



## Biogeochemical evolution of cryoconite holes on Canada Glacier, Taylor Valley, Antarctica

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[1] The cryoconite holes of the McMurdo Dry Valleys are simple, closed biogeochemical systems involving water, ice, mineral and organic debris, which serve as ecosystems for consortia of microorganisms. This study is the first to document the seasonal and annual chemical evolution of solutes in cryoconite holes. Samples of glacier ice, frozen cryoconite holes and those containing water were collected during the austral summer of 2005–2006. The isolation age was calculated from the excess  $\text{Cl}^-$  in the holes, and varied from 0 to 5 years (a), consistent with the last hot summer when the cryoconite holes were open to the atmosphere. The holes progressively deepen with isolation age. Variations in DIC, DOC,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  suggest that dissolution of primary minerals in the cryoconite debris, cyclical precipitation and dissolution of secondary carbonates, net photosynthesis over summer and net respiration during the autumnal freeze are the principal reactions which perturb the seasonal and annual solute concentrations in the holes. DOC is generated in the holes at a rate of  $7.5 \mu\text{g C cm}^{-2} \text{ a}^{-1}$ , and non-sea-salt  $\text{K}^+$  accumulates in frozen holes at a rate of  $0.073 \mu\text{eq cm}^{-2} \text{ a}^{-1}$ . We infer that C cycling is complex even in these otherwise simple systems.

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### 1. Introduction

[2] The McMurdo Dry Valleys are located in southern Victoria Land, Antarctica (Figure 1) and are the largest ice-free expanse on the continent [Cowan and Tow, 2004]. The valleys are polar deserts, with a landscape composed of sandy-gravelly soil, perennially ice covered lakes, polar alpine glaciers and ephemeral streams which flow for 4–10 weeks per year [Fountain *et al.*, 1999b]. Ecosystems within the valleys include glacier surfaces, ephemeral streams, soils, and the perennially ice-covered lakes. They are colonised predominantly by microorganisms. No higher plants or animals are present. All habitats are critically dependant on the supply of water which arises principally from glacier melt, and the productivity of the aquatic ecosystems is dependant on tight nutrient recycling and the supply of new nutrient [Priscu, 1998; Barrett *et al.*, 2007].

[3] Cryoconite holes are an element of glacier surfaces that have been the subject of much recent interest. Cryoconite holes are small, cylindrical depressions which occur on the surface ice of glaciers throughout the world

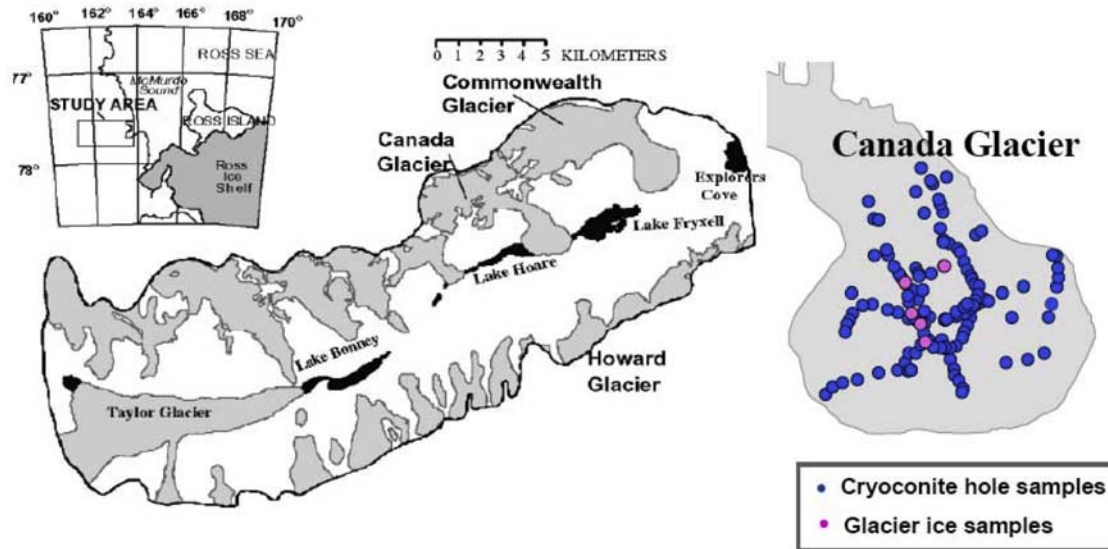
[Podgorny and Grenfell, 1996; Cowan and Tow, 2004; Mueller and Pollard, 2004]. They form when solar radiation heats debris resting on the ice surface, so melting the debris into the ice to form a small, water-filled depression (Figure 2). The debris melts into the ice surface until a steady state depth is reached, when downward melt in rate equals the ablation rate of the glacier surface [Gribbon, 1979]. Cryoconite holes are refugia for life in this extreme environment [Wharton *et al.*, 1985]. The relatively simple systems which operate in the holes also provide an opportunity to study ecosystem dynamics on a simplified scale, and provide an analogue for potential habitats on other icy terrestrial bodies [Priscu and Christner, 2002]. Cryoconite holes in Taylor Valley are unique in often remaining ice-lidded and a significant proportion remaining isolated from the atmosphere and the surrounding supra- and en-glacial drainage systems throughout the ablation season [Fountain *et al.*, 2004]. Consequently, these isolated cryoconite holes may sequester solute and nutrient from glacier ice and debris over time. Recent work suggests that ice-lidded cryoconite holes may contribute at least 13% of the annual surface runoff from Canada Glacier, based on a lower-bound estimate of the proportion of the ice surface covered by cryoconite holes [Fountain *et al.*, 2004]. Whole scale flushing of the glacier surface to downstream ecosystems during warm summers stimulates significant increases in the primary production of the ice-covered lakes [Foreman *et al.*, 2004].

