

Chemical characteristics of hydrologically distinct cryoconite holes in coastal Antarctica

Gautami SAMUI, Runa ANTONY, Meloth THAMBAN

National Centre for Polar and Ocean Research, Headland Sada, Vasco-da-Gama, Goa, India.

E-mail: gautami@ncaor.gov.in

ABSTRACT. Cryoconite holes play a significant role in the nutrient cycling on glaciers and can be regarded as a storehouse of nutrients that are generated through microbial and photochemical activities. In this work, the chemical characteristics of hydrologically connected and isolated cryoconite holes from three geographically distinct regions of coastal Antarctica, namely Larsemann Hills, Amery Ice Shelf and central Dronning Maud Land were studied. Major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and NO_3^-) and total organic carbon in the hydrologically isolated, closed cryoconite holes showed significantly higher enrichment (6–26 times and 9 times, respectively) over the conservative tracer ion Cl^- possibly due to sediment dissolution and microbial synthesis during isolation period. In contrast, depletion of major ions and organic carbon were observed in the open, hydrologically connected holes due to their discharge from the cryoconite holes through interconnected streams. This study suggests that the contribution of cryoconite holes to the nutrient and microbial transport to downstream environments may vary with the extent of hydrological connectivity by virtue of the fact that nutrients and organic carbon which accumulate in the isolated cryoconite holes during isolation could get washed to downstream environments in the event that they get connected through surface or subsurface melt channels.

KEYWORDS: debris-covered glaciers, meltwater chemistry, snow chemistry

INTRODUCTION

Cryoconite holes are common features found in cold and polythermal glaciers of polar regions and higher altitudes (Sävström and others, 2002; Takeuchi, 2002; Fountain and others, 2004; Anesio and others, 2007; Edwards and others, 2011). They are found in the ablation zones of glaciers worldwide (Fountain and others, 2004; Hodson and others, 2013) and also in the temperate regions with low melt rates and deficient runoffs incapable of washing the sediments off the glacier surface (Anesio and others, 2010). The cryoconite holes are formed when windblown dust and organic matter accumulate on the snow surface leading to the melting of ice beneath it, due to the lower albedo of dust and organic matter (McIntyre, 1984; Podgorny and Grenfell, 1996). The depth and diameter of these holes can vary from a few centimetres to >1 m (McIntyre, 1984; Fountain and others, 2004; Tranter and others, 2004). Due to the abundance of microorganisms inoculated by the sediments forming the cryoconite holes, the cryoconite holes are sites for biogeochemical cycling of carbon, nitrogen and other nutrients (Sävström and others, 2002; Fountain and Tranter, 2008; Stibal and others, 2008; Anesio and others, 2009; Hodson and others, 2010; Telling and others, 2014; Cook, 2016) on otherwise relatively passive glaciers and ice sheets.

Depending on the air temperature, cryoconite holes can stay open to the atmosphere favouring air and water exchange (Stibal and Tranter, 2007) or can develop an ice lid and remain isolated to atmospheric exchange processes (Foreman and others, 2007). Open and closed cryoconite holes may have different chemical and biological characteristics associated with them (Mueller and Pollard, 2004; Stibal and Tranter, 2007; Anesio and others, 2010; Bagshaw and others, 2013; Webster-Brown and others,

2015), due to the fact that open holes allow for greater exchange of gases and in wash of microbes, nutrients and water into the cryoconite hole, while closed holes have restricted exchange of materials between a cryoconite hole and surrounding glacier surface (Hodson and others, 2008). These open/closed cryoconite holes can further be differentiated into hydrologically connected and isolated holes (Fountain and others, 2004; MacDonnell and Fitzsimons, 2012). This demarcation is based on the exchange of the cryoconite hole water with nearby streams, channels below the ice surface or other cryoconite holes. In the hydrologically connected cryoconite holes, there is a significant exchange of water, microbes and chemical components with each other and the surrounding area (MacDonnell and Fitzsimons, 2012). Contrastingly, there is an accumulation of chemical constituents due to the dissolution of debris, as well as, due to the photo-chemically and biologically driven reactions in the hydrologically isolated cryoconite holes (Fountain and others, 2004; Telling and others, 2014). The ultimate decay of cryoconite holes can either occur via shrinkage caused by the accumulation of ice on the walls of the cryoconite hole or via breaching of water through the walls by the growing supraglacial drainage (McIntyre, 1984). Thus, cryoconite holes can provide a mechanism for the storage of chemical and microbial constituents on the glacier surface and can significantly affect the rate of their transfer to the supraglacial or subglacial drainage systems. This could potentially impact the ecological balance in downstream ecosystems. Given their significance in biogeochemical cycling (Anesio and others, 2009) and potential to impact downstream ecosystems through the exchange of carbon and nutrients (Foreman and others, 2004; Fountain and others, 2004; Tranter and others, 2005), characterizing the chemical

composition of cryoconite holes and their hydrological connectivity is of importance.

The present study reports the chemical composition (major ions, total organic carbon (TOC) and dissolved inorganic carbon (DIC)) of open and hydrologically connected, as well as, closed and hydrologically connected/isolated holes from three geographically distinct regions in East Antarctica, namely Larsemann Hills (LHS), Amery Ice Shelf (AIS) and central Dronning Maud Land (cDML) in order to understand the characteristics of hydrologically isolated and connected cryoconite holes within Antarctica.

