An influx of glacial meltwater has the ability to alter the properties of marine surface waters and their ability to exchange CO₂ through changes to water column stratification and the inorganic carbon system. Here, we report how inputs of meteoric water affect the physical and biogeochemical properties of both the water column and the sea ice cover on the Wandel Sea shelf, northeastern Greenland, during spring 2015. The observed depleted δ18O-H₂O in the water column, with surface water values as low as −16.3 ‰, suggests a strong input of meteoric water (i.e., water derived from atmospheric precipitation). Depleted δ18O-H₂O observed within sea ice (from −21.5 to −8.0 ‰) reflects its formation from surface water that was already depleted isotopically. In addition, a thick snow cover, as present during the study, promotes the formation of snow ice as well as insulates the ice cover. Within sea ice, the resulting relatively warm temperature and low salinity impedes ikaite formation. However, measurements of total dissolved inorganic carbon and total alkalinity indicate that, in both sea ice and the water column, the dissolution of calcium carbonate was the main process affecting the carbonate system. This finding suggests that inputs of glacial meltwater deliver glacier-derived carbonate minerals to the ocean which become incorporated within the ice structure, increasing calcium carbonate dissolution in the water column in the absence of ikaite precipitation within the sea ice. If widespread in glacial-fed waters, bedrock carbonate minerals could increase CO₂ sequestration in glacial catchments despite the weakening of the sea ice carbon pump.

Keywords: Sea ice, Glacier, Meteoric water, CO₂

1. Introduction
Globally, the rate of mass loss from glaciers is accelerating (Rignot et al., 2011). Increasing glacier meltwater discharge is predicted to fundamentally change hydrography and marine productivity, with consequences on sea level (e.g., Pattyn et al., 2018), ecosystems (Meire et al., 2015), and biogeochemical cycles (Evans et al., 2014; Meire et al., 2016). For instance, subglacial meltwater discharge from the Greenland Ice Sheet has increased nutrient and iron concentrations, primary production, and carbon uptake near glacial fronts in Greenlandic fjords (Statham et al., 2008; Sejr et al., 2011; Meire et al., 2016). Glacial meltwater discharge has also been suggested to play a central role in the CO₂ dynamics of the coastal environment, resulting in a strong undersaturation with respect to atmospheric CO₂ and hence enhancing its uptake (Rysgaard et al., 2012; Evans et al., 2014; Meire et al., 2015). Meltwater supply may affect surface water chemistry, both through dilution of some compounds (e.g., major ions) and addition of others (e.g., minerals from bedrock erosion). High concentrations of dissolved silica (Meire et al., 2016) and increases of both total dissolved inorganic carbon (DIC) and total alkalinity (TA) have been observed in glacial fjords (Sejr et al., 2011; Fransson et al., 2015). In addition, export and dissolution of carbonate-rich bedrock in the surface water have been shown to partly mitigate the effect of ocean acidification (Fransson et al., 2015).

Increasing freshwater inputs also have the potential to affect the formation and physical and biogeochemical properties of sea ice. Lower surface seawater salinity at the time of sea ice formation will result in lower bulk sea ice salinity and brine volume content, which in turn decreases sea ice permeability and its ability to exchange matter (e.g., salts, nutrients, gases) with the atmosphere and/or the underlying water column. This decreased exchange capacity will then impact surface water...
stratification (Nilsen et al., 2008). As sea ice forms, most dissolved components are rejected at the advancing ice–water interface, promoting the release of dissolved gases and solutes to the water column (Papadimitriou et al., 2004). However, some impurities are retained and concentrated into brine inclusions or as gas bubbles within the solid ice matrix. As sea ice thickens, changes in sea ice temperature and salinity increase the concentration of solutes within brines, decreasing the gas solubilities which support the formation of gas bubbles within sea ice (Zhou et al., 2013), and trigger the precipitation of minerals, including ikaite, a metastable form of calcium carbonate (CaCO$_3$.6H$_2$O; Dieckmann et al., 2008). Ikaite precipitation within sea ice brines produces CO$_2$(aq) and reduces both TA and DIC in a ratio of approximately 2:1 (Geilfus et al., 2016).

During sea ice growth, CO$_2$-enriched brines are rejected from the sea ice cover both upward to the atmosphere, resulting in a release of CO$_2$ toward the atmosphere (Geilfus et al., 2013; Fransson et al., 2015), and downward to the water column, resulting in the transport and possible sequestration of CO$_2$ at depth (Anderson et al., 2004; Rysgaard et al., 2007). During sea ice melt, increasing sea ice temperature, decreasing bulk ice salinity, and ikaite dissolution result in a decrease in the partial pressure of CO$_2$ (pCO$_2$) within sea ice brine and surface seawater, promoting the uptake of atmospheric CO$_2$ (Rysgaard et al., 2012; Geilfus et al., 2015). This drawdown of the pCO$_2$ is also enhanced by the development of a biological (photosynthesizing) community at the bottom of the sea ice. Ikaite export from sea ice to the water column where it dissolves has been observed to increase the calcium carbonate saturation state within seawater (Geilfus et al., 2016) with the potential to counteract the effect of ocean acidification. Here, ikaite precipitation and potential export will be affected by warmer temperatures or increasing inputs of freshwater into the marine environment, however, is unknown.

