

1 **Inorganic carbon dynamics of melt pond-covered first year sea ice in the**
2 **Canadian Arctic**

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13 **1. Abstract**

14 Melt pond formation is a common feature of spring and summer Arctic sea ice, but
15 the role and impact of sea ice melt and pond formation on both the direction and size
16 of CO₂ fluxes between air and sea is still unknown. Here we report on the CO₂-
17 carbonate chemistry of melting sea ice, melt ponds and the underlying seawater as
18 well as CO₂ fluxes at the surface of first year landfast sea ice in the Resolute Passage,
19 Nunavut, in June 2012.

20 Early in the melt season, the increase in ice temperature and the subsequent
21 decrease in bulk ice salinity promote a strong decrease of the total alkalinity (TA),
22 total dissolved inorganic carbon (TCO₂) and partial pressure of CO₂ (*p*CO₂) within
23 the bulk sea ice and the brine. As sea ice melt progresses, melt ponds form, mainly
24 from melted snow, leading to a low *in situ* melt pond *p*CO₂ (36 μ atm). The
25 percolation of this low salinity and low *p*CO₂ melt water into the sea ice matrix
26 decreased the brine salinity, TA, and TCO₂ and lowered the *in situ* brine *p*CO₂ (to 20
27 μ atm). This initial low *in situ* *p*CO₂ observed in brine and melt ponds results in air-ice
28 CO₂ fluxes ranging between -0.04 and -5.4 mmol m⁻² d⁻¹ (negative sign for fluxes
29 from the atmosphere into the ocean). As melt ponds strive to reach *p*CO₂ equilibrium
30 with the atmosphere, their *in situ* *p*CO₂ increases (up to 380 μ atm) with time and the
31 percolation of this relatively high concentration *p*CO₂ melt water increases the *in situ*
32 brine *p*CO₂ within the sea ice matrix as the melt season progresses. As the melt pond
33 *p*CO₂ increases, the uptake of atmospheric CO₂ becomes less significant. However,
34 since melt ponds are continuously supplied by melt water their *in situ* *p*CO₂ remains
35 under-saturated with respect to the atmosphere, promoting a continuous but
36 moderate uptake of CO₂ (\sim -1 mmol m⁻² d⁻¹) into the ocean. Considering the Arctic
37 seasonal sea ice extent during the melt period (90 days), we estimate an uptake of
38 atmospheric CO₂ of -10.4 Tg of C yr⁻¹. This represents an additional uptake of CO₂
39 associated to Arctic sea ice that needs to be further explored and considered in the
40 estimation of the Arctic Ocean's overall CO₂ budget.

42

2. Introduction

43

The Arctic Ocean represents a globally important CO₂ sink, with current estimates of net air to sea CO₂ fluxes between -66 and -199 Tg C yr⁻¹ [Bates and Mathis, 2009; Takahashi *et al.*, 2009]. The role of sea ice in these measured air-sea CO₂ exchanges still remains uncertain [Parmentier *et al.*, 2013] although recent studies suggest that sea ice may act as an important control on the *p*CO₂ in the ocean surface layer (*e.g.* Rysgaard *et al.*, [2012b; 2013]). In particular, our understanding of inorganic carbon dynamics during the sea ice melt season and the importance to the annual exchange of CO₂ across the atmosphere-sea ice-ocean interfaces is incomplete. Early studies have invoked melt ponds as significant contributors to the Arctic CO₂ balance through their uptake of CO₂ [Semiletov *et al.*, 2004]. However, their impact on inorganic carbon transport through sea ice remains largely uncharacterized, despite the fact that they are a major and increasing surface feature of Arctic sea ice during spring and summer [Rösel and Kaleschke, 2012].

56

Melt ponds cover up to 50-60% of the Arctic summer sea ice area [Fetterer and Untersteiner, 1998; Eicken *et al.*, 2004]. They result from the accumulation of meltwater on sea ice mainly due to melting of snow. Sea ice melt also contributes to the melt pond formation and growth in advanced stages of melt [Rösel and Kaleschke, 2012], driven by increased short-wave absorption during summer [Taylor and Feltham, 2004]. During melt pond formation, meltwater either drains into the ocean through cracks and other openings in the sea ice or is collected on the ice surface in depressed areas. This meltwater is nearly free of salt and has a density maximum above the freezing point, resulting in radiative heating favouring convection [Fetterer and Untersteiner, 1998]. Convection may be further assisted by winds, increasing temperature erosion of the pond edge and eventually extending the pond area. As sea ice warms during spring its brine volume increases and meltwater ponds located above the freeboard may drain by vertical seepage to the underlying water (brine flushing - *e.g.* Fetterer and Untersteiner [1998]), thereby freshening the upper layer of the ocean. This mechanism is believed to be the primary cause for sea ice desalinisation [Untersteiner, 1968; Cox and Weeks, 1974]. The input of freshwater

72 to the surface layer of the ocean can lead to the formation of under-ice melt ponds,
73 freshwater lenses trapped under thinner ice areas or in depressions in the bottom of
74 thicker ice [Hanson, 1965; Weeks, 2010]. The discharge of melt water through the ice
75 cover is proportional to the ice permeability and the hydraulic pressure gradient in
76 the brine system (Darcy's law). In summer Arctic sea ice, this gradient is mostly
77 determined by differences in hydraulic head that develop as a result of melt over a
78 non-uniform ice surface [Eicken *et al.*, 2002].

79 Melt pond formation has a strong impact on the summer energy and mass budgets of
80 an ice cover through the sea ice-albedo-feedback mechanism [Fetterer and
81 Untersteiner, 1998; Taylor and Feltham, 2004; Perovich *et al.*, 2011]. Melt ponds also
82 alter the physical and optical properties of sea ice [Perovich *et al.*, 2002], have a
83 strong influence of the temporal evolution of sea ice salinity [Untersteiner, 1968; Cox
84 and Weeks, 1974] and affect the salt and heat budget of the ocean mixed layer
85 [Eicken *et al.*, 2002; Perovich *et al.*, 2002]. Although a few studies report surface flux
86 measurements of CO₂ during active surface melt [Semiletov *et al.*, 2004; Geilfus *et al.*,
87 2012b; Nomura *et al.*, 2013], the role of surface melt ponds and the impact of sea ice
88 melt on both the direction and amount of air-sea CO₂ flux is still not well understood.

89 *Semiletov et al.* [2004] documented CO₂ fluxes of -3.9 to -51 mmol m⁻² d⁻¹ (negative
90 flux indicating sea ice uptake of CO₂) across the sea ice-atmosphere interface over
91 melt ponds in June, near to Barrow, Alaska using the chamber method. At that time
92 brine *pCO₂* was under-saturated (from 220 to 280 μatm) with respect to the
93 atmosphere (365 – 375 μatm). This under-saturation was attributed to an increase
94 of photosynthetically active radiation (PAR), which was suggested to have reduced
95 the *pCO₂* in the brine by enhancing photosynthesis [Semiletov *et al.*, 2004]. In June
96 2008, *Geilfus et al.* [2012b] reported CO₂ fluxes over melt ponds and sea ice ranging
97 from -0.02 to -2.7 mmol m⁻² d⁻¹ using the chamber technique over first year sea ice in
98 the Beaufort Sea. These fluxes were substantially smaller than those reported by
99 *Semiletov et al.* [2004], but in the same order of magnitude as those reported during
100 period of melt and surface flooding on Antarctic and Arctic sea ice by *Nomura et al.*
101 [2013]. In the *Geilfus et al.* [2012b] study, sea ice brine and overlying melt ponds

were highly under-saturated in CO₂ relative to atmospheric levels ($p\text{CO}_2$ between 0 and 188 μatm for brine and between 79 and 348 μatm for melt ponds) in 1.2 m-thick landfast sea ice in Amundsen Gulf. At that time, melt ponds were well established and interconnected. It's likely that fresh water originating from internal and surface melting was an important driver of the observed under-saturation in combination with the dissolution of calcium carbonate and primary production. Using micrometeorological techniques, *Papakyriakou and Miller* [2011] also reported CO₂ uptake with the progression of melt over Arctic sea ice, although flux magnitudes are widely diverging from the chamber-based studies highlighted above.

In this study, we examine how melting snow and sea ice and the associated formation of melt ponds affects inorganic carbon dynamics therein and the air – ice CO₂ exchanges. The evolution of the carbonate system was examined using measurements of total alkalinity (TA) and total dissolved inorganic carbon (TCO₂) on melted bulk sea ice, as well as in brine and melt ponds samples. *In situ* $p\text{CO}_2$ was measured on bulk sea ice, brine and melt ponds in association with CO₂ flux measurements over sea ice and melt ponds. Percolation of melt water from melt ponds was tracked using the isotopic ratios δD and $\delta^{18}\text{O}$ within bulk sea ice and brine.

3. Study site, materials and methods

Field data were collected over first-year landfast sea ice in Resolute Passage, Nunavut, from 3 to 23 June 2012 [*Galley et al*, 2012]. The sampling site ($\sim 100 \times 100$ m) was located between Sheringham Point and Griffith Island (74.726°N, 95.576°W, Figure 1). At the site, adjacent 5 x 5 m areas were chosen for regular sampling for carbonate chemistry determination of ice cores and seawater (on 4-day intervals), while the carbonate chemistry of brine and the surface flux of CO₂ were sampled every 2 days. During our survey, the air temperature increased from 0.6 to 4.3°C (Figure 2). During our first ice station (4 June), coarse wet snow was found at the surface of the ice. On 10 June, the first melt ponds were observed (Figure 2). Once the melt ponds started to form, ice core and brine sampling were limited to areas without melt ponds, referred to as melt hummocks.

132 Brine was collected using the sackhole technique (*e.g. Gleitz et al. [1995]*). Sackholes
133 were drilled at incremental depths (20, 40, 75, 100 cm). Brine from adjacent brine
134 channels and pockets was allowed to seep into the sackholes for 5 to 10 min before
135 being collected using a peristaltic pump (Cole Palmer®, Masterflex – Environmental
136 Sampler). Each sackhole was covered with a plastic lid to prevent snow from falling
137 into the hole.

138 Sea ice core samples were collected using a MARK II coring system (Kovacs
139 Enterprises®). Two ice cores were immediately wrapped in polyethylene (PE) bags
140 and stored horizontally on the sampling site at -20°C in a portable freezer
141 (Whynter® FM-45G) to minimize brine drainage during transport. The first core was
142 dedicated to the analysis of TA and TCO₂. The second core was dedicated to partial
143 pressure of CO₂ in bulk ice (noted as *p*CO₂[bulk]) analysis. Two other cores were
144 collected for *in situ* sea ice temperature, bulk ice salinity and ikaite (CaCO₃•6H₂O)
145 content.

146 Seawater was collected at the ice-water interface through an ice core hole using the
147 peristaltic pump. The same pump was used to collected melt pond samples and an
148 articulated arm was used to collect under-ice melt pond samples. We also collected
149 water column samples at six depths (2, 5, 10, 25, 50, 80 m) using 5 L Niskin bottles
150 for determination of TA and TCO₂. Vertical profiles of water temperature and salinity
151 were measured with a newly calibrated Sea-Bird SBE 19plus V2 conductivity-
152 temperature-depth (CTD) probe.