MATERIALS AND METHODS

Study area and sampling

In the present study, cryoconite holes were studied from three geographically distinct sites located in coastal Antarctica, namely Larsemann Hills (LHS), Amery Ice Shelf (AIS) and central Dronning Maud Land (cDML) (Fig. 1). The sampling site at LHS is located in a coastal valley surrounded by hills at the northern and southern region, an ice wall on the eastern side and the Thala fjord on the western side. The open holes in this region seem to be hydrologically connected with supraglacial streams flowing at the study site. The frozen cryoconite holes at cDML are located in a blue ice region immediately to the north of Schirmacher Oasis that is nearly 100 km inland from the sea and is surrounded by many nunataks. Although the cryoconite holes were frozen at the time of sampling in March, they are affected by the surface melting that occurs every year during the summer season. At AIS, frozen cryoconite holes were located 110 km away from the coast in a blue ice region near a prominent rocky promontory.

Seven cryoconite holes each from LHS, AIS and cDML were sampled. Meltwater from the open cryoconite holes at LHS were collected in sterile Whirlpak bags using sterile syringes. The samples for organic carbon analysis were collected in glass bottles which were washed (0.5% HNO₃) and combusted (450°C, 4 h) just a few hours prior to sampling. The frozen cryoconite holes at AIS and cDML were drilled using a KOVACS Mark IV coring device and collected in clean high-density polyethylene bags. All the samples were stored and transported in frozen state in expanded polypropylene boxes. Samples were processed in a cold room (−15°C) and melted in a Class-100 clean room prior to analysis.

Cryoconite hole water

Ionic chemistry

Inorganic anions (Cl[−], SO₄^{2−}, NO₃[−] and F[−]) and carboxylate ions (acetate (Ac[−]), formate (Fo[−]), lactate (Lc[−]) and oxalate (Oxy^{2−})) were measured using a Dionex ICS 2000 Ion chromatography system with a CD25 electrical conductivity detector. The system is equipped with IonPac AS11-HC (4 mm) column and AG11-HC (4 mm) guard column with an ASRS-Ultra Anion Self Regenerating Suppressor. Potassium hydroxide (KOH) was used as the eluent and the sample injection volume was 1 mL. Cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺) were measured using a Dionex DX-2500 ion chromatography system (DS 6 Conductivity Detector) with IonPac CS17 (4 mm) column and an IonPac CG17 Guard column (4 mm) with a CSRS-ULTRA Cation Self

Regenerating Suppressor. Methanesulfonic acid (CH₃SO₃H) was used as the eluent and the sample injection volume was 0.1 mL. Calibration of all the ions was carried out using high-purity standard solutions from Inorganic Ventures. Detection limits achieved were 3 µg L^{−1} (Na⁺, K⁺, Ca²⁺ and Mg²⁺), 3–5 µg L^{−1} (SO₄^{2−}, NO₃[−], Cl[−] and F[−]), 0.1 µg L^{−1} (Ac[−] and Fo[−]), 1 µg L^{−1} (Oxy^{2−}) and 2 µg L^{−1} (Lc[−]). The analytical error of the measurements was <10%.

Total organic carbon

TOC analysis was carried out by the non-purgeable organic carbon method using high sensitivity TOC analyzer (Shimadzu TOC-V_{CPH}) as described in Antony and others (2011). The sample injection volume was 2 mL. Minimum of three measurements were taken for each sample to ensure repeatability. The instrument was calibrated using reagent grade potassium hydrogen phthalate as the organic carbon calibration standard. The detection limit for TOC concentration was 8.0 µg L^{−1}. The instrumental precision based on replicate injections of the standard was better than 10%.

Cell abundance

In order to determine bacterial abundance in the cryoconite hole water, cell counts were determined by filtering 5 mL sample (stained with 4',6-Diamidino-2-phenylindole, final concentration – 5 µg mL^{−1}) through a brown 0.22 µm isopore polycarbonate track-etched membrane filter (Millipore) and counting by epifluorescence microscopy at 1000× magnification (Nikon Ti-U Eclipse). The number of cells in 20 random fields was counted and bacterial abundance in controls comprising filtered ultrapure water was also determined in a similar manner as the samples.

Cryoconite hole sediments

Organic carbon in the sediments collected from Larsemann Hills was analyzed in a TOC Analyzer (TOC-V series SSM-5000A from Shimadzu) with a Non-dispersive Infrared detector (NDIR) and for calibration, glucose was used as the carbon standard. Prior to the organic carbon measurement, each sediment sample was dried, powdered and treated with trace metal grade 2N HCl in order to remove inorganic carbon from the sample. Hundred milligrams of treated sample was placed in a clean ceramic sample boat, which was transferred to a 900°C catalytic combustion chamber inside the analyzer and oxidized to CO₂ in the presence of O₂. Carbon dioxide was then detected by the NDIR detector. The analytical precision of the TOC measurements was <5%. Qualitative analysis of minerals in the sediment samples was carried out by using Rigaku UltimaIV powder diffractometer with CuK_α radiation.

