Arctic Geomicrobiology and Climate Change

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Abstract

Anthropocene is a time of extraordinary change in the Arctic. It has experienced unprecedented variability in both the rates and magnitudes of change in the cryosphere, atmosphere and lithosphere, dependent ecosystem function variability, increased industrial development, and concomitant globalization of local economies. These changes are challenging our ability to respond and to develop a coordinated and scientifically informed policy for the Arctic. The objectives of this project are aligned with the targeted achievements of the Canada Excellence Research Chair on "Arctic Geomicrobiology and Climate Change" to increase understanding on geomicrobial transformations as they occur in Arctic sea ice and sediments, including the regeneration of nutrients required by primary producers and thus the health of all other inhabitants of the Arctic marine system. The project will address 4 key research questions and 2 objectives: (1) What are the relative contributions of dynamic and thermodynamic forcing to the observed change in sea ice areal extent and thickness and how is this related to intra- and extra-Arctic climate processes, variability, and change? (2) What are the consequences of change in Question 1 on biogeochemical cycling, including carbon, nitrogen, sulphur, phosphorous, oxygen, and their stable isotopes? (3) What are the consequences of changes in Questions 1 and 2 on ecosystem function, examined throughout the complete trophic structure: beginning with microbial processes, primary and secondary production, through to apex predators; and on habitat structure: benthic, pelagic, epontic, and within the ocean–sea-ice–atmosphere (OSA) interface? (4) What are the consequences of change on release, transport, and biological impact of chemical contaminants, including both organic and inorganic contaminants, across Arctic biotic and abiotic environmental interfaces? Objective 1: To produce models of coupled physical-biological processes examined in Questions 1 through 4 as a means of making the project science predictive and able to inform future environmental conditions.

Objective 2: To provide and communicate a knowledge base upon which public policy development can build to address the key issues facing the Canadian Arctic (e.g., sustainable development, globalization, socioeconomic stability, and environmental stewardship). Recent evidence suggests that microbial activity and chemical transformations within sea ice greatly influence inorganic carbonate chemistry, playing a far more important role in regulating carbon dioxide (CO_2) uptake by Arctic seas than previously anticipated. The objective of the program is to investigate and quantify the importance of these fundamental microbial activities using state-of-the-art assessment techniques in a comprehensive three-pronged approach of ice tank, in situ, and modelling studies. Combining experimental ice tank and in situ studies will provide important new insight into the regulation of these processes, their seasonal and geographical distribution, and how they are coupled between surface ocean and seafloor. Modelling activities will range from small-scale studies within the sea ice and sediment compartments to local coastal regions of strategic importance and the large-scale systems of the Arctic Ocean and neighbouring seas.

Key Messages

- Ikaite concentrations from this study are higher than any other reported previously; that is 10-fold higher than those measured in Antarctica, and 4 times higher than the ones from Fram Strait.

- Ikaite crystals were located between the interstices of the sea ice matrix between the pure ice platelets, allowing the CO_2 produced during the ikaite formation in sea ice to be rejected with brine, while ikiate can remain entrapped within ice structure.

- Frost flowers, formed initially from atmospheric vapor, consisted primarily of brine skim after 19 hours from ice freeze-up supporting the brine skim wicking hypothesis.

- There was minor secondary atmospheric deposition in the top section of frost flowers later in their evolution.

- We are becoming increasingly aware that the phytoplankton blooms in the water column below the sea ice have likely been and continue to be an important, yet poorly documented, component of the Canadian Arctic ecosystem.

- We are rapidly discovering that sea ice is not simply a barrier to gas exchange between the atmosphere and ocean, but drives its own set of processes that greatly affect this exchange.

Objectives

The overall objective of the CERC program is to investigate and quantify the importance of the fundamental geomicrobial processes in the ice-covered Arctic Ocean using state-of-the-art assessment techniques in a comprehensive three-pronged approach of experimental ice tank, in situ and modeling studies.

We report on two subprojects of the CERC program; a polynya study in Northeast Greenland and a sea ice study Arctic-ICE Resolute program.

In the polynya component of CERC program we investigate the geomicrobial processes in different sea ice types in situ during a field campaign based out of the Zackenberg Research Station located on the north side of the Young Sund-Tyrolerfjord fiord complex in the Northeast Greenland (74º30' N, 21º00' W) in March 2012. Specific aims of that campaign are as follows:

- determine CO_2 dynamics, and construct a CO_2 budget in a polynya setting,

- determine the climatic, chemical and microbial significance of frost flowers on young sea ice.

The underlying objective of the Arctic-ICE (Ice Covered Ecosystem) project was to determine the

physical-biological processes controlling the timing of primary production and their influence on the drawdown/release of climatically active gases. Landfast ice of Resolute Passage/Allen Bay provided a perfect natural laboratory to study these processes in a high Arctic system.

Introduction

As seawater freezes, salts become concentrated in interstitial liquid brine inclusions. Because phase equilibrium must be maintained between these inclusions and the surrounding ice, the salt becomes more and more concentrated as temperatures decrease. Solid salts begin to precipitate out of solution, starting with ikaite ($CaCO_3 • 6H_2O$) at −2.2 °C, mirabilite ($NaSO_4 • 10H_2O$) at −8.2 °C and hydrohalite ($NaCl • 2H_2O$) at −23 °C (Assur 1960). The mineral ikaite has recently been discovered in sea ice in both hemispheres (Dieckmann et al. 2008, Dieckmann et al. 2010). Precipitation of ikaite in standard seawater conditions is described by:

$$Ca_2+ + 2HCO_3- + 5H_2O • CaCO_3 • 6H_2O + CO_2 \quad (1)$$

and if ikaite is trapped within the interstices between the ice platelets, CO_2 could potentially be lost due to brine drainage and/or out-gassed within the brine system. The fate of CO_2 expelled from the sea ice to seawater remains unclear. CO_2 potentially makes it below the mixed layer due to dense brine production in the polynya region, (Anderson et al. 2004), and thus the ikaite production in sea ice will act as a "carbon pump" removing CO_2 from the surface ocean to the deeper water layers (Rysgaard et al. 2009, 2011). Additionally, low density ice meltwater remains at surface facilitating CO_2 atmospheric deposition as a result of ikaite dissolution.

