Influence of glacial water and carbonate minerals on wintertime sea-ice biogeochemistry and the CO$_2$ system in an Arctic fjord in Svalbard

Agneta Fransson, Melissa Chierici, Daiki Nomura, Svein Kristiansen, Tõnu Martma and Gernot Nehrke

Abstract

The effect of freshwater sources on wintertime sea-ice CO$_2$ processes was studied from the glacier front to the outer Tempelfjorden, Svalbard, in sea ice, glacier ice, brine and snow. March–April 2012 was mild, and the fjord was mainly covered with drift ice, in contrast to the observed thicker fast ice in the colder April 2013. This resulted in different physical and chemical properties of the sea ice and under-ice water. Data from stable oxygen isotopic ratios and salinity showed that the sea ice at the glacier front in April 2012 contained on average 54% of frozen-in glacial meltwater. This was five times higher than in April 2013, where the ice was frozen seawater. In April 2012, the largest excess of sea-ice total alkalinity (A$_T$) was carbonate ion ([CO$_3^{2-}$]) and bicarbonate ion concentrations ([HCO$_3^-$]) relative to salinity was mainly related to dissolved dolomite and calcite incorporated during freezing of mineral-enriched glacial water. In April 2013, the excess of these variables was mainly due to ikaite dissolution as a result of sea-ice processes. Dolomite dissolution increased sea-ice A$_T$ twice as much as ikaite and calcite dissolution, implying different buffering capacity and potential for ocean CO$_2$ uptake in a changing climate.

Introduction

The Arctic is warming, with the concurrent rapid decline in sea-ice cover and ice thickness, and is one of the most rapidly changing environments on Earth (IPCC, 2019). The increased melting of Arctic sea ice, and a change from predominantly thicker multi-year sea ice to first-year sea ice, will cause a more easily deformed and more easily melted sea ice (e.g. Meier and others, 2014; Lindsay and Schweiger, 2015; Serreze and Stroeve, 2015; Granskog and others, 2016). Over the past decades, Arctic glaciers have been decreasing in volume, and meltwater discharge to the ocean and fjords has increased (e.g. Kohler and others, 2007; Nuth and others, 2010; IPCC, 2019). Arctic fjords with tidewater glaciers have shown to be particularly affected by increased meltwater from glaciers (e.g. Nilsen and others, 2008; Straneo and others, 2011, 2012). Climate change projections indicate that there will be more freshwater runoff from Svalbard, mainly due to increased glacial meltwater and increased rainfall, and that there will be increased sediment transport from calving marine- and land-terminating glaciers (Hansen-Bauer and others, 2019).

In Greenland and Svalbard fjords sub-glacial melt releases freshwater, which rises to the surface and brings nutrients and other chemical substances from deeper water layers to the surface (e.g. Straneo and others, 2012; Halbach and others, 2019; Hopwood and others, 2020). Increased nutrient concentrations have been observed near the glacier fronts of several fjords, and promoted primary production and carbon uptake in Greenland (Azetsu-Scott and Syvitski, 1999; Sejr and others, 2011; Straneo and others, 2012; Meire and others, 2015, 2016, 2017) and in Svalbard fjords (e.g. Hodal and others, 2012; Hegseth and Tverberg, 2013; Fransson and others, 2016; Halbach and others, 2019). Increased iron concentrations near glacier fronts have been shown to lead increased primary production in fjords (Statham and others, 2008; Bhatia and others, 2013; Hopwood and others, 2020).

Fjords on the west coast of Spitsbergen island (Svalbard) are influenced by warm and saline Atlantic water inflow, and mixing of relatively fresh surface water influenced by river runoff and meltwater from glaciers and sea ice. The freshwater supply affects the surface water chemistry both through the dilution of a chemical compound and due to the addition of minerals as a result of the composition of the bedrock. High concentrations of silicate ([Si(OH)$_4$]) have been observed near glacier fronts in both Greenland and Svalbard, indicating the effect of glacial meltwater (e.g. Azetsu-Scott and Syvitski, 1999; Fransson and others, 2015a, 2016; Meire and others, 2016; Halbach and others, 2019). Increased alkalinity and carbonate ions ([CO$_3^{2-}$])
have been observed near glacier fronts, which has been explained to originate from minerals in the bedrock from the drainage basins (e.g. Sejrup and others, 2011; Fransson and others, 2015a). Dissolution of carbonate-rich bedrock containing minerals such as dolomite (CaMg(CO₃)₂) and calcite (CaCO₃), has been shown to increase A_T and [CO₃²⁻] in the surface water, hence increasing CaCO₃ saturation (Ω; Eqn 1), and counteracting the effect of dilution (Fransson and others, 2015a; 2016).

\[ \Omega = \frac{([CO_3^{2-}] + [Ca^{2+}])}{K_{sp}} \]  

(1)

where \( K_{sp} \) is the condition equilibrium constant at a given salinity, temperature and pressure and [Ca\(^{2+}\)] is calcium-ion concentration, which is proportional to salinity in seawater, according to Mucci (1983). Increased CO₂ in the ocean (i.e. ocean acidification) has led to decreases in [CO₃²⁻] and the CaCO₃ saturation (Ω) in seawater. When Ω < 1, solid CaCO₃ is chemically unstable and prone to dissolution (i.e., the waters are undersaturated with respect to the CaCO₃ mineral).

Sea ice affects physical processes such as deep-water formation/mixing and ventilated, and the salinity and heat budgets of fjords (e.g. Svendsen and others, 2002; Cottier and others, 2007; Nilsen and others, 2008, 2013; Straneo and others, 2011, 2012). During sea-ice formation, salts and chemical substances such as CO₂ are rejected from the ice matrix, which results in the formation of a high-density brine. As sea-ice temperatures decrease, pressure build-up in brine cells forces brine to migrate upward and downward through a process called brine expulsion (Weeks and Ackley, 1986). The brine is released into the underlying water at a rate dictated by the sea-ice growth and by phase relationships (e.g. Cox and Weeks, 1983). In the Arctic, the rejection and transport of CO₂-enriched brine caused increased CO₂ in the under-ice water (UIW) and subsequent sequestering of CO₂ (Anderson and others, 2004; Rysgaard and others, 2007, 2009, 2013; Fransson and others, 2013, 2015b; Ericson and others, 2019). In spring, during sea-ice melt, the surface water had decreased CO₂ and increased Ω (e.g. Rysgaard and others, 2012; Fransson and others, 2013). Consequently, air-ice-sea CO₂ fluxes become affected by the sea-ice processes. Brine can also move upward from hydrostatic pressure, facilitated by the high porosity within a few centimeters of the surface layer (Perovich and Richter-Menge, 1994). The upward expulsion of supersaturated brine brings salts and CO₂-rich brine to the ice surface, and in cold and calm conditions forms frost flowers (Perovich and Richter-Menge, 1994; Martin and others, 1996; Alvarez-Aviles and others, 2008), which can result in the release of CO₂ to the atmosphere (e.g. Fransson and others, 2013, 2015b; Gellius and others, 2013). Moreover, a brine skim layer can be formed by the upward transport of brine, sea-ice flooding or inputs of seawater. As a result of the upward-transported CO₂-enriched brine, outgassing of CO₂ has been observed during the formation of new sea ice in the Arctic (e.g. Else and others, 2011; Miller and others, 2011; Fransson and others, 2013, 2015b; Gellius and others, 2013; Nomura and others, 2013, 2018).

Minerals can precipitate in the highly concentrated brine governed by decreasing temperatures (Assur, 1958). The solid mineral ikaite, a polymorph of calcium carbonate (CaCO₃·6H₂O; Assur, 1958), precipitates in cold brines when calcite formation is inhibited in the Arctic and Antarctic winter sea ice (e.g. Dieckmann and others, 2008, 2010; Rysgaard and others, 2012; Nomura and others, 2013). In warmer ice (>4°C) it decomposes into water and calcium carbonic (Assur, 1958) or dissolves (depending on saturation state, Ω). Precipitation of ikaite (CaCO₃) produces CO₂ (aq) and reduces bicarbonate ions ([HCO₃⁻]), and dissolution of CaCO₃ consumes CO₂(aq) and produces HCO₃⁻, hence affecting the total alkalinity (A_T) and dissolved inorganic carbon (DIC; e.g. Rysgaard and others, 2012, 2013; Fransson and others, 2013, 2015b) according to Eqsns 2, 3a and 3b.

\[ Ca^{2+} + 2HCO_3^- + 5H_2O \leftrightarrow CaCO_3(s) + 6H_2O + CO_2(aq) \]  

(2)

Simplified, A_T is defined as the sum of bicarbonate ions ([HCO₃⁻]), carbonate ions ([CO₃²⁻]), borate ions ([BOH]²⁻), hydroxyl ions ([OH⁻]) and hydrogen ions ([H⁺]):

\[ A_T = [HCO_3^-] + 2[CO_3^{2-}] + [BOH]_2^- + [OH^-] - [H^+] \]  

(3a)

A_T is mainly affected by precipitation and dissolution of CaCO₃ minerals. A_T increases slightly during photosynthesis as nitrate and hydrogen are consumed during protein formation. DIC (Eqn 3b) is mainly affected by primary production and respiration of organic carbon, air-sea CO₂ exchange, and the precipitation and dissolution of CaCO₃ minerals.

\[ DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2(aq)] \]  

(3b)

where [CO₂(aq)] is the concentration of carbon dioxide dissolved in water.