RESULTS

Concentrations of inorganic ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl[−], SO₄^{2−}, NO₃[−] and F[−]) detected in the cryoconite holes from the three study regions are given in Table 1. Mean concentration of all measured carboxylate ions (Ac[−], Fo[−], Oxy^{2−} and Lc[−]) in LHS, cDML and AIS were 54.64 µg L^{−1}, 44.12 µg L^{−1} and 40.46 µg L^{−1}, respectively. Details of carboxylate ion concentrations are provided in Sanyal and others (2018). DIC in the cryoconite hole water samples was estimated using

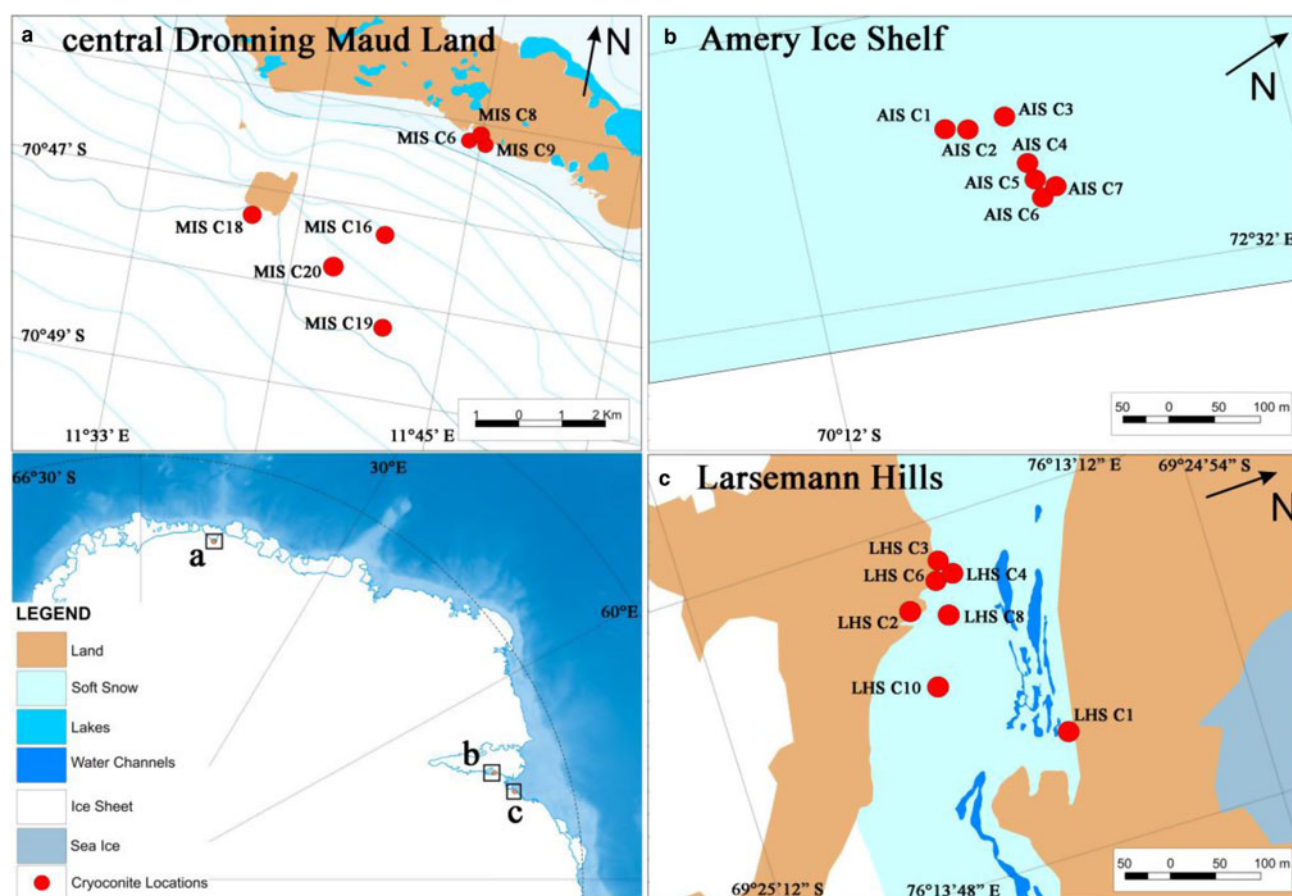


Fig. 1. Map with the inset showing locations of Cryoconite hole sampling in (a) central Dronning Maud Land, (b) Amery Ice Shelf and (c) Larsemann Hills.