Frost flowers are relatively short-lived crystal structures formed on new and young sea ice (Perovich and Richter-Menge 1994), under specific conditions of temperature and relative humidity (Style and Worster 2009) and wind speed. Crystal forms grown from the vapour phase may be related to the air temperature

at which they are formed (Magono and Lee 1966, Perovich and Richter-Menge 1994, Martin et al. 1996) which affects their specific surface area (Domine et al. 2005). Work including that of Style and Worster (2009) has showed frost flowers grow as a result of local super-saturation of the air immediately above a freshwater or sea ice surface sublimating into a cold, dry atmosphere where the surface temperature is much warmer than the far-field air temperature.

Frost flowers present a unique way for the ocean and sea ice volumes to interact with the atmosphere chemically. Frost flowers may be a substantial source of wind blown sea salt (Wagenbach et al. 1998) in the winter months as they form over leads; conclusions of the work of Rankin et al. (2002) include that saline frost flowers contain elevated concentrations of seawater ions, including bromine concentrations three times greater than in seawater. Therefore they argue frost flowers should be considered as a potential source of atmospheric bromine connected to polar tropospheric ozone depletion (Rankin et al. 2002). There is also evidence that frost flowers are a cryospheric microbial habitat. Bowman and Deming (2010) showed that bacterial abundance correlated strongly with salinity in frost flowers formed on sea ice, and extracellular polysaccharide concentrations were elevated in frost flowers and the brine skim they overlay, meaning that bacterial abundance in frost flowers were elevated compared to the sea ice on which they formed.

Activities

In Zackenberg, NE Greenland, a 3-week long field project was conducted in March 2012 primarily to study CO_2 dynamics in a polynya setting where sea ice regularly breaks up (~20-30 cm thick ice; outside the fiord) and contrast it to the land-fast thick ice station (~120 cm thick ice; inside the fiord). An international team of 15 scientists worked towards the main objective focusing their efforts on the following sub-projects:

- CO_2 dynamics in winter sea ice and ikaite distribution within sea ice column

- Ice and snow geophysics and thermodynamics

- CO_2 flux across ocean-atmosphere and ice-atmosphere interface

- Oceanography and brine transport within the water column

As a subproject, an in situ frost flower growing experiment has been designed to study the climatic, chemical and microbial significance of frost flowers on young sea ice. A ~6 x 3 m opening in the ice was cut in a polynya region where the thickness of the surrounding ice was about 30 cm (Figure 1a). The opening froze over, and frost flowers formed on the new ice overnight (Figure 1b). The frost flower field

Figure 1a. Opening cut for the in situ frost flower growing experiment (left; photo: Jakob Sievers).

Figure 1b. Frost flowers formed on new ice overnight (right; photo: Søren Rysgaard).

was sampled between 19 to 119 hours after freeze-up for thermal and geophysical characteristics, viruses and bacteria abundances and genetic analysis, δ18O analysis, ikaite presence and abundance, and CO_2 fluxes.

Currently, the data from the field campaign are being processed and analyzed. The first manuscript has been prepared and submitted to the Cryosphere: Rysgaard S., Søgaard D.H., Cooper M., Pućko M., Lennert K., Papakyriakou T.N., Wang F., Geilfus N.-X., Glud R.N., Ehn J., McGinnis D.F., Attard K., Sievers J.,

