


Assessment and improvement of the sea ice processing for dissolved inorganic carbon analysis

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Abstract

Dissolved inorganic carbon (DIC) is an important parameter to characterize the biogeochemical processes in sea ice and across the ocean-sea ice-atmosphere interface. The main challenge in bulk sea ice processing for DIC analysis is to melt the ice core without exposure to the air, which otherwise might contaminate the sample. A common practice is to seal the ice core in a gas-tight plastic bag and remove the air gently using a syringe or a hand pump. However, this procedure is time-consuming and the uncertainty in DIC concentration processed in this way has not been fully accessed. In this study, we modified the method by using a vacuum sealer and evaluated this procedure by examining the impact of ice sample processing, biological activity, gaseous CO₂ initially present in sea ice, and the presence of ikaite (CaCO₃·6H₂O) crystals. The results show that no loss or gain in DIC occurs during the evacuation and ice melting process and that it might not be necessary to pre-poison the ice samples during the ice melting process. In addition, gaseous CO₂ initially present in sea ice has a negligible impact on DIC analysis. If detectable ikaite crystals are present in sea ice, the measurement results should be referred to total inorganic carbon instead of DIC. The field test at Station Nord in Greenland demonstrates that the modified method is simple and quick to use even under the most remote and extreme environments.

When sea ice grows, most of the brine is expelled to the under-ice seawater due to gravity drainage, while a small portion stays trapped in the ice matrix (Niedrauer and Martin 1979). The chemical composition of brine is primarily a function of salinity and temperature, but can be modified by biological activity and abiotic processes such as gas exchange and mineral formation (Papadimitriou et al. 2007).

Dissolved inorganic carbon (DIC) in sea ice, the measurement of which could include gaseous CO₂ in the bubbles of the ice, is an important parameter to describe the ocean-sea ice-atmosphere CO₂ flux. As described in Tison et al. (2002), sea ice was for many years considered as a lid over seawater preventing CO₂ exchange between the atmosphere and ocean. Some observations suggest that sea ice can be an active source or sink for CO₂ (e.g., Nomura et al. 2010; Miller et al. 2011). A more recent study shows that the effective gas velocity decreases in proportion to sea ice cover,

suggesting that CO₂ flux through sea ice could be minor (Butterworth and Miller 2016). However, direct measurements of the CO₂ flux on sea ice based on the chamber method and eddy covariance tend to largely disagree as pointed out in Geilfus et al. (2013). Since the ice-atmosphere CO₂ flux is limited by the DIC stocks in sea ice (Moreau et al. 2015), improved measurements of DIC in sea ice are needed to better understand the air-ice CO₂ flux. Rysgaard et al. (2011) proposed a conceptual model describing the role of sea ice in controlling air-sea CO₂ exchange (i.e., sea ice carbon pump), and noted that a large dataset of DIC from various types and concentrations of sea ice would be needed in order to better quantify the air-sea CO₂ flux during sea ice formation and decay.

Another important need for DIC measurement is the study of biological activity in sea ice. During phytoplankton growth, major nutrients and DIC are taken up in certain stoichiometric quantities. One of the most common parameterizations is known as the Redfield ratio (C : N : P = 106 : 16 : 1, Redfield 1958). These ratios model the phytoplankton productivity as a function of a limiting nutrient (Günther et al. 1999), but require precise measurements of the DIC stock in sea ice.

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Unlike the gaseous CO_2 determination in the bubbles of terrestrial ice cores, which can be directly extracted from the bubbles by crushing ice samples in a cold closed vacuum system (Neftel et al. 1982; Etheridge et al. 1988), the measurement of DIC in sea ice needs first to melt the ice in an air-free container, with the melt-water being sampled following the procedure for seawater DIC analysis (Dickson et al. 2007). Although DIC of the bulk sea ice has been frequently measured in many studies (e.g., Rysgaard et al. 2007; Rysgaard et al. 2009; Miller et al. 2011; Geilfus et al. 2012; Fransson et al. 2013), a state-of-the-art method for confidently melting ice samples for DIC analysis has not yet been formulated (Miller et al. 2015). The most common practice involves gas-impermeable bags. After the sample is sealed in the bag, the air in the bag is removed manually using a hand pump or a syringe through a valve mounted on the bag (e.g., Fransson et al. 2011; Miller et al. 2011; Geilfus et al. 2012). This method is time-consuming, and it can be cumbersome to take all the air out of the bag, especially under harsh and cold conditions in the field (Miller et al. 2011; Geilfus et al. 2012). Alternatively, ice samples can be melted in a gas-tight syringe by adding a solution of known DIC concentration (Rysgaard et al. 2007). This method can remove the gas entirely but it is not straightforward to operate. Due to the size and/or shape limitation of the syringe, ice samples have to be cut to fit in the syringe. Furthermore, adding a solution to ice samples increases the uncertainty of the DIC analysis.

