Extreme hydrochemical conditions in natural microcosms entombed within Antarctic ice

Abstract

Cryoconite holes are near-vertical tubes that form in the surface of glaciers when solar-heated debris melts into the ice. Those that form in the McMurdo Dry Valleys of Antarctica are distinctive, in that they have ice lids and are closed to the atmosphere for periods of years to decades. Photoautotrophs and heterotrophs grow within this closed environment, perturbing the poorly buffered water chemistry, yet maintaining the potential for photosynthesis. Microbial excretion and decomposition of organic matter produces dissolved organic carbon (DOC): dissolved inorganic carbon ratios of $\sim 1 : 2$. Much of the dissolved nitrogen pool (80–100%) exists as dissolved organic nitrogen (DON). The DON : DOC ratio is $\sim 1 : 11$ (mol/mol), typical of organic particulate material at the Earth’s surface. The combination of photoautotrophy, heterotrophy and weak chemical buffering within these microcosms promotes values of pH, $pCO_2$, $O_2$ saturation and percentage total dissolved nitrogen as DON that reach $10^{-9.9}, 10^{-7.6}$ atm, 160% and 100% respectively, which are a unique combination among the surface waters on Earth. These ice-sealed cryoconite holes could be important analogues of refugia on Snowball Earth and other icy planets. Copyright © 2004 John Wiley & Sons, Ltd.

Key Words cryconite; Antarctica; glacier ice; microcosms

Introduction

Taylor Valley, one of the McMurdo Dry Valleys located in southern Victoria Land, Antarctica, is a polar desert with extreme climatic conditions (Priscu, 1998). The annual average value for air temperature is $\sim -17 ^\circ$C, for precipitation is $<10$ mm, for potential sublimation is 8 cm and for wind speed is 5 m s$^{-1}$. It is the location of the McMurdo Long-term Ecological Research (LTER) project, partly because of the sensitivity of the ecosystem to small variations in climate (Doran et al., 2002). Life has been documented in a wide range of icy environments (Friedmann et al., 1993; Priscu et al., 1998, 1999; McKnight et al., 2002), including near-surface, intraglacial habitats in cryoconite holes (Wharton et al., 1985). Water may be contained within cryoconite holes for several months each year, and the holes are colonized largely by coccoid and filamentous cyanobacteria (Oscillatoriales), with some chlorophytes, diatoms, rotifers and tardigrades (Mueller et al., 2001).

Cryoconite holes initially form as a consequence of solar heating of sediment and dark-coloured algae resident on the glacier surface. The hole depth reaches an equilibrium value based on the heat supplied by solar radiation and heat lost to the colder ice (McIntyre, 1984). The entire hole freezes solid in winter. The hole reforms in summer when solar radiation transmits through the ice and heats the dark sediment and
organic matter at depth. Once formed, it is unlikely that the holes are open to the atmosphere on an annual basis, given the ice lid thickness (30–40 cm) and the rate of sublimation (~8 cm year⁻¹; Fountain et al., 1998). Rather, the holes open during warm spells that reoccur on decadal time scales (Doran et al., 2002). Other hydrological and biological features of cryoconite holes in Taylor Valley are described elsewhere (Fountain et al., 2004; Porazinska et al., 2003).

Solute in cryoconite water is obtained from icemelt and the dissolution of aerosol and debris, but is excluded from the freezing lid. Hence, solute accumulates in the hole over time. Atmospheric gases (e.g., N₂, O₂ and CO₂) are acquired from bubbles in the ice during the downward melting of the hole, and subsequently are either involved in biogeochemical reactions within the hole and/or may contribute to the gases that accumulate in the head space above the water column. Some gas and particulate exchange may occur with the atmosphere during the melt-in of debris through the ice lens, and the melt-out of debris and gas bubbles. These processes have been well documented for lake ice cover (Adams et al., 1998). Further, there is some connectivity between about 50% of the holes (Fountain et al., 2004). Hence, gaseous exchange with the atmosphere is very low in the unconnected holes, and is at least impeded in the connected holes.

The following is a comparison of the chemistries of the unaltered glacier ice and the meltwater in the cryoconite holes, from which we identify the principal biogeochemical processes that operate within these holes that are out of free contact with the atmosphere.