Deming J., and Barber D. (submitted; 19 Nov 2012), Ikaite crystal distribution in Arctic winter sea ice and its implications for CO_2 system dynamics. The second manuscript is being prepared targeted at the Climatic Change: Barber D.G., Ehn J., Deming J., Rysgaard S., Papakyriakou T., Pućko M., Søgaard D.H., and Galley R., Frost flowers on young sea ice: The climatic, chemical and microbial significance of this emerging ice type. Up to ten more manuscripts from the Zackenberg campaign will be prepared and submitted within the next year.
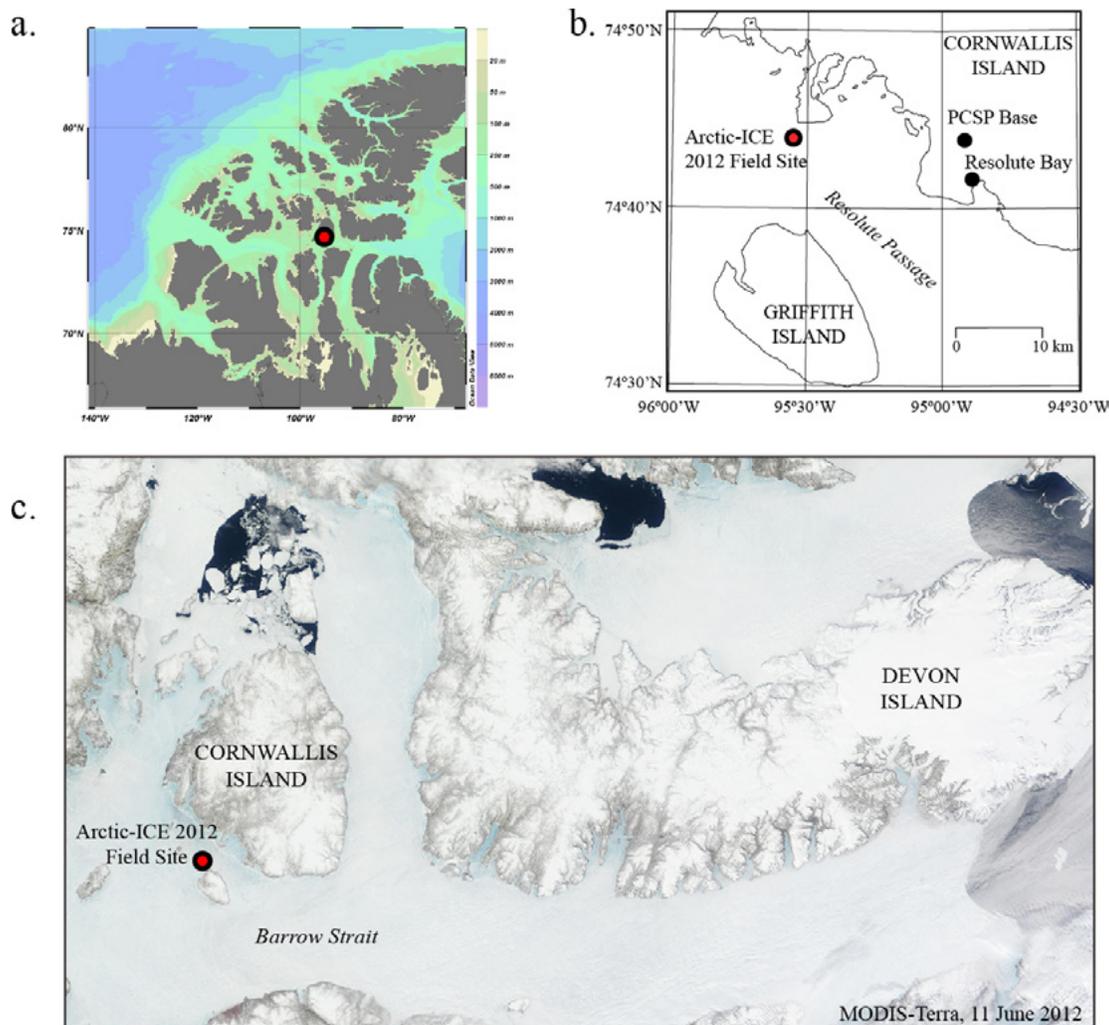
Figure 2. Map of the Arctic-ICE 2012 field study location (red dot; 74.708N 95.250W) relative to (a) the Canadian Arctic Archipelago, (b) the hamlet of Resolute Bay, NU and the PCSP base, and (c) MODIS-Terra image from 11 June, obtained from http://rapidfire.sci.gsfc.nasa.gov/realtime/.

Table 1. List of Arctic-ICE 2012 field participants and their associated field responsibilities, dates in the field and principal investigators (PI).

Field Personnel	Status	Field Responsibilities	Dates in Resolute	PI
C.J. Mundy (CEOS, UM)	Assistant Professor	Camp Manager Sea ice-water column nutrients, algae and bio-optics	11 May to 5 June	C.J. Mundy (CEOS, UM)
Jack Landy (CEOS, UM)	PhD Stu.	Sea ice melt evolution, ice thermodynamics, and microclimate	5 May to 28 June	David Barber (CEOS, UM)
Megan Shields (CEOS, UM)	MSc Stu.	Sea ice melt evolution, SAR validation, and microclimate	11 May to 28 June	David Barber (CEOS, UM)
Matthew Gale (CEOS, UM)	MSc Stu.	Sea ice-water column nutrients, algae and bio-optics	11 May to 28 June	C.J. Mundy (CEOS, UM)
Virginie Galindo (ULaval)	PhD Stu.	Sea ice-water column climate relevant compounds	11 May to 28 June	Maurice Levasseur (ULaval) Michael Scarratt (MLI, DFO)
Margaux Gourdal (ULaval)	MSc Stu.	Sea ice-water column climate relevant compounds	11 May to 28 June	Maurice Levasseur (ULaval)
Alexis Burt (DFO, CEOS)	MSc Stu.	Contaminant tracing in melt ponds	25 May to 28 June	Gary Stern (DFO, CEOS)
Pamela Godin (DFO)	MSc Stu.	Contaminant tracing in melt ponds	25 May to 28 June	Gary Stern (DFO, CEOS)
Randall Scharian (CEOS, UM)	Postdoc	SAR inversion and validation	2 June to 28 June	David Barber (CEOS, UM)
Nicolas Geilfus (CEOS, UM)	Postdoc	Sea ice biogeochemistry and air-ice gas fluxes	2 June to 28 June	Soren Rysgaard (CEOS, UM)
Odile Crabeck (CEOS, UM)	PhD Stu.	Sea ice biogeochemistry and air-ice gas fluxes	2 June to 28 June	Soren Rysgaard (CEOS, UM)
Marjolaine Blais	Technician	Sea ice-water column nutrients, algae and bio-optics	2 June to 28 June	Michel Gosselin (ISMER, UQAR)

From 5 May to 25 July 2012, we accomplished the third field study under the umbrella of the Arctic-ICE program, located in Resolute Passage and based out of the Polar Continental Shelf Program (PCSP) base, located in Resolute Bay, Nunavut, Canada (Figure 2). Also highlighted is the location of the field site relative to the ice edge far away in Lancaster Sound (Figure 2c). Our purpose was to investigate physical and biological aspects of the atmosphere, sea ice and ocean in support of the main objectives of Arctic-ICE stated above. Table 1 lists the Arctic-ICE 2012 field participants and their associated institutions, field activities that they were responsible for, and their principle investigator(s).