The DIC analysis in sea ice samples may also be affected by biological activity during the melting process, gaseous CO_2 initially present in sea ice matrix and the presence of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), none of which has been quantitatively evaluated. It is suggested that ice samples should be poisoned before melting in order to inhibit biological activity (e.g., Rysgaard et al. 2009; Geilfus et al. 2012), and that the gaseous CO_2 trapped in sea ice would be dissolved in the melt water (Rysgaard et al. 2007; Miller et al. 2015). However, to which extent these will affect DIC analysis is unknown. Ikaite is widely observed in sea ice (e.g., Dieckmann et al. 2008, 2010; Nomura et al. 2013; Rysgaard et al. 2013). During the melting of ice samples, ikaite crystals might dissolve and change DIC, which was not considered in most studies (e.g., Fransson et al. 2011; Geilfus et al. 2015) except Miller et al. (2011), which justifiably reported it as total inorganic carbon (TIC).

In this study, we simplified the sea ice processing method for DIC analysis by employing a commercially available plastic bag and a vacuum sealer. We evaluated the performance of the simplified method by addressing the following two questions: (1) is there a loss of DIC during the air evacuation process? and (2) is there an exchange of CO_2 through the new bag during the ice-melting process? With the modified method, we also assessed the impact of the biological activity, gaseous CO_2 initially present in sea ice, and the presence of ikaite crystals on the DIC analysis. The modified method

was then field tested for the measurement of DIC in sea ice at Station Nord in Greenland.

Methods

Ice samples

The ice samples used in this study were collected in an outdoor ice tank experiment at the Sea-ice Environmental Research Facility (SERF) at the University of Manitoba (Winnipeg, Canada) in winter 2015. The SERF outdoor pool has dimensions of 18.3 m (length) \times 9.1 m (width) \times 2.6 m (depth), and was covered by a retractable roof to perform a snow-free ice growth experiment. It contained artificial seawater prepared after the modification of Millero (2006) with a salinity of 32. The entire pool was mixed by an array of sump-pumps (Flygt, Xylem) for a few weeks before the start of ice growth to allow the seawater carbonate system to reach equilibrium with the atmosphere. The experiment ran through January and February and ice grew to a maximum thickness of around 40 cm. Ice samples were extracted using a Mark II core barrel with an internal diameter of 9 cm (Kovacs Ent., Lebanon, U.S.A.).

Ice sample processing

Two methods were used to process the sea ice samples for DIC analysis. Method 1 ("Conventional Method") is the method commonly used by many of the literature studies. It involves placing the ice core in a gas-tight, specially laminated (Nylon, ethylene vinyl alcohol, and polyethylene) plastic bag (Hansen et al. 2000). The bag was sealed by an impulse sealer (AIE-300C) and the air in the bag was evacuated gently using a syringe fitted with a needle that pierced through a valve mounted on one side of the bag. The whole process took up to several minutes. Method 2 ("Modified Method") is to place the ice core in a commercially available plastic bag (Nylon/poly, Cabela's, Sidney, Nebraska, U.S.A.), evacuate and then seal it by placing the open side of the bag in a vacuum sealer (Preservac basic, Cabela's); the whole operation was completed within seconds.

In order to test the effect of air evacuation on sea ice DIC (i.e., whether DIC would be lost during the application of the vacuum), we pushed the testing condition to the extreme: the temperature of ice samples was brought as close as to the seawater freezing point (-1.76°C at salinity 32) when sea ice has the maximum permeability. This was done by bringing three ice cores previously stored at -20°C to a -2°C temperature-controlled room. One ice core was about 40 cm in length and the other two were about 20 cm. After the ice temperature reached the desired value (-2°C), which was checked by a traceable digital thermometer (accuracy $\pm 0.05^\circ\text{C}$, Control Company), those ice cores were cut into 5–6 cm subsections with a stainless steel saw. Each subsection (the top and bottom ones were discarded) was further cut into two halves; one half was processed using the conventional method, and the other half using the modified method.