153 The *p*CO₂ was measured *in situ* (noted as *p*CO₂[*in situ*]) in brine, melt pond water and
154 under-ice seawater using a custom-made equilibration system. The system consists
155 of a membrane contactor equilibrator connected to a non-dispersive infrared gas
156 analyzer (IRGA, Li-Cor 820) via a closed air loop. Brine and airflow rates through the
157 equilibrator and IRGA are approximately 2 l min⁻¹ and 3 l min⁻¹, respectively. The *in*
158 *situ* temperature was measured using a calibrated temperature probe (Testo 720®,
159 ±0.1°C precision) simultaneously at the inlet and outlet of the equilibrator.
160 Temperature correction of *p*CO₂ was applied assuming that the relation of *Copin*
161 *Montégut* [1988] is valid at low temperature and high salinity.

162 Sea ice temperature was measured *in situ* immediately after extraction of the ice
163 cores using a calibrated temperature probe (Testo 720®, $\pm 0.1^\circ\text{C}$ precision) inserted
164 into pre-drilled holes (2.5 cm intervals), perpendicular to core sides. Bulk sea ice
165 salinity and ikaite content was determined on a duplicate ice core sliced into 5 cm
166 sections directly after extraction and placed in sealed containers, which were then
167 placed in a lab fridge to melt at 4°C . These samples were checked regularly, so that
168 the melt water temperature never rose above $1\text{--}2^\circ\text{C}$. Once the samples melted,
169 crystals left in solution were observed on a chilled glass slide under a binocular
170 microscope at room temperature. Finally, the bulk salinity of these samples was
171 measured using a calibrated Thermo-Orion portable salinometer WP-84TPS meter
172 with a precision of ± 0.1 . The sea ice brine volume was calculated according to *Cox*
173 and *Weeks* [1983] for temperatures below -2°C , and according to *Leppäranta* and
174 *Manninen* [1988] between 0°C to -2°C .

175 Samples of melted bulk ice, brine, melt ponds, under-ice melt pond water and
176 underlying seawater were brought back to the University of Manitoba for TA and
177 TCO_2 analyses. Samples were poisoned with a solution of saturated HgCl_2 to prevent
178 any biological activity. The ice core was cut into 10 cm sections in a cold room (-20°C),
179 and each section was placed in a gas-tight laminated (Nylon, ethylene vinyl
180 alcohol, and polyethylene) plastic bag [Hansen *et al.*, 2000] fitted with a 20-cm gas
181 tight Tygon tube and valve. The plastic bag was sealed immediately and excess air
182 was gently removed through the valve using a vacuum pump. The bagged sea ice
183 samples were then melted in the fridge at 4°C and the meltwater mixture and
184 bubbles were transferred to a gas-tight vial (12 ml Exetainer, Labco High Wycombe,
185 UK). TA was determined by potentiometric titration [Haraldsson *et al.*, 1997] with a
186 precision of $\pm 3 \mu\text{mol kg}^{-1}$ while TCO_2 was determined on a TCO_2 auto-analyzer (AS-
187 C3, Apollo SciTech) via sample acidification (H_3PO_4) followed by non-dispersive
188 infrared CO_2 detection (LI-7000) with a precision of $\pm 2 \mu\text{mol kg}^{-1}$. Both TA and TCO_2
189 were calibrated with certified reference material from Dr. A. G. Dickson at the
190 Scripps Institution of Oceanography.

191 The ice cores taken for bulk ice $p\text{CO}_2$ analysis were cut into 10 cm sections and
192 stored at -20°C then shipped frozen so that the bulk ice $p\text{CO}_2$ ($p\text{CO}_2[\text{bulk}]$) could be
193 measured at the Laboratoire de Glaciologie, Université Libre de Bruxelles, using the
194 technique developed by *Geilfus et al.* [2012a]. The general principle of the method is
195 to equilibrate the sea ice samples with a mixture of N_2 and CO_2 of known
196 concentration (referred to as the “standard gas”, 146 μatm) at the *in situ*
197 temperature and rapidly extract the gases into a Varian 3300 gas chromatograph
198 under vacuum. The ice sample is cut to tightly fit the container (4 x 4 x 4.5 cm) to
199 both minimize the headspace volume and keep this headspace constant. The
200 standard gas is injected at 1013 mbar into the container. Then the container with the
201 ice sample is placed in a thermostatic bath at the *in situ* temperature for 24 hours.
202 This timing is chosen to ensure that the sample is re-equilibrated to the brine
203 volume and chemical conditions at the *in situ* temperature. A quick injection into the
204 gas chromatograph then allows the reconstruction of the equilibrium brine $p\text{CO}_2$ at
205 the *in situ* temperature. This method is only valid if the ice is permeable at the *in situ*
206 conditions.

207 Due to differences in the isotopic composition of snowmelt, seawater and sea ice
208 (sea ice is highly depleted in ^{18}O and D), the infiltration of meteoric water can be
209 traced through the sea ice system based on stable isotope measurements [*Eicken et*
210 *al.*, 2002]. Therefore, we determined δD and $\delta^{18}\text{O}$ in 2 ml aliquots of sea ice, brine,
211 under-ice seawater, melt ponds and under-ice melt ponds. Stable isotope
212 measurements were carried out at the University of Manitoba using a Picarro L2130-
213 *i* analyzer. Samples were calibrated against Vienna Standard Mean Ocean Water
214 (VSMOW) with a precision of 0.1‰ for δD and 0.025‰ for $\delta^{18}\text{O}$.

215 CO_2 fluxes at the sea ice surface were measured using a Li-Cor 8100-103 chamber
216 associated with the LI-8100A soil CO_2 flux system. The chamber was connected in a
217 closed loop to the IRGA with an air pump rate at 3 L min^{-1} . $p\text{CO}_2$ in the chamber was
218 recorded every second for 15 minutes and the flux was computed from the slope of
219 the linear regression of $p\text{CO}_2$ against time ($r^2 > 0.99$) according to *Frankignoulle*
220 [1988], taking into account the air volume enclosed within the chamber. The

221 uncertainty of the flux computation due to the standard error on the regression
222 slope was $\pm 3\%$ on average.

223 4. Results

224 a. Sea ice

225 The average ice thickness at the sampling site, as determined from cores, decreased
226 from 130 (± 5) to 105 (± 5) cm over the sampling campaign. Over the course of our
227 study period, the vertical temperature gradient within sea ice decreased, leading to a
228 nearly isothermal ice cover by 21 June. The mean ice temperature increased from -
229 2.9°C on 4 June to -1.5°C on 12 June (Figure 3). From 10 June, the temperature of the
230 top 20 cm of the ice was slightly negative (-0.5°C to 0°C) while the rest of the ice
231 thickness remained around -1.5°C . The anomalous high values reported in the mid
232 section of the core on June 12 are probably due to warming of the ice during the
233 temperature measurement in the field, as a result of positive air temperature at the
234 time of measurement. Bulk ice salinity ranged from 7.5 to 0 (Figure 3). The bulk ice
235 salinity of the upper 15 cm decreased from 5.2 on 4 June to 0.1 on 9 June, then
236 increased to 2.7 on 21 June. The central section of the ice cover (0.2 to 1m depth)
237 decreased from 7.5 to 4 during the survey. The bulk ice salinity at the sea ice
238 interface with the water column decreased from 7.4 on 4 June to 2.7 on 21 June. The
239 salinities associated with the high sea ice temperatures result in brine volumes
240 greater than 5% (data not shown).

241 The $\delta^{18}\text{O}$ and δD isotopic ratios ranged from 1.9 to $-23.9\text{\textperthousand}$ and 2.5 to $-191.2\text{\textperthousand}$,
242 respectively (Figure 3). Profiles of $\delta^{18}\text{O}$ and δD appear to follow the same trend with
243 the lowest values observed in the top 20 cm of the ice cover. Two low events were
244 reported in the upper 20 cm of the ice cover. The first was from 8 to 12 June with
245 isotopic ratios of $\delta^{18}\text{O}$ and δD as low as -23.9 and $-191.2\text{\textperthousand}$, respectively. The second
246 was on 17 June with $\delta^{18}\text{O}$ and δD of -15.4 and $-133.7\text{\textperthousand}$ respectively. The rest of the
247 ice cover ranged from -2 to $1.9\text{\textperthousand}$ for $\delta^{18}\text{O}$ and from -7 to $2.5\text{\textperthousand}$ for δD .

248 The mean total alkalinity in melted bulk sea ice (TA_{ice}) for the entire ice column
249 gradually decreased from $408 \text{ }\mu\text{mol kg}^{-1}$ on 4 June to $283 \text{ }\mu\text{mol kg}^{-1}$ on 21 June

(Figure 3). This decrease of TA_{ice} was more pronounced in the top 20 cm of the ice cover where the minimum value ($106 \mu\text{mol kg}^{-1}$) was observed on 17 June. The same trend was observed for the total inorganic carbon (TCO_{2ice} , Figure 3). The mean TCO_{2ice} of the entire ice column decreased from $332 \mu\text{mol kg}^{-1}$ on 4 June to $225 \mu\text{mol kg}^{-1}$ on 21 June. The minimum values were observed on 17 June, with a mean concentration of $189 \mu\text{mol kg}^{-1}$. To discard concentration – dilution effects, we normalized TA_{ice} and TCO_{2ice} to the mean bulk salinity of our sea ice samples (salinity = 5, noted as nTA_{ice} , $nTCO_{2ice}$, respectively). The main change observed in normalized values occurred in the top 20 cm. From 4 to 17 June, nTA_{ice} and $nTCO_{2ice}$ increased from 468 and $345 \mu\text{mol kg}^{-1}$ to 1762 and $1041 \mu\text{mol kg}^{-1}$ while the rest of the ice cover ranged from 337 to $564 \mu\text{mol kg}^{-1}$ and from 219 to $461 \mu\text{mol kg}^{-1}$, respectively. On 19 and 21 June, in the top 20 cm, nTA_{ice} and $nTCO_{2ice}$ decreased to 376 and $323 \mu\text{mol kg}^{-1}$.

From TA_{ice} and TCO_{2ice} , we computed a bulk ice $p\text{CO}_2$ (noted as $p\text{CO}_2[\text{bulk_calc}]$) using the CO_2 dissociation constants of *Mehrbach et al.* [1973] refitted by *Dickson and Millero* [1987] and correcting the $p\text{CO}_2$ for temperature using the relation of *Copin Montégut* [1988]. This $p\text{CO}_2[\text{bulk_calc}]$ ranged from 0 to $32 \mu\text{atm}$ (Figure 4). On a duplicate ice core, the $p\text{CO}_2[\text{bulk}]$ was also measured on solid ice at the *in situ* temperature, using the sample equilibration technique developed by *Geilfus et al.* [2012a]. The $p\text{CO}_2[\text{bulk}]$ ranged from 6 to $182 \mu\text{atm}$ (Figure 4).

We observed few minerals in the ice, which dissolved within a few minutes at room temperature. Due to technical problems we were unable to take any pictures of the crystals. However, as the overall aspect of these crystals was the same as the crystals found in *Geilfus et al.* [2013a]; [2013b] and *Rysgaard et al.* [2014] and because they dissolved quickly at room temperature, we assumed they were ikaite (after *Rysgaard et al.* [2012b; 2013; 2014]).

b. Brine

From 4 to 10 June, the brine salinity decreased from 55 to 23 (Figure 5). Starting on 10 June, low brine salinities (ranging from 1.6 to 11.8) were found at 20 cm depth

279 while deeper brine salinities ranged from 11 to 30, except on 17 June where low
280 salinity were also found at 40 cm depth. The $\delta^{18}\text{O}$ and δD isotopic ratios ranged from
281 -1.5 to -15.2‰ and from -15.5 to -118.2‰, respectively (Figure 5). Both profiles
282 appear to be similar, with the lowest values observed at 20 cm depth on 10 June (-
283 15.2‰ and -118.1‰, respectively) and at 20 and 40 cm depth on 17 June (-10.4‰
284 and -87.5‰, respectively).