**Methods**

Water samples were collected from cryoconite holes on three glaciers in Taylor Valley (~78°S), namely Commonwealth (n = 2), Taylor (n = 7) and Canada Glaciers (n = 37). The typical hole sampled was 20–120 cm in diameter and 30–80 cm deep. Four main features characterize each hole: (a) an opaque ice lid, 30–40 cm thick; beneath which there is (b) a gas head space (1–10 cm), overlying (c) a clear to tea-coloured water column (30–40 cm), at the bottom of which is (d) a sediment layer (Mueller et al., 2001). The sediment consists of a fine sand, originating from the ground moraine that covers much of the valley, and which is transported by wind to the glacier surface (Fountain et al., 1998). The sediment includes bacteria, cyanobacteria, algae and decaying organic matter (Mueller et al., 2001). Water samples were immediately filtered following collection, and stored in pre-cleaned bottles. Pre-combusted Whatman glass microfibre GF/F filters, with an effective pore size of 0.7 µm, and glass bottles were used for dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) samples. Otherwise, 0.4 µm Nucleopore membranes and polyethylene bottles were used. Measurement of pH and O₂ was made in the field within 4 h of collection using standard procedures (Priscu and Wolf, 1999). Base cations and strong acid anions were measured by ion chromatography. Nutrients (NH₄⁺, NO₃⁻, NO₂⁻ and PO₄³⁻), silicon and DOC were measured by autoanalyser. Full details of analytical methods may be found elsewhere (Priscu and Wolf, 1999). Measurements were conducted within 3 weeks of sample collection at the Crary Laboratory, McMurdo, Antarctica. Dissolved inorganic carbon (DIC) was derived from charge balance deficit. DON was determined by high-temperature catalytic oxidation on a Shimadzu TOC5000A employing chemiluminescent detection (Cauvet, 1999) at Southampton Oceanographic Centre, ~1 year after sample collection. Samples were refrigerated at 4°C and remained in the dark prior to analysis.

**Results and Discussion**

Table I compares the average concentrations of a range of major and minor species in glacier ice and cryoconite holes from Canada Glacier (n = 37). The concentration of Ca²⁺ and SO₄²⁻ in each sample was corrected for seasalt on the basis of the Cl⁻ content. Hence, the asterisk denotes non-seasalt concentrations. Table I shows that the average water in cryoconite holes has a higher pH and major ion concentration than the surface glacier ice of Canada Glacier. This is partially due to the dissolution of seasalt contained in glacier ice during the progressive annual melt in of the holes. Figure 1 shows a scatterplot of "Ca²⁺, "SO₄²⁻ and DIC of cryoconite hole waters versus Cl⁻. There is one clear linear association between Cl⁻ and "SO₄²⁻, and there are two linear associations between Cl⁻ and both "Ca²⁺ and DIC. Variations in the volume of water in the holes, which arise from local enhancement of either melting
or freezing, are one of the key controls on the concentration of solute scavenged from icemelt in the holes. A simple mass balance equation gives rise to a linear association between Cl\(^-\) and the reciprocal of the depth of water in the hole (1/D), assuming that the diameter of the hole remains relatively constant during local enhancement of melting and freezing. The best-fit linear regression equation for the association between Cl\(^-\) (in units of µeq l\(^-1\)) and 1/D (where D has units of centimetres) is

\[
\text{Cl}^- = 9.2(\pm 14) + 1700(\pm 280)/D \\
\left(\rho^2 = 0.755; n = 14\right) \tag{1}
\]

The mass of Cl\(^-\) within the waters of the hole can be used to calculate the approximate duration of closure of the hole from the atmosphere, assuming that the hole was initially full of water formed by icemelt containing the average ice concentration of Cl\(^-\), that the ice lid contains no Cl\(^-\), that additional Cl\(^-\) is dissolved from glacier ice of average Cl\(^-\) composition during melt-in, and that the annual rate of sublimation is 8 cm (Fountain et al., 1998). The duration of closure ranges from 0 to 11 years (based on 15 holes with appropriate data).