After all the ice samples were evacuated and sealed in the cold room (-2°C), they were melted at room temperature in the dark. Tens of milliliter of the melt-water sample processed by the conventional method was slowly taken out of the bag through the valve by a syringe fitted with a needle, without generating air bubbles. For the samples sealed in the new bag, a glass syringe connected with a needle was used. The only difference was that the needle pierced the bag directly and the sample was withdrawn into the syringe. Those samples were further transferred to 12 mL gas-tight vials (Labco, Lampeter, UK) by replacing the needle with a piece of tubing. Samples were measured directly after the transfer.

DIC storage in new bags in the presence and absence of HgCl_2

Two freshly collected sea ice cores, both with a length around 30 cm, were cut into 10 cm subsections immediately after sampling. Three subsections from one ice core were sealed in pre-poisoned bags (0.1% v/m saturated HgCl_2 solution). The other three subsections from the second ice core were sealed without adding HgCl_2 . All samples were evacuated and sealed using the modified method. Those ice cores were melted at room temperature in the dark. After the ice cores were completely melted, tens of milliliter of the melt-water sample was taken as described above; the ice samples that were not initially poisoned were poisoned after transfer to vials. After enough samples were taken, the small hole pierced by the needle was covered with a sealing tape (Uline, U.S.A.) and those bags were then kept in a fridge at a temperature around 4°C until next sampling day. Time series sampling was performed on day 0, 1, 3, 5, 8, 13, and 21.

Sample measurements and calculation

After ice samples were completely melted, salinity was measured with a conductivity meter (Orion Star A212, Thermo Scientific) at room temperature with a precision better than ± 0.01 . DIC was measured on a DIC analyzer (Apollo SciTech) by acidification of a 0.75 mL subsample with 1 mL 10% H_3PO_4 (Sigma-Aldrich), and quantification of the released CO_2 with a nondispersive infrared CO_2 detector (LI-COR, LI-7000). The results were converted from the unit of $\mu\text{mol L}^{-1}$ to $\mu\text{mol kg}^{-1}$ based on sample density that was calculated from sample salinity and temperature when analyzed (Gill 1982). Triplicate measurements were carried out and uncertainty in DIC value was within $\pm 1 \mu\text{mol kg}^{-1}$. Total alkalinity (TA) was measured by the Gran titration (Gran 1952) using a TIM 840 titration system (Radiometer analytical, ATS Scientific), consisting of a Ross sure-flow combination pH glass electrode (Orion 8172BNWP, Thermo Scientific) and a temperature probe (Radiometer analytical). Twelve milliliter sample was titrated with a standard HCl solution (0.05 M, Alfa Aesar); the precision of TA measurement was better than $\pm 3 \mu\text{mol kg}^{-1}$. Both DIC and TA were calibrated with certified reference materials (batch 144) from A. G. Dickson at the Scripps Institution of Oceanography. pCO_2 was calculated from DIC and TA using CO2SYS software

(Pierrot et al. 2006) with the dissociation constants of carbonic acid from Mehrbach et al. (1973) refit by Dickson and Millero (1987), and dissociation constant of KHSO_4 from Dickson (1990). The concentration of dissolved organic carbon (DOC) was determined by catalytic high temperature oxidation at 680°C (Thermolox TOC/TN Analyser, Analytical Sciences) which has a precision of 2.0%.

Assessment and discussion

Comparison between two evacuation methods

Although each ice section was cut into two halves, those two halves were not identical due to the highly heterogeneous nature of brine distribution in sea ice, as indicated from the salinity values (Table 1). Therefore, in order to make the DIC data from two methods comparable, DIC values were normalized to reference salinity (NDIC), which was the average salinity of two halves from the same ice subsection.

The difference in NDIC (ΔNDIC) between each ice sample processed by the modified method and the conventional method ranged from $-3.9 \pm 0.9 \mu\text{mol kg}^{-1}$ to $3.9 \pm 0.5 \mu\text{mol kg}^{-1}$ and yielded a mean ΔNDIC of $0.0 \pm 2.6 \mu\text{mol kg}^{-1}$ for all the samples (Fig. 1; Table 1), indicating that there was no statistically significant difference (paired *t*-test, $p = 0.99$) in ice samples processed using those two methods. It was suggested that after sealing the ice core in the bag, the air remaining in the bag should be gently removed using a syringe (or a hand pump), to ensure that the sample is not exposed to an excessive vacuum as to reduce the loss in DIC (Miller et al. 2015). Although the vacuum degree in the sealed bags processed by two methods was not measured, we noticed that after the ice melted completely, the samples processed by the conventional method always had some headspace left, whereas the samples processed with the modified method were mostly air-free, indicating that the evacuation strength in the modified method is much stronger than in the conventional method. As a result, the H_2CO_3^* component (mainly aqueous CO_2) might be perturbed by the evacuation process, but the impact is expected to be minimal as the diffusion of CO_2 between air and water is kinetically controlled. The evacuation process only takes a few seconds and during the process most of the brine is kept within the ice, which further reduces the perturbation to H_2CO_3^* . Together with the fact that there was no significant difference in DIC between the two methods, we can assume that there was no DIC loss during the evacuation. This is further confirmed by the assessment of the effect of gaseous loss on the sea ice DIC during the gas evacuation in the "Effect of gaseous CO_2 on DIC analysis" section.

