacier, and (C) an extracted ice and sediment core.

tions (Tranter et al., 2004; Bagshaw et al., 2007). These processes have been most intensively studied on Canada Glacier, a large glacier in Taylor Valley (see Fig. 2). Cryoconite holes provide at least 13–15% of glacial meltwater from Canada Glacier (Fountain et al., 2004, 2008), which is typical of the region (Fountain et al.,

1998). Subtle changes in geology and climate, governed by location within Taylor Valley, control the geochemistry and biogeochemistry of the ice-covered lakes and the glacier ice (Lyons et al., 2000, 2003). The same is true for cryoconite holes, which reflect the solute characteristics of the glacier ice in which they are formed



**FIGURE 2.** Location map of Taylor Valley, Antarctica, and location of samples collected on Taylor, Canada, and Commonwealth Glaciers.

(Porazinska et al., 2004; Tranter et al., 2004; Foreman et al., 2007). A gradient of biological diversity and productivity also exists across the valley, with indicators of the highest productivity found in the easterly lake basins (Virginia and Wall, 1999), and so landscape position is an important control on nutrient stoichiometry in the MCMDV (Barrett et al., 2007). This may well be true for cryoconite holes and hence the meltwater which flows from the glaciers, since the first-order biogeochemical characteristics of the cryoconite holes are influenced by the immediate surrounding environments that are a source of dust and inoculi (Christner et al., 2003; Porazinska et al., 2004). To date, the spatial variation in the nutrient content and phase in cryoconite holes of the MCMDV has not been examined. We present a comprehensive survey of the C, N, P, and other biogeochemical characteristics of cryoconite holes on three glaciers in Taylor Valley and assess the factors that influence the potential of glaciers to act as nutrient sources to downstream MCMDV ecosystems.

## Methods

### STUDY SITE

Taylor Valley is located in southern Victoria Land, East Antarctica, is 34 km long, 12 km wide, and trends east–west. The western end is blocked by Taylor Glacier, an outlet of the East Antarctic Ice Sheet (EAIS), and the eastern end is open to the Ross Sea (Fig. 2). Taylor Valley has been intensively monitored since 1993 as part of the Long Term Ecological Research (LTER) program (Priscu, 1999). Meteorological conditions, stream flow, glacier mass balance, and lake levels are monitored annually (Fountain et al., 1999; McKnight et al., 1999; Priscu et al., 1999; Virginia and Wall, 1999). Mean annual temperatures range from  $-15$  to  $-23$  °C. Mean annual wind speeds are  $3.1 \text{ m s}^{-1}$  (Doran et al., 2002), and mean annual accumulation is  $<10$  cm water equivalent (w.e.) (Fountain et al., 2010). The climate is controlled by the prevailing east–west winds, which blow from the Ross Sea or descend from the EAIS. Westerly katabatic winds can reach speeds of  $37 \text{ m s}^{-1}$ , resulting in significant eolian transport of soil and other debris onto the surfaces of the glaciers (Sabacka et al., 2012), and increase local temperatures by up to  $4.3$  °C (Nylen et al., 2004). Mean summer (November to January) temperatures are  $-6$  °C (Foreman et al., 2004). This is sufficient, when coupled with 24-h sunlight and high incident radiation, to cause melting of the polar glaciers and the moats around the edges of the ice-covered lakes. The summer thaw promotes the onset of a period of short, intense biological activity in lakes, streams, soils, and cryoconite holes (McKnight et al., 1999; Barrett et al., 2004; Tranter et al., 2004; Doran et al., 2008).

The glaciers of Taylor Valley have mean ice temperatures of  $-18$  °C and limited surface melting (Fountain et al., 1998). Up to 80% of ablation is due to sublimation. Between 1995 and 1997, total ablation on horizontal ice surfaces ranged from 5.2 to 7.8 cm water equivalent (w.e.) (Lewis et al., 1999; Hoffman et al., 2008). Accumulation ranges from 10 to 50 mm w.e. per year (Fountain et al., 2010). Three glaciers were chosen for study, Taylor, Canada, and Commonwealth, which span the length of the valley (Fig. 2). Taylor Glacier, the easternmost extension of the EAIS, is located in the Lake Bonney Basin; Commonwealth Glacier is closest to

the Ross Sea and in the Lake Fryxell Basin; and Canada Glacier is in the Lake Hoare Basin in the center of the valley.

### SAMPLE COLLECTION AND PROCESSING

Frozen cryoconite holes were sampled at regular intervals along transects across each glacier surface in the austral summer of 2005–2006. The majority of samples was collected on Canada Glacier (90), whereas 30 were collected on each of Taylor and Commonwealth Glaciers (Fig. 2). All sampling locations were recorded using handheld GPS. Hole dimensions (depth, diameter of minor and major axis) were also measured. A 20-cm-diameter core was collected from the center of each frozen hole using a SIPRE corer. Drilling ceased when clean glacier ice below the debris layer was encountered. Cores were stored in Ziploc bags, which had previously been triple-rinsed with deionized water. They were transferred to the field laboratory in Taylor Valley and stored frozen until processing up to 30 days later. Five cores of glacier ice (which contained no cryoconite), drilled to a depth of 40 cm, were collected from the transects on each glacier and treated in the same manner as the cryoconite holes. From late December onwards, meltwater was present in some of the cryoconite holes. In this situation, the ice lid was removed and treated as above, and then a meltwater sample was sucked out with vacuum pump and tubing that had been rinsed six times with meltwater prior to sample collection. A grab sample of sediment was then scooped from the base of the hole with clean plastic gloves. Only one hole on Commonwealth Glacier contained liquid water at the time of sampling, compared with 34 on Canada Glacier and 10 on Taylor Glacier.

Ice and cryoconite hole core samples were melted at room temperature in the Ziploc bags in which they were collected. Meltwater was syringed from the top of the bags, leaving the sediment at the base; 150 mL of melt was filtered through  $0.4 \mu\text{m}$  Nucleopore membranes that were triple-flushed with deionized water and then sample water. The fourth aliquot of filtrate was stored in 60–100 mL Nalgene bottles pre-rinsed with deionized water. These samples were examined for major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ), inorganic nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ , and  $\text{SiO}_2$ ), and pH/conductivity/ $\text{O}_2$ . The pH, conductivity, and  $\text{O}_2$  were determined within one hour of sample melt following standard procedures (McQuaker et al., 1983). Another 100 mL was passed through pre-combusted Whatman GF/F for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analysis, to which 1 mL concentrated HCl was added as a biocide. The samples were stored in combusted amber glass bottles. All filtrates were refrigerated at  $<4$  °C and remained cool during transport. The reserved cryoconite sediments were drained, weighed, and frozen at  $-20$  °C in 60 mL pre-rinsed bottles. They remained frozen until analysis 8 months later.

### ANALYSIS

$\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  were analyzed using a Dionex DX-120 Ion Chromatograph. Analysis was conducted between one and eight weeks after collection at the Crary Lab, McMurdo Station. Precision was  $<5\%$  for all ions. The quantification limits, taken as the concentration of the lowest standard, were (in  $\mu\text{eq L}^{-1}$ ):  $\text{Ca}^{2+}$  2.0;  $\text{Mg}^{2+}$  5.0;  $\text{Na}^+$  2.0;  $\text{K}^+$  0.20;  $\text{Cl}^-$

0.6;  $\text{SO}_4^{2-}$  0.4; and  $\text{NO}_3^-$  0.07. DOC was determined using a Shimadzu TOC-V CPN Total Organic Carbon Analyzer with a high sensitivity catalyst. The detection limit for DOC was  $0.2 \text{ mg L}^{-1} \text{ C}$ , precision was  $\pm 0.1 \text{ mg L}^{-1} \text{ C}$ , and the mean standard error of duplicate samples was 6.4%. Inorganic nutrients were determined on a Brann and Luebbe SEAL colorimetric Autoanalyser 3 at the University of Bristol, approximately 8 months after sample collection. The quantification limits were:  $\text{NH}_4^+$  0.9;  $\text{NO}_3^-$  1.0;  $\text{PO}_4^{3-}$  0.6;  $\text{NO}_2^-$   $0.1 \mu\text{eq L}^{-1}$ ; and  $\text{SiO}_2$   $2.1 \mu\text{mol L}^{-1}$ . Samples were blank-corrected to account for the prolonged storage time. Accuracy was determined against VWR spectrosol standards and was  $\pm 0.2 \mu\text{eq L}^{-1}$ . Dissolved inorganic carbon (DIC, primarily  $\text{HCO}_3^-$ ) was assumed to be equal to alkalinity and was determined by subtracting the sum of the measured positive equivalents from the sum of the measured negative equivalents.