285 From 4 to 21 June, TA_{br} and $\text{TCO}_{2\text{br}}$ decreased from their maximum values of 3487
286 and 3189 $\mu\text{mol kg}^{-1}$, to 234 and 270 $\mu\text{mol kg}^{-1}$, respectively (Figure 5). Two periods
287 of low concentrations were observed during our survey. On 10 June, TA_{br} and $\text{TCO}_{2\text{br}}$
288 minimums of 501 and 401 $\mu\text{mol kg}^{-1}$ respectively occurred at 20 cm. On 17 June, TA_{br}
289 and $\text{TCO}_{2\text{br}}$ were 240 and 275 $\mu\text{mol kg}^{-1}$ respectively at 20 and 40 cm. These two
290 minima in TA_{br} and $\text{TCO}_{2\text{br}}$ coincided with maximums in $n\text{TA}_{\text{br}}$ and $n\text{TCO}_{2\text{br}}$. On 10
291 June, $n\text{TA}_{\text{br}}$ and $n\text{TCO}_{2\text{br}}$ were 596 and 478 $\mu\text{mol kg}^{-1}$, and on 17 June, $n\text{TA}_{\text{br}}$ and
292 $n\text{TCO}_{2\text{br}}$ were 874 and 900 $\mu\text{mol kg}^{-1}$.

293 The brine $p\text{CO}_2$ [*in situ*] was under-saturated with respect to the atmosphere (395
294 μatm in June 2012) with values ranging from 20 μatm to 389 μatm (Figure 4, 5).
295 From 4 to 12 June, the mean brine $p\text{CO}_2$ [*in situ*] decreased from 344 to 70 μatm .
296 Then, it increased to 246 μatm on 17 June before decreasing to 81 μatm on 21 June.

297 c. Melt ponds

298 On 10 June, melt ponds started to form and were present during the rest of the
299 survey. The melt pond salinity increased from 1.5 to 2.4 during the survey with
300 temperatures ranging from 0°C to 0.4°C. The $\delta^{18}\text{O}$ and δD isotopic ratios ranged from
301 -3.8 to -10.1‰ and from -40.6 to -93.4‰ with the minimum values observed on 12
302 June and the maximum values on 21 June (Figure 5).

303 TA_{mp} and $\text{TCO}_{2\text{mp}}$ ranged from 219 to 332 $\mu\text{mol kg}^{-1}$ and from 206 to 306 $\mu\text{mol kg}^{-1}$,
304 respectively. $n\text{TA}$ and $n\text{TCO}_2$ in the melt ponds ranged from 489 to 972 $\mu\text{mol kg}^{-1}$ and
305 562 to 918 $\mu\text{mol kg}^{-1}$, respectively (Figure 5).

306 Melt pond water was also under-saturated with respect to the atmosphere with a
307 $p\text{CO}_2$ [*in situ*] ranging from 36 to 381 μatm . During the initial formation of melt

308 ponds, their $p\text{CO}_2$ [*in situ*] was low (36 – 84 μatm) but increased to 381 μatm on 17
309 June before fluctuating between 150 and 370 μatm (Figure 5).

310 **d. Underlying seawater**

311 During the survey, the temperature of the seawater layer immediately underlying
312 the sea ice increased from -1.7°C to -1.4°C. The salinity of this layer decreased
313 gradually from 33.2 to 31.4 while the salinity of the water column below 10 m
314 changed much less (Figure 6).

315 The $\delta^{18}\text{O}$ and δD isotopic ratio of the surface layer decreased gradually from their
316 respective maximums of -1.3 and -17.3‰ to -2.2 and -19.5‰ on 20 June. Deeper
317 layers of the water column ranged from -1.5 and -14.9‰ to -1.9 and -18.9‰,
318 respectively (Figure 6).

319 TA_{sw} and $\text{TCO}_{2\text{sw}}$ ranged from 2021 and 1920 $\mu\text{mol kg}^{-1}$ to 2239 and 2167 $\mu\text{mol kg}^{-1}$,
320 respectively. On 20 June, a strong decrease in TA_{sw} and $\text{TCO}_{2\text{sw}}$ was observed, leading
321 to the observed minimum values at the surface of the water column. The normalized
322 TA_{sw} and $\text{TCO}_{2\text{sw}}$ ($n\text{TA}_{\text{sw}}$ and $n\text{TCO}_{2\text{sw}}$ to salinity 5) are shown (Figure 6) to allow
323 direct comparison with the sea ice and brine data) ranged from 319 to 350 $\mu\text{mol kg}^{-1}$
324 and 303 to 333 $\mu\text{mol kg}^{-1}$, respectively.

325 The $p\text{CO}_2$ [*in situ*] of the water column ranged from 259 to 469 μatm . The top 2 m of
326 the seawater column was mainly under-saturated with respect to the atmosphere,
327 except on 7 June where the $p\text{CO}_2$ [*in situ*] was at 455 μatm . From there, the $p\text{CO}_2$ [*in*
328 *situ*] decreased to 269 μatm on 23 June (Figure 6).

329 **e. Air – ice CO_2 fluxes**

330 CO_2 fluxes were systematically measured over sea ice and melt ponds (Figure 7)
331 throughout the campaign. Initially, CO_2 fluxes over sea ice were on average at -1.38
332 $\text{mmol m}^{-2} \text{ d}^{-1}$. During the initial formation of melt ponds, the fluxes over sea ice
333 peaked at -5.4 $\text{mmol m}^{-2} \text{ d}^{-1}$ on 10 June and -2 $\text{mmol m}^{-2} \text{ d}^{-1}$ on 12 June. Over melt
334 ponds, the initial uptake of CO_2 was significant at -2.9 $\text{mmol m}^{-2} \text{ d}^{-1}$ on 10 June and -

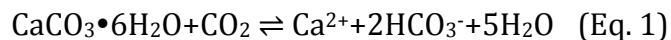
335 4.8 mmol m⁻² d⁻¹ on 12 June. Thereafter the uptake of CO₂ by sea ice and melt ponds
336 decreased over time and stabilized at around -1 mmol m⁻² d⁻¹.

337 5. Discussion

338 Seasonally rising sea ice temperature was associated with decreasing bulk ice
339 salinity, until ultimately values approached 0 at the surface of the ice cover (Figure
340 3). The percolation of snowmelt through the ice cover and its refreezing into the ice
341 matrix formed interposed ice [Landy *et al.*, 2014]. The formation of interposed ice as
342 described by Freitag and Eicken [2003] and Polashenski *et al.* [2012] could explain
343 the low salinity and low values of $\delta^{18}\text{O}$ (down to -23.9‰) and δD (down to -
344 191.2‰) observed in the upper 20 cm of the ice cover. These values are much lower
345 than typical bulk sea ice values ($\delta^{18}\text{O}$ from -0.69 to 1.92‰ and δD from -24.1 to
346 2.53‰, Figure 3).

347 Within the brine system, the low isotopic composition observed at 20 cm depth on
348 10 June (-15.2‰ and -118.1‰, respectively, after melt pond formation) and at 20
349 and 40 cm depth on 17 June (-10.4‰ and -87.5‰, respectively) can be explained by
350 the percolation of melt pond water (-10.1‰ and -93.4‰, respectively) into the
351 underlying sea ice cover (Figure 5). The combination of negative isotopic ratios with
352 low salinities and warm ice temperatures ($\sim 0^\circ\text{C}$) collectively suggest that meltwater
353 percolated into the ice cover, at least to a depth of 40 cm.

354 Previous work has shown brine $p\text{CO}_2$ to change dramatically over the period
355 between sea ice formation and melting [Nomura *et al.*, 2010a; Geilfus *et al.*, 2012b].
356 Increased ice temperatures decrease brine concentration and brine $p\text{CO}_2$. Brine
357 dilution will also promote the dissolution of ikaite that may have precipitated in the
358 sea ice, further decreasing the $p\text{CO}_2$ following the reaction:



360 There are several reports of ikaite precipitation in Arctic sea ice [Dieckmann *et al.*,
361 2010; Rysgaard *et al.*, 2012a; Geilfus *et al.*, 2013a; 2013b; Rysgaard *et al.*, 2013;
362 Søgaard *et al.*, 2013]. In this study, however, only a few crystals were observed and
363 they dissolved within minutes after melting the sea ice. The overall morphology of

364 these crystals are easily recognized as ikaite due to their similarity to crystals
365 identified as ikaite by x-ray diffraction during other campaigns (*after [Geilfus et al.,*
366 *2013a; 2013b; Rysgaard et al., 2013; 2014]*). It is not surprising that only small
367 amounts of ikaite crystals were observed in the ice samples as the combination of
368 elevated temperature and brine dilution associated with melting would support the
369 dissolution of ikaite [*Rysgaard et al., 2012a*]. *Rysgaard et al.* [2014] linked the
370 amount of ikaite content in the ice to the ice temperature, suggesting that as the ice
371 warms up/cools down, ikaite crystals will dissolve/precipitate.

372 The concentrations of TA and TCO_2 reported in melted bulk sea ice, brine and melt
373 ponds in this study are in the same range as those reported from previous studies in
374 the Canadian Archipelago [*Rysgaard et al., 2007; Miller et al., 2011; Geilfus et al.,*
375 *2012b; 2013a*]. Increased temperatures and decreased salinity promote the overall
376 decrease in TA_{ice} and TCO_{2ice} concentrations (Figure 3). The relatively constant
377 nTA_{ice} and $nTCO_{2ice}$ values suggest that the dilution effect dominated. However, the
378 reduction in TA_{ice} and TCO_{2ice} in the top 20 cm of the ice cover was more pronounced
379 after the onset of melt pond formation and the formation of interposed ice. These
380 low TA_{ice} and TCO_{2ice} concentrations are associated with a significant increase of
381 nTA_{ice} and $nTCO_{2ice}$.

382 Decreased brine salinity in response to seasonal warming promoted a decrease in
383 TA_{br} and TCO_{2br} [*Geilfus et al., 2012b*]. Minima in TA_{br} and TCO_{2br} were associated
384 with minimum isotopic ratios of $\delta^{18}O$ and δD , hence we attribute the reduction in
385 carbonate species largely to the percolation of fresh melt water from surface melt
386 ponds into the upper portion of the sea ice volume (Figure 5). nTA_{br} and $nTCO_{2br}$
387 remained relatively constant, until the period of melt water percolation, which
388 corresponded to a significant increase in both nTA_{br} and $nTCO_{2br}$.