When CO₂ is produced during ikaite precipitation, it generally escapes from the ice, either to the atmosphere or to underlying water (if temperatures are not extremely low), while ikaite crystals generally remain within the ice (Rysgaard and others, 2009, 2013). As a result, CaCO₃ stores twice as much A_T as DIC (Eqsns 2, 3a and 3b). The dissolution of ikaite usually occurs at a later stage, when the sea ice becomes warmer and starts to melt, resulting in increased A_T and further decreased CO₂, hence A_T of the melt-water increases relative to DIC in sea ice, and pCO₂ decreases (e.g. Rysgaard and others, 2012, 2013; Eqn 2). When meltwater with excess A_T and higher buffer capacity is mixed with the surface water, pCO₂ in surface water decreases and becomes lower than the atmospheric values, leading to ocean CO₂ uptake from the atmosphere (e.g. Rysgaard and others, 2009; Fransson and others, 2011). Lowering surface-water pCO₂ upon upwelling due to dissolution of CaCO₃ minerals increases the potential for ocean uptake of CO₂ in regions downstream where the ice melts. This seasonal cycle will cause a local net change in the sea-ice carbonate chemistry and fractionation of A_T and DIC (Rysgaard and others, 2009, 2012; Fransson and others, 2013, 2015a, 2015b, 2017). Occasionally, solid ikaite can also escape the ice and sink with the brine to deeper water layers, where it dissolves and adds A_T to the seawater. The depth and timing of the vertical transport of brine-CO₂ and/or ikaite determine whether there is a net change in the ocean carbonate chemistry as A_T gain or loss of A_T. The net effects on A_T, DIC and the buffer capacity will also depend on the bedrock-derived carbonate-mineral species, such as dolomite derived from glacier water according to the dissolution Eqn 4a (Wollast, 1990; Pokrovsky and Schott, 2001).

\[ CaMg(CO_3)_{2(2)} + 2H_2O + 2CO_2 \rightarrow Mg^{2+} + Ca^{2+} + 4HCO_3^- \]  

(4a)

When dolomite dissolves, A_T will increase at twice the rate as when ikaite dissolves (Eqsns 2 and 4a). In addition, dolomite is an external source added to sea ice and seawater; it forms over longer timescales, and does not contribute itself to CO₂ production in the seawater. For bedrock-derived calcite, dissolution will increase A_T at the same rate as when ikaite dissolves (Eqsns 2 and 4b). During dolomite dissolution, A_T will increase by 4 moles and DIC by 2 moles, which is twice as much as the change.
Dieckmann and others (2010) found calcium carbonate (ikaite) in Svalbard fjords. In Kongsfjorden, 322 Agneta Fransson and others (2008) investigated the effects on the sea-ice chemistry and composition, all in the context of the ongoing retreat of tidewater glaciers in Svalbard fjords. The data are used to derive the physical and chemical properties in sea ice, snow, brine and glacial ice, using observations of the CO₂ system, nutrients, and δ¹⁸O during two contrasting winters in Tempelfjorden, a fjord in western Spitsbergen, Svalbard. The data are derived from freshwater fractions and estimate the amount of glacial meltwater in sea ice. We examine the differences in carbonate minerals originating from freshwater sources and sea-ice processes, and evaluate the effects on the sea-ice chemistry and composition, all in the context of the ongoing retreat of tidewater glaciers in Svalbard fjords.

**Study area**

Tempelfjorden is a west-facing fjord, without a distinct sill, located in the easternmost (innermost) part of Isfjorden, on the West-Spitsbergen shelf (Figs 1a and b). The Isfjorden system is influenced by the inflow of cold and less saline Arctic water from Storfjorden and Barents Sea, as well as intrusions of warm Atlantic water from the West Spitsbergen Shelf (Nilsen and others, 2008, 2016). Tempelfjorden comprises two basins, one main basin with a maximum water depth of 110 m (central and outer fjord) and one smaller basin in the inner part of the fjord, with water depths up to 70 m. In March 2012, the water column was warmer and less saline relative to that in April 2013, as reported by Fransson and others (2015a). In March/April 2012, the water column was also more stratified compared to the well-mixed conditions in April 2013. The salinity-homogeneous water column in April 2013 was a result of haline convection due to sea-ice formation and the rejection of salt from the sea ice and into the underlying water, forming denser water that sinks to greater water depths (Fransson and other, 2015a). This sinking of denser surface water will, in turn, result in the transport of deeper waters to the surface, leading to vertical mixing, or haline convection.

Tempelfjorden has active seasonal sea-ice formation and is regarded as a coastal polynya, a so-called 'sea-ice factory'. In Tempelfjorden, sea ice usually starts to form in November and breaks up between April and July (Svendsen and others, 2002; Nilsen and others, 2008, 2013). However, the timing of sea-ice formation and melt, as well as the location of the sea-ice edge, has large interannual variability in western Spitsbergen fjords (Cottier and others, 2007; Gerland and Renner, 2007; Pavlova and others, 2019).

To our knowledge, there are only a few studies on sea-ice CO₂ system (carbonate chemistry) in Svalbard fjords. In Kongsfjorden, Dieckmann and others (2010) found calcium carbonate (ikaite) crystals in sea ice, while Fransson and others (2015b) reported on wintertime carbonate chemistry and CO₂ transport, but without estimating the freshwater content (glacial water) and impact on sea-ice carbonate chemistry. In a study in Tempelfjorden, Alkire and others (2015) presented the effects of glacial water on sea-ice alkalinity, but only measured A₇ and not DIC or carbon ion concentrations. Here we present the distribution of the physical and chemical properties in sea ice, snow, brine and glacial ice, using observations of the CO₂ system, nutrients, and δ¹⁸O during two contrasting winters in Tempelfjorden, a fjord in western Spitsbergen, Svalbard. The data are derived from freshwater fractions and estimate the amount of glacial meltwater in sea ice. We examine the differences in carbonate minerals originating from freshwater sources and sea-ice processes, and evaluate the effects on the sea-ice chemistry and composition, all in the context of the ongoing retreat of tidewater glaciers in Svalbard fjords.

Investigating Arctic fjords with the seasonal sea-ice formation during contrasting years is one useful way to understand the influence and effect of freshwater and water-mass composition on the sea-ice biogeochemistry. Freshwater content in the surface water will affect sea-ice formation and influence sea-ice physics and chemistry, with implications for gas exchange (e.g. Crabeck and others, 2014) or microbiota living in brine channels in the sea ice. Bulk sea-ice salinity affects sea-ice permeability and brine-volume fraction, as well as biogeochemical processes. Since freshwater is lower in chemical species relative to seawater in the ice, there will be a larger volume of fresher ice, with less permeability and less expulsion of substances, resulting in less exchange of nutrients, trace metals, or gases with the surrounding environment (e.g. Loose and others, 2009, 2011; Crabeck and others, 2014). The lower brine volume will in turn decrease the transport of salts and chemical substances to deeper water, hence decreasing the CO₂ sequestration, and influencing biogeochemical processes in the water column, and haline convection, which in turn affects circulation and surface stratification (e.g. Nilsen and others, 2008).

Fjord studies in contrasting years have previously been used to better understand the possible feedbacks of climate change in the Arctic such as warming, increased meltwater and decreased sea ice in winter (e.g. Fransson and others, 2015a, 2016). The sea ice will affect the underlying water column, but the water will also affect the sea ice. The properties in the surface water will pre-condition the characteristics of the sea-ice biogeochemistry so that it will influence the CO₂ system and CO₂ exchange with the surrounding environment.

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by carbonate and evaporitic rock (Dallmann and others, 2002). Tunabreen has surged four times since the first observations were made in the early 1900s (Hagen and others, 1993), most recently in 2002–04 (Flink and others, 2015) and now again, in 2016–18 (Sevestre and others, 2018). Consequently, this means that Tempelfjorden has received varying amounts of freshwater and glacier sediment. Forwick and others (2010) reported further that the waters emanating from Tunabreen and von Postbreen drainage basins consist of ∼30% dolomite (CaMg(CO₃)₂) and 18% calcite (CaCO₃), which can contribute with carbonate (CO₃²⁻) and calcium ions (Ca²⁺) to the fjord water and sea ice. This implies that glacial melt and drainage water from these glaciers have the potential to influence the CO₂ system, ocean acidification state and the oceanic CO₂ uptake (Fransson and others, 2015a). In the outer basin, most particles originate from the river Sassenelva (Fig. 1a), which mostly carries particles of silicate but also carbonates (Forwick and others, 2010).

We used air temperature and precipitation data from the meteorological station at Longyearbyen airport (Webpage: seklima.met.no/observations, Longyearbyen airport) to study the difference in climate between the 2 years. During the period 1971–2017, Svalbard experienced atmospheric warming of between 3 and 5°C, with the largest warming observed in the inner fjords (Hansen-Bauer and others, 2019). The period from December 2011 to March 2012 was significantly warmer than the 50-year long-term mean air temperature from 1964 to 2014. Average air temperature for the period January–March in 2012 was −4.8°C, which was +11°C above the long-term mean (1964–2014). The corresponding values for the same period in 2013 were −11 and +4.6°C above the long-term mean. Although winter 2013 was warmer than the long-term mean, it was much cooler than in 2012. The air temperature in March 2013 was 1.4°C warmer than the long-term average. The sum of precipitation between January and March in 2012 was 97 mm (300% above the long-term mean), three times higher than the corresponding value of 31 mm in the same period in 2013.