Since our above comparison was done at temperature near seawater freezing point when ice has the highest porosity, we are confident that the air evacuation of the ice sample will not cause any significant loss in DIC under most field conditions (i.e., colder environment), as the porosity of

Table 1. DIC concentration ($\mu\text{mol kg}^{-1}$) of eight ice samples. Each ice sample was cut into two halves and processed by two different methods. One half (#-1) is processed by the conventional method and the other half (#-2) by the modified method. NDIC is salinity normalized DIC based on the average of the salinity (#-1 and #-2) from two halve ice sample. ΔNDIC is the difference in NDIC processed by two different methods (#-2 – #-1).

Samples	Salinity	DIC	NDIC	ΔNDIC
# 1-1	5.08	355.1	349.0	2.7 ± 1.0
# 1-2	4.91	345.5	351.7	
# 2-1	4.14	291.1	303.1	0.0 ± 1.1
# 2-2	4.48	315.0	303.1	
# 3-1	4.22	296.6	300.0	0.5 ± 1.1
# 3-2	4.31	304.0	300.6	
# 4-1	3.96	279.0	274.0	-2.9 ± 0.5
# 4-2	3.82	266.2	271.1	
# 5-1	5.44	380.2	374.0	3.9 ± 0.9
# 5-2	5.26	371.5	377.9	
# 6-1	4.84	342.1	342.2	-0.7 ± 0.6
# 6-2	4.85	341.6	341.4	
# 7-1	5.48	384.1	374.0	0.4 ± 1.4
# 7-2	5.19	364.3	374.5	
# 8-1	4.69	332.9	340.0	-3.9 ± 0.5
# 8-2	4.89	343.1	336.1	
Mean	—	—	—	0.0 ± 2.6

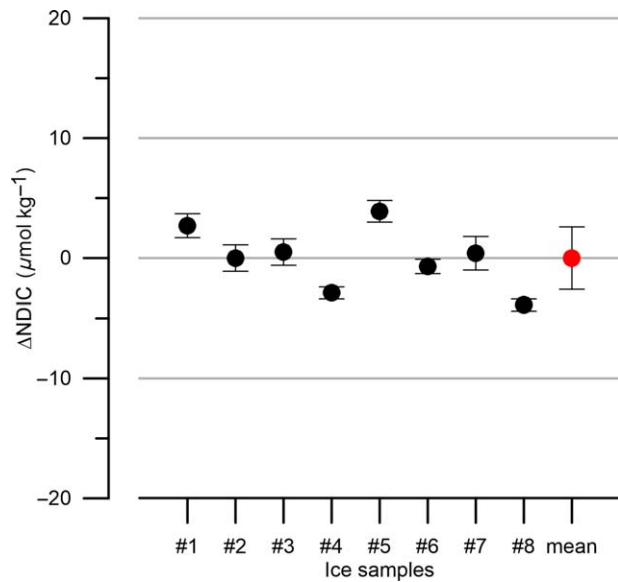


Fig. 1. Difference in NDIC (ΔNDIC) processed by two different methods for eight ice samples (black circle). The red circle is the mean ΔNDIC of all the samples. The error bar is the standard deviation for ΔNDIC .

ice decreases at colder temperatures, making it more difficult for CO_2 to be extracted from the ice segment during air evacuation process.