Table 1. Major ion (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , NO_3^- and F^-) concentrations in the cryoconite holes at Larsemann Hills, central Dronning Maud Land and Amery Ice Shelf

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	NO_3^-	F^-
	($\mu\text{g L}^{-1}$)							
Larsemann Hills								
LHS C1	2550	55	102	142	974	120	48	4
LHS C2	2324	54	141	110	955	160	58	2
LHS C3	3724	313	715	1692	1129	458	158	21
LHS C4	705	17	203	280	105	98	35	6
LHS C6	902	28	117	326	152	199	bD.L.*	7
LHS C8	1060	26	87	99	370	119	48	3
LHS C10	4198	89	411	253	1531	457	90	20
Central Dronning Maud Land								
MIS C6	1839	20	41	379	71	120	107	16
MIS C8	785	38	44	356	47	112	94	9
MIS C9	850	14	38	368	77	66	182	56
MIS C16	732	6	24	139	66	79	19	bD.L.
MIS C18	718	5	11	52	53	63	38	29
MIS C19	1124	426	113	1890	120	28	24	55
MIS C20	1148	10	24	135	78	58	61	8
Amery Ice Shelf								
AIS C1	6669	190	1056	603	2359	636	27	5
AIS C2	2035	40	211	234	727	256	52	4
AIS C3	1271	22	93	149	310	66	77	5
AIS C4	1135	22	49	240	224	97	36	8
AIS C5	1007	27	28	77	259	64	42	7
AIS C6	823	14	22	184	96	46	41	4
AIS C7	1241	15	45	215	211	115	93	5

* Below Detection Limit.

the charge balance equation as $\text{HCO}_3^- (\mu\text{eq L}^{-1}) = (\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+) - (\text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^- + \text{F}^- + \text{Ac}^- + \text{Fo}^- + \text{Lc}^- + \text{Oxy}^{2-})$. Ionic concentrations used in the ion balance equation were in $\mu\text{eq L}^{-1}$. Mean DIC concentration was $112 \mu\text{eq L}^{-1}$, $67 \mu\text{eq L}^{-1}$ and $97 \mu\text{eq L}^{-1}$ for LHS, cDML and AIS, respectively (Table 2), while mean TOC concentrations were $62.3 \mu\text{g L}^{-1}$, $498.7 \mu\text{g L}^{-1}$ and $581.4 \mu\text{g L}^{-1}$ for LHS, cDML and AIS, respectively (Sanyal and others, 2018).

Within the cryoconite holes, the ionic concentration of the water can get significantly affected by microbial activity and dissolution of minerals in the underlying sediment (Tranter and others, 2004; Bagshaw and others, 2016). To understand the sources/sinks of ions and TOC present in the cryoconite holes, Enrichment Factor (EF) of the ion and TOC was estimated as $\text{EF}(i) = (C_i)_{\text{cryoconite hole}} / (C_i)_{\text{snow}}$, where $(C_i)_{\text{cryoconite hole}}$ and $(C_i)_{\text{snow}}$ are the ion or TOC concentrations in a cryoconite hole (Table 1) and surface snow, respectively. Data for ionic and TOC concentrations in surface snow ($(C_i)_{\text{snow}}$) are from this study and from previous studies from the same region. Values of $(C_i)_{\text{snow}}$ are: Na^+ ($16\,976 \mu\text{g L}^{-1}$, Antony and others, 2011), K^+ ($751 \mu\text{g L}^{-1}$), Mg^{2+} ($537 \mu\text{g L}^{-1}$), Ca^{2+} ($382 \mu\text{g L}^{-1}$), Cl^- ($5878 \mu\text{g L}^{-1}$), SO_4^{2-} ($1200 \mu\text{g L}^{-1}$), NO_3^- ($186 \mu\text{g L}^{-1}$) and TOC ($420 \mu\text{g L}^{-1}$, Antony and others, 2011) for LHS; Na^+ ($199 \mu\text{g L}^{-1}$, Antony and others, 2011), K^+ ($22 \mu\text{g L}^{-1}$), Mg^{2+} ($14 \mu\text{g L}^{-1}$), Ca^{2+} ($34 \mu\text{g L}^{-1}$), Cl^- ($418 \mu\text{g L}^{-1}$), SO_4^{2-} ($182 \mu\text{g L}^{-1}$), NO_3^- ($145 \mu\text{g L}^{-1}$) and TOC ($134 \mu\text{g L}^{-1}$, Antony and others, 2011) for cDML; Na^+ ($77 \mu\text{g L}^{-1}$), K^+ ($7 \mu\text{g L}^{-1}$), Mg^{2+} ($11 \mu\text{g L}^{-1}$), Ca^{2+} ($17 \mu\text{g L}^{-1}$), Cl^- ($161 \mu\text{g L}^{-1}$), SO_4^{2-} ($25 \mu\text{g L}^{-1}$), NO_3^- ($9 \mu\text{g L}^{-1}$) and TOC ($65 \mu\text{g L}^{-1}$) for AIS (Samui and others, 2017). EF of the ions in the cryoconite hole samples from the three study regions are given in Table 3, where, $\text{EF}(i) > 1$ represents the enrichment of ion i and $\text{EF}(i) < 1$ indicates the depletion of the ion (Telling and others, 2014). Enrichment of the conservative tracer Cl^- is used to determine the hydrological connectivity and isolation of the cryoconite holes (Fountain

and others, 2004). Range of $\text{EF}(\text{Cl}^-)$ in the three regions were: LHS, 0.0–0.3 (mean, 0.1); cDML, 0.1–0.3 (mean, 0.2) and AIS, 0.6–14.7 (mean, 3.7) (Table 3). EF of $\text{Cl}^- > 1$ represents the accumulation of Cl^- during isolation and aging of the hole, while $\text{EF}(\text{Cl}^-) < 1$ indicates water exchange with other meltwater implying that the cryoconite hole is hydrologically connected. Previous studies on snow chemistry in the LHS (Antony and others, 2011), AIS (Samui and others, 2017) and cDML (Mahalinganathan and others, 2012) region have shown that surface snow concentrations of Cl^- in these regions are heavily influenced by marine inputs, with sea-spray contributing to at least 80% of the Cl^- in these regions.