Data and methods

Sampling

We sampled sea ice, brine, snow/brine skim, glacier ice, and the upper water column (ice/water interface, 0–2 m), from the glacier front to the outer parts of the fjord near the fast ice edge (ice edge Fig. 1. (a) Map of study area in Tempelfjorden, northeast of Longyearbyen, Svalbard. Black dots indicate sampling stations (see also Table 1), dashed lines show the approximate location of the fast-ice edge in April 2012 and April 2013. (b) Tempelfjorden in April, surrounded by carbonate-rich mountains and the glaciers of Tunabreen, Bogebreen and Von Postbreen in the inner part of the fjord, (c) the glacier front of Tunabreen (station 1). Photos: Agneta Fransson.
in 2012; Figs 1a–c; Table 1). Table 1 summarizes the station locations, dates, types of sample, snow and sea-ice thickness, brine sampling depths, air temperature and a number of samples. The most extensive sampling was performed in April 2012 (five stations) and April 2013 (four stations), with limited sampling performed in January (one station), March 2012 (three stations) and September 2013 (two stations).

Sea-ice cores were sampled using an ice corer (Kovacs®, Ø = 0.09 m). The sea ice in January was collected using a stainless-steel saw to cut chunks from the thin ice. The ice cores were divided into 10 cm sections, which were individually placed in plastic bags and put into an insulated box to avoid further ikaite precipitation due to freezing outdoor temperatures. The samples were transported to the laboratory at the University Centre in Svalbard (UNIS, Longyearbyen), and immediately transferred to gastight Tedlar® bags, to initiate the ice melting as soon as possible and avoiding long-term storage in −20°C (to avoid producing more ikaite crystals). Saturated mercuric chloride was added (100 μL for 10 cm ice, ~500 mL melted ice) to halt biological activity. The same treatment was performed on ice samples cut directly from the glacier or from ice pieces found on the beach at the glacier front. After sealing the bags, the air was removed from the bag using a vacuum pump. The bulk sea-ice samples (hereafter referred to as sea ice) were thawed in darkness and at +4°C to preserve the potential ikaite crystals within the sample; melting time was ∼24–48 hour. While thawing, the sea-ice samples were regularly checked visually for the presence of different forms of solid calcium carbonate. If detected, crystals were carefully removed from the melted sea-ice sample bag using a pipette and stored in 50% ethanol at −20°C for analysis. Smaller calcium carbonate crystals will not be detected using this method, and are dissolved during the melting. This is therefore qualitative rather than a quantitative method to identify crystals present in the samples.

Fig. 2. Sea-ice cover in the Isfjorden system with Tempelfjorden indicated in the black square for selected dates: (a) 15 December 2011, (b) 16 January 2012, (c) 15 February 2012, (d) 16 March 2012, (e) 16 April 2012, (f) 28 December 2012, (g) 15 January 2013, (h) 15 February 2013 (i) 15 March 2013 and (j) 15 April 2013. Data were obtained from the Ice Service of the Norwegian Meteorological Institute (MET, http://cryo.met.no/). Ice chart color scheme shows very open drift ice (1–4/10ths, green), open drift ice (4–7/10ths, yellow), close drift ice (7–9/10ths, orange), very close drift ice (9–10/10ths, red) and fast ice (10/10ths, grey).
During the ice-coring, brine samples were collected (Table 2) into 100 mL borosilicate glass bottles from partially drilled holes in the ice, so-called sackholes. The brine, which had seeped into sackholes in the ice (Table 1) was collected with a plastic syringe with PVC tubing and transferred to bottles. During seepage, the sackholes were covered with a lid to ensure that snow was not falling into the hole and alter the measurements. The seeping time for the brine was up to 30–40 min, for sample volumes of 50–100 mL, hence some gas exchange may have taken place.

Samples of snow at the ice surface were sampled in duplicates with a Teflon® ladle from a surface area of 1 m² for each sample. Where the snow thickness was >5 cm (Table 1), we sampled snow at 5 cm vertical depth intervals. Occasionally, the snow samples at the ice surface contained brine, referred to as brine skim. All snow samples were placed in Ziplock® plastic bags in the field, put into an insulated box, and thereafter transferred into gastight Tedlar® bags in the laboratory. Air was gently removed from the bag using a vacuum hand pump, and the samples melted. The brine-skim and snow samples were placed in Ziplock® plastic bags in the field, with a Teflon® ladle from a surface area of 1 m² for each sample.

Determination of physical properties

Sea-ice temperature was measured on site, immediately after the ice core was recovered, at 5-cm intervals using a digital probe (Testo 720) with a precision and accuracy of ±0.1°C. The holes for temperature measurement were slowly drilled with a clean stainless-steel bit, such that heating induced by drilling was negligible. The temperature of brine was measured in the sackhole before the transfer to a sample bottle, and the temperature of the UIW was measured in the sample bottle immediately after sampling, using the same handheld digital probe.

Salinity of the melted sea ice (bulk ice), brine skim, snow and UIW were measured using a WTW Cond 330i conductivity meter, with a precision and accuracy of ±0.05.

The brine-volume fraction (BV) in sea ice can be determined, based on the requirement that there is phase equilibrium between brine and ice, using the parameterizations of Cox and Weeks (1983). Since more than 78% of the sea ice was colder than −2°C, BV can be described as a function of bulk-ice salinity (S) and absolute (ABS) ice temperature (T, °C) using a simplified formulation by Frankenstein and Garner, (1967) derived from Assur, (1960):

$$ BV = \frac{S}{1000} \left( 0.04915 - 0.532 \frac{T}{ABS(T)} \right) $$ (5)

This simplified BV formulation introduces an uncertainty of a maximum of 0.2% (at the coldest temperatures) in the calculations.

Concepts of percolation theory have previously been applied to sea ice (Golden and others, 1998) to explain the origin of the critical porosity (percolation threshold) of sea ice, i.e. the porosity below that sea ice becomes virtually impermeable to fluid flow. Cox and Weeks (1975) report that no brine drainage from sea ice was observed for total porosities below a BV of 0.05. Ice temperature fundamentally controls the ice porosity (Petrich and Eicken, 2010). Golden and others (1998) investigated the sea-ice

### Table 1. Summary of the sampling dates, and locations for each station (Stn#), sampling type, and data on sea ice thickness (Th, m), snow depth, brine sampling depths and air temperature (Ta, °C).

<table>
<thead>
<tr>
<th>Sampling date dd/mm/yyyy</th>
<th>Stn#</th>
<th>Location</th>
<th>Type</th>
<th>Station latitude (°N)</th>
<th>Station longitude (°E)</th>
<th>Th, m</th>
<th>Snow depth (m)</th>
<th>Brine depth (m)</th>
<th>Ta, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25/01/2012</td>
<td>5</td>
<td>Fredheim</td>
<td>ice, uiw</td>
<td>78.04</td>
<td>16.92</td>
<td>0.04</td>
<td>N/a</td>
<td>N/a</td>
<td>−5.0</td>
</tr>
<tr>
<td>21/03/2012</td>
<td>1</td>
<td>GF</td>
<td>ice, gluc, uiw, snow, brine</td>
<td>78.44</td>
<td>17.38</td>
<td>0.36</td>
<td>0.07</td>
<td>0.15</td>
<td>−11.3</td>
</tr>
<tr>
<td>11/04/2012</td>
<td>2 Ice edge</td>
<td>ice, uiw, snow, brine</td>
<td>78.42</td>
<td>17.31</td>
<td>0.32</td>
<td>0.08</td>
<td>0.15</td>
<td>−11.5</td>
<td></td>
</tr>
<tr>
<td>3 Ice edge</td>
<td>1</td>
<td>GF</td>
<td>ice, gluc, uiw, snow</td>
<td>78.42</td>
<td>17.23</td>
<td>0.27</td>
<td>0.07</td>
<td>0.15</td>
<td>−11.5</td>
</tr>
<tr>
<td>11/04/2012</td>
<td>2 Ice edge</td>
<td>ice, uiw, snow, brine</td>
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<td>0.08</td>
<td>0.20</td>
<td>−9.8</td>
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<tr>
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<td>GF</td>
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<td>0.30</td>
<td>0.05</td>
<td>0.15</td>
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<td>GF</td>
<td>ice, uiw, snow</td>
<td>78.41</td>
<td>17.15</td>
<td>0.25</td>
<td>0.04</td>
<td>N/a</td>
<td>−9.5</td>
</tr>
<tr>
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<td>5</td>
<td>5 km from ice edge</td>
<td>ice, uiw, snow</td>
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<td>0.05</td>
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<tr>
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<td>N/a</td>
<td>N/a</td>
<td>N/a</td>
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GF, indicates the locations of sampling of glacial ice, three samples at each location; N/a, not applicable.
Table 2. Median, standard deviation (Std dev), minimum (min) and maximum (max) values of physical and chemical properties of temperature (T, °C), salinity (S), total alkalinity (A<sub>T</sub>, μmol kg<sup>-1</sup>), total dissolved inorganic carbon (DIC, μmol kg<sup>-1</sup>), pH in situ, partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>, μatm), carbonate ion ([CO<sub>3</sub>]<sup>2-</sup>, μmol kg<sup>-1</sup>), calcium carbonate saturation for calcite ([Ca<sup>2+</sup>], nitrate ([NO<sub>3</sub>]<sup>-</sup>), μmol kg<sup>-1</sup>), phosphate ([PO<sub>4</sub>]<sup>3-</sup>, μmol kg<sup>-1</sup>), and silicate ([Si(OH)<sub>4</sub>]<sup>-</sup>, μmol kg<sup>-1</sup>) concentrations, and isotopic oxygen ratio (δ<sup>18</sup>O, ‰) in sea ice (ice), brine, snow (snow, including brine skim), glacier ice (glacier), and under-ice water (UIW).