A study looking at contaminent enrichment in melt ponds was added for the Arctic-ICE 2012 field program. Some current use pesticides (CUPs), such as e.g. endosulfan or chlorothalonil may be heavily deposited from the atmosphere to the melt pond water over the course of the summer. Potential implications of this process involve increased exposures of biota below sea ice to some CUPs during the melt season. In this sub-project, we collected melt pond water, under-ice sea water, air, phytoplankton and zooplankton samples for current use and legacy pesticides analysis. Results are still being processed, and will be reported at a later date.

Results

Ikaite distribution and abundance in winter sea ice

We investigated two different ice locations (Figure 2): a fast ice location (ICE 1, 112 cm ice, 70 cm snow) situated in the fjord 3.5 km off the shore and a polynya site (POLY I, 15-30 cm ice, 17 cm snow) located in the recently frozen polynya outside the fjord. Due to a thick snow cover at ICE I, sea ice surface temperatures were relatively warm, -10 °C, with a gradient to -2 °C towards the sea ice-water interface. Bulk salinities ranged from 10-12 in the top layers to 4 at the bottom. Despite low air temperatures, the insulating effect of snow resulted in relatively high brine volumes ranging
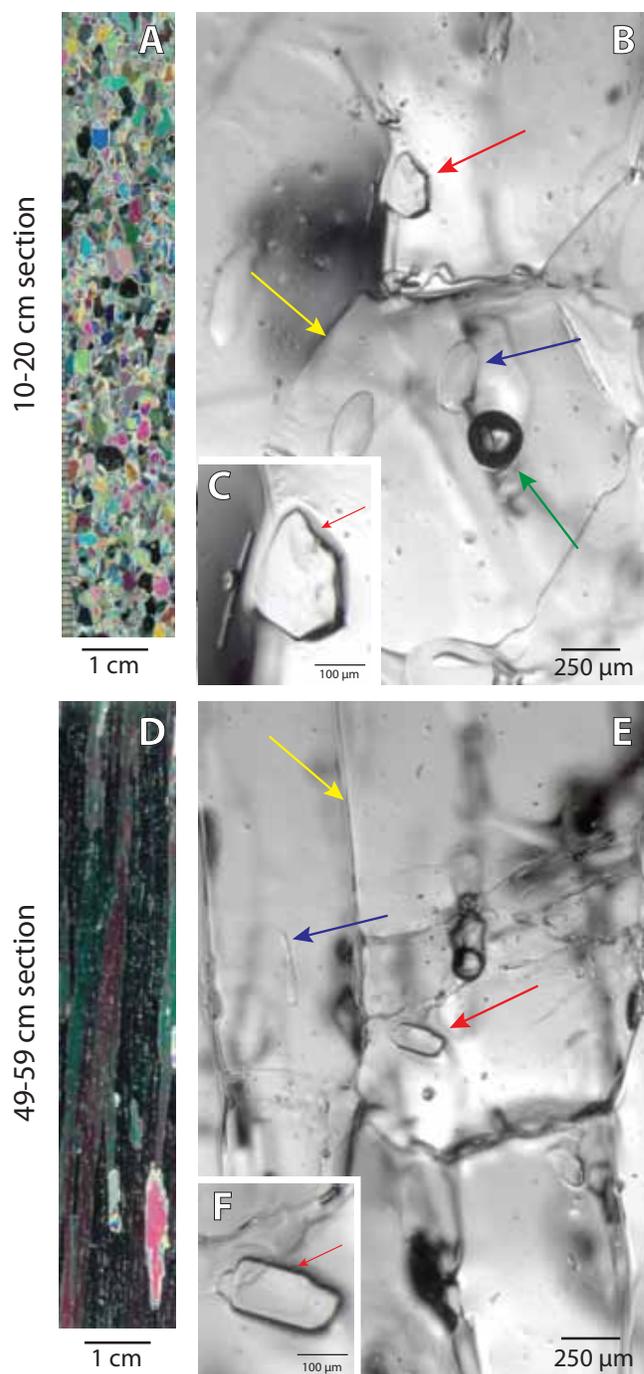

Figure 3. Location of an ikaite crystal in sea ice.

from less that 5 % in surface layers to 12 % near the bottom. The calculated brine salinities ranged from 200 in the surface sea ice to 33 in the bottom layers. At

POLY I, surface sea ice temperatures were only -5 °C with a downward gradient to -2 °C at the sea ice-water interface due to the rapid freezing with concurrent heat release and proximity to the water column (thin ice). Bulk salinities ranged from 10 in surface ice layers to 7 in the lower ice layers. Given high bulk salinities and temperatures, brine volumes ranged from 10 % in the top layers to 20 % in the bottom layers, and brine salinities were lower that at ICE I ranging from 93 at the surface to 33 at the bottom.

The upper 35 cm of sea ice at the ICE I location was composed of orbicular granular ice, formed presumably through consolidation of frazil ice. Daily images with automatic camera systems (MarinBasis Program, c/o Greenland Institute of Natural Resources) show that sea ice started to form locally outside the fjord in early October, and that those ice floes drifted into the fjord and consolidated with local ice to form a uniform ice cover that lasted until our arrival. Thus, the top layers of the ICE I location may have been produced outside the fjord. The layer from 35-112 cm consisted of columnar sea ice. Microscopic

Table 2. δ18O, S, T, and Vb in sea ice, brine, fresh snow, frost flower and brine skim samples throughout the duration of the frost flower growing experiment.