Sediment samples were thawed and excess water removed under suction, then weighed into ceramic crucibles and baked at  $120^\circ\text{C}$  for 12 h. Samples were reweighed to determine pre-baked water content as a proxy for porosity, and then suspended in water for laser particle size analysis (0.3 to  $300 \mu\text{m}$ ) using a Malvern Mastersizer Micro 2.12. A calibrated standard of known particle size was run after every 10 samples, and the largest gravel particles were excluded from analysis.

The organic C and N content of the cryoconite was determined using a Eurovector EA3000 Elemental Analyser, calibrated with certified acetanilide [ $\text{C}_6\text{H}_5\text{NH}(\text{COCH}_3)$ ]. The detection limit was 10 ppm, and the working range was from 0.01 to 100% organic C or organic N. Precision was dependent on range, being  $0.10\% \pm 0.01\%$ ,  $1.00\% \pm 0.02\%$ ,  $10.00\% \pm 0.10\%$ , and  $50.00\% \pm 0.30\%$ . The inorganic carbon (or carbonate) content was measured on a Strohlein Coulomat 702 Analyser, calibrated with certified barium carbonate. The detection limit was 1 ppm as DIC, and precision was  $\pm 0.5\%$ . Output from both instruments was validated with a Eurovector reference soil standard.

The concentration and comparative bioavailability of P in the cryoconite sediment was assessed via sequential extraction (Hodson et al., 2004). Five operationally defined P fractions were measured: loosely adsorbed (extracted with  $1 \text{ mol L}^{-1} \text{ MgCl}_2$ ); Fe and Al hydroxide bound (extracted with  $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ); calcite and apatite bound (extracted with  $1 \text{ mol L}^{-1} \text{ HCl}$ ); organic bound (extracted with 30%  $\text{H}_2\text{O}_2$ ); and the residual phase (extracted with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ ). Extractions were performed on 18 samples using the following method. The cryoconite (0.2 g) was shaken continuously for 16 h in a centrifuge tube with 12 mL of extractant (in the first instance,  $1 \text{ mol L}^{-1} \text{ MgCl}_2$ ), using an end to end shaker. After shaking, the tubes were centrifuged at 2600 rpm for 12 min, and the supernatant was filtered through  $0.45 \mu\text{m}$  cellulose nitrate membrane filters and collected. An additional 12 mL of extractant was added to the same sediment, shaken for 2 h, and the centrifugation and filtration procedures were repeated. Finally, 12 mL of deionized water were added to the sediment and shaken for 2 h before centrifugation and filtration as above. The sediment was then treated with the next extractant and the procedure repeated. The supernatant from the organic-bound extraction required boiling with  $1 \text{ mol L}^{-1} \text{ NaOH}$  (pH 10.5) to remove excess oxidizing agent before analysis. The residual P fraction was extracted using acidi-

fied potassium dichromate, autoclaved at  $121^\circ\text{C}$  at 15 psi for 1 h, and then cooled and filtered through  $0.45 \mu\text{m}$  cellulose nitrate membrane filters before dilution in a 1:14 ratio with deionized water. The filtered supernatants were analyzed using the molybdenum blue method on a Shimadzu UV-Mini 1240 Spectrophotometer at 880 nm wavelength. Some 4 mL of extract was mixed with 0.64 mL of combined reagent ( $5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ ,  $(\text{NH}_4)_6\text{MO}_7\text{O}_{24}$ , and ascorbic acid), and the resulting blue color was analyzed. Potassium dihydrogen phosphate standards, with the same matrix as the samples, were prepared, ranging from 0 to 1 ppm P. The detection limit was 0.1 ppm P and precision was  $<5\%$ . Results are reported in units of  $\mu\text{g Pg}^{-1}$  of cryoconite, and corrections for deionized water blanks were made. Blanks had very high and variable concentrations for the organic fraction, with a mean of 57% of the total P measured, although some corrections approached 85% of the total P measured. The high blank values were thought to arise from possible contamination during the prolonged boiling or incomplete removal of excess oxidizing agent. Hence, values of P in the organic fraction reported here are best estimates only.

## Results and Discussion

### PHYSICAL PROPERTIES OF CRYOCONITE HOLES

The largest (radius  $38 \pm 18 \text{ cm}$ ) and deepest ( $47 \pm 22 \text{ cm}$ ) cryoconite holes were found on Taylor Glacier, whereas the holes on Commonwealth and Canada Glaciers were about  $20 \pm 15 \text{ cm}$  in radius and about  $18 \pm 6 \text{ cm}$  depth (Table 1). Cryoconite sediment thickness was relatively uniform on all glaciers, in agreement with previous studies in the Antarctic and in Svalbard (Porazinska et al., 2004; Cook et al., 2010), although thicknesses ( $\sim 0.8 \text{ cm}$ ) were generally greater than Arctic holes ( $0.3 \pm 0.1 \text{ cm}$ ; Telling et al., 2012). Maximum thicknesses (up to 10 cm) were found on Taylor Glacier. The majority ( $>90\%$ ) grain size distribution of cryoconite sediment was sand ( $>50 \mu\text{m}$ ) with some silt ( $2-23 \mu\text{m}$ ). On Taylor Glacier the sediment had the highest proportion of large particles, with 69% of particles  $>160 \mu\text{m}$ , compared with Canada Glacier, 57%  $>160 \mu\text{m}$ , and with Commonwealth Glacier, 12% particles  $>160 \mu\text{m}$ , furthest down-valley (Fig. 3).

The spatial pattern of particle size distributions supports earlier findings from eolian sediment traps at 1 m height on the glaciers (Lancaster, 2002). The proportion of sand-sized particles ( $>50 \mu\text{m}$ ) in the sediment traps ranged from 5% on Commonwealth to 16% on Canada and 21% on Taylor Glaciers (Lancaster, 2002). That the particle size in the cryoconite sediment is larger than the sediment traps reflects the difference in sediment transport between saltation and suspension. A later study with passive eolian traps and counters situated closer to the surface, at 30 cm height, found that  $<1\%$  material captured was  $<50 \mu\text{m}$  (Sabacka et al., 2012). The relationship between longitude (down-valley distance) and median grain size in the cryoconite holes is significant ( $P = 0.00$ ,  $F = 22$ , d.f. = 1; Fig. 4). Higher wind speeds are much more common up-valley at the western end of Taylor Valley (Nylen et al., 2004), and it has been shown that 95% of eolian material at 30 cm height is transported by down-valley winds, generally southwesterlies in excess of  $20 \text{ m s}^{-1}$  (Sabacka et al., 2012). The majority of the larger cryoconite sediment is thus transported by katabatic

TABLE 1

Mean dimensions of cryoconite holes (cm), total area of ablation zone (km<sup>2</sup>), and percentage area covered by cryoconite holes (after Fountain et al., 2004).