<table>
<thead>
<tr>
<th>Date</th>
<th>Type</th>
<th>stn</th>
<th>T</th>
<th>S</th>
<th>DIC</th>
<th>pH in situ</th>
<th>pCO&lt;sub&gt;2&lt;/sub&gt; (μatm)</th>
<th>[Ca&lt;sup&gt;2+&lt;/sup&gt;] (μmol kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>[NO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt; (μmol kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>[Si(OH)&lt;sub&gt;4&lt;/sub&gt;]&lt;sup&gt;-&lt;/sup&gt; (μmol kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>δ&lt;sup&gt;18&lt;/sup&gt;O (‰)</th>
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<td>17.3</td>
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<td>1050</td>
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<td>63 72</td>
<td>1.86 48</td>
<td>0.28 3.60</td>
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<td>Std dev</td>
<td>5.0</td>
<td>0.9</td>
<td>61 68</td>
<td>0.02</td>
<td>6 4</td>
<td>0.10 0.8</td>
<td>0.03 0.15</td>
<td>0.11</td>
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</tr>
<tr>
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<td>950</td>
<td>8.53</td>
<td>53 67</td>
<td>1.73 3.9</td>
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<tr>
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<tr>
<td></td>
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<td>Std dev</td>
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<td>0.8</td>
<td>83 72</td>
<td>0.12</td>
<td>5 4</td>
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<td>339</td>
<td>321</td>
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<td>15 12</td>
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<td>7.2</td>
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<td>502</td>
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<tr>
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<td>342</td>
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<tr>
<td></td>
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<td>1.39</td>
<td>12 11</td>
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<td>0.51 1.0</td>
<td>0.06 4.15</td>
<td>-0.9</td>
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</tbody>
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...Continued...

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porosity and the percolation threshold of sea ice. Below a given BV threshold (below 5% for ideal, columnar ice) (Golden and others, 1998, 2007), sea ice becomes impermeable to fluid flow, and above this threshold chemical substances dissolved in sea-ice brine are highly mobile (Cox and Weeks, 1975, 1983; Loose and others, 2009, 2011). Gas-bubble transport in brine channels is thought to be possible above a brine-volume threshold of ∼7.5% (Zhou and others, 2013). The ice becomes less permeable as BV decreases, (e.g., Golden and others, 1998, 2007; Loose and others, 2009, 2011), and both gas and liquid transport decreases.

For the calculation of meteoric water fractions in sea-ice cores, the isotopic composition of a sample can be used to indicate to what extent a sample is of marine or meteoric origin. Stable oxygen isotopes ($\delta^{18}O$) have previously been used to better understand Arctic estuarine processes (e.g. Macdonald and others, 1995; Kuzyk and others, 2008; Crabeck and others, 2014). To estimate the amount of meteoric water in sea ice (FMW) we use the relation derived by Macdonald and others (1995):

$$FMW = (\delta^{18}O_{\text{ice}} - \varepsilon - \delta^{18}O_{\text{sw}})/(\delta^{18}O_{\text{MW}} - \delta^{18}O_{\text{sw}})$$  \hspace{1cm} (6)$$

where $\varepsilon$ (1.8) is the fractionation factor estimated from $\delta^{18}O$ values measured from upper 20 m of the surface water (UIW) in this study, which agrees with the fractionation factor estimated by Alkire and others (2015) in Svalbard fjords. Here we used a $\delta^{18}O$ value of ∼15.7% for glacier ice ($\delta^{18}O_{\text{Glacier}}$) and 0.5% for seawater ($\delta^{18}O_{\text{sw}}$) endmembers (Fransson and others, 2015a). The $\delta^{18}O_{\text{ice}}$ values are from this study. Sea-ice formation causes fractionation ($\varepsilon$) in $\delta^{18}O$, relative to the water from which it is formed. Due to fractionation upon evaporation and precipitations, snow or rain precipitating from an air mass are progressively depleted in $\delta^{18}O$, with respect to the seawater source (Eicken and others, 2005). Using the $\varepsilon$ of 2.2 from the study in a Hudson Bay estuary in the Arctic (Kuzyk and others, 2008), the FMW estimates would be 3% larger.

In 2012 and 2013, field observations and ice charts from the Ice Service of the Norwegian Meteorological Institute (MET, http://cryo.met.no/) were used to map the ice conditions. Figs 2a–j show the sea-ice coverage for the Isfjorden system and Tempelfjorden before and during part of our field periods, where the ice chart color scheme delineates very open drift ice (1–4/10ths, green), open drift ice (4–7/10ths, yellow), close drift ice (7–10/10ths, orange), very close drift ice (9–10/10ths, red) and fast ice (10/10ths, grey).

**Determination of chemical properties**

Melted ice (sea ice and glacier) and snow (including brine skim), brine and UIW were analysed for total alkalinity ($A_T$), total dissolved inorganic carbon (DIC), dissolved inorganic nutrients: nitrate-nitrite ($[NO_3^-]$), phosphate ($[PO_4^{3-}]$) and silicate ($[Si(OH)_4]$), and stable oxygen isotopic ratio ($\delta^{18}O$). DIC and $A_T$ were analyzed within 6 months after collection, either in the laboratory at University Centre in Svalbard (UNIS, Longyearbyen) or at the Institute of Marine Research, Tromsø, Norway. Analytical methods for DIC and $A_T$ determination in seawater samples are described in Dickson and others (2007). DIC was determined using gas extraction of acidified sample followed by coulometric titration and photometric detection using a Versatile Instrument for the Determination of Titration carbonate (VIDTDA 3C, Marianda, Germany). The DIC instrumentation was used for all types of samples. Routine analyses of Certified Reference Materials (CRM, provided by A. G. Dickson, Scripps Institution of Oceanography, USA) ensured the accuracy and precision of the measurements. The average standard deviation from triplicate CRM analyses was within ±1 μmol kg$^{-1}$ for all sample varieties.

Total alkalinity ($A_T$) in UIW was determined from potentiometric titration with 0.1 N hydrochloric acid in a closed cell using a Versatile Instrument for the Determination of Titration Alkalinity (VIDTDA, Marianda, Germany). Samples with $A_T$ are significantly different from seawater $A_T$, such as melted ice, snow, brine skim or brine, were determined using an automated system for potentiometric titration in an open cell using 0.05 N HCl (Methrohm® Titran system, Switzerland), described in Mattsdotter and others (2014). This method allows a smaller sample volume (40 mL) and a low HCl concentration allowed for improved determination of low $A_T$ in melted sea-ice samples, as well as analyses of samples with low volume such as brine samples. The average standard deviation for $A_T$ determined from
triplicate CRM measurements, was ±2 μmol kg⁻¹ for both A_T instrumentation systems.

We used DIC, A_T, salinity, temperature, and depth for each sample as input parameters in a CO₂-chemical speciation model (CO2SYS program, Pierrot and others, 2006) to calculate all the other parameters in the CO₂ system, such as CO₂ concentration ([CO₂]), carbonate-ion concentration ([CO₃²⁻]), bicarbonate-ion concentration ([HCO₃⁻]) and partial pressure of CO₂ (pCO₂). We used the HSO₄⁻ dissociation constant of Dickson (1990), and the CO₂-system dissociation constants (K₁ and K₂) estimated by Mehrbach and others (1973) modified by Dickson and Millero (1987), since they have been shown to be valid also for sub-zero temperatures (Millero and others, 2002; Fransson and others, 2015b) down to −21.4°C (Marion, 2001). Brine concentrations of A_T (A_T(BRINE)) were calculated using the brine-volume fraction (BV, Eqn 4) and the bulk sea-ice concentrations of A_T.

An internal consistency check performed on 100 data points of each A_T, DIC and pH from measurements in Antarctic bulk sea ice showed a bias between calculated and measured DIC of ±11 μmol kg⁻¹ (Fransson and others, 2011). Similar results were showed in bulk sea ice from winter in the Kongsfjorden, where DIC deviated <±3 μmol kg⁻¹ with a standard error of 11 μmol kg⁻¹ using the same dissociation constants as here. Using a standard error of 11 μmol kg⁻¹ in DIC data and ±2 μmol kg⁻¹ for A_T for sea ice and brine results in a calculated uncertainty of ±5 μatm in calculated pCO₂. Delille and others (2007) found a consistency of ±25 μatm in sea-ice melt, based on comparison between direct and calculated pCO₂ values. Brown and others (2015) estimated consistency in high salinity sea-ice brines and estimated consistency to be ±4.5 μatm in the calculated pCO₂ from a combination of A_T and DIC for the same carbonate dissociation constants used in this study in the CO2SYS program. In summary, the uncertainty range in calculated sea-ice brine pCO₂ between 5 and 85 μatm indicated that the internal pCO₂ variability in sea-ice brine is larger than the uncertainty.