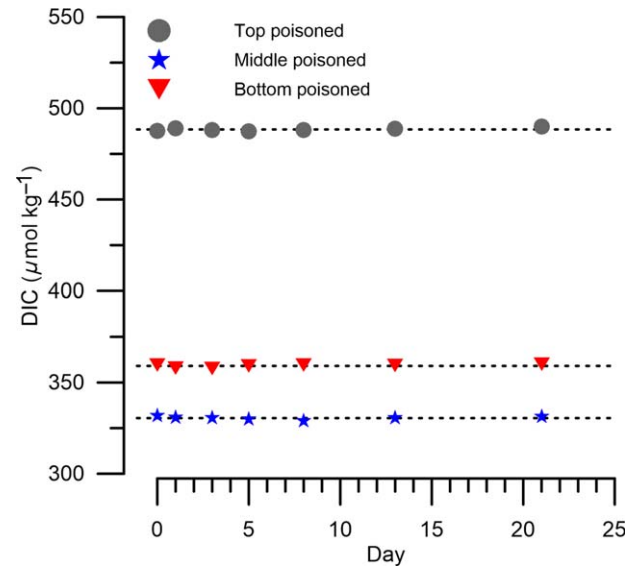


Fig. 2. The evolution of DIC concentration for three poisoned ice samples (top, middle, and bottom subsections from a 30 cm ice core) during a 21-d time series experiment using the modified sample processing method.

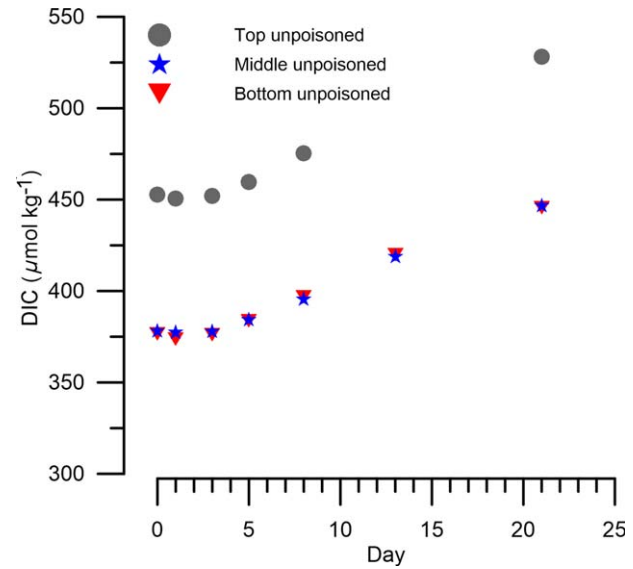


Fig. 3. The evolution of DIC concentration for three unpoisoned ice samples (top, middle, and bottom subsections from a 30 cm ice core) during a 21-d time series experiment using the modified sample processing method.

DIC storage in new bags

Figure 2 shows the evolution of DIC with time for the three poisoned ice samples during a 21-d time series experiment using the modified method. No significant change in DIC was observed over the entire experimental period. The mean of DIC values of the three samples were $488.4 \pm 0.9 \mu\text{mol kg}^{-1}$, $330.5 \pm 1.0 \mu\text{mol kg}^{-1}$, and $359.1 \pm 1.0 \mu\text{mol kg}^{-1}$, respectively; for all tested samples, ΔDIC ($\text{DIC} - \text{mean}$)

Table 2. The carbonate system (DIC, TA, and $p\text{CO}_2$) for all the poisoned and unpoisoned ice samples on day 0 in the time series experiment. T. P., M. P., and B. P. represent top 10 cm, middle 10 cm, and bottom 10 cm, respectively, of poisoned ice samples from a 30 cm ice core; T. un-P., M. un-P., and B. un-P. represent top 10 cm, middle 10 cm, and bottom 10 cm, respectively, of unpoisoned ice samples from a 30 cm ice core.

Samples	Salinity	DIC ($\mu\text{mol kg}^{-1}$)	TA ($\mu\text{mol kg}^{-1}$)	$p\text{CO}_2^*$ (μatm)
T. P.	7.19	488.4	507.2	86.1
M. P.	4.68	330.5	350.1	39.4
B. P.	5.10	359.1	375.8	52.7
T. un-P.	6.66	451.7	487.5	43.3
M. un-P.	5.36	377.6	399.4	46.7
B. un-P.	5.47	375.5	393.5	54.7

$p\text{CO}_2^*$ is calculated based on DIC and TA at the temperature of 4°C.