[4] Cryoconite holes in Taylor Valley are typically 30 to 80 cm deep, and 20 to 120 cm in diameter [Tranter *et al.*,

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**Figure 1.** Location, key landscape features of Taylor Valley, McMurdo Dry Valleys, Antarctica, 77°S, 163°E and sampling locations on Canada Glacier [after Fountain *et al.*, 2004].

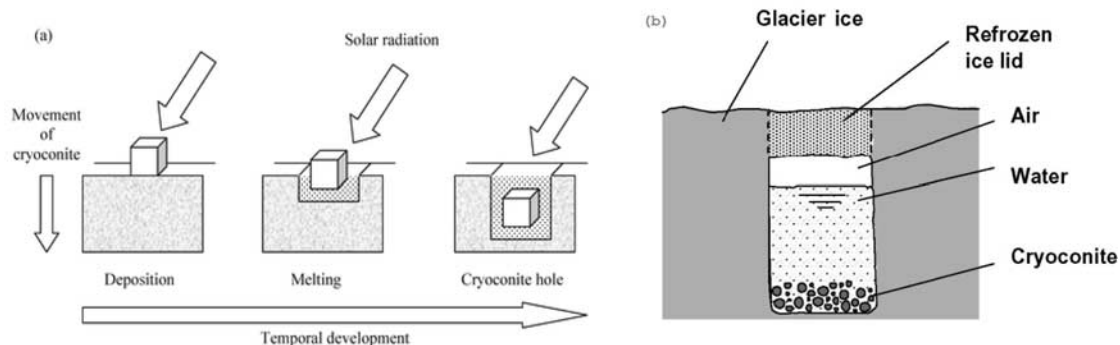
2004]. An ice lid between 10 and 30 cm may form over the hole, below which is a head space (Figure 2b). Water in summer is generally clear, but can be tea-coloured. The cryoconite material at the base of the hole is derived from aeolian sources [Lyons *et al.*, 2003], and acts as a substrate for microorganisms such as heterotrophic bacteria, fungi, cyanobacteria, green algae, rotifers and tardigrades [Mueller and Pollard, 2004; Porazinska *et al.*, 2004]. The cyanobacteria, in particular, photosynthesize when sunlight illuminates the holes [Tranter *et al.*, 2004]. The holes freeze solid over winter and reform during the following spring. Heterotrophy and photoautotrophy by biota in the holes, coupled with weak chemical buffering, can cause extreme chemical conditions to develop: pH values approach 11 and O<sub>2</sub> saturation may approach 160%. Biochemical cycling between periods of net photosynthesis and net respiration produces large quantities of dissolved organic carbon (DOC) and much of the dissolved nitrogen pool (>99%) is in the form of dissolved organic nitrogen (DON).

[5] The previous biogeochemical studies of cryoconite holes in Taylor Valley [Fountain *et al.*, 2004; Porazinska *et*

*al.*, 2004; Tranter *et al.*, 2004] dealt with relatively small sample sets and have not examined the biogeochemical evolution of the holes from a frozen state, through the thaw and throughout successive ablation seasons, largely because no means of dating the holes was available. In addition, the consequences of photosynthesis and biogeochemical cycling on the C cycle in these closed systems have yet to be explored. This paper addresses these issues by analysing a comprehensive survey of cryoconite holes from Canada Glacier, which was undertaken in the austral summer of 2005–2006.

## 2. Site Description

[6] Canada Glacier is situated within Taylor Valley, one of the three McMurdo Dry Valleys, which is 34 km long and 12 km wide (Figure 1). Average annual temperatures on the valley floor are between –15 and –30°C, with summer temperatures close to zero [Doran *et al.*, 2002]. Precipitation is less than 10 cm water equivalent per year (a), most of which sublimates before making any hydrologic contribu-



**Figure 2.** Schematic showing (a) the development [from Cowan and Tow, 2004] and (b) the internal structure [from Fountain *et al.*, 2004] of a typical cryoconite hole.

tion [Fountain *et al.*, 1999b]. Katabatic winds descend from the Antarctic Plateau at speeds of 20 to 35 m s<sup>-1</sup> [Nylen *et al.*, 2004]. These winds transport the sediment from the valley floor onto the glaciers, creating the observed cryoconite holes.

[7] Canada Glacier is typical of most glaciers in the valley, being small, polar and alpine type in morphology, with an ablation area of <10 km<sup>2</sup> [Fountain *et al.*, 1998]. The ice temperature is well below freezing throughout, with an average of ~-18°C [Fountain *et al.*, 1999a]. Canada Glacier descends from the Asgard Range (Figure 1). Yearly mass exchange is relatively small compared to glaciers in temperate regions; about 10 to 30 cm a<sup>-1</sup> water equivalent of snow accumulation occurs in the upper zones of the glaciers and 6 to 15 cm water equivalent ablation occurs in the lower zones, of which 30% is from melting and 70% from sublimation [Fountain *et al.*, 1999b]. Limited melting occurs on the horizontal ice surfaces, but more occurs on vertical surfaces because the angle of incidence of incoming solar radiation is higher [Lewis *et al.*, 1999]. Meltwater on cold, polar glaciers is confined to the surface or very near-surface. Canada Glacier has a near-surface drainage system which is maintained by the heating of subsurface debris in otherwise frozen supraglacial channels, lakes and cryoconite holes. Wholescale melting of the glacier surface only occurs during relatively warm summers. Then, the subsurface drainage network is exposed to form the basis of a supraglacial drainage system, which includes melt channels and ponds [Fountain *et al.*, 2004]. Simultaneously, the lids of the cryoconite holes melt out and the holes are flushed of their solute [Foreman *et al.*, 2004].