The ratio between A_T and DIC (A_T/DIC) can theoretically be used to investigate the effect of precipitation and dissolution of CaCO₃ (Rysgaard and others, 2009, 2012; Fransson and others, 2013). However, due to larger seasonal variability in DIC as a result of biological processes and air-sea CO₂ exchange than in A_T, the ratio between A_T and salinity (A_T/S) is less affected by these processes, hence is used here. The A_T/S ratio has previously been used to estimate the effect of precipitation and dissolution of ikaite on A_T in sea ice (e.g. Rysgaard and others, 2009, 2013; Fransson and others, 2013). A seawater A_T/S ratio of 66 is used in this study, derived from averages of A_T and salinity in Fransson and others (2015a). A higher A_T/S ratio in sea ice than that of seawater indicates the addition of A_T mainly due to dissolved CaCO₃. The seawater A_T/S ratio can vary both spatially and temporally, and may include effects from sea-ice derived brine, which is not accounted for. Insignificant effects due to biological processes are not considered.

By normalizing A_T to a reference salinity and assuming insignificant effect on A_T from biological production, the main cause for the A_T change is attributed to CaCO₃ dissolution or precipitation. To compare the chemical concentrations in sea ice (lower salinity) with the concentrations in seawater, the sea-ice concentrations were salinity-normalized (using dilution line) to a salinity of 34.9, obtained from Tempelfjorden seawater salinity in April 2013 (Fransson and other, 2015a). Based on salinity-normalized A_T and DIC to a seawater reference salinity of 34.9, we calculated [CO₃²⁻]norm and [HCO₃⁻]norm in the sea ice, using CO2SYS (Pierrot and others, 2006).

The nutrient concentrations (nitrate + nitrite, [NO₃⁻]) phosphate ([PO₄³⁻]) and silicate ([Si(OH)₄]) were analyzed in liquid phase in all samples by colorimetric determinations on a Flow Solution IV analyzer (O.I. Analytical, USA) with routine seawater methods adapted from Grasshoff and others (2009). The Analyzer was calibrated using reference seawater from Ocean Scientific International Ltd. UK, and analytical detection limits were obtained from three replicate analyses on the reference seawater. Analytical detection limits were 0.15 μmol kg⁻¹ for nitrate + nitrite, and 0.02 μmol kg⁻¹ for phosphate and silicate, respectively.

Stable oxygen isotopic ratios (δ¹⁸O) were analyzed using a Picarro L2120-i Isotopic Liquid Water Analyser with High-Precision Vaporizer AO211 and Thermo Fisher Scientific Delta V Advantage mass spectrometer with Gasbench II. Different methods were used because we used different laboratories for the samples collected in 2012 and 2013. The isotope values using both methods are reported in the common delta (δ) notation relative to Vienna Standard Mean Ocean Water (VSMOW). The reproducibility of replicate analysis for the δ¹⁸O measurements was ±0.1 % for both the Picarro (2012 samples) and for the Gasbench II (2013 samples).

Section plots and interpolation were performed in Ocean Data View software version 4.7 (Schlitzer, 2015).

**Qualitative analysis of crystals in particles**
Mineralogical phase identification was done using a WITec alpha 300 R (WITec GmbH, Germany) confocal Raman microscope. The measurements were done using an excitation wavelength of 488 nm and an ultra-high throughput spectrometer (UHTS 300, WITec GmbH, Germany) with a grating, 600 mm. 500 nm blaze. The samples were placed in a glass Petri dish filled with crushed ice and immediately measured using a water submersible objective (20 × Olympus). Raman measurements allow a reliable identification of carbonate minerals based on their distinct molecular spectra, which are related to the inelastic scattering of light (e.g. Gillet and others, 1993; Nehrke and Nouet, 2011).

### Results

#### Physical and chemical characteristics

The contrasting sea-ice conditions between the 2 years were confirmed by our field observations and measurements (Table 1). The sea-ice thickness in April 2012 was at a maximum of 54 cm at the glacier front (station 1, Figs 1a–c, Table 1), and decreased towards the ice edge, where it reached 23 cm (station 5, Table 1). In April 2013, the maximum sea-ice thickness was 84 cm at the glacier front (station 1) and 64 cm at station 5, ~5 km from the ice edge in 2013 (Table 1). The thinnest sea ice in April 2012 was likely due to slower sea-ice growth due to warmer atmospheric conditions in 2012 than in 2013 (Table 1).

Snow thickness was 6 cm at the glacier front (station 1) and 5 cm at the ice edge (station 5) in April 2012 (Table 1). In 2013, the snow thickness was 6 cm at the glacier front (station 1) and 4 cm at station 5 (Table 1). Freeboard was positive for all stations and years.

Vertical profiles of sea-ice temperature, salinity, stable oxygen isotopic ratio (δ¹⁸O), brine-volume (BV) fraction and freshwater fraction along the fjord in April 2012 and April 2013 show the physical characteristics of the sea ice from the glacier front to the ice edge (Figs 3a–j). In both years, the coldest sea ice was found at the snow/ice interface (top); temperatures increased almost linearly towards the bottom ice (Figs 3a and b), which was at the seawater freezing point (~−1.9°C). In April 2012 and 2013, the top ice was ~−8°C at the glacier front. In April 2012, the top ice gradually increased towards the ice edge to reach ~−6°C. In April 2013, the top ice was generally colder (~−12°C) throughout the rest of the stations. The bottom sea ice
in 2012 was slightly colder at the glacier front than in 2013, likely
due to the colder glacial water.

Sea-ice salinity (Figs 3c and d) was generally higher in the top
and bottom ice than in the middle, a typical C-shape pattern indi-
cating first-year ice (Malmgren, 1927; Thomas and others, 2010).

This pattern was more pronounced in April 2013 than in April
2012. The lowest sea-ice salinity measured was ∼2 in April
2012 and ∼5 in April 2013, both observed in the middle of the
sea ice at the glacier front (Figs 3c and d). In April 2012, there
was no pronounced salinity increase towards the bottom ice,
which was likely due to warmer UIW in the outer part of the fjord, than in April 2013 (Table 2). Sea-ice salinity increased towards the ice edge (station 5) in both years. The highest salinity was 11 in April 2012 (in the top 10 cm of the ice at station 4) and 9 in April 2013 (at the bottom ice at station 2) (Figs 3c and d). The δ18O values in the sea ice were mostly positive (0–2.5 ‰), except for some negative values found in a few ice cores near the glacier in 2012 and at the outermost station (station 5) in 2012 (Fig. 3e). In April 2012, there was large δ18O variability along the section, with the lowest δ18O values of −8 ‰ near the glacier front (station 1), decreasing from top to bottom, and as high as 2.5 ‰ (near the ice edge) (Fig. 3e). At station 4, the salinity in the top 10 cm ice in 2012 was the highest and δ18O was negative, which indicates that it was not only influenced by seawater. In 2013, a few negative δ18O values of −2.8 ‰ were found at the bottom ice near the glacier front; otherwise δ18O values were positive in all other ice depths with a median value of 1.8 ‰ and a maximum of 2.4 ‰ (Fig. 3f).

In April 2012, BV ranged between 2% (fraction 0.02) in top 10 cm of the sea ice at the glacier front (station 1) and 13% (0.13) at bottom ice at station 2 (Fig. 3g). In general, the sea ice was permeable (BV>5%, 0.05), except for at the upper 40 cm at the glacier front. This contrasted with April 2013, in which most of the sea ice was impermeable (BV<5%, 0.05) at all stations, indicating that the sea ice was not porous enough for gas and brine transport (Fig. 3h). In April 2013, the 3% (0.03) limit of BV was observed in the upper 50 cm of the ice at the glacier front (station 1) and in the upper 30 cm at the station near the ice edge (station 5). Consequently, it was only at the bottom part of the ice gas and brine could be transported to the underlying water (Fig. 3h).

The freshwater fraction (FMW) of 0.6 in April 2012 was largest near the glacier front (Station 1; Fig. 3i) decreasing towards the ice edge to zero (station 5), except for in the upper 10 cm of the ice at stations 4 and 5 (Fig. 3i). In April 2013, the FMW of 0.2–0.3 was only observed at the bottom ice and mid-ice (30 cm) near the glacier front. All other ice depths had the FMW of <0.1 (Fig. 3j). Figures 4a–l show the vertical concentrations in melted sea ice (bulk) of, total alkalinity (A, Figs 4a and b), total inorganic carbon (DIC, Figs 4c and d), carbonate ion concentrations ([CO3$^{2-}$], Figs 4e and f), silicate ([Si(OH)4]$_4^-$, Figs 4g and h), and nitrate concentrations ([NO3$^-$], Figs 4i and j) along the sections in April 2012 and 2013.

In general, A$_T$ and DIC increased from the glacier front to the ice edge (Figs 4a–d). At the glacier front, A$_T$ and DIC were lower than close to the ice edge, in a similar pattern as δ18O. In 2012, near the glacier front, A$_T$ and DIC were lower than the corresponding values at the same station in 2013. This coincided with higher [CO3$^{2-}$] near the glacier front in 2012 compared to the values in 2013 (Figs 4e and f). A$_T$ (Figs 4a and b) and DIC (Figs 4c and d) followed salinity (Figs 3c and d), with the highest values typically at the top and bottom. In 2012, the [CO3$^{2-}$] concentrations (Figs 4e and f) in the top ice were generally higher than in the top ice in 2013 (Fig. 4f). In 2013, on the other hand, [CO3$^{2-}$] was generally lower at bottom ice close to the ice edge.