389 Melt pond formation and the subsequent percolation of melt water into the ice cover
390 affects TA_{br} and TCO_{2br} and also appear to affect the *in situ* brine pCO_2 (Figure 5).
391 From 4 to 10 June, the decrease of the brine pCO_2 [*in situ*] is mainly due to the
392 concurrent decrease in brine salinity associated with rising ice temperatures and the
393 dissolution of ikaite. As melt ponds begin to form, their initial pCO_2 is much lower

(36 – 84 μatm) than the atmosphere (395 μatm). The percolation of low $p\text{CO}_2$ melt pond water into the ice matrix resulted in a strong decrease in the brine $p\text{CO}_2$ [*in situ*] observed at 20 cm depth on 9 and 10 June. However, over time, the melt pond $p\text{CO}_2$ [*in situ*] increased as it continued to equilibrate with the atmosphere (Figure 5). The subsequent percolation of this higher $p\text{CO}_2$ melt water into the ice matrix resulted in an increase in brine $p\text{CO}_2$ within the sea ice observed on 17 June. The melt pond $p\text{CO}_2$ [*in situ*] decreased slightly (150 μatm on 19 June) as did the brine $p\text{CO}_2$ (to <100 μatm) as a result of melt water being added to the pond. By 21 June, the $p\text{CO}_2$ in the melt pond had increased as a result of atmospheric CO_2 uptake.

The sea ice $p\text{CO}_2$ [bulk] measured on solid ice samples (Figure 4) are in the same range as those reported by *Geilfus et al.* [2012a] on landfast sea ice sampled during the same season in Barrow, Alaska. The ice characteristics in the Barrow study were similar to this Resolute Bay survey; a nearly isothermal ice cover (approaching 0°C), low salinity in the sea ice surface layer (0-20 cm) and melt ponds at the surface of the ice [Zhou *et al.*, 2013]. *Crabeck et al.* [2014] also reported sea ice $p\text{CO}_2$ [bulk] from SW Greenland. However, the concentrations reported in this work are on the lower end compared with the concentrations of 77-330 μatm reported by *Crabeck et al.* [2014] due in part to warmer sea ice leading to a lower $p\text{CO}_2$ due to brine dilution by fresh melt water (Figure 5) and/or dissolution of ikaite. These concentrations can be compared with the sea ice $p\text{CO}_2$ [bulk_calc] (Figure 4). However, the sea ice $p\text{CO}_2$ [bulk_calc] values rely on the validity of four equilibrium constants of the aqueous carbonate system. The thermodynamic constants are assumed to be valid at subzero temperatures, but this assumption needs to be tested. Moreover, the sea ice $p\text{CO}_2$ [bulk_calc], which is derived from TA and TCO_2 analyses, is not representative of the *in situ* concentration because the ice sample must be melted. Moreover, melting samples will dissolve ikaite crystals that may have formed, which will strongly impact both the TA and the TCO_2 of the resulting meltwater. On the contrary, the sea ice $p\text{CO}_2$ [bulk] measured the CO_2 concentration at the *in situ* temperature, therefore takes into account the CO_2 dissolved within the brine as well as the gaseous CO_2 (bubbles) in the ice sample. The average $p\text{CO}_2$ [bulk_calc] is in the

lower end of the $p\text{CO}_2[\text{bulk}]$ range. However, both sea ice $p\text{CO}_2[\text{bulk_calc}]$ and $p\text{CO}_2[\text{bulk}]$ show an over-all drop in $p\text{CO}_2$ associated with brine dilution and the dissolution of ikaite. While the ice $p\text{CO}_2[\text{bulk_calc}]$ only shows a slight decrease over time, the ice $p\text{CO}_2[\text{bulk}]$ reveals that larger changes may occur, especially in the upper 20 cm of the ice cover (Figure 4). The ice $p\text{CO}_2[\text{bulk}]$ and brine $p\text{CO}_2[\text{in situ}]$ differ in that a significant decrease in the brine $p\text{CO}_2[\text{in situ}]$ was observed on 12 June just after melt pond formation, whereas only a slight decrease was observed in the ice $p\text{CO}_2[\text{bulk}]$ at that point. The percolation of melt water with low *in situ* $p\text{CO}_2$ initiated a decrease in the brine $p\text{CO}_2[\text{in situ}]$ to similar concentrations as in the melt ponds. Other examples are observed on 17 June, then again on 19 and 21 June. On 17 June, high *in situ* $p\text{CO}_2$ melt water percolation through the ice matrix was associated with an increase in brine $p\text{CO}_2[\text{in situ}]$ whereas the ice $p\text{CO}_2[\text{bulk}]$ remained constant. On 19 and 21 June, the brine $p\text{CO}_2[\text{in situ}]$ decreased to the ice $p\text{CO}_2[\text{bulk}]$ value. Therefore, changes in sea ice $p\text{CO}_2[\text{bulk}]$ are less variable than brine $p\text{CO}_2[\text{in situ}]$, reflecting mostly internal melting due to temperature and resultant salinity changes in the ice cover. Brine $p\text{CO}_2[\text{in situ}]$ highlight rapid changes in the brine network such as infiltration of melt water from melt ponds [Geilfus *et al.*, 2014].

To evaluate if the sackhole technique yielded uncontaminated brine, we compared TA_{br} and $\text{TCO}_{2\text{br}}$ with TA and TCO_2 estimated from TA_{ice} and $\text{TCO}_{2\text{ice}}$ and the calculated brine volume (Figure 8) [Cox and Weeks, 1983; Leppäranta and Manninen, 1988]. Both methods yield similar TA and TCO_2 concentrations (from 274 to 3554 $\mu\text{mol kg}^{-1}$ and from 283 to 3189 $\mu\text{mol kg}^{-1}$, respectively), with a similar relationship between TA and TCO_2 with a R^2 's of 0.84 and 0.85, respectively. The scatter between the two methods could be due to the impossibility of determining the exact original depth from which the brine seeped, especially if melt ponds are present at the surface of the ice cover.

As melt ponds developed, freshwater percolation through the ice matrix may form a freshwater layer beneath the sea ice [Hanson, 1965] though an accumulation of under-ice melt water was not observed during our survey. Perhaps this is because the stage of ice melt was not sufficiently advanced and/or under-ice currents

454 effectively mixed the freshwater layer beneath the ice. The only noticeable impact of
455 the percolation of melt pond water on the underlying seawater was observed on 20
456 June where the decrease of TA_{sw} and TCO_{2sw} was associated with the low isotopic
457 ratio of $\delta^{18}O$ and δD captured over a very short period (Figure 6).

458 As in previous studies, the relationships between nTA and $nTCO_2$ in seawater, brine
459 and sea ice may determine the main processes affecting the carbonate system. In
460 Figure 9, the dotted lines represent the response of inorganic carbon and alkalinity
461 to different processes (after Zeebe and Wolf-Gladrow [2001]). An exchange of $CO_{2(gas)}$
462 will affect TCO_2 while TA will remain constant. The precipitation – dissolution of
463 ikaite will affect TA and TCO_2 in a ratio of 2:1. Biological activity will increase TA
464 slightly and reduce TCO_2 slightly in the ratio $TA:TCO_2 = -0.16$ [Lazar and Loya, 1991].
465 To calculate these theoretical effects we assumed that seawater sampled at 50 m (on
466 average: $T = -1.62^\circ C$; $S = 32.43$; $TA = 2229 \mu mol kg^{-1}$ and $TCO_2 = 2135 \mu mol kg^{-1}$,
467 Figure 6), was not influenced by the overlying melting sea ice. Sea ice nTA and $nTCO_2$
468 data fall along the ikaite dissolution line while brine and melt pond samples fall
469 between the ikaite dissolution line and the CO_2 uptake line, suggesting both
470 processes occurred in combination (Figure 9). We posit that ikaite crystals formed in
471 winter were dissolved during spring, thereby lowering pCO_2 and enhancing CO_2
472 uptake. The dissolution of the ikaite crystals increased nTA and $nTCO_2$ (in a ratio 2:1)
473 in the upper brine layer and melt ponds while the uptake of CO_2 only increased
474 $nTCO_2$. This explains the high nTA and $nTCO_2$ in Figure 5. This theory is lent further
475 credibility by ikaite crystals observed in the sea ice. The mean concentration of algal
476 biomass ($Chl\ a$) in bulk sea ice decreased from decreased from $23.2 \mu g L^{-1}$ in 4 June
477 to $1.1 \mu g L^{-1}$ on 12 June and $Chl\ a$ concentration in melt ponds ranged from 0.1 to 0.4
478 $\mu g L^{-1}$ (unpublished data, C. Mundy and V. Galindo). The loss of biomass could result
479 from the warming and melting of the ice [Zeebe *et al.*, 1996; Galindo *et al.*, 2014].
480 These concentrations are in the same range as those reported by Mundy *et al.* [2011]
481 and Geilfus *et al.* [2012b] on melting landfast sea ice in the Beaufort Sea. From the
482 brine profiles in Figure 5 and from the trend of the sea ice samples in Figure 9, we
483 surmise that brine dilution and calcium carbonate dissolution are the main factors

484 controlling CO₂ exchange during our observation period. However, most of the
485 calcium carbonate dissolution trend holds in 4-5 samples located in the top 20 cm of
486 the sea ice cover. When *n*TA and *n*TCO₂ are less than 500 μmol kg⁻¹ (80% of the sea
487 ice cover including the bottom Chl *a* rich 10 cm layer), the ice samples pull the trend
488 to the left of the calcium carbonate dissolution line, suggesting an increasing
489 influence of algal CO₂ uptake, strong enough to maintain the bottom ice and brine
490 *p*CO₂ at low values close to the nearly saturated water values at the ice-water
491 interface. This biological effect on TCO₂ is probably limited to the very bottom
492 decaying section of the sea ice cover [Søgaard *et al.*, 2013; Glud *et al.*, 2014]. This is
493 similar to what has been described in the Beaufort Sea (Arctic, Geilfus *et al.* [2012b])
494 and in the Weddell Sea (Antarctica, Papadimitriou *et al.* [2012]) on landfast sea ice,
495 although during early spring, i.e. at ice temperatures colder than those observed
496 during the present study. Therefore sea ice and brine samples from these other
497 studies are located on the other side of the seawater value, i.e. lying between the
498 precipitation of calcium carbonate and the release of CO₂, in the *n*TA/*n*TCO₂ space.

499 The CO₂ fluxes reported here are lower than fluxes reported by Semiletov *et al.*
500 [2004] over melt ponds, but similar to fluxes reported by Geilfus *et al.* [2012b] over
501 sea ice and melt ponds and similar to fluxes reported by Nomura *et al.* [2013] on
502 Antarctic and Arctic sea ice during periods of snowmelt and surface flooding. CO₂
503 fluxes over sea ice depend on the ice permeability and the CO₂ concentration
504 gradient between the ice surface and the atmosphere conveyed through the liquid
505 phase (*i.e.* brine and melt water). Brine and melt ponds were under-saturated with
506 respect to the atmosphere (Figure 5). The sea ice uptake of atmospheric CO₂ was at
507 first moderate (~ -1 mmol m⁻² d⁻¹, Figure 7) due to brine being slightly under-
508 saturated. Then the decrease of the brine *p*CO₂[*in situ*] due to the percolation of melt
509 water with low *in situ* *p*CO₂ intensified the uptake of atmospheric CO₂ (up to -5.4
510 mmol m⁻² d⁻¹) by the ice. As the brine *p*CO₂[*in situ*] increased, the uptake of CO₂
511 decreased accordingly (~ -1 mmol m⁻² d⁻¹). In addition, insignificant fluxes (in the
512 range of -0.005 mmol m⁻² d⁻¹) were detected over interposed ice, similar to Nomura
513 *et al.* [2010b] and Geilfus *et al.* [2012b] who reported fluxes ~0 mmol m⁻² d⁻¹ on

514 superimposed ice. During the initial formation of melt ponds, the low *in situ* $p\text{CO}_2$
515 yielded a strong uptake of atmospheric CO_2 (-3.8 $\text{mmol m}^{-2} \text{d}^{-1}$). However, as the melt
516 pond $p\text{CO}_2$ [*in situ*] approached equilibrium with the atmosphere, melt pond CO_2
517 uptake decreased and stabilized around $\sim -1 \text{ mmol m}^{-2} \text{ d}^{-1}$.