	Radius	Total hole depth	Sediment thickness	Ablation zone area	% hole coverage	<i>n</i>
Commonwealth	19.4	17.4	0.85	10.9	4.8	30
<i>s.d.</i>	8.97	6.60	2.31			
Canada	22.8	18.5	1.13	8.5	4.5	90
<i>s.d.</i>	13.2	7.19	2.48			
Taylor	37.7	46.7	0.50	61.3	3.4	30
<i>s.d.</i>	20.4	16.2	2.36			

storms, when particulate deposition is high and coarser debris may be saltated or blown onto the glacier surface.

ICE CHEMISTRY

The mean chemical composition of the ice sampled from the three glaciers is dominated by NaCl (Table 2). Marine aerosols are a significant source of solute to glacier ice, transported into Taylor Valley on up-valley sea breezes that are common in summer (Nylen et al., 2004). Commonwealth Glacier, closest to the Ross Sea (Fig. 2), has the highest concentration of Cl<sup>-</sup>, then Canada Glacier, and finally Taylor Glacier, furthest from the coast, contains the lowest Cl<sup>-</sup> concentration. The total dissolved solute concentration also follows this pattern, although there are subtleties in the relative ion concentrations, as shown below. Our concentrations, taken from ice cores of up to 40 cm depth, are more dilute than those of Lyons et al. (2003), who collected ice cores to a depth of 5 cm. To evaluate the importance of marine aerosols as the source of solutes to the ice and cryoconite, we calculated mean enrichment factors as follows (Chester, 2000):

$$EF_x = \frac{X / Cl_{ice}^-}{X / Cl_{seawater}^-}, \tag{1}$$

where the *EF* is the enrichment factor of species *x*, and *X* is the concentration of species *x*, relative to the Cl<sup>-</sup> of ice and seawater. Chloride is used because it generally behaves conservatively in solution. We assume, given the number of samples collected and the analytical uncertainties, that *EF* that are 1.0 ± 0.2 are not enriched (*EF* > 1.2) or depleted (*EF* < 0.8) relative to sea salt.

The large *EF* (≥2) values in Table 2 show that glacier ice is clearly enriched in Ca<sup>2+</sup> > K<sup>+</sup> > Mg<sup>2+</sup> > SO<sub>4</sub><sup>2-</sup> when compared with sea salt. These ions are derived from the dissolution of dust during ice melt (Lyons et al., 2003). Glacier ice in Taylor Valley is particle-rich by polar ice-sheet standards (5–100 mg L<sup>-1</sup>), with concentrations at least two orders of magnitude higher than most other Antarctic snow and ice, which are typically in the range of 0.002–0.015 mg L<sup>-1</sup> (Lyons et al., 2003). The relatively high dust loading in the MCMDV snow and ice is derived from the valley floor and sidewalls. The general availability of dust for eolian trans-

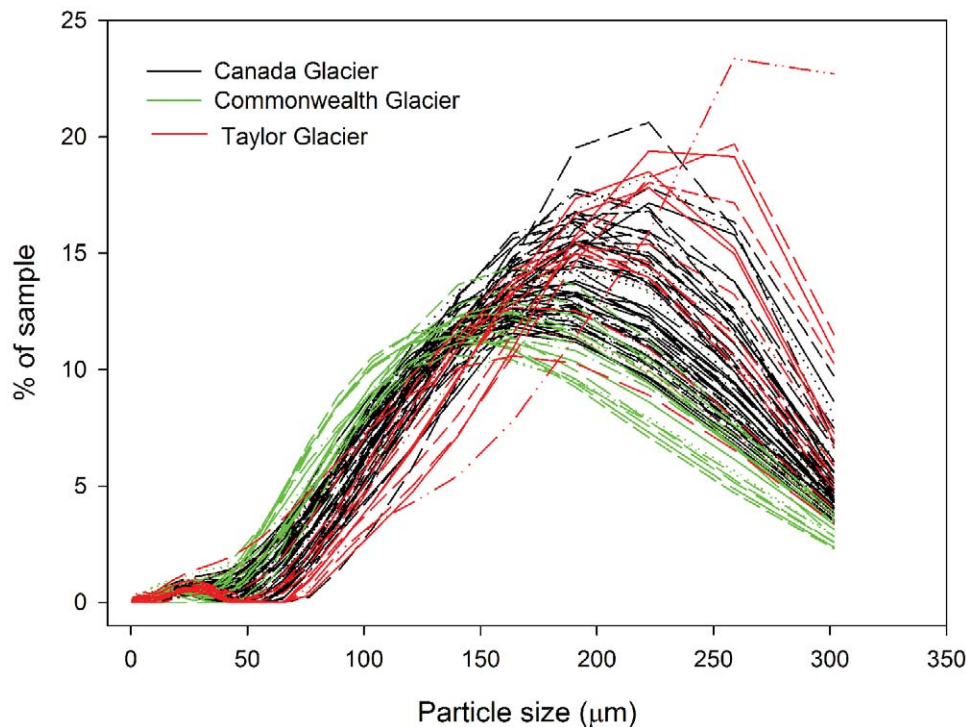


FIGURE 3. Grain-size distribution of cryoconite hole debris from Commonwealth, Canada, and Taylor Glaciers.

TABLE 2

Mean major ion, organic carbon, and inorganic nutrient concentrations for glacier ice and cryoconite hole waters on Commonwealth, Canada, and Taylor Glaciers, with enrichment factors (EF) calculated according to Equation (1).

	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	DOC	NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>	DIN	DON	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>2</sub>
<b>Glacier ice</b>															
<b>Commonwealth</b>															
Mean	17.8	0.23	4.40	15.6	2.28	11.3	15.5	21.9	0.29	2.18	*	0.04	*	*	1.99*
St dev	4.45	0.06	1.51	3.27	0.52	2.53	5.64	9.58	0.20	*	*	0.01	*	*	*
EF	1	ND	2.38	1.02	6.83	3.23	23.1	ND	ND	ND	ND	ND	ND	ND	ND
±	0	ND	0.23	0.04	0.14	0.08	2.63	ND	ND	ND	ND	ND	ND	ND	ND
n	5	5	5	5	5	5	5	5	5	1		5		1	1
<b>Canada</b>															
Mean	9.21	0.41	3.45	6.00	1.54	11.0	6.51	12.0	0.34	*	0.06	0.03	*	*	*
St dev	2.97	0.12	1.98	1.97	0.50	2.96	2.55	2.46	0.20	*	*	0.01	*	*	*
EF	1	ND	3.61	0.76	8.94	6.15	18.7	ND	ND	ND	ND	ND	ND	ND	ND
±	0	ND	0.91	0	0.01	0.33	1.28	ND	ND	ND	ND	ND	ND	ND	ND
n	5	5	5	5	5	5	5	5	5	5	1	5		1	5
<b>Taylor</b>															
Mean	5.07	0.12	1.33	4.31	1.46	4.72	2.51	5.53	0.44	*	0.08	0.01	*	*	*
St dev	2.40	0.04	0.43	2.00	0.62	5.52	1.46	5.72	0.18	*	0.12	0.01	*	*	*
EF	1	ND	2.54	0.99	15.35	4.78	13.2	ND	ND	ND	ND	ND	ND	ND	ND
±	0	ND	0.38	0.01	0.72	3.33	1.41	ND	ND	ND	ND	ND	ND	ND	ND
n	5	5	5	5	5	4	5	5	5	4	3	4		1	3
<b>Cryoconite hole waters (sampled when frozen)</b>															
<b>Commonwealth</b>															
Mean	187	5.75	57.2	138	20.7	101	203	212	0.79	0.51*	0.04	0.05	0.17	0.19*	14.1
St dev	158	20.2	46.5	110	9.78	62.3	127	119	0.38	1.32	0.05	0.07	0.15	0.27	7.01
EF	1	2.43	1.24	0.84	0.84	0.85	1.23	0.9	0.18	ND	ND	ND	ND	ND	ND
±	0	6.43	0.07	0.01	0.3	0.18	0.13	0.09	0.01	ND	ND	ND	ND	ND	ND
n	26	24	26	26	26	26	26	26	26	16	12	18	21	22	26
<b>Canada</b>															
Mean	91.9	6.45	51.1	56.5	15.9	49.8	231	202	0.72	0.97	0.35	0.07	0.20	*	10.6
St dev	93.2	23.3	63.1	46.9	9.02	41.1	145	102	0.32	1.39	0.47	0.08	0.20	*	7.23
EF	1	1.59	1.49	0.94	1.03	0.45	3.55	1.69	0.21	ND	ND	ND	ND	ND	ND
±	0	4.1	0.05	0.17	0.46	0.05	1.13	0.66	0.06	ND	ND	ND	ND	ND	ND
n	89	89	89	89	89	89	89	89	87	73	85	89	77	18	89
<b>Taylor</b>															
Mean	18.6	1.77	17.7	19.0	4.37	22.9	55.9	63.3	0.41	0.78*	0.15	0.04	0.16	*	7.74
St dev	16.8	2.29	22.0	14.3	1.94	14.9	31.8	31.2	0.17	0.77*	0.15	0.07	0.11	*	3.75
EF	1	4.13	3.61	1.20	0.82	1.32	6.05	3.11	0.25	ND	ND	ND	ND	ND	ND
±	0	1.10	0.69	0.17	0.34	0.59	1.38	0.47	0.11	ND	ND	ND	ND	ND	ND
n	20	20	20	20	20	20	20	20	14	14	19	14	10	3	20