Silicate concentrations (Figs 4g and h), were generally depleted (near detection limit) in the fjord ice. However, notably higher [Si (OH)$_4$]$_4$ were observed throughout the ice core at the glacier front in 2012 and at the bottom ice near the glacier front in 2013. The high [Si(OH)$_4$]$_4$ near the glacier coincided with low salinity and low δ18O in 2012. Also in 2013, the high [Si(OH)$_4$]$_4$ in the bottom ice coincided with the lowest δ18O, although salinity was higher than in 2012. Nitrate concentrations ([NO3$^-$], Figs 4i and j) were low and almost depleted near the glacier front in 2012. In 2013, generally higher [NO3$^-$] were observed in all fjord ice than were observed in 2012, with higher concentrations at the bottom ice. Phosphate concentrations ([PO4$^{3-}$], were depleted ≤0.1 μmol·kg$^{-1}$ in April 2012 at all sites (not shown), and in April 2013, there were higher concentrations at the bottom ice (ice/water interface, not shown).

Table 2 shows the averages of physical and chemical characteristics of sea ice, brine, snow (including brine skim, glacier ice and UIW). The brine temperatures were similar for both years with mean values of −3.6°C and −4.4°C in 2012 and 2013, respectively. The mean brine salinity was lower in 2012 (salinity of 65) than in 2013 (salinity of 80). The snow temperatures varied with air temperatures, and the snow was ∼7.1°C and warmer in April 2012 than that in April 2013 of −13.8°C (Table 2). The snow salinity was about twice as high in April 2012 than in 2013. This may be caused by a larger component of brine incorporated into the snow (brine skin layer), due to warmer ice and larger BV in April 2012. The more permeable ice in April 2012, facilitated upward brine transport relative to the conditions in April 2013 (Figs 3e and f). Brine A$_T$ and DIC were highly elevated compared to A$_T$ and DIC in bulk sea ice and in the UIW, with the highest brine A$_T$ and DIC (>5000 μmol·kg$^{-1}$) observed in April 2013 (Table 2). In both years, the [CO3$^{2-}$] and calcite saturation (ΩCa) were higher in brine than in bulk sea ice and UIW, where the brine ΩCa was clearly oversaturated (ΩCa > 4, Table 2). Brine [CO3$^{2-}$] varied between 17 and 1061 μmol·kg$^{-1}$. Brine and snow [NO3$^-$] were relatively high, particularly in 2012, with the maximum [NO3$^-$] of 27 and 20 μmol·kg$^{-1}$, respectively (Table 2). Brine pCO2 ranged between 73 and 1134 μatm and the highest A$_T$ and DIC values coincided with relatively high salinity. Bulk sea ice was undersaturated (ΩCa<1) for both years (Table 2). Glacier ice was not significant saline, nor did it contain significant amounts of nutrients, and only small amounts of A$_T$ and DIC were found in one of the samples (Table 2).

**Effects of glacial water and sea-ice processes**

In glacier ice, δ18O ranged between −10 and −15.7 ‰, and snow (including brine skin) between −6 and −17.5 ‰, for a salinity interval between 0 and 30 (Fig. 5a; Table 2). The δ18O and salinity relationship indicate three mixing lines depending on the different endmembers, such as seawater and meteoric water (Fig. 5a). The sea-ice δ18O (~2.5 to 1 %) and salinity ranges were larger in 2012 than in 2013. In 2013, the sea-ice δ18O and salinity (from 4 to 9) were generally higher in δ18O and similar to δ18O in seawater (0.47–0.67 ‰; Table 2; Fig. 5a). Snow δ18O and salinity indicate a clear influence of brine skim. The δ18O in brine varied between −1.5 and −9 ‰, in a salinity range of 30–80 (Fig. 5a; Table 2). The negative sea-ice δ18O between −2.5 and −7.5 ‰ suggest incorporation of meteoric water, snow or brine in the sea ice in 2012 (Fig. 5a). The δ18O in snow generally followed the mixing line between glacial ice and seawater, indicating a source of brine from the ice/snow interface (brine skin) (Fig. 5a).

Increased meteoric water in sea ice was observed from March to April 2012 at each station, reaching the highest integrated freshwater fraction of 54% in April 2012 at the glacier front (Fig. 6a). The fraction of meteoric water decreased towards the ice edge with the lowest values of <10% in March and April 2012 at station 3, and the lowest of <5% at the ice edge in April 2013. Figure 6b shows the vertical distribution of freshwater fractions in the ice, where FMW of 0.6 (60%) was found in bottom ice in March and April 2012 at the glacier front station (Fig. 6b). This was nearly five times higher than found at any other station in April 2012 (0.1–0.15; 10–15%), and substantially higher than at any station in April 2013 (0.1–0.10; Figs 6a and b). It is evident that there was higher freshwater fractions in the bottom sea ice at stations near the glacier front (station 1) than elsewhere, for all three sampling campaigns, (Fig. 6b).
In April 2012, the highest \([\text{Si(OH)}_4]\) values were observed in the ice and seawater and show large deviation from the dilution line, suggesting excess \([\text{Si(OH)}_4]\) relative to salinity (Fig. 5b). In April 2013, the \([\text{Si(OH)}_4]\) values in both seawater and sea ice were generally lower than in April 2012, and were clustered around the dilution line (Fig. 5b).

The vertical distribution of \(A_T:S\) in sea ice shows elevated \(A_T:S\) values relative to seawater \(A_T:S\) of 66 throughout the ice core in both years. This was particularly evident at the glacier front in 2012 (Fig. 7), where the highest \(A_T:S\) ratios (>80) was found in March and April 2012, with ratios up to 141 in the mid-part of the ice (Fig. 7). The highest \(A_T:S\) ratios coincided with the highest...
FMW near the glacier front in April 2012 (Figs 6a and b). In April 2013, the AT:S ratios were lower than that in 2012, ranging between 64 and 87 (Fig. 7).

δ18O is a good tracer for meteoric contribution, and, when combined with the [CO32−]norm and [HCO3−]norm, gives a clue to the possible excess of [CO32−] and [HCO3−] in sea ice, relative to an average seawater salinity of 34.9. We used pure glacial ice (zero salinity) values of δ18O of −16 ‰ assuming zero [CO32−]norm and [HCO3−]norm and average seawater δ18O, and [CO32−]norm and [HCO3−]norm as endmembers for the dilution lines (Figs 8a and b). The seawater [CO32−]norm values were ∼100–110 μmol kg−1 and [HCO3−]norm were on average 2000 μmol kg−1. The values below the respective dilution line indicates a loss of [CO32−] and [HCO3−] compared to that of seawater, and above indicates a gain (excess) of [CO32−] and [HCO3−] relative to seawater. In 2012, most of the sea ice had an excess of [CO32−] and [HCO3−], while in 2013 both excess and loss of [CO32−] and [HCO3−] were observed relative to seawater (Figs 8a and b). Consequently, the outstanding [HCO3−]norm of up to 4600 μmol kg−1 were found at the lowest sea-ice δ18O. This implies that these elevated values are a result of dolomite dissolution.

Sea ice with δ18O values below −2.8 ‰ and AT:S ratios above 84 are assumed to be influenced by meteoric water and higher δ18O values indicate more influence of seawater, with sea-ice AT:S ratios varying between 66 and 100 (Fig. 8c). The difference (of ∼1.8 ‰) between the positive sea-ice δ18O values and seawater δ18O is caused by δ18O fractionation during sea-ice formation (e.g. Macdonald and others, 1995). The excess of [CO32−]norm and [HCO3−]norm at the lowest sea-ice δ18O values in 2012 also coincided with the high AT:S ratio of up to 141, possibly indicating a contribution of carbonate ions from dissolved bedrock minerals in glacial water/meteoric water (Fig. 8c). Indeed, crystals of CaCO3 minerals were identified in sea ice, snow (including brine skim) and glacier ice (Table 3; Fig. S1). In April 2012, no minerals were found in sea ice. However, dolomite was the main mineral found in snow and glacier ice. Sea-ice samples in April 2013 contained calcite (not bedrock-transported type) while dolomite was absent in 2013. In April 2013, the snow contained mainly ikaite and calcite, particularly at station 2 and 4.

Discussion

Effects of glacial water on sea-ice characteristics

In April 2012, both seawater and air temperatures were warmer than in April 2013, more precipitation fell as rain, and therefore the fresh water may have originated from several sources such as rain, snow, glacial meltwater and river runoff. Positive δ18O
indicates that sea-ice meltwater is the predominant source, negative $\delta^{18}O$ indicate mostly meteoric water (precipitation, glacial meltwater or river runoff). Alkire and others (2015) argued that it is challenging to distinguish between glacial water and river runoff. However, Killingtveit and others (2003) found that the Spitsbergen freshwater sources were mainly from precipitation and glacial meltwater. The main outlet of the river Sassenelva is located at the outer part of Tempelfjorden and near Fredheim (Fig. 1a). Incorporation of freshwater flowing under the ice was found in a river-influenced shelf in the Canadian Arctic (Macdonald and others, 1995), an estuary in Hudson Bay (Kuzyk and others, 2008) and in a Greenland fjord (Crabeck and others, 2014). The lowest $\delta^{18}O$ values in both the sea ice and seawater were found at the glacier front in 2012, not at the middle or outer stations, where a more riverine influence could be expected. The role of freshwater freeze-in in our study was indicated by the change of FMW from the glacier front to the outer station. This was particularly evident in 2012, when the mean freshwater fraction decreased abruptly from 54% at station 1 to the lowest FMW of 8% at station 3 (Fig. 6a). After station 3, FMW increased again to $\sim$13% at the ice edge (station 5) in 2012. This slight increase could perhaps be a result of riverine influence at the outer stations. However, the FMW increase was not evident in 2013 and was generally lower (<10%) at all stations compared to that in 2012.