### 3. Methods

[8] Three types of sample, frozen cryoconite holes, cryoconite holes containing water (hereafter, wet holes) and glacier ice, were collected. Some 123 cryoconite holes (89 frozen and 34 wet) were sampled between October 2005 and February 2006. Five cores of glacier ice were also collected from locations shown in Figure 1.

[9] Cryoconite holes were randomly sampled at regular intervals along transects. All sampling locations were recorded using handheld GPS. Hole dimensions (depth, diameter of minor and major axis) were also measured. Transects radiated out from the permanently sited meteorological station on the lower ablation zone (Figure 1). Frozen holes were sampled by drilling a 20 cm diameter core from the centre of the hole using a Badger drill and Sipre corer. Drilling ceased when clean glacier ice below the basal debris layer was encountered. Cores were stored in Ziploc bags triple-rinsed with deionised water, transferred to the field laboratory and stored frozen in a chest freezer until processing up to 30 days later. Wet holes were sampled by drilling through the centre of the ice lid. The core from the ice lid was retained and treated as above. A water sample of ~500 ml was collected using a hand pump. Samples were returned to the field laboratory and stored in a refrigerator at 1–4°C for a maximum of 1 day. Glacier ice cores were drilled to 40 cm depth, and treated in the same manner as the ice samples above.

[10] Ice samples were melted at room temperature. Some 150 ml of meltwater was filtered through 0.4 μm Nucleo-

pore membranes and stored in three 60 ml prerinsed bottles, and used for major ion, nutrient and pH/conductivity/O<sub>2</sub> analysis. An additional aliquot of 100 ml was filtered through precombusted Whatman GF/F for DOC analysis, to which 1 ml concentrated HCl was added as a biocide. Filtrates were refrigerated at <4°C.

[11] Conductivity, dissolved oxygen and pH was measured on filtered samples in the field laboratory within a few hours of filtration using portable meters: YSI 30, YSI 58 and a Thermo-Orion pH meter, respectively. The pH probe was calibrated daily with pH 4 and 7 buffers. Major ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) were measured using a Dionex DX-120 ion chromatograph, DOC using a Shimadzu TOC-V CPN Total Organic Carbon Analyzer (with high sensitivity catalyst) at the Crary Lab, McMurdo Station. Full details can be found in Priscu and Wolf (1999). Analysis was conducted between one and eight weeks after filtration. Precision was <5% for all ions. The quantification limit was taken as the concentration of the lowest standards, which are: F<sup>-</sup> 0.3; Cl<sup>-</sup> 0.6; NO<sub>3</sub><sup>-</sup> 0.07; SO<sub>4</sub><sup>2-</sup> 0.4; Na<sup>+</sup> 2; Mg<sup>2+</sup> 5; K<sup>+</sup> 0.2 and Ca<sup>2+</sup> 2 μeq/l. The detection limit for DOC was 0.2 ppm (or mg/l). C. DIC (dissolved inorganic carbon) 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.

[12] Factor Analysis was employed to aid interpretation of the data set using Minitab 14.20 Statistical Software. Factor Analysis, like Principal Components Analysis, attempts to reduce the number of variables in a complex data set by finding a small number of linear combinations of variables, or factors, which explain most of the variability in the data set. Factor Analysis is similar to Principal Components Analysis, except that factor weights are scaled so that their sum of squares is equal to the associated eigenvalue of the correlation or covariance matrix, and so are related to the total variance explained by the factor. Varimax rotation was employed. Kaiser's criterion was used to select factors with eigenvalues greater than or equal to 1 [Bryman and Cramer, 1996].

### 4. Results

[13] Cryoconite holes on Canada Glacier contained generally fine-grained sediment, with some coarse particles. Areas of developing cryoconite holes were visible on the ice surface, with very small, shallow pockets containing wind-blown debris, especially on the western flank of the glacier. Relict surface meltwater channels, last containing waters at high flow in 2001 [Foreman *et al.*, 2004], were key features on the glacier surface, especially at low elevations. Liquid water flowed in the base of these channels by the end of the ablation season, either open to the atmosphere or covered by a thin layer of ice. Large sediment volumes in the base of these channels catalysed the development of 'extreme' cryoconite holes [Fountain *et al.*, 2004] which persist throughout the ablation season and engulf smaller holes around them. The ice surface was becoming rotten by the end of the ablation season, but some cryoconite holes still remained ice-lidded.