was less than $2 \mu\text{mol kg}^{-1}$. Figure 3 shows the evolution of DIC with time for the three unpoisoned ice samples during a 21-d time series experiment. The DIC values stayed essentially unchanged for 3 d with mean values of $451.7 \pm 1.1 \mu\text{mol kg}^{-1}$, $377.6 \pm 0.4 \mu\text{mol kg}^{-1}$, and $375.5 \pm 1.5 \mu\text{mol kg}^{-1}$, respectively. After day 3, all the three samples showed a significant increase in DIC with time, reaching a DIC value of $528.2 \mu\text{mol kg}^{-1}$, $446.6 \mu\text{mol kg}^{-1}$, and $445.7 \mu\text{mol kg}^{-1}$ at the end of the experiment. The initial $p\text{CO}_2$ values from all melt-water samples ranged from $39.4 \mu\text{atm}$ to $86.1 \mu\text{atm}$ (Table 2), suggesting that all the melt-water samples were far undersaturated with respect to the ambient CO_2 of around $400 \mu\text{atm}$ (Tans 2015). Thus, if the bags were permeable to CO_2 , an increase in DIC in all the tested samples would be expected. Nevertheless, no change in DIC was observed in the poisoned samples, suggesting that this new bag is gas-impermeable for DIC storage for at least 21 d. The increase in DIC in unpoisoned samples after 3 d stored in the fridge is thus most likely due to bacterial activity in melted ice water, which could convert organic carbon into DIC (Bendtsen et al. 2002). The organic carbon of the melt sea ice was partly originated from the SERF seawater with a background concentration of DOC measured around $180 \mu\text{mol L}^{-1}$ and partly due to the releasing from the plastic vacuum bag (whose material is made of organic carbon) over time as can be seen from the Table 3.

Effect of biological activity on DIC analysis

A common concern in DIC measurement is whether DIC will be affected due to the biological activity during the ice melting process. To this end, some researchers added HgCl_2 to ice samples to inhibit biological activity (e.g., Rysgaard et al. 2009; Geilfus et al. 2012). Our results show that for the unpoisoned samples stored in the plastic bags, DIC can stay unchanged for at least 3 d in a fridge. This suggests that it is not necessary to pre-poison ice samples before the ice

Table 3. DOC concentrations of the melted ice samples and their change over 21 d in the plastic bags. T. P., M. P., and B. P. represent top 10 cm, middle 10 cm, and bottom 10 cm, respectively, of poisoned ice samples from a 30 cm ice core; T. un-P., M. un-P., and B. un-P. represent top 10 cm, middle 10 cm, and bottom 10 cm, respectively, of unpoisoned ice samples from a 30 cm ice core.

	Day 0	Day 21
	DOC ($\mu\text{mol L}^{-1}$)	DOC ($\mu\text{mol L}^{-1}$)
T. P.	82.1 ± 0.6	139.2 ± 2.2
M. P.	62.5 ± 1.3	112.2 ± 1.0
B. P.	88.0 ± 1.9	109.2 ± 2.0
T. un-P.	86.2 ± 1.5	120.0 ± 2.6
M. un-P.	71.9 ± 1.0	105.0 ± 1.2
B. un-P.	64.4 ± 1.3	132.7 ± 2.9

melting, as long as they are analyzed shortly after the melting is complete (e.g., within 3 d). There are many advantages of skipping the pre-poisoning step, as larger amount of HgCl_2 is required to poison the ice samples while not all the melted ice samples are collected, and poisoning the ice samples with HgCl_2 in the field under extremely cold conditions often results in HgCl_2 spill and thus pollution to the environment; the high HgCl_2 concentration used is also dangerous to people who handle the melted ice samples afterward (Miller et al. 2015). We need to note that the ice samples used in this study were derived from the SERF tank, which has low biological activity during the ice growth period (Rysgaard et al. 2014). The results derived here should be applicable for natural ice samples with low biological activity. For those ice samples with high biological activity, such as at the ice bottom (e.g., Meguro et al. 1967; Meiners et al. 2009), HgCl_2 poisoning before melting the ice samples might still be needed. It should also be noted that if the samples cannot be analyzed within a short time, they need to be transferred to vials and poisoned by HgCl_2 .