518 To estimate a total uptake of atmospheric CO_2 (Figure 7) over the sampling area (F_{tot} ,
519 crosses), we used the pond coverage (fraction $0 \leq x \leq 1$) (Figure 2) to weight the
520 fluxes over sea ice (F_{ice} , open circles) and over melt ponds (F_{mp} , black triangles)
521 respectively, using the following equation:

$$F_{tot} = F_{ice} \cdot (1 - x) + F_{mp} \cdot x$$

522 The melt pond coverage (Figure 2) was obtained six times between the date of pond
523 onset (10 June) and the final sampling date with a terrestrial laser scanner. The
524 scanner was used to measure the surface topography of an untouched 80 x 160 m
525 area of sea ice and could differentiate between ice cover and melt ponds at the
526 surface, providing the pond fraction [Landy *et al.*, 2014]. F_{tot} peaked during the initial
527 formation of the melt ponds, and then returned to previous values (-1 $\text{mmol m}^{-2} \text{ d}^{-1}$)
528 when melt ponds were the dominant surface feature. $p\text{CO}_2$ conditions in melt ponds
529 are determined by a balance between equilibration with atmospheric CO_2 and the
530 continuous supply of low- $p\text{CO}_2$ melt water from melting snow and sea ice. This
531 allows melt ponds to be a continuous but moderate CO_2 sink. Considering the mean
532 F_{tot} after melt pond onset (= -1.15 $\text{mmol m}^{-2} \text{ d}^{-1}$) over $8.4 \times 10^6 \text{ km}^2$ of sea ice (i.e. the
533 difference between the maximum and the minimum annual Arctic sea ice extents
534 (Dieckmann and Hellmer, 2010)) over a 90-day duration (the length of the spring and
535 summer melt period), we derive an uptake for this annual melt period of -10.4 Tg C
536 yr^{-1} , in addition to existing annual estimates of Arctic oceanic CO_2 uptake. However,
537 mixing the melt of the sea ice observed during this study (with average
538 characteristics of $T = -1.1^\circ\text{C}$, $S = 3.8$, $\text{TA} = 296 \mu\text{mol kg}^{-1}$ and $\text{TCO}_2 = 228 \mu\text{mol kg}^{-1}$) in
539 a 20 m-thick mixed layer (with average water column characteristics of $T = -1.62^\circ\text{C}$;
540 $S = 32.4$; $\text{TA} = 2229 \mu\text{mol kg}^{-1}$ and $\text{TCO}_2 = 2135 \mu\text{mol kg}^{-1}$), will result in a 9.4 μatm
541 $p\text{CO}_2$ decrease in the seawater and an oceanic uptake of 0.55 $\text{mmol of CO}_2 \text{ m}^{-2} \text{ d}^{-1}$
542 over the 90-day melt period. This corresponds to a total oceanic uptake of -5 Tg of C

543 yr^{-1} . These estimations are in the same range as previous work from *Rysgaard et al.*
544 [2011] who estimated an overall budget for Arctic sea ice between 14 and 31 Tg of C
545 yr^{-1} depending on whether the precipitation of calcium carbonate took place in the
546 ice or not. Other estimates of carbon uptake by the Arctic Ocean include *Takahashi et*
547 *al.* [2009], who estimated oceanic uptake of 121 Tg of C yr^{-1} for an area north of 66°N
548 while *Bates and Mathis* [2009] estimated an uptake between 66 and 199 Tg of C yr^{-1}
549 for the Arctic Ocean. However, these studies considered sea ice an impermeable
550 barrier, ignoring the potential role of ice-covered seas on gas exchange between the
551 ocean and the atmosphere. We surmise that melting sea ice may play an important
552 role in mediating the exchange of CO_2 between the atmosphere and ocean at high
553 latitudes and could provide an additional uptake to previous estimates [*Bates and*
554 *Mathis* (2009) and *Takahashi et al.*, (2009)].

555 6. Conclusions

556 We investigated the evolution of inorganic carbon within landfast first-year sea ice in
557 Resolute Passage, Nunavut, from 3 to 23 June 2012 during the spring and summer
558 melt period. Temperature profiles became isothermal ($\sim -1^\circ\text{C}$) with low salinity at
559 the surface (~ 0). Melt ponds started to form at the surface of the ice on 10 June.

560 Early in the melt period, increased ice temperatures and subsequent decreased bulk
561 ice salinity and dissolution of ikaite crystals promoted a strong decrease of TA, TCO_2
562 and $p\text{CO}_2$ observed in bulk sea ice and brines (Figure 10a). The decrease of $p\text{CO}_2$
563 caused sea ice to act as a sink for the atmospheric CO_2 ($\sim -1 \text{ mmol m}^{-2} \text{ d}^{-1}$). This sink
564 increased (up to $-5.4 \text{ mmol m}^{-2} \text{ d}^{-1}$) during the initial formation of melt ponds due to
565 their very low $p\text{CO}_2$ levels. Percolations of melt pond water into the ice matrix
566 increased brine dilution and decreased brine TA, TCO_2 and $p\text{CO}_2$ (Figure 10b). Low
567 TA_{br} and $\text{TCO}_{2\text{br}}$ concentrations observed were associated with the percolation of
568 melt water from melt ponds, and the brine $p\text{CO}_2$ [*in situ*] was controlled by the melt
569 ponds. The melt pond $p\text{CO}_2$ [*in situ*] was low (36 μatm) because melt ponds formed
570 from melted snow and surface sea ice melt. The percolation of this low $p\text{CO}_2$, low
571 salinity melt water into the sea ice matrix decreased the brine $p\text{CO}_2$ [*in situ*] to 20
572 μatm . As sea ice temperatures rose, melt water was continuously supplied to the

573 ponds, which prevented melt ponds from fully equilibrating with the atmospheric
574 CO₂ concentration. Instead, $p\text{CO}_2$ in the melt ponds fluctuated between 0 μatm and
575 the atmospheric concentration (395 μatm). As melt ponds reached equilibrium with
576 the atmosphere, their uptake became less significant, but because melt ponds are
577 continuously supplied with fresh melt water while simultaneously draining to the
578 ocean, the melt pond $p\text{CO}_2$ [*in situ*] remained under-saturated and promoted a
579 continuous but moderate uptake of CO₂ from the atmosphere ($\sim -1 \text{ mmol m}^{-2} \text{ d}^{-1}$).

580 Based on the present study, we estimate an atmospheric CO₂ uptake due to the melt
581 of the seasonal sea ice in the Arctic to be in the order of -10.4 Tg of C yr⁻¹. This
582 represents an additional uptake by 5 to 15% for the Arctic Ocean from previous
583 estimated as reported when sea ice was considered a barrier to these fluxes [Bates
584 and Mathis, 2009; Takahashi *et al.*, 2009].

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592 manuscript.

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595 **8. Figure captions**

596 Figure 1: Location map of the sampling area in the Resolute Passage, Nunavut. The
597 sampling site was located between Sheringham Point and Griffith Island
598 (74.726°N, 95.576°W).

599 Figure 2: (a.) Evolution of the atmospheric temperature in Resolute from the end of
600 May to the end of June 2012. The black dots represent the air temperature
601 during our survey (from 3 to 23 June). (b.) Evolution of the melt ponds
602 (black dots) and sea ice (white dots) fraction coverage at the sampling site.
603 The bold dashed line on 10 June represents the initial formation of melt
604 ponds at the surface of the ice cover. Aerial photo were taken over the field
605 study site on 13 June (pond fraction = 0.9; width of the picture = 4472m),
606 23 June (pond fraction = 0.65; width of the picture = 2212m), 29 June
607 (pond fraction = 0.61; width of the picture = 4426m).

608 Figure 3: Temporal evolution of sea ice temperature (°C), salinity, isotopic
609 composition of $\delta^{18}\text{O}$ and $\delta\text{D}(\text{\textperthousand})$, TA_{ice} and $n\text{TA}_{\text{ice}}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and
610 $n\text{TCO}_{2\text{ice}}$ ($\mu\text{mol kg}^{-1}$). Open squares on the X-axis mark the sampling dates.

611 Figure 4: Profiles of sea ice $p\text{CO}_2[\text{bulk_calc}]$ (calculated from TA_{ice} and $\text{TCO}_{2\text{ice}}$, grey
612 diamonds), sea ice $p\text{CO}_2[\text{bulk}]$ (white diamonds), brine and melt ponds
613 $p\text{CO}_2[\text{in situ}]$ (black dots and triangle, respectively).

614 Figure 5: Temporal evolution of brine (0.2, 0.4, 0.75 and 1m depth) and melt ponds
615 (0m) $p\text{CO}_2[\text{in situ}]$ (μatm), salinity, isotopic composition of $\delta^{18}\text{O}$ and
616 $\delta\text{D}(\text{\textperthousand})$, TA and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and $n\text{TCO}_2$ ($\mu\text{mol kg}^{-1}$). Open
617 squares on the X-axis mark the sampling dates.

618 Figure 6: Temporal evolution of water column temperature (°C), salinity, isotopic
619 composition of $\delta^{18}\text{O}$ and $\delta\text{D}(\text{\textperthousand})$, TA and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and $n\text{TCO}_2$
620 ($\mu\text{mol kg}^{-1}$) and calculated $p\text{CO}_2$ (μatm). Open squares on the X-axis mark
621 the sampling dates.

622 Figure 7: CO_2 fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) measured over sea ice (white diamonds), melt
623 ponds (black triangle). The total fluxes are represented by the black cross.

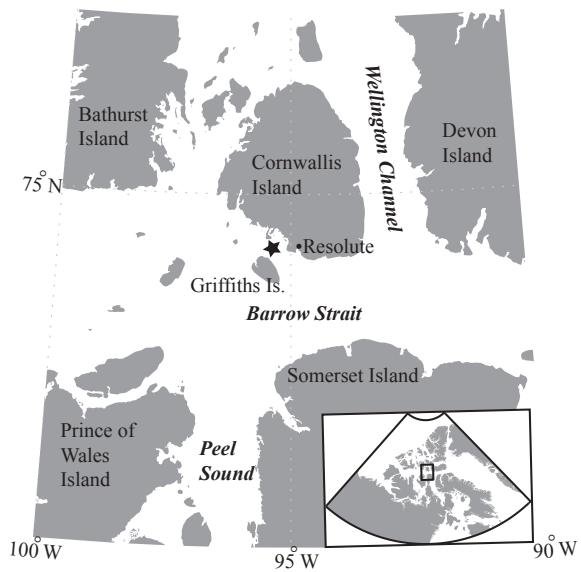
624 Figure 8: Comparison between brine TA and TCO_2 measured on brine collected using
625 the sackholes technique and the brine TA and TCO_2 estimated from TA_{ice} ,
626 $\text{TCO}_{2\text{ice}}$ and the brine volume.