Total cell counts in the cryoconite hole water ranged from 0.47×10^4 to 11.8×10^4 cells mL^{-1} (LHS); 0.07×10^4 – 1.62×10^4 cells mL^{-1} (cDML) and 0.13×10^4 – 9.57×10^4 cells mL^{-1} (AIS) and include diverse heterotrophic bacteria and eukarya (Sanyal and others, 2018). X-Ray Diffraction analysis carried out on cryoconite sediments from LHS showed the presence of quartz, orthoclase, plagioclase feldspar, biotite, spinel and magnetite as the major minerals. TOC in these sediments ranged from 0.4 to 1.8 mg C g^{-1} . Sediment samples were not retrieved from cryoconite holes in the cDML and AIS regions due to the frozen state of the holes during sampling. The composition of cryoconite hole sediments and TOC concentration from these regions could therefore not be determined.

DISCUSSION

Hydrological connectivity

Chloride ion (Cl^-) behaves as a relatively conservative tracer ion in nearly all hydrological streams with the high sea salt

Table 2. Dissolved inorganic carbon (DIC) concentration in the cryoconite holes

Sample ID	DIC ($\mu\text{eq L}^{-1}$)
Larsemann hills	
LHS C1	96
LHS C2	88
LHS C3	268
LHS C4	56
LHS C6	57
LHS C8	45
LHS C10	175
Central Dronning Maud Land	
MIS C6	96
MIS C8	49
MIS C9	49
MIS C16	35
MIS C18	29
MIS C19	156
MIS C20	54
Amery ice shelf	
AIS C1	331
AIS C2	92
AIS C3	58
AIS C4	56
AIS C5	40
AIS C6	42
AIS C7	59

Table 3. Enrichment factor of ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , NO_3^- and Cl^-) and Total Organic Carbon (TOC) detected in the cryoconite hole water samples

	EF							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	NO_3^-	TOC	Cl^-
Larsemann Hills								
LHS C1	0.2	0.1	0.2	0.4	0.1	0.3	0.0	0.2
LHS C2	0.1	0.1	0.3	0.3	0.1	0.3	0.3	0.2
LHS C3	0.2	0.4	1.3	4.4	0.4	0.8	0.4	0.2
LHS C4	0.0	0.0	0.4	0.7	0.1	0.2	0.1	0.0
LHS C6	0.1	0.0	0.2	0.9	0.2	0.0	0.1	0.0
LHS C8	0.1	0.0	0.2	0.3	0.1	0.3	0.1	0.1
LHS C10	0.2	0.1	0.8	0.7	0.4	0.5	0.2	0.3
Central Dronning Maud Land								
MIS C6	9.2	0.9	2.9	11.1	0.7	0.7	4.2	0.2
MIS C8	3.9	1.7	3.1	10.5	0.6	0.7	4.4	0.1
MIS C9	4.3	0.6	2.7	10.8	0.4	1.3	0.9	0.2
MIS C16	3.7	0.3	1.7	4.1	0.4	0.1	9.1	0.2
MIS C18	3.6	0.2	0.8	1.5	0.3	0.3	1.1	0.1
MIS C19	5.6	19.3	8.1	55.6	0.2	0.2	2.7	0.3
MIS C20	5.8	0.4	1.7	4.0	0.3	0.4	3.2	0.2
Amery ice shelf								
AIS C1	86.6	27.2	96.0	35.5	37.4	3.0	1.9	14.7
AIS C2	26.4	5.7	19.2	13.7	15.0	5.8	15.2	4.5
AIS C3	16.5	3.2	8.5	8.8	3.9	8.6	2.2	1.9
AIS C4	14.7	3.2	4.4	14.1	5.7	4.0	13.3	1.4
AIS C5	13.1	3.9	2.6	4.5	3.8	4.7	9.6	1.6
AIS C6	10.7	2.0	2.0	10.8	2.7	4.6	7.7	0.6
AIS C7	16.1	2.1	4.1	12.6	6.8	10.3	11.8	1.3

input of Cl^- (Zellweger, 1994; Gooseff and others, 2004; Svensson and others, 2012). Similarly, Cl^- in cryoconite holes, which is primarily sourced from sea salt aerosols present in the snowmelt, is considered to behave conservatively as long as they are hydrologically isolated and is only affected by the deepening and aging of the holes (Fountain and others, 2004). In the present study, the calculated EFs indicate a depletion of Cl^- in LHS (mean EF, 0.1) and cDML (mean EF, 0.2), suggesting that the cryoconite holes in both the study regions are hydrologically connected, resulting in the discharge of solutes from the holes. The elapsed time or age (Δt) of a cryoconite hole was also estimated to confirm the hydrological connectivity of the cryoconite holes at LHS using the equation $\Delta t = [(M_t / (a \times i)) - h] / (dz/dt)$ (Fountain and others, 2004), where M_t is the amount of Cl^- present in the hole at a particular time t , a is the cross-sectional area of the hole, i is the Cl^- concentration in the surrounding ice, h represents the depth of the hole and dz/dt represents the melt rate of the ice which is assumed to be equal to the ablation rate of the ice surface. We used an ablation rate value of 1.8 cm a^{-1} which is based on the average value determined for this region (personal communication from Mohd. Yunus Shah). The $\Delta t < 0$ observed at LHS indicate hydrological connectivity of the holes with the nearby streams. The hydrological connectivity of the holes at LHS is corroborated by the depletion of other ions (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} and NO_3^-) (Table 3) and also by the observed exchange of water with the nearby flowing stream during the sampling. The TOC concentration in the LHS cryoconite holes also showed depletion in concentration (Table 3), further indicating that hydrological connectivity could result in the flushing out of the organic carbon and microbes.