The $\delta^{18}O$ in the glacier ice ranged between $-13.6$ and $-15.7$ ‰ (Fig. 5b), which is in fair agreement with observations of $\delta^{18}O$ in solid precipitation from Ny-Ålesund (Svalbard), whose means is $-13 \pm 5$ ‰ ($n=63$) (D. Divine, unpublished data, 2016). One means to identify the freshwater source and to distinguish glacial meltwater from snow, rain or river inputs is to investigate the silicate concentrations. The correlation of high [Si(OH)$_4$] and glacial water has been reported previously in Svalbard (Fransson and others, 2015a) and Greenland (Azetsu-Scott and Tan, 1997; Azetsu-Scott and Syvitski, 1999). In April 2012, the surface water had high [Si(OH)$_4$] near the glacier front, suggesting the impact of glacial-water contribution, mainly by sub-glacial meltwater (Fransson and others, 2015a; Halbach and others, 2019). Indeed, the high [Si(OH)$_4$] in sea ice were only observed at the glacier front in 2012, coinciding with the lowest $\delta^{18}O$ values and the highest content (68%) of frozen-in freshwater. Flink and others (2015) found that...
Tunabreen front retreat had caused the following surge events, introducing increased glacial and sub-glacial meltwater input to Tempelfjorden. Alkire and others (2013) found no evidence in 2013 for the incorporation of glacial meltwater in the sea ice. This supports our findings that glacial meltwater had insignificant effect in the sea ice in 2013. We conclude that most part of the fresh water incorporated in the sea ice in 2012 originated from glacial meltwater.

Calcium carbonate minerals from glacial water and sea ice

Dolomite is a common rock-forming mineral and is transported in several ways; by wind, through glacial- and sub-glacial meltwater, and through riverine transport from the drainage basin to seawater. Dolomite cannot precipitate in the sea ice as ikaite does. As seawater freezes, dolomite is incorporated in the sea ice and then transported to the surface of the ice through upward brine transport. While Alkire and others (2015) speculated that carbonate minerals in the glacial water could explain the elevated $A_{T}$ found in sea ice in 2013, they did not have any observations of minerals or measurements of DIC. Their hypothesis was confirmed in 2012, 2013, and 2014 for all sea-ice stations in March 2012 (red, filled symbols), April 2012 (red, open symbol) and April 2013 (black symbol) in Tempelfjorden. Dashed line denotes the $A_{T}$:S ratio of 66 in the water column in Tempelfjorden in April 2012 and April 2013 (Fransson and others, 2015a).

In both April 2012 and 2013, parts of the sea-ice $A_{T}$:S ratios were below 100, indicating that the excess $A_{T}$ was mainly explained by ikaite dissolution, based on this and previous studies. However, wind-transported bedrock-originated minerals such as calcite and dolomite to seawater could be incorporated in sea ice during formation, and contributed to the $A_{T}$:S ratios, when dissolved (Fig. 8b). The observations of sea-ice $A_{T}$:S ranging between 66 and 85 in April 2013 and ikaite crystals identified in snow confirm that the sea ice in 2013 was influenced by $A_{T}$-rich seawater, brine expulsion and ikaite dissolution in the top 30 cm of sea ice, combined with less glacial-water influence. High carbonate ion concentrations may trigger the precipitation of ikaite in sea ice. It is interesting that ikaite was not identified in any 2012 samples although the $[\text{CO}_3^{2-}]$ was relatively high in the top 10 cm in the ice in 2012, even higher than in 2013. Ikaite typically precipitates at temperatures below $-2^\circ\text{C}$, thus the colder and more saline ice in 2013 with high brine concentrations of chemical solutes in sea ice and brine such as $[\text{CO}_3^{2-}]$, had a more favorable environment for ikaite precipitation than in the relatively warmer and fresher sea ice in 2012, which possibly had the presence of ikaite before the sampling in March/April. Dolomite was found in the snow in 2012, which could explain the high $[\text{CO}_3^{2-}]$ in the upper 10 cm of the ice in 2012.

Ikaite in sea ice has previously been observed and explained to result in $A_{T}$:S ratios up to 84 in winter sea ice, which is clearly elevated compared to the UIW $A_{T}$:S of 71 in the Canadian Arctic (Fransson and others, 2013). Rysgaard and others (2009) also found a $A_{T}$:S ratio in wintertime sea ice of up to 84, which was explained to be caused by ikaite dissolution. In Kongsfjorden, $A_{T}$:S ratios up to 73 were found in land-fast sea ice in March/April, elevated from the $A_{T}$:S of 66 (Fransson and others, 2015b). This supports our findings from this study that ikaite dissolution in sea ice explained the excess sea ice $A_{T}$:S ratios between 66 and 84 (Fig. 8c). Fransson and others (2013) reported $A_{T}$:S ratios between 87 and 97 in frost flowers in the Canadian Arctic in November and March (Fransson and others, 2013). This suggest that $A_{T}$:S ratios between 84 and 100 in our study may have been a result from upward-transported brine, including ikaite crystals, which were then subsequently introduced to the top sea ice. This mechanism could explain the excess $A_{T}$:S ($<100$) and $[\text{CO}_3^{2-}]$ in the top 10 cm in the ice in 2012 (Fig. 7; Fig. 4c). Although no ikaite crystals were identified, there may have been ikaite crystals at an earlier stage that were rapidly dissolved due to CaCO$_3$ undersaturation and melting, or too small to discover.

Ikaite can either become trapped in the sea-ice matrix and later dissolve (gain of [CO$_3^{2-}$]) or escape from the ice and dissolve further down in the water column (loss of [CO$_3^{2-}$]; Fransson and others, 2013). Such a loss may explain the low sea ice $[\text{CO}_3^{2-}]$$_{\text{norm}}$ relative to seawater values found in 2013 (Fig. 8a). Decreased
[CO$_3^{2-}$] and Ω were reported in the upper 2 m surface layer in the Canadian Arctic Archipelago in March by Fransson and others (2013), which was explained to be due to ikaite precipitation within the sea ice and the downward expulsion of CO$_2$-rich brine, increasing surface-water pCO$_2$ and decreasing Ω. In May, increased [CO$_3^{2-}$] and Ω were observed in the upper 2 m, mainly due to ikaite dissolution in the surface water (Fransson and others, 2013). In 2012, most of the sea ice indicated an excess (gain) of [CO$_3^{2-}$], while in 2013 both excess and loss of [CO$_3^{2-}$] were observed (Fig. 8a). The [CO$_3^{2-}$]$_{norm}$ of seawater was 100 at the salinity of 34.9, meaning that the excess [CO$_3^{2-}$] in sea ice varying between 50 and 370 μmol kg$^{-1}$ was due to dissolved carbonate minerals. Rysgaard and others (2013) found that dissolved ikaite contributed by as much as 900 μmol kg$^{-1}$ to [CO$_3^{2-}$] at the

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**Fig. 8.** Plots of δ$^{18}$O (‰) vs (a) salinity normalized [CO$_3^{2-}$] to a seawater reference salinity of 34.9 ([CO$_3^{2-}$]$_{norm}$, μmol kg$^{-1}$), (b) salinity normalized [HCO$_3^{-}$] to a seawater reference salinity of 34.9 ([HCO$_3^{-}$]$_{norm}$, μmol kg$^{-1}$) and (c) the ratio between total alkalinity and salinity (A$_T$:S) in sea ice (ice), glacier ice (glacial) and seawater (sw) in 2012 and 2013. Dashed line in Figure 8a and 8b shows the dilution line between the seawater values and the glacial values assuming zero [CO$_3^{2-}$] and [HCO$_3^{-}$], respectively, at zero salinity in glacier ice. Blue dashed box in Figure 8c denotes the glacial-water transported dolomite dissolution area; magenta dashed box denotes the area where ikaite and calcite dissolution is the main explanation for the A$_T$:S values, which refer to literature A$_T$:S values for the maximum ikaite dissolution of 84 in sea ice and 97 in frost flowers (Fransson and others, 2013, 2015b; Rysgaard and others, 2013), and the seawater value of 66 (black, Fransson and others, 2015a). The fractionation between sea ice and seawater, ε, is denoted with a black arrow in Figure 8c.
ice surface, and to ~100 μmol kg⁻¹ at the ice bottom. Gelfus and others (2016) estimated that up to 167 μmol kg⁻¹ of [CO₃²⁻] in sea ice was due to ikaite dissolution and Fransson and others (2013) found [CO₃²⁻] values between 300 and 600 μmol kg⁻¹ due to the dissolved ikaite.

The relatively large supply of [CO₃²⁻] and an elevated Aₜ as a result of dolomite dissolution near the glacier front in 2012 compared to in 2013 was further confirmed by the calculated Aₜ concentration in brine (A_brine). In April 2012, the A_brine (Fig. 9a) in the top 30 cm were higher at the glacier front compared to the other stations. This was not observed in the following year, but the A_brine was clearly elevated in the top 30 cm of the ice at all other locations in the fjord in April 2013 (Fig. 9b). This supports the idea that different conditions resulted in the excess Aₜ between the two study years. The sea ice contained five times more glacial meltwater in 2012 than in 2013, resulting in the largest excess Aₜ at the glacier front. One explanation for the increased FMW in the upper 10 cm of the sea ice observed in 2012, between station 3 and the ice edge (station 5), together with high salinity, [CO₃²⁻], DIC, Aₜ and negative (−60) δ¹⁸O, could be a result of snow-ice formation including ikaite (Granskog and others, 2017), and not due to dissolution of dolomite transported by either meteoric water or wind. In 2013, the high A_brine at all stations except at the glacier front, was explained by progressing ice formation that caused incorporation of seawater and dissolution of ikaite.