627 Figure 9: Relationship between the $n\text{TCO}_2$ and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$) in bulk sea ice (white
628 diamonds), melt ponds (grey triangle) and brine samples (black dots). The
629 different dashed lines represent the theoretical evolution of $n\text{TA}$: $n\text{TCO}_2$
630 ratio following the precipitation/dissolution of calcium carbonate,
631 release/uptake of $\text{CO}_{2\text{(g)}}$ and biological photosynthesis/respiration.

632 Figure 10: Schematic illustration of the inorganic carbon dynamics of melt pond-
633 covered first year sea ice. (a.) The increase of the ice temperature and the
634 decrease of the salinity, associated with the dissolution of ikaite crystals
635 promote the decrease of the bulk ice and brine $p\text{CO}_2$. (b.) Formation of melt
636 ponds at the surface of the ice and percolation of meltwater into the ice
637 matrix further decreases the $p\text{CO}_2$ with episodes of partial recovery, due to
638 surface exchanges with the atmosphere. The $p\text{CO}_2$ level is indicated by the
639 size of the writing. The intensity of the CO_2 uptake is indicated by the size
640 of the arrow.

641

642 Figure 1: Location map of the sampling area in the Resolute Passage, Nunavut. The
643 sampling site was located between Sheringham Point and Griffith Island
644 (74.726°N, 95.576°W).

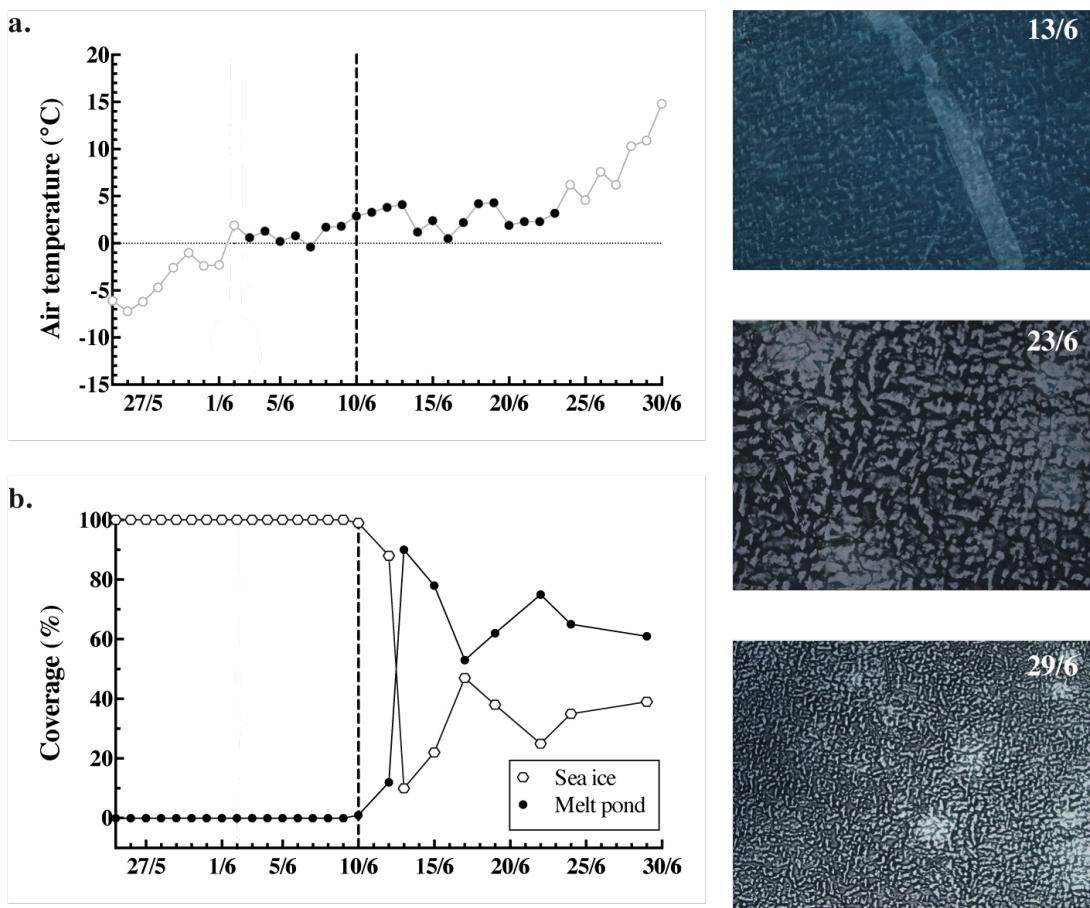


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647 Figure 2: (a.) Evolution of the atmospheric temperature in Resolute from the end of
 648 May to the end of June 2012. The black dots represent the air temperature
 649 during our survey (from 3 to 23 June). (b.) Evolution of the melt ponds
 650 (black dots) and sea ice (white dots) fraction coverage at the sampling site.
 651 The bold dashed line on 10 June represents the initial formation of melt
 652 ponds at the surface of the ice cover. Aerial photo were taken over the field
 653 study site on 13 June (pond fraction = 0.9; width of the picture = 4472m),
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 655 (pond fraction = 0.61; width of the picture = 4426m).

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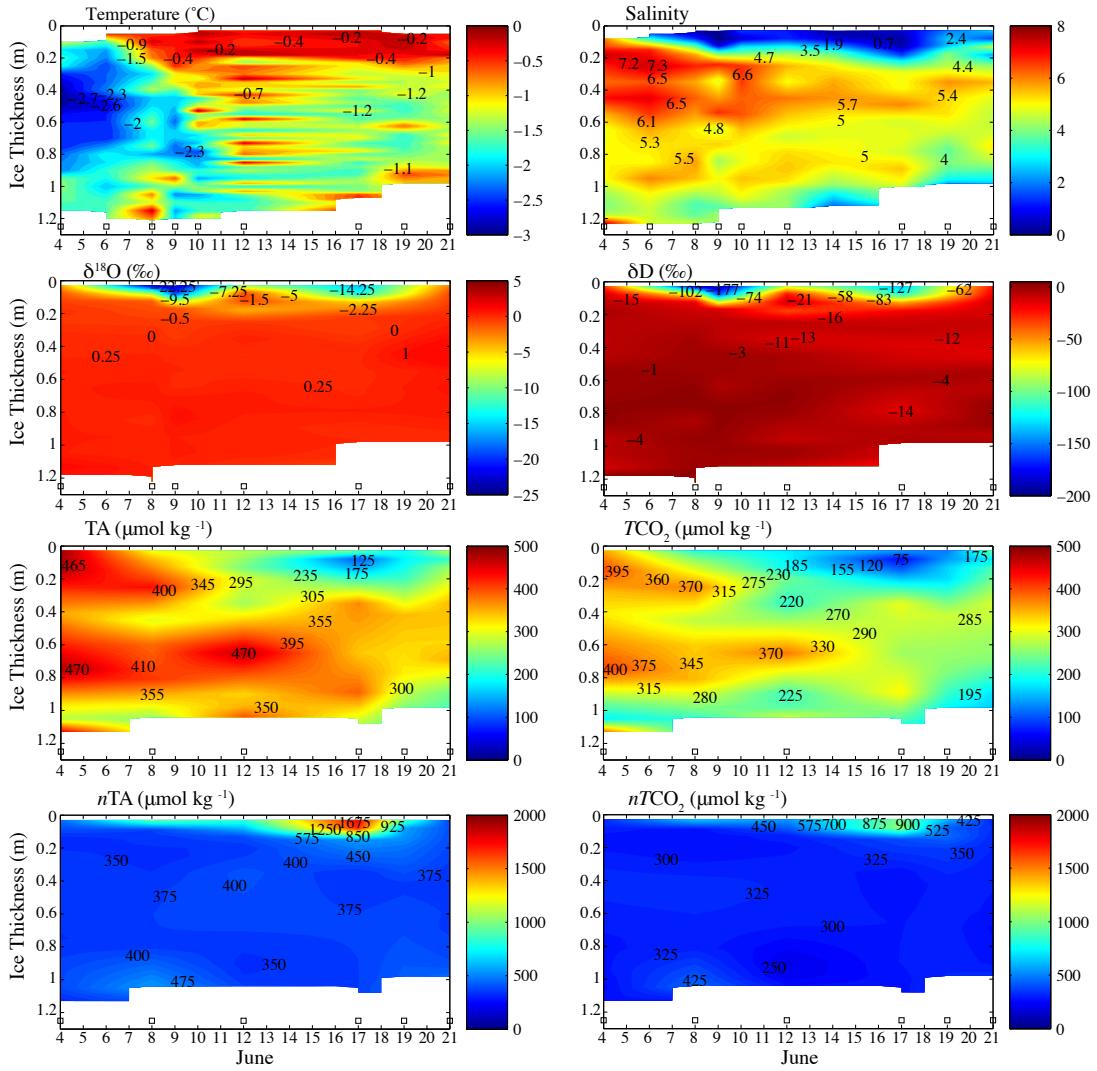
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Figure 3: Temporal evolution of sea ice temperature ($^{\circ}\text{C}$), salinity, isotopic composition of $\delta^{18}\text{O}$ and $\delta\text{D}(\text{‰})$, TA_{ice} and $n\text{TA}_{\text{ice}}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and $n\text{TCO}_{2\text{ice}}$ ($\mu\text{mol kg}^{-1}$). Open squares on the X-axis mark the sampling dates.