\*Denotes a sample below the detection limit, ND denotes no data. Concentrations are in µeq per liter, except DOC, DON, and DIN, which are in mg C or N per liter.

port increases with distance from the coast, due to factors such as decreasing snowfall and decreasing soil moisture (Barrett et al., 2007), and higher wind speeds, which can transport more material (see above).

#### MAJOR ION CHEMISTRY OF CRYOCONITE HOLES

The major ion content of the water or ice within the cryoconite holes arises largely from solute scavenged from glacier ice as the hole melts in during its annual cycle, and from chemical interactions between ice melt and eolian debris, which forms the hole. Once the debris is deposited and encased in a cryoconite hole, it

may remain there for years (Tranter et al., 2004), so allowing greater chemical weathering of the mineral surfaces. The *EF* for the cryoconite holes was calculated using Equation (1) but substituting *Cl*<sup>-</sup> in the cryoconite hole (*CH*) for *Cl*<sup>-</sup> in the ice:

$$EF_x = \frac{X / Cl_{CH}^-}{X / Cl_{ice}^-} \quad (2)$$

Water from cryoconite holes on Commonwealth Glacier had *EF* for major ions close to 1, showing little enrichment (Table 2). Those on Canada Glacier were enriched in SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and DIC, but depleted in Mg<sup>2+</sup>, whereas holes on Taylor Glacier were more enriched in all four species. The higher *EF* from Taylor Glacier



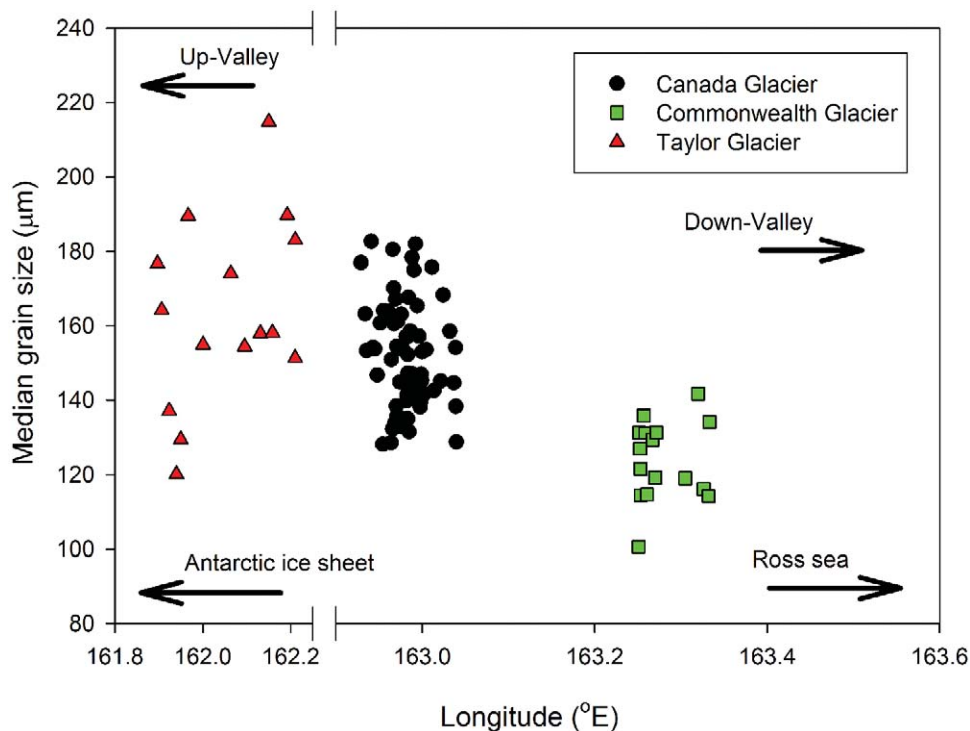


FIGURE 4. Median grain size of cryoconite debris compared to longitude on Commonwealth, Canada, and Taylor Glaciers.

may be explained by longer residence times (hydrologic isolation) of water and sediment in the larger holes (Bagshaw et al., 2007), which promotes greater dissolution despite the coarser grain size (see Fig. 4).

It is likely that the salinity of the cryoconite sediment is one of the key controls on the overall ion concentrations in the holes. Sediment deposited on Taylor Glacier is likely to originate from medial moraines or nunataks upwind of the glacier (Speirs et al., 2008), whereas sediment on Canada and Commonwealth Glaciers more likely originates from the soils on the valley floor (Witherow et al., 2006). These soils have variable salinity, from 127  $\mu\text{S cm}^{-1}$  in the Lake Hoare Basin to 549  $\mu\text{S cm}^{-1}$  at Lake Fryxell Basin and 706  $\mu\text{S cm}^{-1}$  at Lake Bonney Basin (Barrett et al., 2004). The salinity effect is confounded by the different wetting histories that the sediment has experienced before it is incorporated into the cryoconite hole. Soils that first contact meltwater in the hole are

likely to be very saline, but if they have previously been exposed to water, for example, in a stream bed or at the base of an ice cliff, they are likely to be much less saline. The *EF* therefore depends on the potential of the debris for new silicate dissolution and the concentration of evaporite minerals other than NaCl, such as CaSO<sub>4</sub> (Lyons et al., 2000).

#### PARTICULATE ORGANIC C AND N

The rank order of organic C and N in the cryoconite sediment, Commonwealth > Canada  $\geq$  Taylor (Table 3), is the same as found in the surrounding soils in the respective basins, as would be anticipated since the sediment is locally sourced. However, there is several times more organic C (total carbon [TC] – total inorganic carbon [TIC]) in the cryoconite sediment than in the soils, by a factor of ~7 on Canada Glacier (0.29 cf. 0.04%), ~5 on Commonwealth Glacier (0.10 cf. 0.02%), and ~2 on Taylor Glacier (0.04

TABLE 3

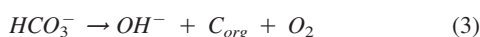
Mean C, N, and P, plus C:N:P content of soils (data from Barrett et al., 2007) and cryoconite hole debris in the three lake basins. More than 90% of C in the cryoconite holes is organic, thus it is directly compared with soil organic carbon.