[14] Table 1 shows the chemical compositions of the samples. Concentrations of all ions other than Cl<sup>-</sup> have

**Table 1.** Chemical Composition of Glacier Ice, Frozen Cryoconite Holes, Wet Cryoconite Holes and Their Ice Lids on Canada Glacier<sup>a</sup>

	F <sup>-</sup> , μeq/l	Cl <sup>-</sup> , μeq/l	NO <sub>3</sub> <sup>-</sup> , μeq/l	*SO <sub>4</sub> <sup>2-</sup> , μeq/l	*Na <sup>+</sup> , μeq/l	*K <sup>+</sup> , μeq/l	*Mg <sup>2+</sup> , μeq/l	*Ca <sup>2+</sup> , μeq/l	*DIC, μeq/l	pH	pCO <sub>2</sub> , atms	DOC, ppm C	DO, % sat.	Depth, cm	Width, cm
Glacier ice n = 5	$\bar{x}$ 0.00	9.2	0.40	2.49	-1.91	1.37	9.22	6.16	12.0	5.30	-2.59	(0.34)		40	
	Δ 0.00	2.97	0.12	1.98	1.97	0.50	2.96	2.55	2.46	0.76	0.80	(0.20)		20.8	52
Frozen holes n = 89	$\bar{x}$ 1.0	92.0	6.40	41.6	-22.5	14.1	31.9	227	202	6.50	-2.54	0.72		5.74	26
	Δ 0.58	93.2	23.3	63.1	46.9	9.02	41.7	145	102	0.47	0.88	0.32		28.3	26
Wet holes n = 35	$\bar{x}$ 1.50	116	1.40	56.0	-19.4	9.01	12.1	155	97.9	7.22	-3.68	0.71	106	6.24	8.06
	Δ 0.79	86.9	1.66	55.5	64.2	8.95	23.3	109	81.4	0.98	0.57	0.64	0.43	8.75	26
Hole lids n = 33	$\bar{x}$ 0.70	25.9	0.40	10.3	-1.74	3.88	7.23	56.6	54.6	6.42	-3.20	0.58	96.5	3.40	8.06
	Δ 0.20	18.7	0.31	9.91	14.6	3.69	7.86	47.9	47.5	0.84	2.64	1.81	0.20	3.40	8.06

<sup>a</sup>Data on the dimensions of the holes and the lids that were sampled are also given. The DOC concentrations for glacier ice are close to detection limit and are indicative values only.

been corrected for sea salt, denoted by \*, assuming that all Cl<sup>-</sup> is derived from sea water. There might be local sources of Cl<sup>-</sup> which are not associated with sea salt, since some of the \*Na<sup>+</sup> are negative. Frozen cryoconite holes usually contain an order of magnitude more solute than the surrounding glacier ice, and have variable chemical compositions. Concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> are particularly higher in the frozen holes, whereas DOC concentrations are apparently only a factor of two higher. We note that DOC concentrations in the glacier ice are usually close to detection limit, and therefore are unlikely to be a true representation of the actual concentrations.

[15] The concentration of ions in waters within the wet holes (Table 1) is variable and is comparable to those sampled in previous studies [Tranter *et al.*, 2004; Fountain *et al.*, 2007]. The concentration of solutes in the wet holes is usually less than those of the frozen holes, except for Cl<sup>-</sup>, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Concentrations of \*DIC are notably lower. However, the standard deviations are so high that there is little statistical difference between the mean values of the individual ions. The ice lids contain mean concentrations that are between ~2–5 times less than the underlying waters. Hence solute is not totally rejected from the ice lids during freezing.

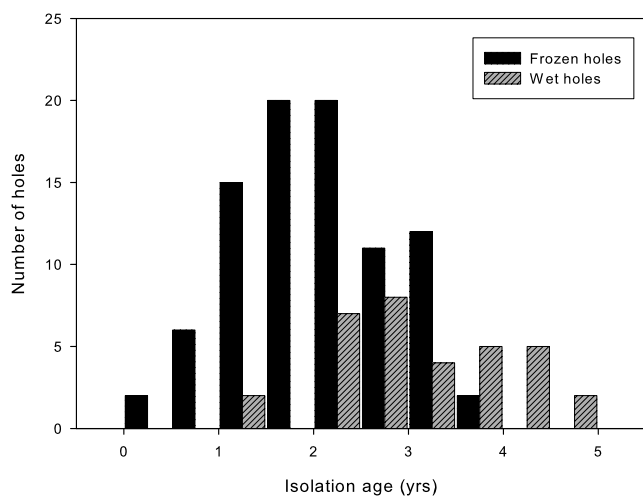
[16] The glacier ice (Table 1) is more dilute than the frozen and wet holes. It is also more dilute than that sampled on the lower ablation zone by Lyons *et al.* [2003]. However, the cores collected in this study were all to a depth of ~40 cm, while the majority of samples collected in the previous study were to a depth of 5 cm. Hence, the effect of any dry deposition to the surface or solute enhancement due to sublimation is mitigated. The mean measured concentration of Cl<sup>-</sup> in the glacier ice is of significance because the isolation ages of waters that are calculated below are inversely related to Cl<sup>-</sup>.