Effect of gaseous CO_2 on DIC analysis

Another major concern in sea ice DIC measurement is the fate of gaseous CO_2 initially present in the air bubbles in the ice. It was assumed that gaseous CO_2 would be dissolved in the melt-water that typically has low $p\text{CO}_2$ (Miller et al. 2015), which might affect DIC concentration. Here, we consider two extreme scenarios for the fate of gaseous CO_2 initially present in the air bubbles in sea ice: first, air bubbles trapped in the ice matrix are completely removed during the air evacuation process; second, the air trapped in the ice matrix remains in sea ice during the air evacuation process and gaseous CO_2 reaches equilibrium with the melt-water. At our experimental conditions (i.e., ice temperature of -2°C , and bulk salinity of ice samples between 3 and 5), the gas content in sea ice was estimated to be around 1–2% by volume according to the equation of Cox and Weeks (1983)

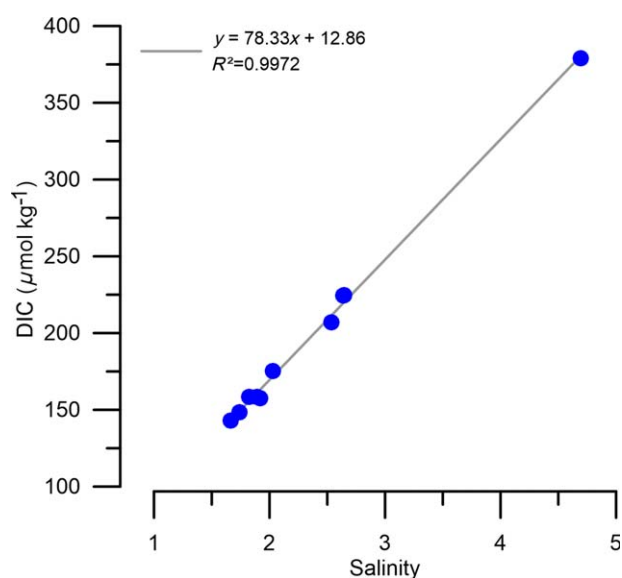


Fig. 4. The correlation between bulk DIC and bulk salinity of ten ice sections (Blue circles) from a complete sea ice core retrieved at Station Nord, Greenland processed by the modified method.

based on an average ice density of 910 kg m^{-3} (Timco and Frederking 1996). Assuming the air bubbles in the ice are in equilibrium with the ambient air with a pCO_2 value of around $400 \text{ } \mu\text{atm}$ (Tans 2015), calculations following the method of Dickson et al. (2007) reveals that the difference in DIC caused by the gaseous CO_2 between the two extreme scenarios will be less than $0.5 \text{ } \mu\text{mol kg}^{-1}$. Even at a pCO_2 as high as $2000 \text{ } \mu\text{atm}$ (Geilfus et al. 2012) and an air bubble volume as large as 5% (Crabeck et al. 2015), it only causes a difference in DIC of about $4 \text{ } \mu\text{mol kg}^{-1}$. These calculations are done with the consideration of two opposite fates for gaseous CO_2 in sea ice and combined conditions of extreme high pCO_2 value and air bubble percentage. In reality, the contribution of gaseous CO_2 to DIC should be much less. Therefore, the effect of gaseous CO_2 in the ice on DIC analysis can be safely neglected.

Effect of ikaite dissolution on DIC analysis

When melting ice samples, ikaite, if present in the ice, might also dissolve which will contribute to an increase in DIC concentration. In practice, the amount of ikaite is normally estimated by melting ice samples at 0°C and assuming that ikaite will not dissolve to any significant extent during the ice melting process (e.g., Dieckmann et al. 2008; Geilfus et al. 2013). Since ikaite is very unstable at temperatures above 4°C , it will be completely dissolved within a few hours when brought to room temperature (Rysgaard et al. 2012). Thus, it is possible to quantify the contribution of ikaite to DIC analysis by measuring the difference in DIC or TA between the samples taken immediately after the ice melt and samples brought to the room temperature. In this study, only a few ikaite crystals on the top of the SERF sea ice cores

were observed under the microscope, which is consistent with earlier findings in field studies where ikaite was mainly found on the top of sea ice cores (e.g., Dieckmann et al. 2008; Fischer et al. 2013). The maximum amount of ikaite at the ice growth experiment at SERF 2015 was found at the top 0.5 cm of the ice core, with a value below $10 \text{ } \mu\text{mol kg}^{-1}$ (melt-water); the concentration of ikaite in the rest of the ice core was lower than the measurement uncertainty ($\pm 1 \text{ } \mu\text{mol kg}^{-1}$). The maximum contribution of ikaite from a 10 cm ice-subsection to DIC concentration was thus less than $1 \text{ } \mu\text{mol kg}^{-1}$. Therefore, the effect of ikaite dissolution could be ignored. Nevertheless, higher ikaite concentration ($> 10 \text{ } \mu\text{mol kg}^{-1}$) in sea ice has been observed in the field study (e.g., Fischer et al. 2013; Rysgaard et al. 2013). In such cases, the contribution of ikaite dissolution to DIC measurement during the ice melting process should be kept in mind; the measurement results should be referred to TIC instead of DIC, as was done in Miller et al. (2015).