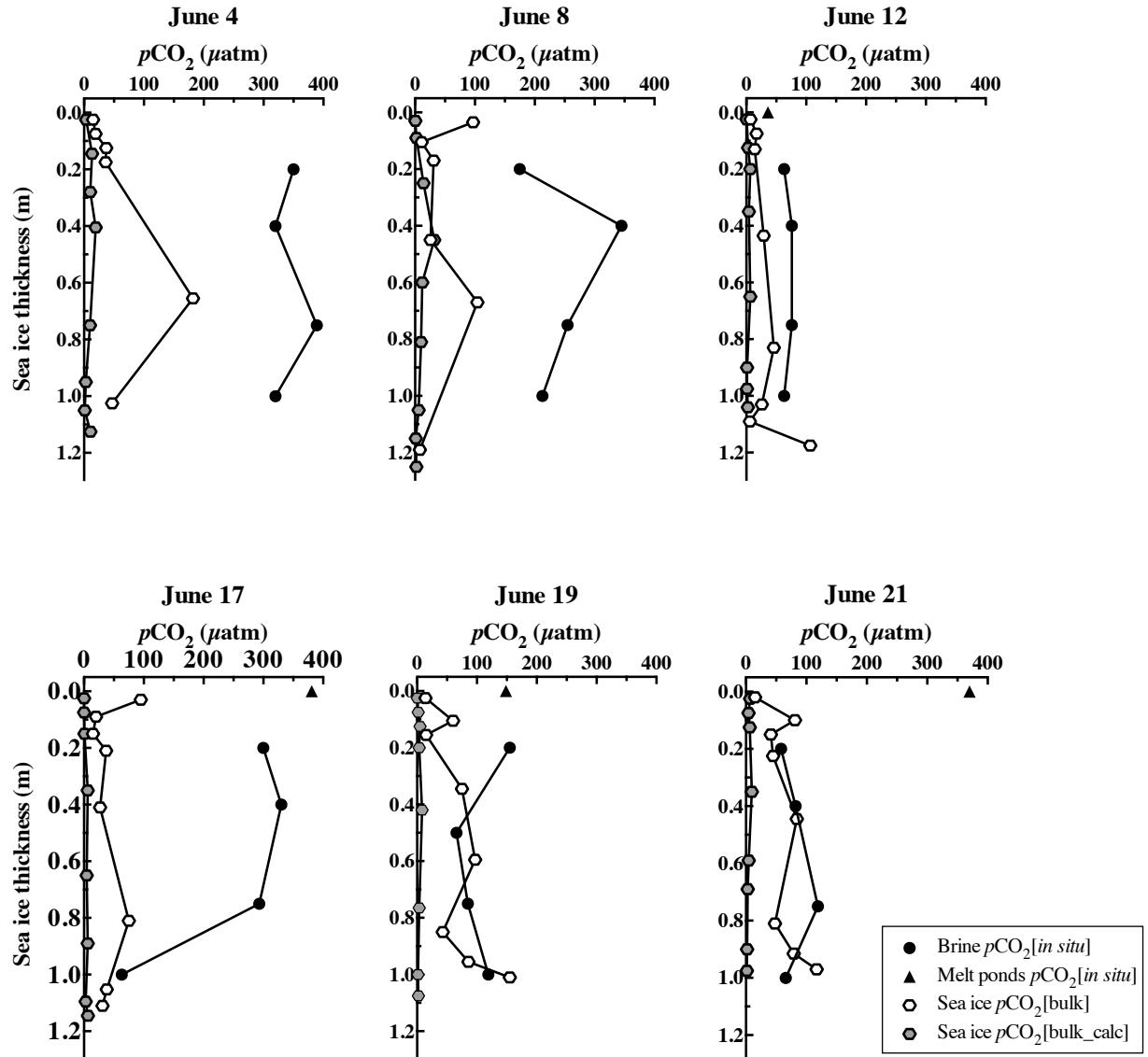
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665 Figure 4: Profiles of sea ice $p\text{CO}_2[\text{bulk_calc}]$ (calculated from TA_{ice} and $\text{TCO}_{2\text{ice}}$, grey
 666 diamonds), sea ice $p\text{CO}_2[\text{bulk}]$ (white diamonds), brine and melt ponds
 667 $p\text{CO}_2[\text{in situ}]$ (black dots and triangle, respectively).

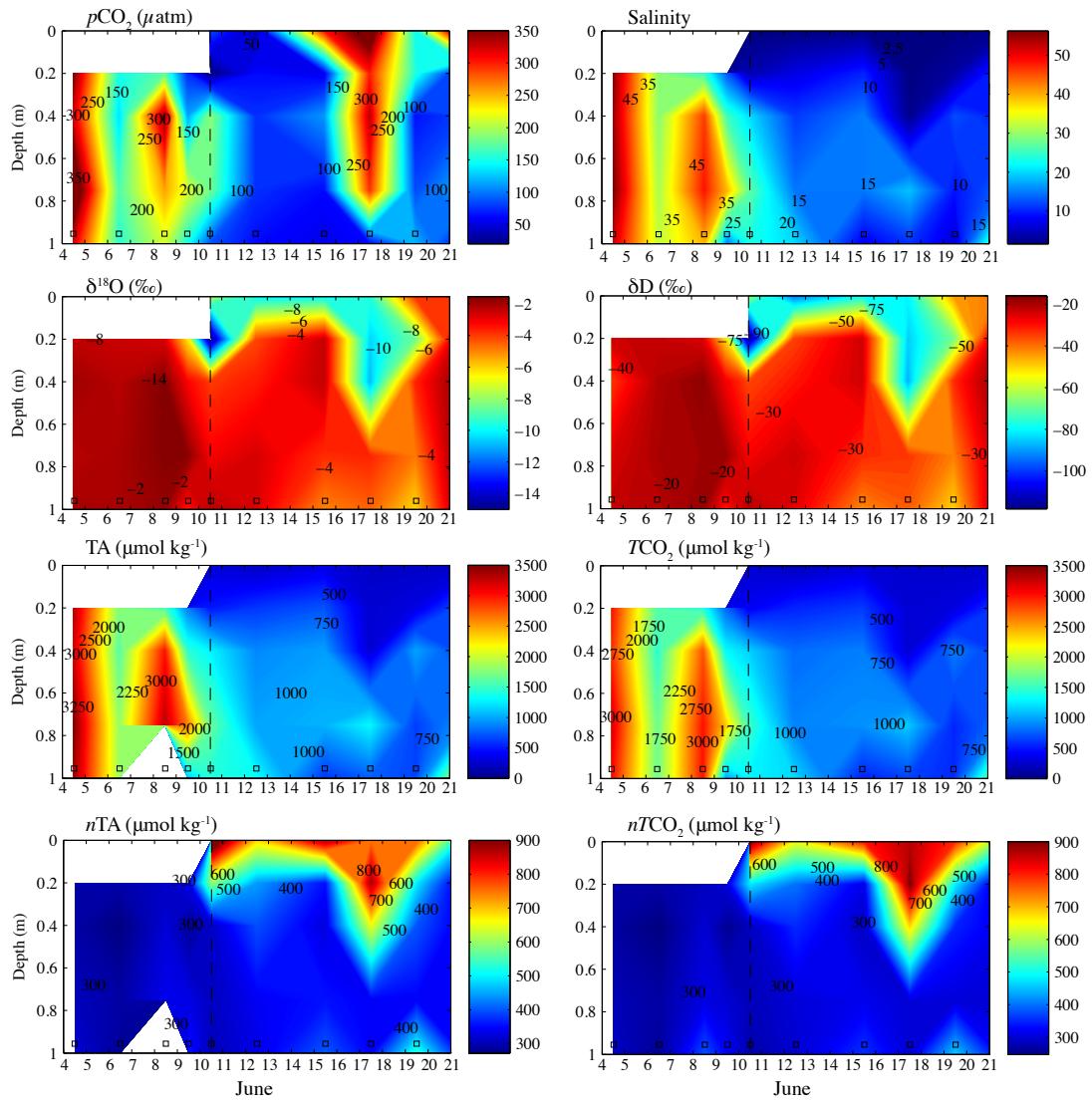


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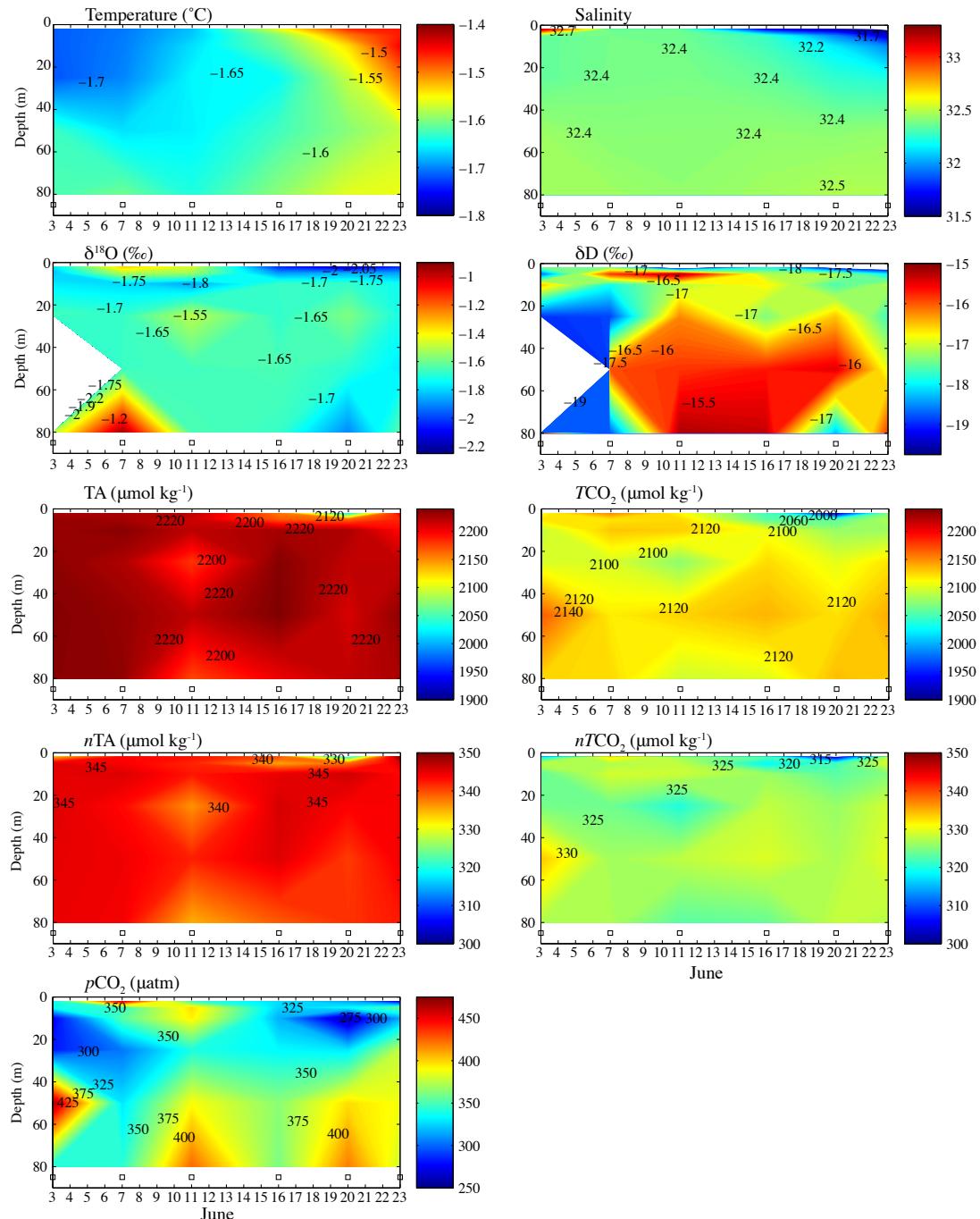
671 Figure 5: Temporal evolution of brine (0.2, 0.4, 0.75 and 1m depth)
672 (0m) $p\text{CO}_2$ [*in situ*] (μatm), salinity, isotopic composition of $\delta^{18}\text{O}$ and
673 $\delta\text{D}(\text{\textperthousand})$, TA and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and $n\text{TCO}_2$ ($\mu\text{mol kg}^{-1}$). Open
674 squares on the X-axis mark the sampling dates.