## 5. Isolation Age

[17] It is useful to know how long the cryoconite hole has been isolated from the near surface drainage system, since this gives a time frame over which to examine annual changes in the biogeochemistry of water in the isolated holes. The excess mass of Cl<sup>-</sup> in the cryoconite hole, in comparison to the mass of Cl<sup>-</sup> in an equivalent volume of glacier ice, gives an index of how long the hole has been accumulating Cl<sup>-</sup>. An estimate of the isolation of the hole from the supraglacial drainage system can be obtained when the excess Cl<sup>-</sup> is normalised to the sublimation rate. The confounding factors which caution against the uncritical use of isolation ages are discussed in detail below. Isolation ages, Δ*t*, were calculated for each hole using the method of Fountain *et al.* [2004], modified to include the mass of Cl<sup>-</sup> found in the ice lid. Equation (1) shows that

$$\Delta t = \left( \left( \frac{M_i}{ai} - h \right) + \left( \frac{M_{lid}}{ai} - h_{lid} \right) \right) \left( \frac{dz}{dt} \right)^{-1} \quad (1)$$

where *h* is the depth and *a* is the cross-sectional area of the hole, *i* is the average concentration of chloride in the surrounding ice and *dz/dt* is equal to the melt rate at the base of the hole, assumed to be equal to the ablation rate. The value for *dz/dt* is assumed to be 8 cm a<sup>-1</sup> [Fountain *et al.*,



**Figure 3.** Histogram of isolation ages for frozen and wet cryoconite holes on Canada Glacier.

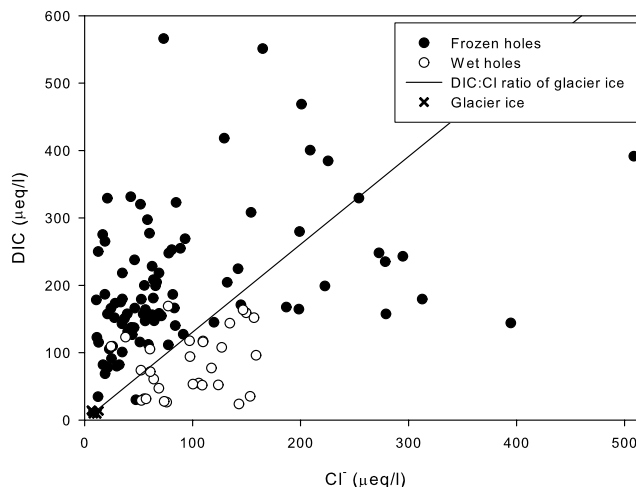
2004], and  $i$  is assumed to be  $9.2 \mu\text{eq/l}$  (Table 1). All the wet holes and most of the frozen holes (92%) sampled were isolated according to this classification. *Fountain et al.* [2004] estimated that up to 50% holes on Canada Glacier were isolated based on a smaller sample size. All the holes sampled have been apparently isolated for less than 5 a, with the majority between 1 and 4 a (Figure 3). This is consistent with the last period of exceptionally warm weather in 2001, which led to melting and flushing of solutes from the glacier surfaces [*Foreman et al.*, 2004]. Wet holes appear to be isolated longer than the frozen holes because the wet holes scavenge  $\text{Cl}^-$  when melting into glacier ice during the thaw, equating to a gain of up to 1 a in their isolation age.

## 6. Discussion

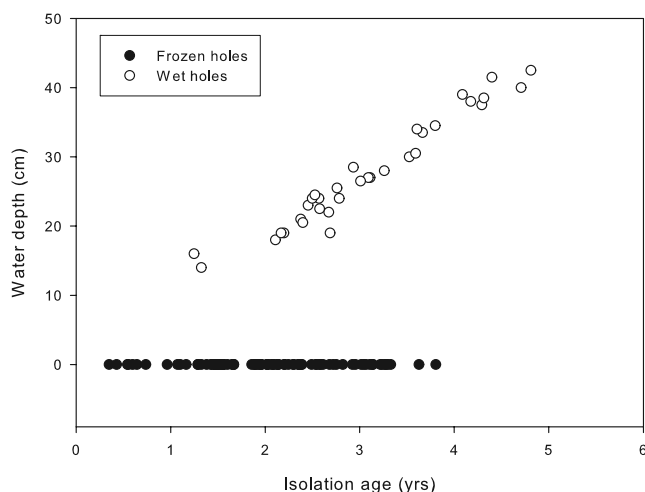
[18] Cryoconite holes melt out and refreeze on seasonal and subseasonal timescales (*Fountain et al.*, submitted manuscript, 2007). The cyclical melting and freezing may impact on C-cycling within the holes, which involves both organic and inorganic phases. DIC is fixed into organic matter during the summer, when there is copious liquid water in the holes and photosynthesis exceeds respiration [*Tranter et al.*, 2004; *Stibal and Tranter*, 2007]. It is likely that net respiration occurs during freezing, when environmental stresses on photosynthetic organisms will be high. Net respiration may occur over winter if some liquid water is present despite the subzero temperature of the glacier ice, for example in solute-rich quasi liquid layers around ice crystals [*Ushakova and Toshkina*, 1974] or in ice veins [*Price*, 2000]. Net respiration returns DIC to solution, along with some DOC [*Tranter et al.*, 2004]. Over-winter freezing produces secondary carbonate precipitates from the predominantly  $\text{Ca}^{2+}\text{-HCO}_3^-$  waters within the holes. These largely dissolve during the thaw. It is possible that photosynthesis in the wet holes may lead to localised precipitation of carbonates in the vicinity of the cyanobacterial flakes and mats on the surface of the cryoconite debris because of the local elevation of pH. Evidence for the cyclical dissolution and precipitation of carbonates in the closed cryoconite

holes is provided by Figure 4, which shows a scatterplot of DIC versus  $\text{Cl}^-$ . The first order feature of this scatterplot is that most of the frozen hole samples lie above the line defining the DIC: $\text{Cl}^-$  ratio of glacier ice, and most of the wet hole samples lie below. This is consistent with the dissolution of carbonates in the cryoconite debris during the thawing and processing of the frozen hole samples, which produces DIC concentrations higher than those found in glacier ice for a given  $\text{Cl}^-$  concentration. The source of this additional DIC is likely to be from  $\text{CO}_2$  scavenged from glacier ice during melt in and dissolution of debris in the holes. By contrast, DIC concentrations are usually lower in the wet holes for a given  $\text{Cl}^-$  concentration, suggesting depletion either directly by photosynthesis [*Stibal and Tranter*, 2007] due to incorporation of inorganic C into new organic matter, or perhaps indirectly because of carbonate precipitation in the vicinity of cyanobacterial flakes and mats.