The concentrations of \(^{+}\text{Ca}^{2+}\), DIC, \(^{+}\text{SO}_4^{2-}\) and NO\(_3^-\) in ice from Canada Glacier are shown in Table I and are similar to those published elsewhere (Lyons et al., 2003). Dissolution of debris is suggested, since the enrichment factors for \(^{+}\text{Ca}^{2+}\), DIC, silicon and \(^{+}\text{SO}_4^{2-}\) are greater than unity. \(^{+}\text{SO}_4^{2-}\) concentrations increase by a factor of ~2.4 with respect to Cl\(^-\), suggesting that the oxidation and/or dissolution of trace sulphides and sulphates in dust (Lyons et al., 2003) is an important supply of SO\(_4^{2-}\) to waters within the holes. The chemical composition of the dust also impacts on the \(^{+}\text{Ca}^{2+}\) and DIC concentrations. Those waters in the group that defines the lower linear association in Figure 1 are undersaturated with respect to both polymorphs of CaCO\(_3\) (aragonite and calcite), whereas those in the group that define the upper linear association are supersaturated. This suggests that there is an excess of carbonate in the dust of the latter samples over that necessary to saturate the water in the holes. The dissolution of carbonate into dilute waters may produce waters that are supersaturated with respect to CaCO\(_3\) (House, 1981). Additionally, increases in pH as a result of freezing or photosynthesis may also produce supersaturation, since the kinetics of carbonate precipitation may be relatively slow, particularly if compounds such as DOC poison nucleation sites (Morse, 1983). Local sources of carbonate aerosol include evaporitic salts in the soil and marble from the mountains that overlook Canada Glacier to the west (Lyons et al., 2003).

The pH values of the cryoconite holes’ waters rise to exceptionally high values, approaching 11 (Figure 2). Hydrolysis of CaCO\(_3\) (Equation (2)) in the dust at 0°C increases the pH to ~10.5, generates a low pCO\(_2\) (~10\(^{-6}\) atm) and saturates the waters with respect to CaCO\(_3\) (Tranter et al., 2002). Algal photosynthesis increases the pH in closed systems (Equation (3)), so further increasing saturation with respect to CaCO\(_3\). Figure 2 shows the increase in pH as \(^{+}\text{Ca}^{2+}\) and DIC increase in solution, due to the combination of the dissolution of debris, freezing and photosynthesis. The pCO\(_2\) falls systematically as pH rises, from near-atmospheric values of 10\(^{-3.7}\) to 10\(^{-7.6}\) atm at high pH, drawing into solution most of the CO\(_2\) in the air space overlaying the water column. These alkaline pH values of >10 are some of the highest values recorded in pristine natural aquatic ecosystems at or near the Earth’s surface, and are only commonly recorded in arid African soda lakes.

### Table I. Concentrations of selected major ions and nutrients in the surface ice (n = 10) of Canada Glacier and all cryoconite waters (n = 46). The glacier ice concentrations are derived from 10 surface ice samples, chosen from random locations. Asterisk denotes sea salt-corrected concentrations. Enrichment factors are calculated as \((X/\text{Cl}^-)_{\text{cryoconite holes}}/(X/\text{Cl}^-)_{\text{glacier ice}}\) where X is the chemical species of interest.

<table>
<thead>
<tr>
<th>Species</th>
<th>Glacier ice</th>
<th>Cryoconite holes</th>
<th>Enrichment factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-) (µeq l(^-1))</td>
<td>32 ± 28</td>
<td>106 ± 160</td>
<td>1</td>
</tr>
<tr>
<td>(^{+}\text{Ca}^{2+}) (µeq l(^-1))</td>
<td>36 ± 36</td>
<td>230 ± 300</td>
<td>1.9</td>
</tr>
<tr>
<td>DIC (µeq l(^-1))</td>
<td>35 ± 36</td>
<td>150 ± 160</td>
<td>1.3</td>
</tr>
<tr>
<td>(^{+}\text{SO}_4^{2-}) (µeq l(^-1))</td>
<td>7.8 ± 5.2</td>
<td>63 ± 78</td>
<td>2.4</td>
</tr>
<tr>
<td>Si (ppb)</td>
<td>18 ± 16</td>
<td>1000 ± 860</td>
<td>2.4</td>
</tr>
<tr>
<td>NO(_3^-) (ppb-N)</td>
<td>99 ± 62</td>
<td>24 ± 35</td>
<td>5.7</td>
</tr>
<tr>
<td>NH(_4^+) (ppb-N)</td>
<td>99 ± 63</td>
<td>4.7 ± 12</td>
<td>5.2</td>
</tr>
<tr>
<td>PO(_4^{3-}) (ppb-P)</td>
<td>3.1 ± 2.6</td>
<td>2.6 ± 2.7</td>
<td>0.25</td>
</tr>
<tr>
<td>pH</td>
<td>7.8 ± 1.7</td>
<td>6.2 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 1. Scatter plot of (a) $[^*]Ca^{2+}$ and DIC, and (b) $[^*]SO_4^{2-}$ versus Cl$^-$ for cryoconite waters from Canada, Taylor and Commonwealth Glaciers. Asterisk denotes that concentrations are seasalt corrected. DIC is the sum of HCO$_3^-$ and CO$_3^{2-}$, since H$_2$CO$_3$ is small by comparison (Drever, 1988).