While no obvious conduits were visible at the AIS and cDML cryoconite hole sites at the time of sampling, hydrological connectivity between the frozen holes in these sites via fractures within the ice or via channels below the ice surface cannot be ruled out. At cDML, the surface melting occurs annually during the summer season (Bøggild and others, 1995). While the EF (Cl^-) in cDML was depleted indicating dilution of cryoconite hole water with surrounding meltwater, the observed enrichment of Na^+ (EF: 3.6–9.2, mean 5.2), K^+ (EF: 0.2–19.3, mean 3.4), Mg^{2+} (EF: 0.8–8.1, mean 3.0) and Ca^{2+} (EF: 1.5–55.6, mean 13.9), indicate that there is interaction of the cryoconite water with the underlying sediment. This suggests limited hydrological connectivity or a slower rate of exchange of water with the surface meltwater pool allowing the sediment to affect the ion concentration of water within the holes. The high EF (Cl^-) at AIS (mean, 3.7) indicates that the holes in this region are isolated. In addition, higher EFs observed for Na^+ , K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} as compared with EF(Cl^-) suggest dissolution of minerals containing these ions from the cryoconite sediments at AIS. Presence of minerals comprising Na^+ , K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} is further supported by the significant correlation ($p < 0.001$) observed among these ions.

Additionally, previous studies show $\text{EF}(\text{Cl}^-) < 1$ in open cryoconite holes (Hodson and others, 2008; Bagshaw and others, 2013) and $\text{EF}(\text{Cl}^-) > 1$ in closed cryoconite holes (Telling and others, 2014). In this study, open cryoconite holes in LHS exhibited $\text{EF}(\text{Cl}^-) < 1$, consistent with earlier studies. Closed and frozen cryoconite holes in cDML, however, also exhibited $\text{EF}(\text{Cl}^-) < 1$. This discrepancy in EF values in the closed cryoconite holes in cDML is attributed

to the hydrological connectivity of these holes as explained above.

TOC values recorded in the cryoconite hole water in cDML and AIS were 1–15 times (mean EF, 6) higher than that found in the surface snow (Table 3). This observation is consistent with that of other studies, which reports significantly higher concentrations of organic carbon in the cryoconite hole water than in the surrounding glacier ice (Bagshaw and others, 2007, 2013). This could be due to the dissolution of organic matter from the cryoconite debris in the closed cryoconite hole, which results in organic carbon concentrations higher than those found in the glacier ice. Thus, higher TOC concentration in the cryoconite hole water at AIS and cDML compared to LHS could be attributed to the interaction of organic-rich sediment (0.4 to 1.8 mg C g^{-1}) with the overlying water. However, apart from sediment dissolution, microbial synthesis of organic matter could also contribute to the higher TOC concentration in cryoconite holes, as observed in previous studies (Anesio and others, 2009, 2010). Further, Bagshaw and others (2013) suggested that lower photolytic degradation of organic matter occurs in closed holes due to the limited amount of solar radiation reaching the water through the lids. This observation is consistent with the high $\text{EF}(\text{TOC}) > 1$ in the closed holes at AIS and cDML compared with the melted holes at LHS.

Ionic trend and sources

In addition to snowmelt, various minerals present in the cryoconite sediments can significantly influence the ionic composition in the overlying cryoconite water through sediment dissolution. For instance, mineral dissolution occurring in cryoconite sediments has been observed to significantly enrich certain ions over Cl^- in the overlying water (Tranter and others, 2004; Telling and others, 2014). However, the extent of connectivity of any cryoconite hole with the hydrological streams also determines the enrichment and depletion of ionic constituents. Ion concentrations obtained in the cryoconite holes from the three study regions are consistent with previous studies carried out in Antarctica (Table 4).