	OC (%)		IC (%) Hole	N (%)		P (%)		C:N		N:P	
	Soil	Hole		Soil	Hole	Soil	Hole	Soil	Hole	Soil	Hole
Fryxell	0.04	0.35	0.06	0.002	0.05	0.07	0.05	25	8.2	0.06	2.39
<i>s.d.</i>	0.004	0.12	0.01	0.0001	0.02	0.006	0.02	2.7	7.0	0.01	2.21
Hoare	0.02	0.18	0.08	0.004	0.02	0.03	0.04	7	7.0	0.28	1.89
<i>s.d.</i>	0.004	0.23	0.11	0.0004	0.03	0.001	0.01	6.3	1.2	0.16	6.64
Bonney	0.02	0.06	0.02	0.003	0.02	0.03	0.05	6.4	3.5	0.28	0.94
<i>s.d.</i>	0.003	0.01	*	0.002	0.01	0.002	0.04	6.5	1.2	0.25	0.55

\*Only one sample from Taylor Glacier analyzed for IC.

cf. 0.02%). The percentage composition of N in the cryoconite sediment and Dry Valley soil is small (<0.05%), but there is nonetheless ~25 times more N in Commonwealth cryoconite (0.05 cf. 0.002%), and ~5 times more in Canada and Taylor cryoconite (0.02 cf. 0.004 and 0.003%, respectively) than in the soils.

Soils in the Lake Fryxell Basin are the most productive in Taylor Valley, as indicated by the higher algal mat density and greater microbial abundance (Virginia and Wall, 1999; Barrett et al., 2004; McKnight et al., 2007). Observations of windblown algal flakes were most frequent on the surface of Commonwealth Glacier, and mat-like material was frequently observed in the cryoconite from Commonwealth Glacier but not on the other two glaciers. The mean pH of the holes can be used as a crude proxy for net photosynthesis in closed systems (Tranter et al., 2004), with higher pH associated with greater degrees of net photosynthesis [Equation (3)]. The mean pH of Commonwealth Glacier cryoconite hole waters was 6.98, compared with 6.45 and 6.10 on Canada and Taylor Glaciers, respectively (ANOVA test,  $p = 0.007$ ). This crude proxy for net photosynthesis reflects the rank order of the overall organic C and N content of the cryoconite sediment.



#### DISSOLVED C AND N SPECIES

The highest concentrations of dissolved C and N were found in cryoconite hole waters on Commonwealth Glacier (3.5 mg C L<sup>-1</sup>, 0.17 mg N L<sup>-1</sup>), and the lowest on Taylor Glacier (0.85 mg C L<sup>-1</sup>, 0.16 mg N L<sup>-1</sup>) (Table 2). The difference in total dissolved carbon (TDC) concentrations is significant between the glaciers, although TDN concentrations are similar (ANOVA Kruskal-Wallis TC  $p = 0.014$ , total nitrogen (TN)  $p = 0.606$ ). Most of the dissolved C is inorganic, with mean proportions ranging from 60 (Taylor) to 76% (Commonwealth). By contrast, most of the dissolved nitrogen is organic, with average values ranging from 69 (Canada) to 78% (Taylor). N concentrations in glacier ice are at or below detection limits, with no detectable dissolved organic nitrogen (DON), and dissolved inorganic N (DIN) concentrations of 0.01 to 0.04 mg L<sup>-1</sup>. The mean *EF* of NO<sub>3</sub><sup>-</sup> in the cryoconite hole waters ranges from 1.6 (Canada) to 4.1 (Taylor). DOC is detectable in the ice on all three glaciers, ranging from 0.29 to 0.44 mg C L<sup>-1</sup>. Blanks were below detection limit, ranging from 0.01 to 0.1 mg C L<sup>-1</sup>. The values recorded in the cryoconite hole waters are thus significantly higher than the glacier ice. However, the *EF* of DOC in the cryoconite hole waters is depleted on all three glaciers (0.18 on Commonwealth, 0.21 on Canada, and 0.25 on Taylor), suggesting that DOC has been removed from the cryoconite holes over time. This observation is consistent with recent work on glaciers in Alaska and northeastern U.S.A., which reports that glacial DOC, although present in relatively low concentrations, is labile (Hood et al., 2009; Stubbins et al., 2012). Photolytic degradation of DOC is also possible (Mopper et al., 1991), although the ice lids significantly limit the proportion of solar radiation that reaches the waters below.

Together, these data suggest that there is significant biogeochemical cycling as a result of microbial activity in the cryoconite holes. Depletion of DOC is indicative of heterotrophic activity and bacterial production (Foreman et al., 2007), while enrichment in

NO<sub>3</sub><sup>-</sup> suggests that net nitrification is occurring, as has been found in streams in Taylor Valley (Gooseff et al., 2004; McKnight et al., 2004), in the maritime Antarctic (Hodson, 2006), and in cryoconite holes in Svalbard (Hodson et al., 2005, 2008). Nitrogen fixation has been observed in cryoconite holes in Svalbard (Telling et al., 2011) and in sediment contained within the lake ice cover in Taylor Valley (Paerl and Priscu, 1998), so it is reasonable to suggest that it also occurs in the cryoconite holes of Taylor Valley glaciers. Paradoxically, nitrification occurs when NO<sub>3</sub><sup>-</sup> concentrations are low (Telling et al., 2011) and most likely when microbial production is high during the peak summer ablation season, which explains the high particulate N and organic C in cryoconite debris. By contrast, denitrification occurs during the autumn freeze (Tranter et al., 2004). Comparison of samples collected when the holes were completely frozen with those that contained meltwater beneath the ice lid further supports this hypothesis. NO<sub>3</sub><sup>-</sup> concentrations in cryoconite holes containing liquid water at the time of sampling were depleted with respect to glacier ice (*EF* = 0.28 on Canada Glacier), whereas the holes sampled earlier in the season when they were completely frozen were enriched (*EF* = 1.6 on Canada Glacier; Table 2). Hence, successive annual cycles of nitrification and denitrification may result in higher concentrations of labile N in the cryoconite holes overall, and often higher NO<sub>3</sub><sup>-</sup> concentrations in the waters of the cryoconite holes, but this depends on the time of sampling.

#### DIP, DOP, AND PHASE ASSOCIATION OF PARTICULATE BOUND P

Concentrations of dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP) were below detection limits (<0.6 μeq L<sup>-1</sup> and 0.2 μmol L<sup>-1</sup>, respectively) in all ice and cryoconite hole water/ice samples (Table 2). The Lakes Bonney and Hoare in Taylor Valley are among the most P-limited aquatic ecosystems on Earth (Foreman et al., 2004; Barrett et al., 2007; Bate et al., 2008), despite the pools of inorganic P in the glacial tills (Bate et al., 2008). The low concentrations of DIP and DOP in cryoconite hole waters (Table 2) suggest that they too may be P-limited (Tranter et al., 2004). Much higher concentrations of P are found in the cryoconite debris (Table 4). Between 24% (Canada) and 45% (Taylor) of total P is bound in the residual fraction, which may not be bioavailable on annual timescales. The remainder of the particulate P is potentially bioavailable. The most readily available phase, that extracted by MgCl<sub>2</sub>, comprises just 0.06% of total P on Commonwealth Glacier, but 0.12 and 0.18% on Canada and Taylor Glaciers, respectively. This quantity of P may potentially fix ~100 times the amount of C (Redfield, 1958), thus even small amounts are significant to the biological function of the cryoconite hole ecosystem. The availability of the remaining P fractions (NaOH and HCl extractable, organic, and residual) is dependent on the chemical characteristics of microenvironments within the cryoconite debris. For example, to utilize the next most available fraction (extracted with NaOH), alkaline conditions are needed, which might occur during periods of high photosynthesis. There is a relatively large proportion of NaOH-extractable P in the Commonwealth cryoconite, 7.2%, compared to 1.9 and 1.5 on Canada and Taylor, respectively. Acidic conditions may extract mineral-bound phases (HCl extractable) (Liang et al., 2010), which contrib-

TABLE 4

Concentration of P ( $\mu\text{g P g}^{-1}$  debris) in each sequential extract, with the relative percentage of total P. The highest concentrations of P are found in extracts from Commonwealth Glacier sediment, which also has the highest proportion of bioavailable P.