[19] A problem with the interpretation of scatterplots such as Figure 4 is that there is no overt time element on the plot. Further, concentration is influenced by factors such as whether the hole is melting into glacier, causing dilution, or whether the hole is freezing, when concentration will occur. We use mass per unit area rather than concentration in the following figures to remove this effect. The isolation age is useful for providing a crude means of dating the holes. We assume that the isolation age provides an index of how long biogeochemical processes have been operating in a relatively closed system. However, it is important to be critical of this interpretation of the isolation age since variations in the recharge and isolation histories of the holes of the upstream holes may have an important effect on the apparent isolation age of the hole. For example, holes that are flushed and recharged with dilute waters when they connect to the supraglacial drainage system have appropriate isolation ages. However, some holes may be recharged with concentrated waters, depending on the flushing history of holes and hydrology upstream [*Fountain et al.*, 2004]. The isolation age may even increase if the  $\text{Cl}^-$  concentra-



**Figure 4.** Scatterplot of DIC ( $\mu\text{eq/l}$ ) versus  $\text{Cl}^-$  ( $\mu\text{eq/l}$ ) for frozen and wet cryoconite holes on Canada Glacier. Data for glacier ice are also plotted. The line denotes the DIC: $\text{Cl}^-$  ratio of glacier ice.

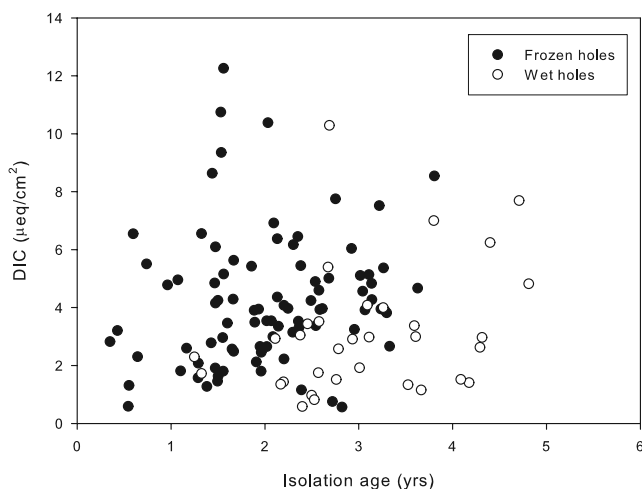


**Figure 5a.** Scatterplot of water depth versus isolation age (years) for frozen and wet cryoconite holes on Canada Glacier.

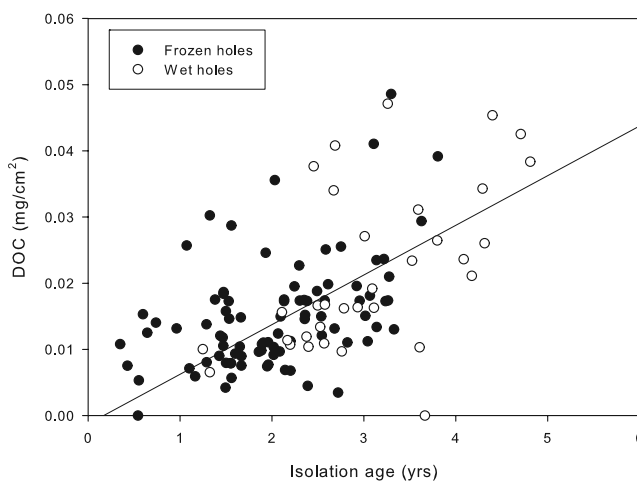
tion of the incoming water is greater than that of waters in the hole. Therefore the isolation age must be seen as indicative, rather than an absolute.

[20] Figure 5a shows a plot of water depth versus isolation age for the wet holes. The frozen holes are also shown for comparative purposes. There is a striking linear association between water depth and isolation age. It seems that processes within the holes may serve to deepen the hole over time. This has the advantage of providing better thermal inertia to the system over time, and may serve to preserve water in the holes for longer during each ablation season, so providing an ecological benefit. We explore which processes may give rise to this effect below.

[21] The previous discussion of C cycling in isolated cryoconite holes revealed that several processes serve to either increase or decrease DIC concentrations over time. This is confirmed by Figure 5b, which shows a scatterplot of the mass per unit area of DIC versus isolation age. There



**Figure 5b.** Scatterplot of the mass of DIC ( $\mu\text{eq}/\text{cm}^2$ ) versus isolation age (years) for frozen and wet cryoconite holes on Canada Glacier.