Ionic concentration in the cryoconite hole samples from all the three study regions was dominated by Na^+ . At LHS, the dominance of Na^+ in cryoconite holes is similar to the trend shown in surface snow samples at the coast (Antony and others, 2011). The observed similarity between cryoconite hole and surface snow samples could be due to the hydrological connectivity of the holes preventing longer interaction between cryoconite water and sediment within the holes which further leads to Na^+ depletion in the holes (Table 3). In contrast, at cDML and AIS, the dominance of Na^+ over Cl^- in the cryoconite holes is contradictory to the trend observed in surface snow samples from these two regions. This dominance is most likely a result of cryoconite sediment dissolution which is corroborated by the higher enrichment of Na^+ (cDML: mean EF, 5.2; AIS: mean EF, 26.3) compared to Cl^- enrichment (cDML: mean EF, 0.2; AIS: mean EF, 3.7) in the cryoconite holes (Table 3). EF (Ca^{2+}) in cryoconite holes at cDML (mean EF, 13.9) and AIS (mean EF, 14.3) exhibited a similar trend as that of Na^+ (Table 3), suggesting possible mineral dissolution. Minerals containing Na^+ and Ca^{2+} such as plagioclase feldspar are commonly found in the study regions at cDML (Ravich and Kamenev, 1975; Sengupta, 1986; Joshi and Pant, 1995)

Table 4. Mean concentration of various inorganic ions in cryoconite holes from Larsemann Hills (LHS), central Dronning Maud Land (cDML) and Amery Ice Shelf (AIS) observed in this study and from other regions of Antarctica

Study area	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	DIC	References
	µg L ⁻¹				µeq L ⁻¹				
Larsemann Hills	2209	83	254	415	745	230	62	112	This study
central Dronning Maud Land	1028	74	42	474	73	75	75	67	This study
Amery Ice Shelf	1626	55	139	337	407	151	71	97	This study
Commonwealth glacier	3174	819	1212	4060	6639	2746	372	212	Bagshaw and others (2013)
Canada Glacier	1311	624	600	4620	3266	2448	434	202	Bagshaw and others (2013)
Taylor Valley	437	156	276	1120	675	864	124	64	Bagshaw and others (2013)
McMurdo Dry Valley	1495	468	492	1680	4367	†	558	†	MacDonell and others (2016)
McMurdo Dry Valley	552	234	72	1660	959	288	124	242	Telling and others (2014)
McMurdo Dry Valley	n.r.*	n.r.	n.r.	4600	3763	3024	1488	150	Tranter and others (2004)

* Not reported is denoted as n.r..

† SO₄²⁻ + HCO₃⁻ = 69 µeq L⁻¹ (MacDonell and others, 2016).

and AIS (Manton and others, 1992; Mikhalsky and others, 2001). Weathering of rocks containing such minerals and subsequent wind borne deposition could contribute to the sediment composition in the cryoconite holes in the study regions and lead to the enrichment of Na⁺ and Ca²⁺ over Cl⁻ in the overlying water through sediment dissolution (Table 3). In addition to plagioclase feldspar, NaCl and CaCO₃ in the sediments can also influence the Na⁺ and Ca²⁺ concentration in the overlying water. The cDML and AIS regions, which receive high sea salt inputs from the marine sea spray (Antony and others, 2011; Samui and others, 2017), could have significant contributions of NaCl in the cryoconite sediments, thereby resulting in an enrichment of Na⁺ in the cryoconite water. Similarly, the presence of CaCO₃ in the promontories at cDML (Sengupta, 1986; Bauer and Fitzner, 2003) and AIS (Manton and others, 1992) supports its possible presence in the cryoconite sediments, thereby contributing to the enrichment of Ca²⁺ in the overlying water. Possible presence of minerals like gypsum-containing Ca²⁺ and SO₄²⁻ at AIS is also indicated by a significant correlation ($p < 0.001$) between these ions. The presence of such minerals could also contribute to the enrichment of Ca²⁺ in the cryoconite hole. Dissolution of minerals like calcite, gypsum and the evaporites also influence the concentration of HCO₃⁻ and SO₄²⁻, respectively. This is supported by the high concentration of HCO₃⁻ observed in cryoconite holes in cDML and AIS, as well as, the significant enrichment of SO₄²⁻ (mean EF, 10.8) in AIS. Enrichment of SO₄²⁻ due to the dissolution of gypsum is also supported by previous studies where evaporite minerals have been found to enrich SO₄²⁻ over Cl⁻ in Antarctic cryoconite holes and lakes (Lyons and others, 2003; Tranter and others, 2004; Bagshaw and others, 2013). In addition to the dissolution of gypsum, oxidation of sulphur rich minerals during the isolation period can also result in the enrichment of SO₄²⁻ in AIS. Unlike AIS, SO₄²⁻ in cDML was found to be depleted. Depletion of SO₄²⁻ was also accompanied by depletion in Cl⁻ indicating the possibility of dilution during the melt season. The observed depletion in SO₄²⁻ concentrations in cDML could also be a result of the lower initial concentration of minerals rich in sulphur within the cryoconite sediment (Bagshaw and others, 2007). This is supported by a weak correlation observed between SO₄²⁻ and the cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺). However, limited information on sediment composition of the cryoconite holes at this site

precludes any inferences on the depletion of SO₄²⁻. Similar to Na⁺ and Ca²⁺, significant enrichment of Mg²⁺ and K⁺ were observed at both AIS and cDML. This can be attributed to the high sea spray influence in these regions. In addition to the sea spray, dissolution of Mg²⁺ and K⁺ containing minerals like biotite, feldspar and cordierite commonly present in the AIS (Manton and others, 1992; Mikhalsky and others, 2001) and cDML region (Sengupta, 1986; Musta and Tahir, 2012) could also contribute to the enrichment.