	MgCl <sub>2</sub>	NaOH	HCl	H <sub>2</sub> O <sub>2</sub>	Residual
Commonwealth	0.28	33.5	140	155	133
<i>s.d.</i>	0.00	12.2	43.9	24.4	80.0
% of total P	0.06	7.23	30.3	33.6	28.8
<i>n</i>	2	5	5	5	5
Canada	0.41	6.67	115	144	84.3
<i>s.d.</i>	0.31	3.27	48.1	88.4	141
% of total P	0.12	1.90	32.8	41.2	24.0
<i>n</i>	5	12	18	18	17
Taylor	0.86	6.98	95.3	153	214
<i>s.d.</i>	0.06	0.95	18.3	5.16	182
% of total P	0.18	1.49	20.3	32.5	45.6
<i>n</i>	2	2	4	3	5

ute 30% of the total P on Commonwealth, 32% on Canada, and 20% on Taylor Glaciers. These conditions may occur, for example, in microenvironments within the debris that are predominantly heterotrophic (Gahoonia and Nielsen, 1992).

The organic P fraction is estimated to contribute 30–40% of the total P on the three glaciers, and only becomes available as microbes degrade the organic material in the cryoconite hole. Particulate organic P is recycled through respiration, but the virtual absence of direct consumers in the cryoconite hole microbial communities limits the rapidity of this process (Stibal et al., 2008). An alternative method of extracting P from organic material is via enzymatic mechanisms. Phosphatase activity has been detected in cryoconite holes on glaciers in the Arctic (Stibal et al., 2009) and the Antarctic (Foreman et al., 2007), indicating that microbes can cleave phosphate from complex P-containing organic molecules. Phosphatase activity is also detected in the ice-covered lakes of Taylor Valley (Dore and Priscu, 2001) and is a strategy that has been proposed as a means of coping with P deficiency (Stibal et al., 2009). Stibal et al. (2009) estimated that the store of organic P in cryoconite on Werenskioldbreen, Svalbard, may be turned over in 46–180 days and is sufficient to supply the entire supraglacial community over the ablation season. Phosphatase activity on Commonwealth Glacier was higher than on Taylor and Hughes Glaciers (see Fig. 2) (Foreman et al., 2007). Our data, which shows that readily bioavailable P in cryoconite is lower at Commonwealth than at Taylor Glacier, is consistent with these observations, since utilization of organic P sources is most required in cryoconite holes on glaciers at the eastern end of Taylor Valley.

The physiochemical form of P in MCMDV cryoconite sediment agrees with the patterns found in cryoconite at Werenskioldbreen, Svalbard (Stibal et al., 2008), although total concentrations of P are lower since allochthonous sources in the Dry Valleys are less abundant than in Svalbard. The total P content of cryoconite at Werenskioldsbreen was  $2.2 \text{ mg P g}^{-1}$ , compared with  $0.09$  to  $0.69 \text{ mg P g}^{-1}$  in Taylor Valley. There are different relative proportions of potentially bioavailable and less available P in the soils of each glacier basin. Soils of the Lake Fryxell Basin have higher P concentrations in all fractions than those in the Lake Bonney Basin (Blecker et al., 2006), and up to 8 times more labile P (Bate et

al., 2008). The cryoconite holes on Commonwealth Glacier are therefore likely to receive local debris with higher concentrations of total P and higher proportions of bioavailable P than Taylor Glacier, which is consistent with results of the extractions (Table 4). The relative lack of loosely adsorbed or labile P (0.06%) is most likely an indication of the increased levels of biological activity in the cryoconite holes on Commonwealth Glacier, which rapidly exhausts the most readily available P, instead fixing the P into organic fractions. The lack of detectable DOP or DIP in the holes (Table 2) also suggests that any available P is quickly utilized by microbial communities. The dissolved and particulate P data show that microbial communities existing in the cryoconite holes are stressed by a lack of immediately bioavailable P, but that they are likely able to respond to stress by producing phosphatase in order to extract P from the potentially large stores of particulate organic P in the cryoconite.

#### EFFECT OF GEOGRAPHY ON CHARACTERISTICS OF CRYOCONITE HOLES

There is a clear gradient in the geochemical characteristics of cryoconite holes across the three glaciers, which are situated along the length of Taylor Valley (Fig. 2), in common with other landscape components within the valley (Lyons et al., 2000; Welch et al., 2010). Of the sampled cryoconite holes, those on Taylor Glacier, at the western end of the valley, are larger and deeper, with the largest particles and waters that are most enriched in ions from mineral dissolution. They have the lowest concentrations of marine-derived aerosols, and the lowest particulate organic carbon and nitrogen. The waters have the lowest pH, which, when used as a proxy for photosynthesis, suggests low biological activity. This is supported by the highest proportion of easily available particulate P, the highest ratios of DOC:DIC and DON:DIN, the lowest total DOC and dissolved nitrogen (DN), and the highest enrichment of  $\text{NO}_3^-$  with respect to glacier ice, indicating low uptake by active microbial communities. The opposite is true for cryoconite holes on Commonwealth Glacier, and those on Canada Glacier are generally intermediate.

This pattern maps clearly onto the position of each glacier

within the landscape, and the relative influence of local climate. We have demonstrated that the highest wind speeds are found at the western end of the valley, as a result of a microclimate dominated by katabatic winds (Nylen et al., 2004; Speirs et al., 2010), which control the deposition of material that forms the cryoconite holes onto the glacier surfaces. The first-order control on biological productivity of the cryoconite holes is also the relative position within the landscape and the associated impact of the climate. Higher snowfall at the easterly (seaward) end of the valley increases soil moisture in the Lake Fryxell Basin, which supports higher biological productivity in the valley floor ecosystem components (Virginia and Wall, 1999). Since the cryoconite holes are principally seeded by the immediate surrounding area (Christner et al., 2003), a greater proportion of biological material, including microorganisms, fragments of algal mat, and other organic matter, will be deposited on glaciers at the eastern end of the valley. This promotes elevated levels of biological activity compared to cryoconite holes at the western end of the valley, and hence relative depletion in easily accessible phases of particulate C, N, and P, reduced DIC and DIN, and augmented accumulation of DOC and DON. An accumulation of algal material on Falconer Ridge (T. Nylen, personal communication), at the sidewalls of Commonwealth Glacier, further enhances this effect by delivering additional algal material to the glacier surface for incorporation into cryoconite holes, and maximizes the observed differences in biological activity at opposite ends of the valley.

#### CRYOCONITE HOLES AS C, N, AND P RESERVOIRS

The MCMDV contain depauperate ecosystems in which biotic communities are limited by physical constraints, access to organic matter, and nutrient availability (Zeglin et al., 2009). Nutrients are often in low quantities and in proportions outside the ratios required for balanced growth (Barrett et al., 2007). Overall, rates of microbial activity are directly related to the quality and quantity of available organic matter (Barrett et al., 2006; Zeglin et al., 2009). Any process that serves to maximize the production of organic matter and nutrient storage is thus important on the landscape scale, particularly if the organic matter and nutrient are potentially exportable

in the future via increased hydrological connectivity between landscape elements (Ball et al., 2011; Levy et al., 2011). We have shown unequivocally that the biological processes that occur in cryoconite holes increase the C and N content of cryoconite with respect to the soils, and the dissolved fractions with respect to glacier ice. Next, we quantify the magnitude of the dissolved and particulate C, N, and P stored in the cryoconite holes and assess the significance of this reservoir to the Dry Valley ecosystem as whole.