		$\delta^{18}O \pm SD$ [‰]	$S \pm SD$	T [°C]	υ_b [%]
brine		-4.9 ± 0.7	88.8		
fresh snow		-24.6 ± 0.4	0.0		
ice 19h	0.0-2.5 cm	-1.6 ± 0.1	10.4	-8.7	8.0
	2.5-5.0 cm	-1.9 ± 0.5	11.2	-5.4	14.1
	5.0-8.0 cm	-1.2 ± 0.3	8.7	-2.1	23.9
ice 26h	0.0-2.0 cm				
	2.0-5.0 cm		7.6	-5.3	6.6
	5.0-8.0 cm		8.6	-2.2	17.7
	8.0-11.0 cm		9.2	-1.8	23.6
	11.0-14.0 cm		6.6	-1.8	16.8
	14.0-17.0 cm		9.5	-1.7	25.9
frost flowers	19h	-0.8 ± 0.3	125.1	-12.7	43.8
	26h	-1.6 ± 0.3	94.9 ± 13.8	-7.8	56.6
	46h	-2.1 ± 0.3	90.9 ± 10.1	-7.1	58.9
	46h (tops)	-4.0 ± 0.2	92.2 ± 16.5		
	46h (bottoms)	-0.1 ± 0.4	89.6 ± 3.8	-7.1	58.9
	70h	-4.4 ± 1.2	87.0 ± 9.7		
	90h	-4.4 ± 0.3	64.4		
	90h (tops)	-7.7	50.2		
	90h (middles)	-4.6 ± 0.4	78.8		
	90h (bottoms)	-0.9 ± 0.3	64.1		
	114h	-4.3 ± 0.1	77.4		
brine skim	19h	-0.1 ± 0.5	48.2	-10.3	22.7
	26h	-0.9 ± 0.4	66.2 ± 7.6		
	46h	2.1 ± 0.9	77.4 ± 19.1	-8.7	41.7
	70h	-0.4 ± 0.5	72.7 ± 11.0		
	90h	-0.4 ± 0.0	52.9		
	114h	-1.3 ± 0.5	72.3		

examination of different vertical and horizontal ice thin sections showed the presence of ikaite crystals in the entire ice column. In general, ikaite crystals were located in the interstices between the ice platelets and well separated from brine pockets in both granular and columnar ice (Figure 3).

The sea ice at POLY I was less than one week old when first sampled. The upper 5 cm of the sea ice consisted of polygonal granular ice crystals, followed by transitional granular/columnar texture from 5 to 12 cm. The surface ice transformed into columnar sea ice towards the bottom (12-29 cm). Similarily to ICE I, microscopic examination of thin ice sections from POLY I revealed ikaite crystals presence in the entire ice column. Ikaite crystals were also mostly located in the interstices between the ice platelets. However, in layers where many small air bubbles were observed between the interstitial spaces closer to the bottom of the ice, few ikaite crystals were present.

At ICE I, the numbers of ikaite crystal per kg of melted ice ranged from ~ 25 x 106 kg^{-1} in the upper layers to about 1 x 106 kg^{-1} in the bottom layers. At POLY I, similar ikaite abundances were observed in upper ice layers, whereas abundances in bottom ice layers reached ~7 x 106 kg^{-1}. The molar concentration of ikaite per kg melted ice at ICE I decreased with depth from surface values of 900 μmol kg^{-1} to 100 μmol kg-1 in bottom layers. At POLY I, the highest concentrations (700 μmol kg^{-1}) were observed between 5-10 cm from the ice surface, decreasing to ~200 μmol kg^{-1} in the bottom ice layers.

Frost flower formation on new sea ice

$\delta^{18}O$, salinity, temperature and brine volume fraction (Vb) data from the in situ frost flower growing experiment are summarized in Table 2.

There has been considerable amount of debate on whether the surface crystals commonly referred to as frost flowers are indeed frost flowers grown from the vapor phase or rather salt flowers formed from

crystallized solid salts. Recent research suggests that majority of those structures present in the Arctic have indeed vapor origin (Perovich and Richter-Menge 1994, Style and Worster 2009), however continuous wicking of brine skim supplies brine to frost flowers since early hours of formation as shown by laboratory experiments (Roscoe et al. 2011). In this study, δ18O signature of frost flowers from 19 to 114 hours after freeze-up suggests that they are composed primarily of brine skim (Figure 4A). High brine volume fractions of both frost flowers and brine skim (Table 2), greatly exceeding the critical value of 5 % for brine mobility (Golden et al. 1998), support the brine skim wicking hypothesis. Fresh (19h) unsectioned frost flowers had $\delta^{18}O$ value of -0.8 ± 0.3 ‰ which was similar to the brine skim signature (-0.1 ± 0.5 ‰), and decreased gradually with time to -4.3 ± 0.1 ‰ after 114 hours after freeze-up. Brine skim $\delta^{18}O$ signature remained considerably lower than that of frost flowers after 114 hours reaching -1.3 ± 0.5 ‰, pointing to the influence of secondary atmospheric deposition either from vapor or from blowing snow ($\delta^{18}O$ value of -24.6 ± 0.4 ‰) later in the evolution. Influence of that secondary atmospheric deposition is particularly pronounced in the top sections of frost flowers, while bottom sections remained composed almost exclusively by brine skim. Lack of data prior 19 hours after freeze-up prevents a definite determination of frost flower initial origin; however, frozen brine origin seems implausible for two reasons: 1) salinities of frost flowers are too low to be formed by freezing brine (Figure 4B), and 2) $\delta^{18}O$ signature of frozen brine should be about -2.3 ‰ as calculated from fractionation, which is not the case.