**Table 3.** Mineral composition of particles identified in sea ice, snow, and glacier ice in April 2012 and April 2013

<table>
<thead>
<tr>
<th>Month/year</th>
<th>Type of sample</th>
<th>Station#</th>
<th>Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 2012</td>
<td>Snow 3</td>
<td></td>
<td>Dolomite, calcite, quartz</td>
</tr>
<tr>
<td>April 2012</td>
<td>Snow 4</td>
<td></td>
<td>Mainly dolomite, quartz</td>
</tr>
<tr>
<td>April 2012</td>
<td>Glacier ice 1</td>
<td></td>
<td>Dolomite, calcite, quartz</td>
</tr>
<tr>
<td>April 2012</td>
<td>Sea ice 1-5</td>
<td></td>
<td>No data</td>
</tr>
<tr>
<td>April 2013</td>
<td>Snow 2.4</td>
<td></td>
<td>Calcite, aragonite, lots of ikaite</td>
</tr>
<tr>
<td>April 2013</td>
<td>Glacier ice 1</td>
<td></td>
<td>Calcite, calcite crystals not dissolved ikaite</td>
</tr>
<tr>
<td>April 2013</td>
<td>Sea ice 3</td>
<td></td>
<td>‘bedrock-transported-like’, sulphate mineral</td>
</tr>
</tbody>
</table>

**Implications for CO₂ fluxes**

Precipitation and dissolution of ikaite have consequences for CO₂ concentrations in the brine and CO₂ gas exchange. The ikaite crystals found in 2013 in the upper 30 cm of the ice indicates that precipitation had taken place in the sea ice, resulting in release of CO₂ to the brine. However, the sea ice in April 2013 was not permeable (BV<0.05) in the top ice, hence no CO₂ exchange with the atmosphere occurred. The brine pCO₂ (Table 2) was higher (above 700 μatm) than atmospheric pCO₂ (~400 μatm) in both years. The highest pCO₂ of 11 000 μatm observed in the brine could be explained by local effects, such as bacterial respiration producing CO₂. The presence of locally distributed bacteria was suggested by Fransson and others (2015b) to be partly responsible for the elevated brine pCO₂, ranging between 2983 and 18 139 μatm (median of 10 561 μatm) in a wintertime sea-ice study in Kongsfjorden in Svalbard. Miller and others (2011) reported high brine pCO₂ > 20 000 μatm, using silicone cone chamber sampler (‘peepers’) to absorb CO₂ from the brine and measure pCO₂, in the Canadian Arctic winter, where low sea-ice temperatures below −15°C resulted in low BV and high concentrations in the brine. In our study, the sea ice was warmer, and BV was larger in April 2012, than in the study by Miller and others (2011), hence higher brine pCO₂ could have been expected. The reason for the lower pCO₂ than expected, was likely due to brine-CO₂ transport through expulsion to the bottom ice (BV >0.05), where CO₂ could escape to the underlying water, so-called brine pump, or escape to the top ice and atmosphere, particularly in April 2012.

Due to relatively cold temperatures and low BV, the sea ice in April 2013 was mostly impermeable (BV<5%) for gas transfer, limiting exchange with the atmosphere, such that no CO₂ exchange may have occurred at this time. However, the CO₂ exchange could have occurred during new ice formation, earlier than our observations. The maximum pCO₂ of 1600 μatm in sea ice in April 2013 indicated a limited exchange with the surrounding, whereas in April 2012, the maximum sea-ice pCO₂ was similar to that in UIW (Table 2). The top 10 cm ice in 2012 had high carbonate ion concentrations and BV >5% (permeable), allowing gas exchange, except for at the glacier front. The maximum pCO₂ in snow was 5344 μatm (Table 2), suggesting brine-CO₂ upward expulsion and/or ikaite precipitation mixed with snow at the ice surface, and CO₂ exchange with the atmosphere. In the future climate warming scenario, the ice will become warmer, thinner and more porous and allow for increased gas permeability. However, with increased freshwater incorporated in the sea ice, the permeability may decrease. In April 2013, the bottom sea ice showed signs of ongoing primary production, which was not significant in the thinner sea ice of 2012 (Fransson and Chierici, unpublished data). The high [NO₃⁻] values observed at the bottom ice can be either explained by brine rejection or by seawater intrusions at the ice/water interface. High [NO₃⁻] was observed mostly in the thicker and more sea-water influenced sea ice in April 2013, compared to the thinner ice of April 2012, which could explain the primary production in the bottom ice. The warmer ice (BV>5%) will have increased potential for CO₂ exchange with atmosphere and water (increased mobility in warm ice). Bacterial respiration and the turnover rate of the microbial carbon loop in sea ice may increase at higher temperatures (e.g. Torstensson and others, 2015), hence outgassing or the transport of CO₂ to the surface water may continue. On the other hand, a fresher source water resulted in less formation of dense CO₂-rich brine derived from ikaite formation and decreased transport of CO₂ to underlying water through the brine pump.

**Scenarios of warming and increased glacial meltwater**

Projections of climate change towards the end of the century show a large increase of annual runoff, caused mainly by increased glacial melting in response to strong warming, and to increased precipitation associated with the warming (Hansen-Bauer and others, 2019). The Svalbard archipelago is covered by ~60% glaciers, all of which are retreating over decadal timescales, and all of which are losing mass (e.g. Kohler and others, 2007; Moholdt and others, 2010). This mass loss is mainly caused by increased melting through warming (e.g. Kohler and others, 2007), thus increasing the freshwater and sediment supply to the nearby fjords and ocean. In future, warming of the air and ocean increases the melting of glaciers, ice caps and sea ice and increase river runoff in the Arctic. Consequently, this results in increased freshwater content in the surface water and sea ice, affecting the sea-ice physical and chemical characteristic and biogeochemical processes. This will have further consequences for brine rejection from sea ice, carbon transport and ocean...
circulation, biological processes, air-sea CO2 exchange and ocean acidification.

In our study, the colder winter 2013 led to more sea-ice formation and more brine formation, which in turn resulted in haline convection. This convection explained the elevated salinity above 35 observed under the sea ice in the top 5 m in April 2013 (Fransson and others, 2015a). Haline convection likely decreases because of increased freshwater runoff, similar to the situation in Tempelfjorden in winter 2012 (Fransson and others, 2015a). Ultimately this results in less wintertime mixing of water and stronger surface stratification when sea ice melts and additional meltwater is added from the glaciers. This may also cause less nutrient addition from subsurface waters, hence less primary production. Another consequence of increased freshwater runoff is the increased silt and sediment load to the fjord, which restricts light and limits primary production, as has been found near the glacier fronts in Kongsfjorden (Halbach and others, 2019). Increased freshwater fluxes enhances ocean acidification and decreases CaCO3 saturation states, as observed on the freshwater-influenced shelves in the Canadian Arctic (Chierici and Fransson, 2009) as well as in Kongsfjorden (Fransson and others, 2016). Decreased biological CO2 consumption and possibly less contribution from buffering ions from ikaite dissolution will have a positive feedback on ocean acidification.

Conclusion

The two contrasting winters clearly showed that the amount of freshwater content in the fjord influenced the chemical and physical characteristics of sea ice. It was obvious that the lowest alkalinity, δ18O and nitrate, and the highest silicate concentrations at the glacier front coincided with the highest freshwater fractions. Glacial and sub-glacial meltwater contributed to alkalinity in April 2012 due to the incorporation of carbonate minerals (mainly from dissolved calcite and dolomite) originating from the bedrock-influenced glacial freshwater runoff. The result of dissolved ikaite due to sea-ice processes was the main cause of the elevated alkalinity relative to salinity in the sea ice in April 2013. Since ikaite has a seawater source, precipitates in sea ice, and dissolves in the melted sea ice, brine or in underlying water, CO2 is either produced or consumed, depending on the season. This means that the magnitude as well as the net effect of CO2 exchange with the surrounding environment is difficult to predict. Regarding the bedrock-derived carbonate minerals added from an external source and not produced in sea ice, the net effect will be decreased CO2 since these minerals contribute to the seawater buffering capacity against CO2, when dissolved. This study demonstrated that the different sources and species of CaCO3 minerals play an important role in determining the final impact in the water-column chemistry. Moreover, dolomite dissolution produces twice as many bicarbonate ions as ikaite (and calcite), and hence contributes twice as much to alkalinity and buffering capacity in the water column compared to ikaite and calcite dissolution. As a result of the contrasting winters in Svalbard, glacial-water influenced fjords are affected by carbonate-rich bedrock. Accordingly, these fjords can be considered as climate laboratories and be used to project climate-change effects in other freshwater-influenced areas, such as Greenland fjords and shelves, and the shallow shelves of the Canadian Arctic Archipelago. In the context of retreating glaciers, ice caps and increased meltwater in the Arctic Ocean and fjords, the result from this study suggests that in a warmer climate, with increased glacial melt, sea ice would be formed in the fresher water, potentially with less ikaite in the sea ice and a larger influence of bedrock minerals on sea ice and water. Regardless of the specie of carbonate mineral, the contribution to the water column increases ocean CO2 uptake due to increased buffer capacity.

Fig. 9. Vertical profiles of brine-volume corrected total alkalinity (ATBr, μmol kg⁻¹) of the chemical variables in April 2012 and April 2013 along the section in the fjord, from the glacier front (GF, station #1) to station #5.
Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1017/aog.2020.52.

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