The total mass of sediment stored in the cryoconite holes on each glacier can be estimated from the average sediment depth, the estimated area of the ablation zone, and the percentage of the glacier ablation area that is occupied by cryoconite holes on each glacier (see Table 1). In these calculations we assume a mean dry cryoconite particle density of  $2.64 \text{ g cm}^{-3}$  and mean porosity of 33%. The values for total cryoconite sediment mass are 18,400, 7830, and 760 tonnes for Taylor, Commonwealth, and Canada Glaciers, respectively. The total mass of particulate organic carbon (POC), particulate organic nitrogen (PON), total phosphorus (TP), and particulate organic phosphorus (POP) in cryoconite on each glacier can then be calculated from the total debris mass, given the mean %C, %N, and %P in the debris, as shown in Tables 3 and 4. The calculated values are 11,000, 27,400, and 1370 kg for POC; 3670, 3920, and 230 kg for PON; 2800, 1220, and 110 kg for POP; and 8620, 3620, and 270 kg for TP, respectively (see Table 5). Our estimates of POC and PON for Canada Glacier are higher than those of Foreman et al. (2007), largely because they estimated that the sediment layer was only a few millimeters in depth, whereas our measurements show that they are consistently of the order of a centimeter.

The average water depth of the holes, the percentage of the accumulation area covered, and the mean dissolved C and N concentrations can be combined to calculate the total dissolved C and N reservoir in the cryoconite holes on each glacier (Table 5). The calculated values are 900, 286, and 18.5 for TDC, and 175, 16.4, and 1.46 kg for TDN, respectively (Table 5). The TDC and TDN stores are typically 2–3 orders of magnitude smaller than the particulate reservoirs, and the ratio of solid phase to dissolved reservoir

TABLE 5

**Total dissolved (TD), dissolved inorganic (DI), dissolved organic (DO), and particulate (TP) C, N, and P (kg) stored on the surface of the three glaciers, and in different Taylor Valley landscape components (stream and soil data from <http://www.mcmllter.org> and Barrett et al., 2007). Totals were estimated using mean concentrations and the area covered by each landscape element.**

	DOC	DIC	TDC	DON	DIN	TDN	TPC	TPN	TPP
Commonwealth	68.0	220	287	12.1	4.32	16.4	27,400	3910	3670
<i>Standard error</i>	38.4	91.2	201	13.1	5.22	26.6	18,500	2410	1680
Canada	4.66	13.8	18.5	0.99	0.46	1.46	1370	230	270
<i>Standard error</i>	2.20	4.74	10.8	1.41	0.51	2.65	1760	232	86
Taylor	366	542	910	135	38.5	173	11,000	3670	8630
<i>Standard error</i>	228	366	835	52.3	48.4	228	2470	1920	7450
All glaciers	886	2450	3340	203	75.8	280	153,000	25,830	33,200
<i>Standard error</i>	480	1010	2280	196	90.7	431	124,000	18,500	18,800
All streams	6.00	64.1	70.1	ND	ND	8.00	120,000	10,000	ND
<i>Standard error</i>	1.08	10.4	17.1			2.47	12,000	1000	
All soils	n/a	n/a	n/a	n/a	n/a	n/a	13,000,000	11,100,000	7,390,000
<i>Standard error</i>	n/a	n/a	n/a	n/a	n/a	n/a	2,330,000	758,000	1,110,000

decreases from Commonwealth to Taylor Glaciers. Comparison of the ratios of dissolved to particulate stores for each glacier suggests that biological activity is more efficient at scavenging C and N from the dissolved phase into the solid phase at Commonwealth > Canada > Taylor Glaciers. There is considerable uncertainty in these estimates, particularly with respect to dissolved and particulate N (Table 5). Nevertheless, they provide a useful assessment of the relative magnitude of the C, N, and P stores on the glaciers in relation to other landscape units.

Soils cover  $\sim 105 \text{ km}^2$  of the floor of Taylor Valley (Burkins et al., 2001). Permafrost is found at a near constant depth of 10–30 cm across the valley (Virginia and Wall, 1999), and we consider the top 20 cm to be the location of the potentially biologically active store of C, N, and P. The mean C, N, and P by weight are 0.03, 0.003, and 0.02%, respectively (Burkins et al., 2001; Barrett et al., 2007) (Table 3). Thus, assuming porosity of 30% (measured mean water content), and particle density of  $2.64 \text{ g cm}^{-3}$ , the total stores of C, N, and P are 12,900, 1110, and 7390 tonnes, respectively. The other significant biologically active landscape components in Taylor Valley are the ephemeral streams, which cover an area  $\sim 0.2 \text{ km}^2$ . The steam algal mats have an estimated carbon density of  $\sim 600 \text{ g C m}^{-2}$  (Burkins et al., 2001). The organic C stored in the algal mats is therefore  $\sim 120,000 \text{ kg}$ . The C:N ratio in the algal mats is 11–13 (Lee Stanish, personal communication), so we estimate that the likely N store is of the order of 10,000 kg.

Comparing these pools, we see that the cryoconite holes (and hence the glacier surfaces) represent a store of C and N that is slightly larger than that of the algal mats located in ephemeral stream beds, but only 1.2% of C, 2.3% of N, and 0.5% of the P stored in the soils (Fig. 5). However, the C, N, and P in the cryoconite holes are much more accessible to the hydrological drainage system than that in the soils, and present in more bioavailable fractions. The cryoconite holes play an active part in the annual hydrological cycle (for example, contributing 13–15% of runoff from Canada Glacier; Fountain et al., 2008) and hence are connected to other parts of the ecosystem, whereas the majority of the

soil environments remain disconnected (Doran et al., 2008). Even the benthic fraction of the holes is relatively mobile, since connected cryoconite holes can have their sediment flushed into supraglacial streams (Fountain et al., 2004). The proportion of sediment liberated from the cryoconite holes varies according to the magnitude of surface melting, but in a “warm summer,” when the majority of cryoconite holes lose their ice lids and are flushed out (Foreman et al., 2004), a large proportion of the sediment store of C, N, and P is mobile. This means that it can play a part in contemporary biological processes.

Present day models of ecosystem processes in the MCM DV tend to combine the contribution from the cryoconite holes with that from the ephemeral streams (Moorhead et al., 2005; Barrett et al., 2008; Doran et al., 2008), which potentially allows misinterpretation of important processes controlling nutrient cycling. However, we have shown the total cryoconite hole store of C and N is larger (Table 5) than that in the streams and thus should be considered as a separate entity. The 2001/2002 “warm year” is used to illustrate the potential impact of a nutrient flush from cryoconite holes to the ice-covered lakes. In the summer of 2001/2002, abnormally warm air temperatures induced an extreme melt event in Taylor Valley (Foreman et al., 2004). Ephemeral stream discharge was at a record high, lake levels rose (Doran et al., 2008), soil moisture increased (Barrett et al., 2008), supraglacial streams were widespread (Fortner et al., 2005), and the majority of cryoconite holes lost their ice lids and connected to the supraglacial drainage system (Fountain et al., 2004). There was significant mass loss at all elevations on the glaciers during the warm summer (Fountain et al., 2008), which fueled increases in ephemeral stream discharge of as much as 6000-fold (<http://www.mcmlter.org>), so we anticipate that much of the nutrient stored in the cryoconite holes was flushed from the glacier in this large meltwater pulse. In the year following the “flood,” primary production (PP) in the top 5 m of Lake Fryxell increased by  $12.8 \mu\text{g C L}^{-1} \text{ d}^{-1}$  from the long-term average of  $2.4 \mu\text{g C L}^{-1} \text{ d}^{-1}$  (Foreman et al., 2004). Foreman et al. (2004) hypothesized that this increase was fueled by nutrient previously stored in the cryoconite holes.