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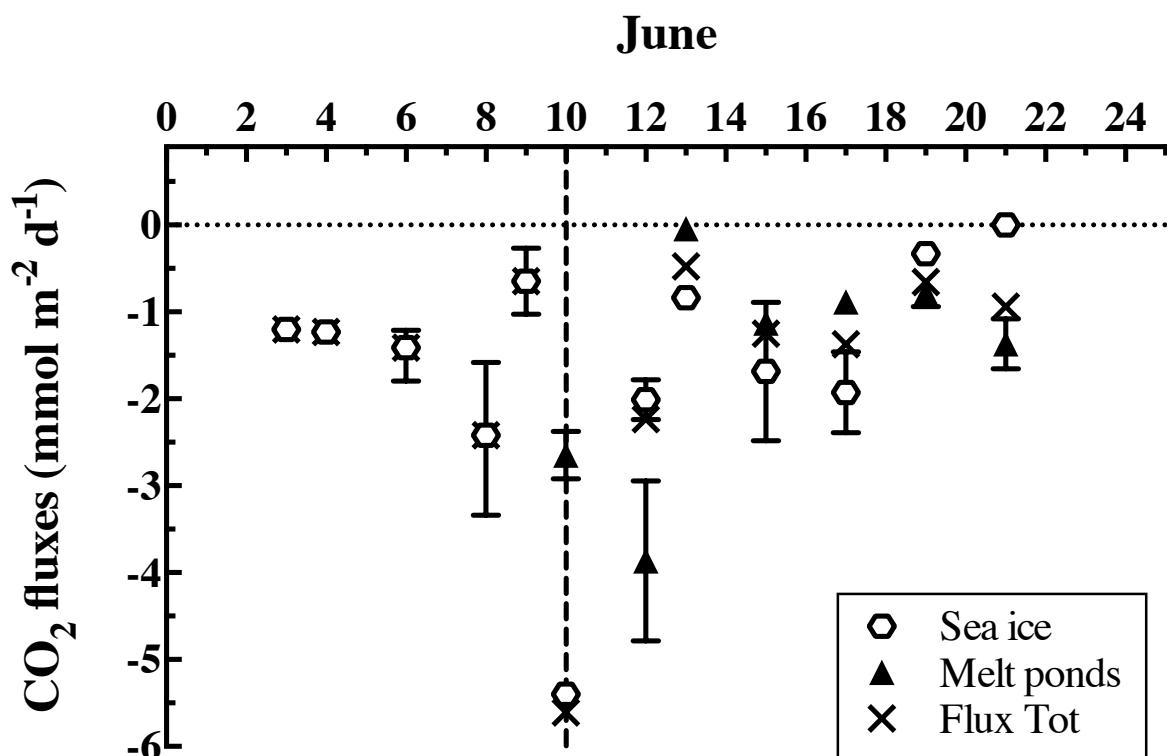
Figure 6: Temporal evolution of water column temperature (°C), salinity, isotopic composition of $\delta^{18}\text{O}$ and $\delta\text{D}(\text{\textperthousand})$, TA and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$), TCO_2 and $nTCO_2$ ($\mu\text{mol kg}^{-1}$) and calculated pCO_2 (μatm). Open squares on the X-axis mark the sampling dates.



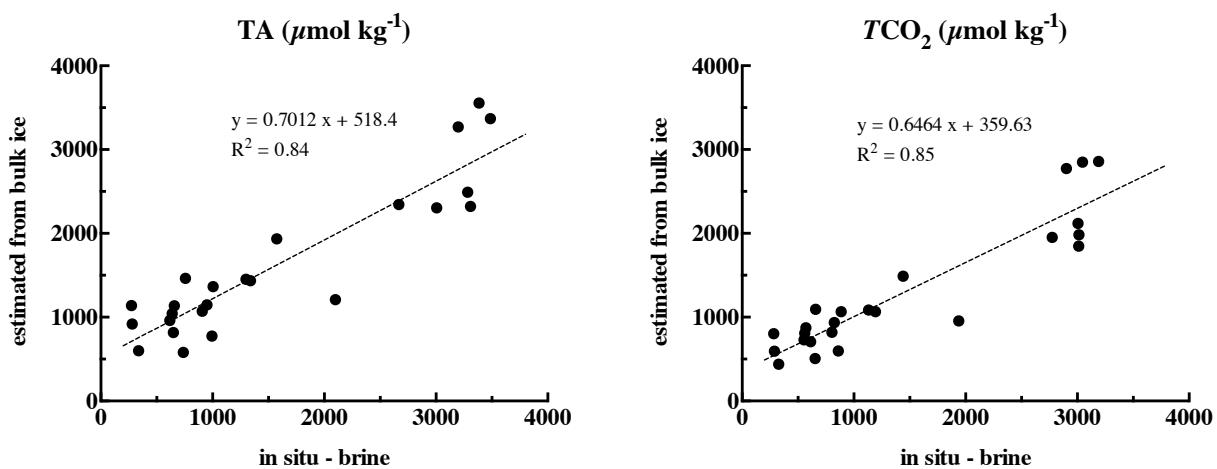
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685 Figure 7: CO₂ fluxes (mmol m⁻² d⁻¹) measured over sea ice (white diamonds), melt
686 ponds (black triangle). The total fluxes are represented by the black cross.
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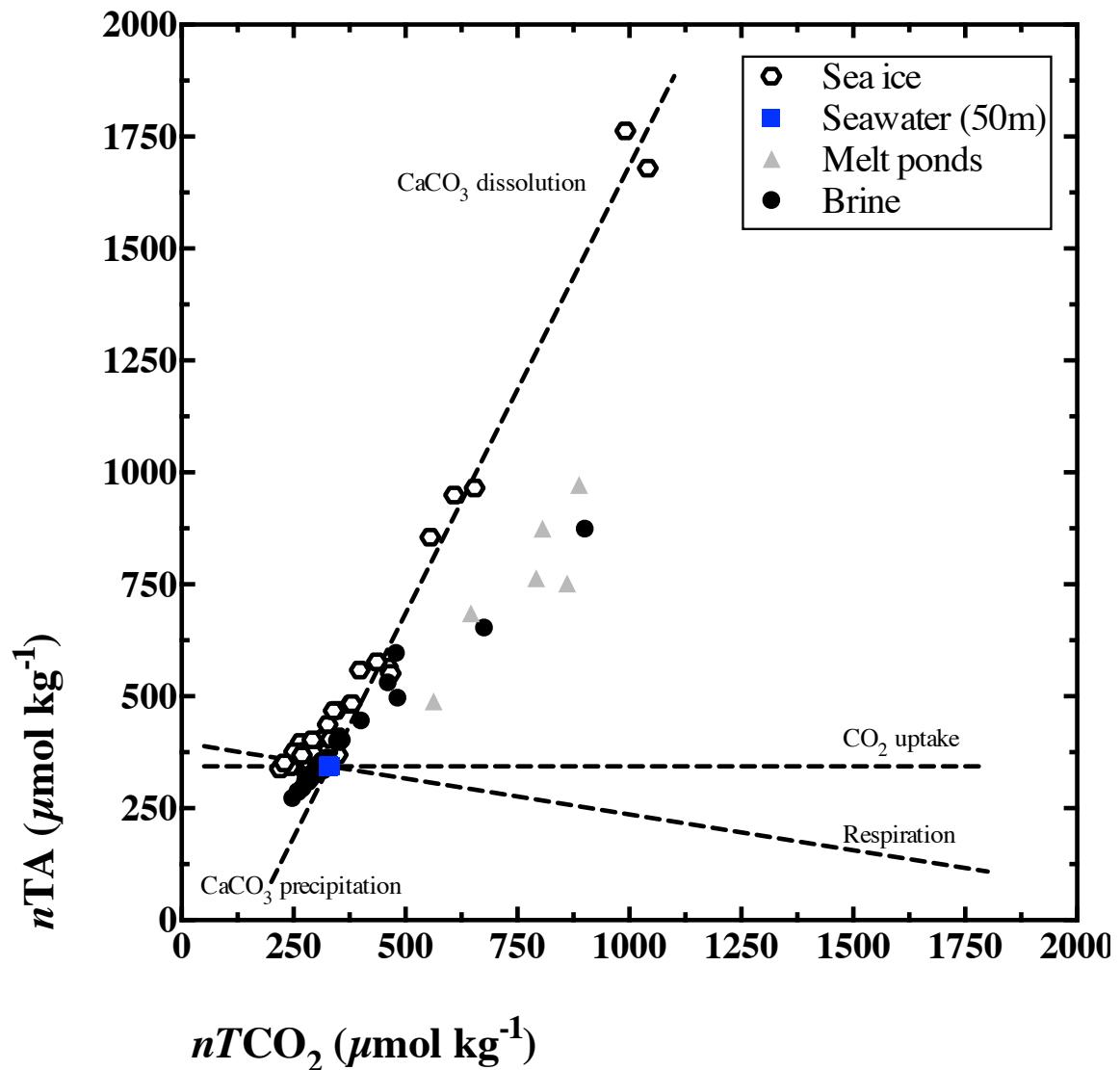


692 Figure 8: Comparison between brine TA and TCO_2 measured on brine collected using
693 the sackholes technique and the brine TA and TCO_2 estimated from TA_{ice} ,
694 TCO_{2ice} and the brine volume.
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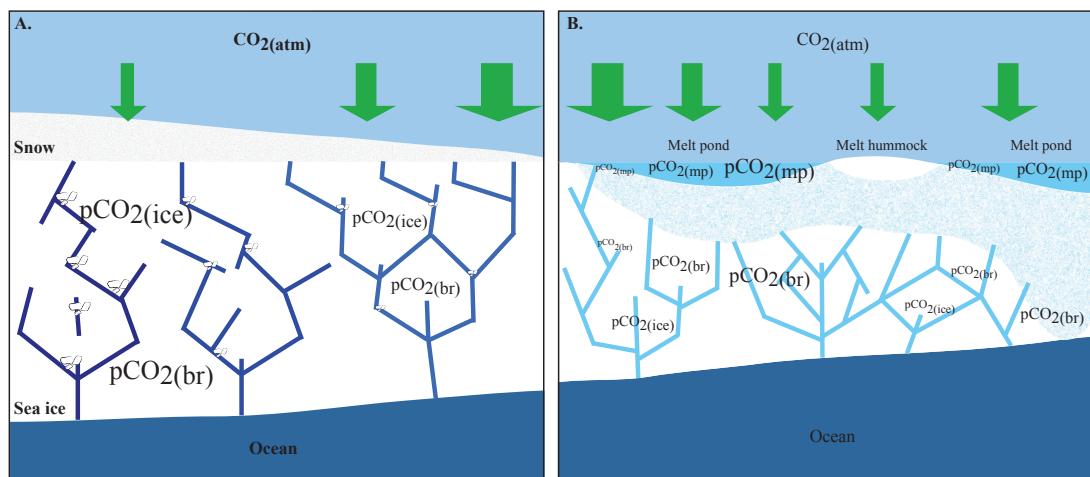
699 Figure 9: Relationship between the $n\text{TCO}_2$ and $n\text{TA}$ ($\mu\text{mol kg}^{-1}$) in bulk sea ice (white
700 diamonds), melt ponds (grey triangle) and brine samples (black dots). The
701 different dashed lines represent the theoretical evolution of $n\text{TA}$: $n\text{TCO}_2$
702 ratio following the precipitation/dissolution of calcium carbonate,
703 release/uptake of $\text{CO}_{2\text{(g)}}$ and biological photosynthesis/respiration.



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707 Figure 10: Schematic illustration of the inorganic carbon dynamics of melt pond-
708 covered first year sea ice. (a.) The increase of the ice temperature and the
709 decrease of the salinity, associated with the dissolution of ikaite crystals
710 promote the decrease of the bulk ice and brine $p\text{CO}_2$. (b.) Formation of melt
711 ponds at the surface of the ice and percolation of meltwater into the ice
712 matrix further decreases the $p\text{CO}_2$ with episodes of partial recovery, due to
713 surface exchanges with the atmosphere. The $p\text{CO}_2$ level is indicated by the
714 size of the writing. The intensity of the CO_2 uptake is indicated by the size
715 of the arrow.

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