The EF of TOC and ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻ and NO₃⁻ in the open cryoconite holes in LHS were low (<1), which is consistent with previous observations from open holes (Bagshaw and others, 2013). Chemistry of open holes in LHS also reflects the continuous addition of water due to ice melting in summer, the shorter residence time of meltwater within the cryoconite holes and associated water exchange due to hydrological connectivity as previously reported (Hodson and others, 2008). EF>1 of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻ and TOC in cryoconite holes at AIS is consistent with the closed state of these holes. However, at cDML, few ions (Na⁺, Mg²⁺ and Ca²⁺) and TOC showed EF>1, while rest of the ions (K⁺, Cl⁻, SO₄²⁻ and NO₃⁻) showed EF<1. This complex trend in the closed cryoconite holes in cDML is attributed to the hydrological connectivity of the cryoconite holes with the surrounding glacier during the melt season.

Influence of microbial activity

Estimated DIC concentrations in the three study regions ranged from 44 to 268 µeq L⁻¹ (LHS, mean 112 µeq L⁻¹); 29–156 µeq L⁻¹ (cDML, mean 67 µeq L⁻¹) and 40–331 µeq L⁻¹ (AIS, mean 97 µeq L⁻¹) (Table 2). In a previous study, a significant fraction of carbon (60–76%) in the cryoconite holes was found to be present as DIC (Bagshaw and others, 2013). Likewise, in the present study, the concentration of DIC (HCO₃⁻; 1742–20 197 µg L⁻¹) is significantly higher compared with the TOC concentration (7–1213 µg L⁻¹) in all the samples.

In spite of a considerable difference in the ion concentration in the three study regions, DIC concentration was found to be comparable between the sites. A recent study has shown that these samples harbour diverse heterotrophic bacteria and eukarya that are metabolically active, thereby significantly impacting the chemistry of these environments

(Sanyal and others, 2018). Several other studies from the Arctic (Anesio and others, 2010; Hodson and others, 2010), Antarctic (Foreman and others, 2007; Anesio and others, 2010; Telling and others, 2014) and Alpine region (Anesio and others, 2010) have also reported microbial activity within the cryoconite holes.

Microbial activity in the cryoconite holes produces CO₂, which, in turn, replenishes the HCO₃⁻ in the cryoconite hole water (Tranter and others, 2004). Carbon dioxide produced by heterotrophic activity in cryoconite holes results into weathering of carbonate and silicate minerals thereby increasing the concentration of certain ions like K⁺, Mg²⁺ and Ca²⁺ (Bagshaw and others, 2016). These findings are corroborated by other studies which show that microbial activity in cryoconite holes can appreciably affect the nutrient cycling within the holes (Hodson and others, 2005; Bagshaw and others, 2016). Thus, in spite of isolation and resulting accumulation of the ions in an isolated hole, charge balance is most likely preserved due to the continued heterotrophic activity within the holes. This is supported by the presence of diverse and active microbial communities in these samples (Sanyal and others, 2018), with differences in bacterial abundance, activity, doubling times and diversity being detected between open and closed holes (Mueller and Pollard, 2004; Anesio and others, 2010; Sanyal and others, 2018) owing to open and closed systems exerting different environmental pressures on the microbial communities.

CONCLUSIONS

Considering EF (Cl⁻), cryoconite holes at LHS were found to be hydrologically well connected and open and at AIS they were isolated and closed. In cDML, cryoconite holes, EF (Cl⁻) suggested that the ice-lidded cryoconite holes had limited hydrological connectivity. Major ions (Na⁺, K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻) in the closed isolated holes at AIS were enriched by 7–26 times, while the conservative tracer Cl⁻ was enriched by 4 times. The higher enrichment of the ions at AIS is attributed to the leaching of ions from the underlying sediment during the isolation period. These cryoconite holes can therefore be considered an important store of inorganic nutrients on the glacier surface. In contrast, the open and hydrologically connected cryoconite holes at LHS showed that all ions were depleted due to the flushing of the ions from the cryoconite holes via the interconnected streams and meltwater channels. Ion EFs in the cryoconite holes at cDML indicate limited hydrological connectivity. Thus, constraints in hydrological connectivity, as well as differences between open and closed cryoconite holes, can affect the extent of ion and organic matter accumulation within the holes. This study also shows that closed and isolated holes store an abundance of nutrients and carbon compared with open and connected holes which may further affect the extent of microbial activity within the holes and also their impact on nutrient and carbon transport to the downstream environments.

ACKNOWLEDGEMENTS

We thank the Director, National Centre for Polar and Ocean Research for support and encouragement. We are grateful to the Ministry of Earth Sciences for financial support through the project 'Cryosphere and Climate'. This work forms part of the doctoral research being undertaken at the

Department of Marine Sciences of the Goa University. Gautami Samui was supported by a fellowship from the Council of Scientific and Industrial Research, India. We thank the logistic and crew members of the 33rd Indian Scientific Expedition to Antarctica for field support. Many thanks to Ashish Painginkar for the laboratory assistance. Norwegian Polar Institute is acknowledged for the Quantarctica QGIS package. Thanks to Girish Prabhu (National Institute of Oceanography) for help with X-Ray Diffraction analysis and V. Purnachandra Rao (National Institute of Oceanography) for helping in the interpretation of X-ray Diffraction data. This is NCPOR contribution No. 56/2018.

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