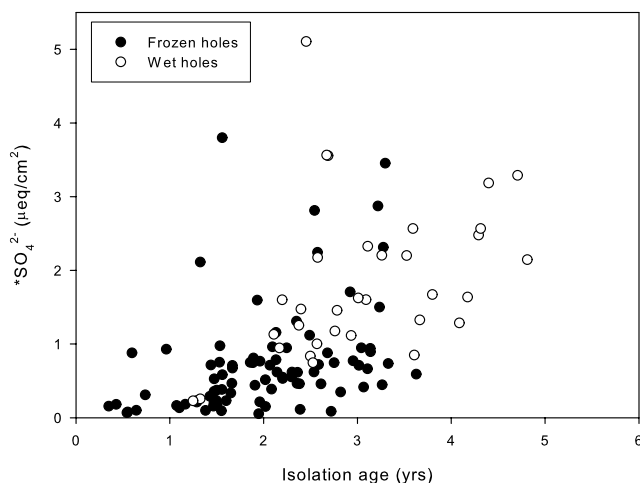


**Figure 5c.** Scatterplot of the mass of DOC ( $\text{mg C}/\text{cm}^2$ ) versus isolation age (years) for frozen and wet cryoconite holes on Canada Glacier. The best fit linear regression line is also shown:  $\text{DOC} = 0.0075 * \text{Isolation Age} - 0.0013$  ( $r^2 = 0.2992$ ,  $n = 118$ ).

is considerable scatter in the data. The wet holes appear "older" and contain slightly less DIC than the frozen holes, which is consistent with the assertion that DIC is lost during the thaw due to photosynthesis and possibly local precipitation of carbonates. The overall scatter of the data in Figure 5b is not only the consequence of biological processes in the holes. There is likely to be an influence of factors such as the original carbonate content of the debris which formed the holes and the exchange of gases between the holes and the atmosphere if the ice lids become rotten and permeable during the ablation season, in addition to the hydrological factors noted above. For example, the cryoconite debris may be sourced from different locations within Taylor Valley according to available debris, wind direction and speed [Lancaster, 2002; Lyons *et al.*, 2003], and this may significantly affect the chemical composition of the hole waters. Dust from more saline soils [Barrett *et al.*, 2007] will introduce more solute to the holes initially and holes in proximity to stream algal mats [McKnight *et al.*, 1998] are likely to have much higher organic matter content. Finally, holes formed from the deposition of new dust are likely to contain more carbonate than those which reform following melt out and flushing of the holes during relatively warm years.

[22] Figure 5c shows how, on average, the mass of DOC in the holes on Canada Glacier increases over time. There is considerable scatter in the data set, which is testament to the variable nature of physical processes in cryoconite holes (Fountain *et al.*, submitted manuscript, 2007), cryoconite debris [Lyons *et al.*, 2003] and inoculi [Nkem *et al.*, 2006]. The best fit linear regression of the mass of DOC in both wet and frozen holes versus isolation ages has a correlation coefficient,  $r$ , of 0.547 ( $n = 118$ ), which is significant at the 1% level. The best fit linear regression equation has a slope of  $\sim 0.0075 \text{ mg C cm}^{-2} \text{ a}^{-1}$ , which is our best estimate of the average rate of accumulation of DOC in these holes.

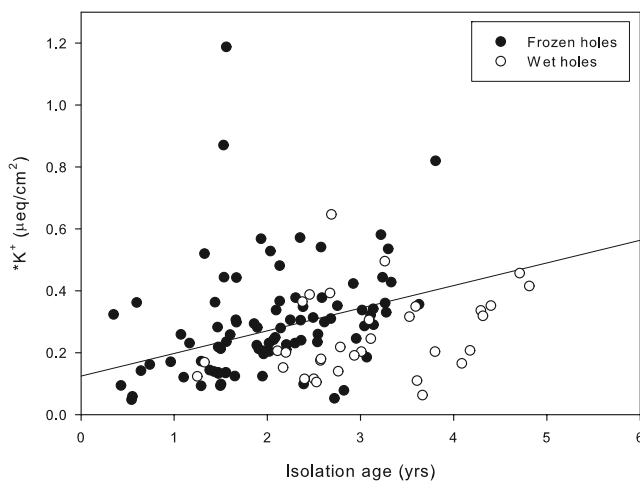
[23] Figure 5d shows that  $\text{SO}_4^{2-}$  is largely constant in frozen holes, but some individual frozen holes have relatively high masses of  $\text{SO}_4^{2-}$ . We attribute these high con-



**Figure 5d.** Scatterplot of the mass of  $*SO_4^{2-}$  ( $\mu\text{eq}/\text{cm}^2$ ) versus isolation age (years) for frozen and wet cryoconite holes on Canada Glacier.

concentrations of  $SO_4^{2-}$  to variability in the original S content of cryoconite debris. For example, a higher proportion of gypsiferous soil dust [Campbell and Claridge, 1987] could produce such high concentrations. The wet holes appear to have relatively higher masses of  $SO_4^{2-}$  when compared to the frozen holes, which suggests that  $SO_4^{2-}$  is generated from the cryoconite debris during the ablation season.