Arctic-ICE

In this project, we tracked the formation and evolution of melt ponds on the ice surface using an innovative laser scanning technique. We found that snowdrifts and ice deformation controlled the initial locations of ponds, whereas the prevalence of melt water drainage flaws in the ice (including seal breathing holes) controlled the spatial evolution of ponds throughout the melt season.
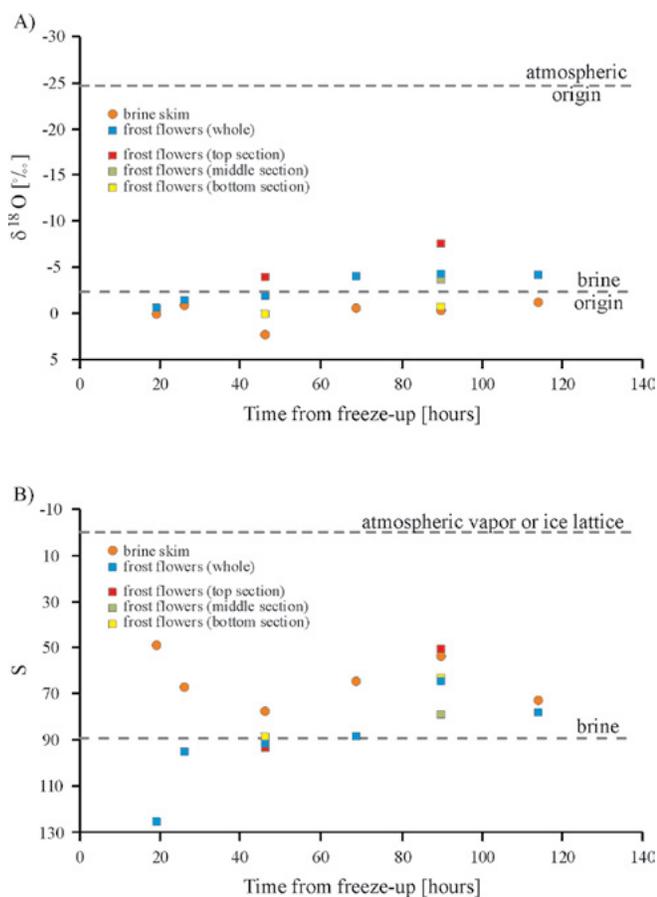
Figure 4. Temporal evolution of δ18O (A) and salinity (B) in frost flowers and brine skim over the duration of the frost flower growing experiment.

This study examined the CO_2 in water, sea ice, and atmosphere and the resulting fluxes between ice and atmosphere the in Canadian Arctic Archipelago from winter conditions into the melting season until sea ice break up. Carbon dioxide partial pressures within the ice were consistent with thermodynamic predictions, with high values (about 5 times atmospheric values) early in the season (early May), dropping as the temperatures increased, primary production advanced, and brine channels expanded, to become under saturated by the end of the study season (late June).

The Arctic-ICE project helped advance our understanding of key processes influencing the timing of primary producers in the ice-covered ecosystem.

In particular, we focused on the bottom ice algae, the melt water algae, and the under-ice phytoplankton (water column) blooms. For the first time, we applied a naturally transmitted irradiance technique to remotely estimate ice algal biomass at a single location from the winter through to melt of the sea ice. We applied the method to process studies and snow removal experiments that have further uncovered the important roles of ice temperature gradients, under-ice currents and snow depth as controlling variables on the timing of ice algal biomass loss from the sea ice (Campbell, 2012 M.Sc. thesis).

Bacteria, which are known to use DMSP as a source of carbon and sulfur, could be responsible for the rapid disappearance of the DMSPd released from the ice. The DMSPd consumed by the bacteria could be efficiently converted into DMS, especially if the bacteria use DMSP mostly as a carbon source. This hypothesis was tested during our field program in 2012 and the results show that brine could represent an important source of DMS. These new observations suggest that ice algae and under-ice phytoplankton blooms could be responsible for the high concentrations of dimethylsulfide (DMS) generally measured at the marginal ice zone.

Discussion

Ikaite distribution and abundance in winter sea ice

Ikaite concentrations from this study are higher than any other reported previously; that is 10-fold higher than those measured in Antarctica (Dieckmann et al. 2008), and 4 times higher than the ones from Fram Strait (surface summer ice, 160-240 μmol kg^{-1} melted sea ice; Rysgaard et al. 2012). One plausible explanation relates to differences in the quantification procedure between studies (prolonged melting in previous studies versus immediate analysis in the field in this study). The discrepancies could also represent real differences between sites and seasons as we present results from the winter, while other studies were conducted in the spring and summer

with melt already apparent. As a result, a fraction of ikaite crystals may have been already dissolved due to ice melting or lost via brine drainage in previous studies. Higher surface concentrations of ikaite are also predicted by the FREZCHEM model. Assuming that a standard seawater (S=35, [Na+] = 0.4861, [K+] = 0.01058, [Ca$_2$+] = 0.01065, [Mg$_2$+] = 0.05475, [C$_l$-] = 0.56664, [SO$_{42}$-] = 0.02927, [HCO$_3$-] = 0.0023; ions concentration unit: mol kg-1 water) freezes in an open system with a pCO$_2$ = 320 μatm, the FREZCHEM model (Marion et al. 2010) predicts an ikaite concentration of up to 620 μmol kg^{-1} sea ice in the cold surface layer of ICE I, decreasing exponentially downwards. Both the concentration range and distribution pattern agreed very well with the empirical data at ICE I. It should be noted that

the FREZCHEM modeling assumes that the system reaches thermodynamic equilibria and is always open to a constant pCO$_2$, both of which are not the case in the dynamic sea ice environment. Nevertheless, it supports the observation that the ikaite concentration increases with decreasing temperature, and is thus expected to be highly variable between seasons.