Field practical

The modified method was tested during a field campaign at Station Nord ($81^\circ 36'\text{N}$, $16^\circ 40'\text{W}$), northeastern Greenland in April 2015 when air temperatures were as low as -20°C . Sea ice cores were cut into 10 cm sections, and per section, transferred to the aforementioned plastic vacuum bags without adding HgCl_2 . The bags were evacuated and sealed in situ by a vacuum sealer. This ensured the ice samples had minimal exposure to the atmosphere, which reduced the CO_2 exchange between the ice samples and ambient air. The ice samples were transported in a cooler to Villum Research Station at Station Nord, where the ice samples were processed following the methods described in “Ice samples processing” section. The melted ice samples were stored in 12 mL vials and poisoned by HgCl_2 ; and were analyzed within 2 months. Figure 4 shows the DIC results from a complete first-year ice core (ice thickness 102 cm) as a function of bulk ice salinity. The DIC concentration (ranging from $148.5 \text{ } \mu\text{mol kg}^{-1}$ to $379.1 \text{ } \mu\text{mol kg}^{-1}$) is linear with respect to salinity at salinities from 1.74 to 4.70 with an $R^2 = 0.997$, suggesting that the sea ice DIC concentration is primarily controlled by physical processes (i.e., brine drainage). The nonzero intercept of the DIC-salinity relationship (i.e., $\text{DIC} = 12.9 \text{ } \mu\text{mol kg}^{-1}$ at $S = 0$) is likely due to the dissolution of atmospheric CO_2 in seawater from where sea ice forms, as well as the impact of riverine inputs with high DIC concentration (Friis et al. 2003). The modified method is simple and fast to operate, allowing collection of a large number of sea ice DIC samples in the field under extreme conditions. Such a large dataset of DIC, together with the mass of ice segments, would allow us to readily calculate the carbon stock in ice cores and estimate the amount of carbon being exported to the underlying seawater during ice formation as well as the air-sea CO_2 flux when sea ice melts (Rysgaard et al. 2011).

Comments and recommendations

We assessed the sea ice processing method for DIC analysis and proposed a modified method. In general, DIC of the bulk sea ice can be processed with the existing method. However, the modified method is faster and easier to handle compared to the previous one; it can be used conveniently in the field to ensure that the ice samples for DIC analysis can be processed immediately after the ice core is retrieved. In the field practical tested in this study, the vacuum sealer was powered by a generator, but it is possible to use a battery-based vacuum sealer. We need to mention that if the ambient air temperature is too low, the vacuum sealer needs to be warmed up before use and it is necessary to press “vacuum & seal” button twice to ensure that the bag is well sealed. When processing warm or wet ice cores, there is a risk that the brine might get lost during the evacuation process. In this case, it is possible to stop the evacuation manually by pressing the “seal only” button once the brine is about to leave the bag. If the ice samples are to be melted at room temperature rather than in the fridge, it is better to keep the samples cold for a while before bringing them to room temperature, making sure there is absolutely no leak in the bags. Thus, even if the bag is broken, it is still not too late to save the ice sample by changing to a new bag and evacuate/seal it again.

The vacuum sealer is inexpensive; it is light, easy to carry and operate. The plastic bags are sturdy, with different sizes available, which can meet different processing requirements for different length of ice samples. We believe this modified method will make it possible for high density (in space and in time) sampling and measurement of sea ice DIC under even the most extreme field conditions, which will improve our understanding of the exchange of CO₂ across the ocean-sea ice-atmosphere interface.

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Acknowledgments

We thank David Binne for his kind help during the SERF experiment. This work is a contribution to the ArcticNet Networks of Centres of Excellence and the Arctic Science Partnership (ASP) asp-net.org. We gratefully acknowledge the financial contributions of the Fundamental Research Funds of Shandong University, the Canada Excellence Research Chair (CERC; Rysgaard) and Canada Research Chair (CRC; Barber and Wang) programs. Support was also provided by the Natural Sciences and Engineering Research Council (NSERC; Wang) of Canada, the Canada Foundation for Innovation and the University of Manitoba.

Conflict of Interest

None declared.

Submitted 15 June 2017

Revised 03 November 2017

Accepted 16 November 2017

Associate editor: Mike DeGrandpre