[24] Figure 5e shows that the mass of  $*K^+$  increases in both wet and frozen holes over time, most likely from dissolution of silicates in the cryoconite debris. The three outliers above  $0.8 \mu\text{eq}/\text{cm}^2$  have been omitted from the following analysis. Simple linear regression analysis of the mass of  $*K^+$  in frozen holes versus isolation age gives a correlation coefficient,  $r$ , of 0.433 ( $n = 89$ ), which is significant at the 1% level. The slope of the best fit linear



**Figure 5e.** Scatterplot of the mass of  $*K^+$  ( $\mu\text{eq}/\text{cm}^2$ ) versus isolation age (years) for frozen and wet cryoconite holes on Canada Glacier. The best fit linear regression line for frozen holes is also shown:  $*K^+ = 0.073 * \text{Isolation Age} + 0.12$  ( $r^2 = 0.1873$ ,  $n = 89$ ).

**Table 2.** Factor Analysis of Constituents Within Frozen and Wet Cryoconite Holes on Canada Glacier<sup>a</sup>

Variable	Factor1	Factor2	Factor3	Communality
Isolation age, years	0.171	0.946	-0.164	0.951
$*SO_4^{2-}$ , $\mu\text{eq}/\text{cm}^2$	0.396	0.224	-0.842	0.917
DIC, $\mu\text{eq}/\text{cm}^2$	0.897	-0.078	-0.112	0.824
DOC, $\text{mg C}/\text{cm}^2$	0.559	0.451	-0.522	0.789
$*K^+$ , $\mu\text{eq}/\text{cm}^2$	0.899	0.151	-0.203	0.873
Water depth, cm	-0.282	0.681	-0.570	0.868
Variance	2.1926	1.6408	1.3873	5.2206
% Var	0.365	0.273	0.231	0.87

<sup>a</sup>The water depth is equal to zero in the frozen holes. Varimax rotated factor loadings and communalities are shown.

regression line is  $0.073 \mu\text{eq cm}^{-2} \text{ a}^{-1}$ , which is our best estimate of the average accumulation of  $*K^+$  in the frozen holes. There is a suggestion that lower masses of  $*K^+$  occur in wet holes, which has been observed in laboratory incubation experiments and may be related to biological activity [Stibal and Tranter, 2007].

[25] Factor Analysis of these data was undertaken to determine the principal underlying features of the data sets. A water depth of zero was used for the frozen holes, to compare and contrast their properties with those of the wet holes. The results are shown in Table 2. Three factors account for 87% of the variance. The first factor accounts for  $\sim 37\%$  of the variance. The masses of  $*K^+$ , DIC and DOC load preferentially on this factor, as to some extent does the mass of  $*SO_4^{2-}$ . This factor can be regarded as an index of dust dissolution, in that all these ions can be sourced from cryoconite debris. Isolation age does not load highly on this factor, suggesting that the initial composition of the dust is important in controlling the solute content of water in the holes. This is consistent with simple dissolution experiments conducted with dust from a variety of locations on the glacier and soil (M. Tranter, unpublished data).

[26] Isolation age, water depth and DOC load more heavily on the second factor, which explains a further  $\sim 27\%$  of the variance. This suggests that the wet holes become deeper as they age, and that their DOC contents increase on average. This may be a direct consequence of the increasing DOC, since the waters become darker in colour and may absorb more solar radiation as a consequence. Other factors that could increase water depth include the possibility of the biomass within the sediment increasing with time. The biomass is darker than the sediment, and greater adsorption of solar radiation could occur as a consequence.

[27] The mass of  $*SO_4^{2-}$ , DOC and water depth load negatively on the third factor, which accounts for a further  $\sim 23\%$  of the variance. This suggests that frozen holes generally contain lower masses of  $SO_4^{2-}$  and DOC than wet holes. The loss of  $SO_4^{2-}$  in the frozen holes may be the result, perhaps, of the generation of reduced S compounds, such as sulfides, during the autumnal freeze and possibly over winter, when anoxic conditions may prevail in micro-environments in the freezing debris. The loss of DOC may be due to precipitation of more refractory compounds during freezing, which take longer to fully dissolve than the processing of the frozen hole samples allows. Alterna-

tively, it could be the consequence of heterotrophic uptake during the fall and winter.

## 7. Conclusions

[28] The main processes controlling the chemical composition of solutes in both frozen and water-containing or wet cryoconite holes on Canada Glacier, Taylor Valley, Antarctica, have been documented. These are dissolution of cryoconite debris, cyclical precipitation and dissolution of carbonates, net photosynthesis over summer and net respiration during the autumnal freeze. Dissolution of primary carbonate and sulfate minerals in the debris which forms the hole produces a water chemistry that reflects the heterogeneous nature of the debris. Thereafter, slower dissolution of silicates adds ions such as  $K^+$  to the holes. Net photosynthesis occurs during the summer months, and DIC may be lost from the waters. Net respiration is likely to occur during the autumnal freeze, and possibly over winter. There is some equivocal evidence for  $SO_4^{2-}$  reduction during this period, presumably in anoxic environments in the cryoconite debris. DOC is regenerated during the thaw, and the mass of DOC accumulates annually. Some DIC accumulates annually in the holes because of scavenging of  $CO_2$  during the annual melt in of the holes, but the variety of processes in which DIC is involved confounds a simple patterning in the data set we present. The isolation age, based on the mass of excess  $Cl^-$  in the holes, appears to be crudely indicative of the extent of isolation of these simple, closed biogeochemical systems from the near surface drainage system. The holes progressively deepen over time. Our best estimate of DOC generation in the cryoconite holes is of the order of  $7.5 \mu g C cm^{-2} a^{-1}$ , and the accumulation of  $*K^+$  in frozen holes is of the order of  $0.073 \mu mole cm^{-2} a^{-1}$ .

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