Ikaite crystals were located between the interstices of the sea ice matrix between the pure ice platelets. In contrast, solutes and gases (CO$_2$) are entrapped and transported within the brine system, which was visible under the microscope as small particles and air bubbles moved between the interstices of ice platelets. Increasing the temperature by a few degrees significantly accelerated the transport velocity. Hence, our observations confirm previous hypotheses (Rysgaard et al. 2007, 2009, 2011) that ikaite crystals are trapped within the sea ice matrix, whereas CO$_2$ released through ikaite production (Eq. 1) and dissolved within the brine can be lost from the sea ice. As a result, TA increases relative to TCO$_2$ in sea ice in spring and summer. When ikaite crystals dissolve during sea ice melt, surface water salinity and pCO$_2$ will decrease.

Frost flower formation on new sea ice

There has been considerable amount of debate on whether the surface crystals commonly referred to as frost flowers are indeed frost flowers grown from the vapor phase or rather salt flowers formed from crystallized solid salts. Recent research suggests that majority of those structures present in the Arctic have indeed vapor origin (Perovich and Richter-Menge 1994, Style and Worster 2009), however continuous wicking of brine skim supplies brine to frost flowers since early hours of formation as shown by laboratory experiments (Roscoe et al. 2011). In this study, δ18O signature of frost flowers from 19 to 114 hours after freeze-up suggests that they are composed primarily of brine skim (Figure 4A). High brine volume fractions of both frost flowers and brine skim (Table 2), greatly exceeding the critical value of 5 % for brine mobility (Golden et al. 1998), support the brine skim wicking
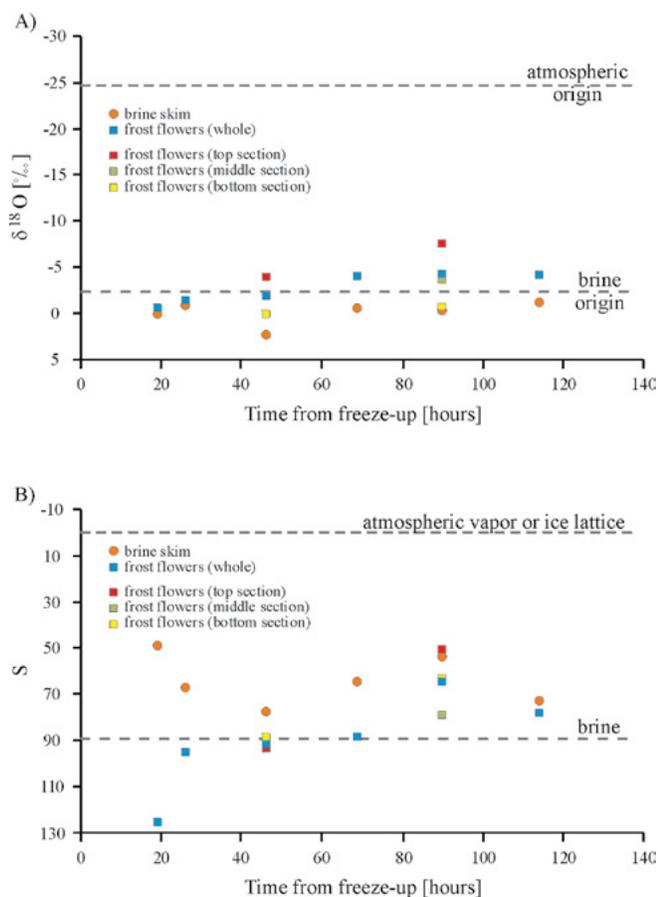
Figure 4 Temporal evolution of δ18O (A) and salinity (B) in frost flowers and brine skim over the duration of the frost flower growing experiment.

hypothesis. Fresh (19h) unsectioned frost flowers had δ18O value of -0.8 ± 0.3 ‰ which was similar to the brine skim signature (-0.1 ± 0.5 ‰), and decreased gradually with time to -4.3 ± 0.1 ‰ after 114 hours after freeze-up. Brine skim $\delta^{18}O$ signature remained considerably lower than that of frost flowers after 114 hours reaching -1.3 ± 0.5 ‰, pointing to the influence of secondary atmospheric deposition either from vapor or from blowing snow ($\delta^{18}O$ value of -24.6 ± 0.4 ‰) later in the evolution. Influence of that secondary atmospheric deposition is particularly pronounced in the top sections of frost flowers, while bottom sections remained composed almost exclusively by brine skim. Lack of data prior 19 hours after freeze-up prevents a definite determination of frost flower initial origin; however, frozen brine origin seems implausible for two reasons: 1) salinities of frost flowers are too low to be formed by freezing brine (Figure 4B), and 2) $\delta^{18}O$ signature of frozen brine should be about -2.3 ‰ as calculated from fractionation, which is not the case.

Arctic ICE

Since the fractional coverage of melt ponds controls the albedo of the sea ice surface and therefore the amount of solar radiation absorbed by and transmitted through the ice, these new findings are an important step towards properly modelling the energy balance of sea ice during the melt season. We also investigated the evolution of ice bottom topography and the fate of draining surface water as the ice melted. Early results show that ice bottom melt is delayed several days by the formation of a continuous layer of fresh melt water and a false ice bottom between the sea ice and ocean, which may influence the roughness of the ice underside and the timing of ice break-up.