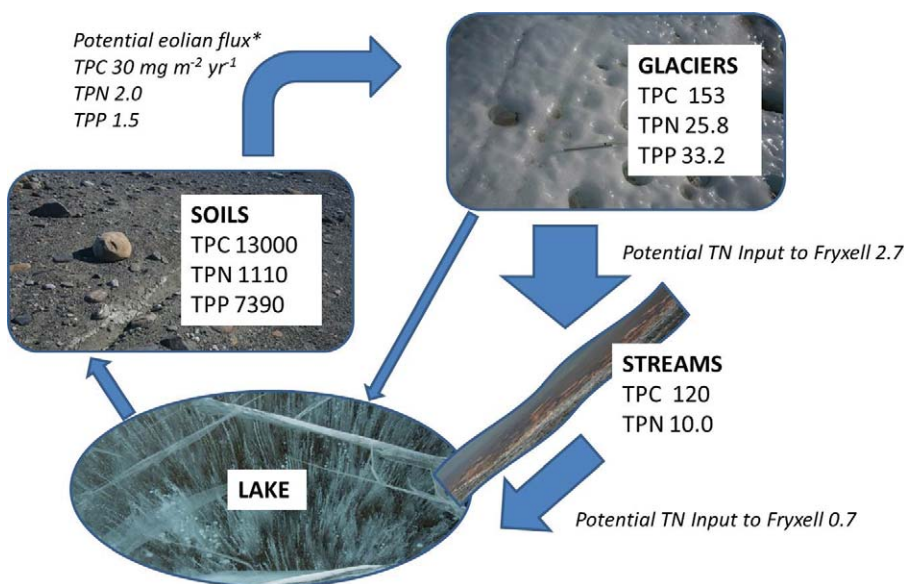


FIGURE 5. Estimated stores (tonnes) of particulate C, N, and P in different landscape components of Taylor Valley, with example fluxes of N from the glaciers and streams into Lake Fryxell. \*Eolian flux data from Sabacka et al. (2012) show the mean flux of C, N, and P recorded in sediment traps in the central Lake Hoare Basin.

In order to examine this hypothesis, we used a simple mass balance model to estimate the nutrient requirements of this increase in PP and the potential sources (Appendix). The total N required to support the observed increase in PP is 1640 kg. The likely contribution from streams is 730 kg N, although there may be additional PON input from algal mat scouring associated with higher streamflows (McKnight et al., 1999). The dissolved nitrogen (DN) content of the cryoconite holes is negligible in comparison to that in the lake (<10 kg; Table 5), but the potential contribution of particulate N from the cryoconite sediment is 2700 kg. Supporting an increase in PP in Lake Fryxell would thus require less than 20% of the total N store on Canada and Commonwealth Glaciers to be flushed from the holes into the lake. This is certainly plausible, given the magnitude of the melt and the observed flushing of the cryoconite holes. Our model is constrained by a number of assumptions, namely that PP occurs at the mean rate for 30 days, and that the nutrient requirement follows the Redfield ratio. We also have no way of estimating the actual contribution of cryoconite sediment to the lake during the warm year. We also have ignored the microbial recycling loop within the lake, diffusion across the chemocline, the potential of N inputs from stream hyporheic zones (Gooseff et al., 2002), and direct contributions from melting permafrost or groundwater seeps (Harris et al., 2007; Wall, 2007). However, we believe that these simple calculations illustrate the importance of considering cryoconite hole biogeochemical processes, along with those in the streams, soils, and lakes, when modeling ecosystem processes in the MCMDV.

## Conclusions

Our assessment of the nutrient status and store in cryoconite holes of three glaciers in Taylor Valley has shown that there is active biogeochemical cycling as a result of microbial activity, and that this results in a larger proportion of bioavailable C, N, and P present in the cryoconite than exists in the source material, with 2–7 times more POC, 5–25 times more particulate nitrogen (PN), and up to 8 times more labile P. The position of the parent glacier within the Taylor Valley landscape exerts a key control on the geochemical character of the holes, since the holes are seeded by the surrounding environment. Mean DOC and DON concentrations in the holes are 0.4–0.8 and 0.2 mg L<sup>-1</sup>, respectively, and estimates of the total quantity of dissolved carbon and nitrogen on the glacier surfaces are 3340 and 280 kg, respectively. The cryoconite sediment fraction represents a much larger nutrient store than the water/ice layer, where total particulate carbon (TPC) comprises up to 0.35% of the sediment, total primary nitrogen (TPN) up to 0.05%, and total particulate phosphorus (TPP) 0.05%, and hence the total store of C, N, and P in the cryoconite holes of Taylor Valley is 150,000, 25,800 and 33,200 kg, respectively. The magnitude of the cryoconite nutrient reservoir is similar to that found in the ephemeral streams, but smaller than the total quantity present in the poorly developed soils that cover much of the Dry Valley landscape, where C and N stores are approximately 80 and 40 times larger, respectively. Crucially, however, the fractions present in the cryoconite holes are more bioavailable to microorganisms, and also more mobile. A proportion of the cryoconite sediment store will be flushed to downstream aquatic ecosystems during the summer melt, when about 50% of cryoconite holes connect to the near-surface supragla-

cial drainage system (Fountain et al., 2004, 2008). The meltwaters and material from the cryoconite holes pass through the ephemeral stream network to oligotrophic, perennially ice-covered lakes. During warm summers, which occur with approximately decadal frequency (Ball et al., 2011), the majority of the cryoconite holes are flushed and their contents are redistributed throughout the Dry Valley ecosystem mosaic. Simple calculations show that an increase in primary productivity recorded in the ice-covered Lake Fryxell in the summer following the 2001/2002 warm period could be supported by an influx of nutrient from cryoconite holes, and hence cryoconite holes are an integral part of the Dry Valley ecosystem.

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## APPENDIX

### Chemical Mass Balance Model

Redfield stoichiometry can be used to estimate the nutrient requirements for the increase in particulate production (PP) in Lake Fryxell, following the 2001/2002 warm event (Redfield, 1958). Over a 30-day growing season, a PP rate of  $12.8 \mu\text{g C L}^{-1} \text{d}^{-1}$  in the top 5 m of Lake Fryxell requires 1640 kg N. This is a maximum estimate, since this calculation does not account for the likely nutrient recycling that occurs in the surface waters of the lake. We calculate the probable sources of this N as follows: The concentration of particulate organic nitrogen (PON) in the top 5 m of the lake at the end of winter prior to the flood (27 October 2001) was  $15.7 \mu\text{g L}^{-1}$ , while dissolved inorganic nitrogen (DIN) was negligible at  $0.02 \mu\text{M}^{-1}$  (data from <http://www.mcmlter.org>). The volume of the surface 5 m of water in Lake Fryxell is  $2.8 \times 10^{10}$  L, and hence the PON in the surface lake waters was of the order of 445 kg, and the DIN was  $<1$  kg. Doran et al. (2008) estimated that the total stream water input to Lake Fryxell during

the flood year was  $2.5 \times 10^9$  L (from Canada, Aiken, Von Guerard, Harnish, Crescent, and Delta streams), and the mean N in stream waters was  $0.3 \text{ mg L}^{-1}$  (<http://www.mcmlter.org>). The total nitrogen (TN) input from the streams is thus approximately 730 kg N. This input from the streams when compared to the background total organic nitrogen (TON) content of the lake surface water is still  $\sim 500$  kg less than the N required for the observed levels of PP. The dissolved nitrogen (DN) content of the cryoconite holes is negligible in comparison to that in the lake ( $<10$  kg; Table 5), but the larger particulate nitrogen (PN) store was likely flushed during this flood event. The topography of Canada and Commonwealth Glaciers is such that approximately half the holes on Canada and two-thirds on Commonwealth will drain to Lake Fryxell, so the potential total particulate nitrogen (TPN) input to the lake from cryoconite is approximately 2700 kg.