\[
CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \quad (2)
\]

\[
CO_3^{2-} + 2H_2O \rightleftharpoons O_2 + CH_2O + 2OH^- \quad (3)
\]

The low $pCO_2$ and high pH may inhibit photosynthesis (Riebesell et al., 1993); hence, in these poorly pH-buffered closed systems, there may be biochemical buffering on the amount of photosynthesis, since new sources of atmospheric CO$_2$ and organic matter in dust are limited.

The dissolved carbon in the waters is partitioned between DOC and DIC reservoirs. There is a good association between DOC and DIC concentrations (Figure 3a), given the high potential for variability...
Figure 2. Scatterplot of $p$CO$_2$, *Ca$^{2+}$ and DIC versus pH for cryoconite waters from Canada, Taylor and Commonwealth Glaciers. $p$CO$_2$ is the pressure of CO$_2$ in a hypothetical atmosphere with which the water is in equilibrium.

in the amount and composition of debris in the holes. The best-fit linear regression equation is

$$\text{DOC} = 0.06(\pm 0.06) + 0.56(\pm 0.09)\text{DIC}$$

($r^2 = 0.57; n = 29$) (4)

Equation (4) suggests that the ratio of DIC : DOC is $\approx 2:1$. One possible ecological benefit is that the DOC helps to preserve the DIC pool by blocking the precipitation of CaCO$_3$ (Morse, 1983), which becomes supersaturated at higher pH. Hence, there is feedback between decomposition and the potential for photosynthesis. Oxygen is consumed and CO$_2$ is generated in the manufacture of DOC, as crudely shown by

$$2\text{CH}_2\text{O}(s) + \text{O}_2(\text{aq}) \rightleftharpoons \text{xCO}_2(\text{aq}) + \text{yH}_2\text{O}(l)$$

$$+ \text{C}_{(2-x)(2-y)}\text{H}_{(2-y)}\text{O}_{(2-2x-y)}(\text{aq})$$ (5)

where $\text{C}_{(2-x)(2-y)}\text{H}_{(2-y)}\text{O}_{(2-2x-y)}$ is a simplistic representation of DOC. The association between oxygen saturation, which approaches $\approx 160\%$, and pCO$_2$ is largely inverse, but is not simple (Figure 3b). This suggests that there are complex linkages between the rate of photosynthesis, the rate of microbial decomposition of organic matter, DOC, DIC and pH in these relatively simple closed systems. Indeed, experiments on the bacterial primary production $P$ and respiration $R$ of debris slurries from cryoconite holes on Canada Glacier show a wide range of $P : R$ ratios, from 0-01 to 1-3 (C. H. Fritsen, unpublished data). This implies that there is either temporal and/or spatial variation in the ability of the holes to generate conditions of net photosynthesis, which further suggests complex linkages between the above variables.