Observed CO_2 results are very different from results from very cold, wintertime conditions in other places in which pCO_2 values measured in situ have been substantially less than predicted by theory. We also found that sea ice brine analyses alone are not sufficient to unravel the inorganic CO_2 cycle within sea ice and that frequency and quantity of gas bubbles within sea ice potentially play a crucial role. Thus,

future studies have to take bubble formation within sea ice into account to fully assess the polar carbon cycle. We note that we now require data collection from different regions and for full annual cycles to improve our knowledge of the influence of a complete seasonal cycle of sea ice on atmosphere-ocean CO_2 fluxes and to hopefully provide a more realistic Arctic budget.

It was concluded that rain and warm air intrusion events, which can rapidly melt the snow cover and are becoming increasingly more common in the Arctic, would result in an earlier bloom termination if they occur in late spring. However, if these events occur earlier in the spring when ice temperatures are still sufficiently low, the ice algae were shown to continue to accumulate at the ice bottom, likely acclimating to the rapid changes in ice bottom irradiances.

Through collection and analysis of a series of sectioned sea ice cores collected from Resolute Passage, we have also demonstrated that the accumulation of the sea ice specific biomarker IP25 occurs at the same time as the spring algal bloom. This observation from Resolute reinforces the outcomes from a related study carried out in the Amundsen Gulf in 2008, although the Resolute dataset is more complete. Further, the datasets reveal some temporal differences between the two locations and some further insights into the relationships between ice-derived biomarkers and those found in water column (under ice) have also been found. This work is feeding into the exciting application of this biomarker for not only paleo-oceanographic studies, but also Arctic food web studies.

Formation of the ice melt layer typically occurs during peak solar insolation, resulting in consistent exposure of the environment to the highest annual levels of UV and visible radiation that are further amplified by light scattering at the ice surface and within the sea ice. Subsequently, the melt water flora have been suggested exhibit significant photoprotective strategies including production of UV screening compounds known as mycosporine-like amino acids (MAAs), which inferred from algal absorption spectra (see: Mundy et al. 2011; Polar Biology, DOI 10.1007/s00300-011-0998-x).

Indeed, from the Resolute data we have confirmed the presence of MAAs associated with the melt pond algae (work of an undergraduate student of Dr. F. Wang at University of Manitoba). Interestingly, we are also finding MAAs in the upper 10 m of the water column. This was somewhat surprising in that we did not expect high enough UV radiation in the water column for algae to respond through the production of MAAs. However, this photoprotective response of the algae can be explained by the presence of melt ponds on the sea ice that let > 50 % surface irradiance through the ice cover.

The inter-annual variability of under-ice phytoplankton within the three years of Resolute Passage/Allen Bay data has been incredible. In both 2010 and 2011, we observed significant under-ice phytoplankton blooms with biomass concentrations reaching more than an order of magnitude greater than that found in the sea ice. However, the processes behind bloom formation were completely different as were the species composition of these two years. In 2010, the bloom was associated with a reduction in water column turbulence due to weak tidal currents and the onset of sea ice melt; whereas in 2011, the water column was strongly stratified at 25 m leading to the occurrence of the bloom and depletion of surface nutrients before the ice broke up. Finally, in 2012, we did not observe a bloom prior to the end of the study due to strong tidal mixing that caused the water column to be mixed well below a critical depth needed for the occurrence of positive net primary production.

Dimethylsulfide (DMS) is produced through bacterial degradation of dissolved dimethylsulfoniopropionate (DMSPd), the latter a product of primary producers. The importance of DMS stems from its role as a cloud condensation nucleate through which it is hypothesized to have a negative feedback on climate warming. Both ice algae and phytoplankton contributed to the increase in particulate DMSP (DMSPp) in the water column during the spring-summer transition. The concentrations of DMSPd were very high at the bottom of the ice, but less than 10 % of the dissolved DMSP lost from the ice during the warming period was found

in the water column. This intriguing 'vanishing' of DMSPd was observed in 2010, 2011, and 2012.

Conclusion

The precipitation of ikaite ($CaCO_3 \cdot 6H_2O$) in polar sea ice is critical to the efficiency of the sea ice-driven carbon pump and potentially important to the global carbon cycle, yet the spatial and temporal occurrence of ikaite within the ice is poorly known. We report unique observations of ikaite in unmelted ice and vertical profiles of ikaite abundance and concentration in sea ice for the crucial season of winter. Ikaite crystals, ranging in size from a few μm to 700 μm, were observed to concentrate in the interstices between the ice platelets in both granular and columnar sea ice. Their concentration decreased with depth from surface-ice values of 700–900 μmol kg^{-1} ice (~ 25 x 106 crystals kg^{-1}) to bottom-layer values of 100–200 μmol kg–1 ice (1–7 x 106 kg^{-1}), all of which are much higher (4–10 times) than those reported in the few previous studies. Direct measurements of TA in surface layers fell within the same range as ikaite concentration, whereas TA concentrations in bottom layers were twice as high. This depth-related discrepancy suggests interior ice processes where ikaite crystals form in surface sea ice layers and partly dissolved in bottom layers. The result is a C-shaped pH profile with high pH (>9) in surface and bottom ice layers, and lower pH (~ 8) in interior layers. Based on results presented here, enhanced ice production in winter polynyas would add considerable amounts of TA to the surface waters in the form of ikaite crystals from sea ice, lowering surface water pCO^2 upon ice melt and crystal dissolution, and increasing the potential for seawater uptake of CO^2.

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