Enrichment factors for phosphorus and nitrogen in hole waters are less than unity (Table I), consistent with biological uptake. Concentrations of PO$_4^{3-}$ are low (Figure 4), but fairly constant, despite the high pH of the waters, which enhances desorption (Langmuir, 1997). By contrast, silicon concentrations increase with pH, suggesting that dissolution of silicates in the dust may be enhanced at higher pH (Gratz and Bird, 1993). This may increase the environmental stress on diatoms that live in the holes (Mueller et al., 2001), since production and maintenance of silica tests will take place in waters that are more aggressive to the tests. Concentrations of NO$_3^-$ and NH$_4^+$ generally decrease in the more concentrated waters (Figure 4). This suggests that there is efficient conversion of new nitrogen scavenged from icemelt.
Figure 3. (a) Scatterplot of DOC versus DIC for cryoconite waters from Canada and Commonwealth Glaciers. The best-fit line is given by Equation (4). (b) Scatterplot of oxygen saturation versus $pCO_2$ for cryoconite waters from Canada and Commonwealth Glaciers.

(Table I) into organic species. The ratio of inorganic nitrogen (DIN) to inorganic phosphorus approaches $\sim 10:1$ in the concentrated waters, compared with $\sim 30:1$ in the icemelt. $^{15}$N-isotope dilution experiments (J. C. Priscu, unpublished data) revealed that ammonium uptake : regeneration molar ratios always exceeded one (range: 1.6–3.2). Turnover of the ammonium pool from uptake and regeneration ranged from 3.8 to 18.3% day$^{-1}$ and 1.5 to 9.7% day$^{-1}$ respectively. Successive cycles of microbial uptake and regeneration will produce a positive association between DOC and DON (Figure 5). The best-fit linear association between DON and DOC, excluding one outlier, is

$$\text{DON} = 2.9(\pm 3.9) + 0.086(\pm 0.0014)\text{DOC}$$

($r^2 = 0.69; n = 19$)

suggesting a molar DON : DOC ratio of $\sim 0.09$. This is similar to that found in particulate organic matter in a wide variety of natural waters (Guildford and Hecky, 2004).
Figure 4. Scatterplot NO$_3^-$, NH$_4^+$, silicon and PO$_4^{3-}$ versus DIC concentrations in cryoconite waters from Canada and Commonwealth Glaciers. DIC is an index of the progressive dissolution of debris in the cryoconites, an assertion supported by the positive association with silicon

2000), suggesting that decomposition of organic matter is the source of DON and DOC in the hole waters. At least ~80%, and often >95–100%, of the total dissolved nitrogen is present as DON. The occurrence of photosynthesis, as suggested by the high saturation of O$_2$ and the experimental $P:R$ ratios, in holes with low DIN may suggest that the DON is labile, and that the ecosystem has adapted to derive nitrogen from dissolved organic compounds.

**Conclusions**

These new findings on the hydrochemistry of intraglacial aquatic habitats show that the weak
Figure 5. Scatterplot of DON versus DOC in cryoconite waters from Canada Glacier. The best-fit regression equation is given by Equation (6).

+ denotes the outlier.

pH buffering of these systems, when coupled with heterotrophic and photosynthetic activity, results in extreme values of pH, pCO₂ and oxygen saturation in a seemingly inhospitable cryogenic regime. These systems still allow net photosynthesis to occur in some circumstances, as crudely measured by the high oxygen saturation and P : R > 1. In common with other extreme environments on Earth (Rothschild and Manicelli, 2001), given the presence of water, algae and microbial communities survive in an extreme range of physico-chemical conditions in which life-sustaining energy is harvested and utilized to support the cycling of materials that are necessary for the survival, adaptation and radiation of life forms. This ice-sealed environment provides potential analogues for the survival of life in glacial surface environments on ‘Snowball Earth’ (Vincent et al., 2000) and other planetary ecosystems (Nisbet and Sleep, 2001). Given the existence of dust, e.g. from volcanoes, nunataks and a variety of moraines, inoculi and an energy balance that enables liquid water to form below the ice surface, biological activity may adapt to dissolve gases, substrates and nutrients from rock and ice, and recycle material in a manner that enables biological activity to continue even in extreme hydrochemical conditions. Feedbacks between physical, chemical and biological processes serve to maintain the ecosystem in a suitable form for continued colonization (e.g. feedbacks between photosynthesis, pH, DOC production and CaCO₃ saturation). This study lends weight to the contention that near-surface cryogenic environments on other planetary bodies, such as the polar ice caps of Mars and the icy shell of Europa, could be targets in the search for life or evidence of life’s past existence therein, since biological activity in sealed ice refugia has the potential to modify chemical conditions to sustain colonization.

References