A common way to estimate the relative contribution of meteoric water in the marine environment is to use the stable isotope composition of oxygen in water, $\delta^{18}$O–H$_2$O (herein referred to as $\delta^{18}$O; Macdonald et al., 1995; Eicken, 1998; Alkire et al., 2015). The $\delta^{18}$O is typically expressed in ‰, relative to Vienna Mean Standard Ocean Water, as:

$$
\delta^{18}O(\%o) = \left( \frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \right) \times 1000, \tag{1}
$$

where $R = ^{18}O/^ {16}O$. Both equilibrium thermodynamic and kinetic effects favor the accumulation of lighter isotopes of water in the vapor phase and heavier isotopes in the liquid phase (Craig and Gordon, 1965). As water molecules travel toward the poles, repeated cycles of evaporation and precipitation cause polar latitude meteoric waters to be highly depleted in $^{18}$O relative to $^{16}$O, resulting in more negative $\delta^{18}$O values in meteoric water compared to seawater. As such, glacial ice has a typical $\delta^{18}$O ranging from $\approx$20 ‰ to $\approx$30 ‰, with some values as low as $\approx$40 ‰ (Dansgaard and Tauber, 1969; Johnsen et al., 2001). In contrast, sea ice formation slightly favors heavier isotope incorporation into the solid phase, with an apparent fractionation factor ($\epsilon_{\text{app}}$) ranging from 1.9 to 2.3 ‰ (Souchez et al., 1988; Macdonald et al., 1995; Eicken, 1998). The term $\epsilon_{\text{app}}$ is used here and in previous publications to underscore that, despite the occurrence of equilibrium fractionation ($\epsilon_{\text{eq}} = 3$ ‰) at the freezing interface, the impact of the growth rate of the sea ice on the seawater isotopic signature at the freezing interface and the heterogeneous nature of the sea ice (brine inclusions) results in an observed (apparent) fractionation that differs (is generally lower) from equilibrium (Souchez et al., 1988; Eicken, 1998). Glacial and sea ice meltwater thus have $\delta^{18}$O values distinguishable from that of seawater ($\delta^{18}$O of approximately 0 ‰).

In this study, we investigated how meteoric water inputs can affect inorganic carbon transport in sea ice and CO$_2$ exchange between sea ice and the underlying seawater. Based on $\delta^{18}$O and salinity measurements, we estimated the contribution of meteoric water in the marine environment, while the carbonate system, including precipitation–dissolution of ikaite, was estimated based on TA and DIC measurements.

2. Methods

2.1. Study area

Between May 5 and 21, 2015, we sampled 13 first-year sea ice (FYI) and 2 multiyear sea ice (MYI) sites on the Wandel Sea shelf, in the vicinity of the Villum Research Station (VRS; Figure 1; Table 1), located at the Danish military outpost Station Nord (81°36′N, 16°40′W) in the northeastern corner of Greenland. The Wandel Sea is predominantly covered by landfast MYI year round, yet it is strongly influenced by freshwater that originates from the summer snow melt, sea-ice melt (Dmitrenko et al., 2017), and glacial melt and runoff (Willis et al., 2015; Bendtsen et al., 2017). Fjord interiors may become ice-free during late summer forming open water separated from the deep ocean by an MYI landfast ice fringe (about 3.5 m or thicker) present throughout the year (Dmitrenko et al., 2017; Kirillov et al., 2017). This ice fringe has been suggested to trap meltwater from sea ice, snow, and glaciers that accumulates in the surface layer of the inner part of the Wandel Sea (Dmitrenko et al., 2017; Kirillov et al., 2017). Several outlets of the Greenland Ice Sheet, including the Flade Isblink ice cap, are draining both subglacial and surface meltwater into the Wandel Sea via marine-terminating glaciers (Palmer et al., 2010). The Flade Isblink ice cap represents a surface area of approximately 5,000 km$^2$ with a maximum ice thickness of about 600 m overlying the bedrock at an average of 100 m below the sea level (e.g., Palmer et al., 2010; Rinne et al., 2011). Dmitrenko et al. (2017) suggested that the water column on the Wandel Sea shelf was composed of 6 distinct layers (Figure 2). Immediately below the ice cover (top 2.5 m), the first layer has its temperature slightly increasing and salinity decreasing with depth to reach local maxima and minima, respectively, at about 2.5 m depth. Low surface salinities are due to summer snow melt, sea ice melt, and freshwater from glacial melt (Bendtsen et al., 2017; Dmitrenko et al., 2017). During the melt season, this layer freshens to salinities between 1 and 8 (Bendtsen et al.,...
Below the surface layer, the subsurface halocline is characterized by a strong vertical salinity gradient down to about 15-m depth (Figure 2). This layer separates the fresh surface water layer from a layer with weak vertical salinity gradients and temperature near the freezing point, reaching about 75-m depth. Dmintrenko et al. (2017) refer to this layer as the “halostad.” Below the halostad, seawater temperatures increase through the halocline and Atlantic modified water. The halocline is further distinguished from the halostad and the Atlantic modified polar water by its high vertical salinity gradient. Seawater temperatures eventually exceed 0°C, the commonly accepted upper boundary of the Atlantic water, at approximately 140-m depth, indicating the presence of modified Atlantic Water below this depth.

2.2. Sampling procedure
At each site, snow thickness was measured and a temperature profile within the snow cover was established at vertical intervals of 5–10 cm using a calibrated temperature probe (Testo 720, Lenzkirch, Germany, ± 0.1°C precision). Snow was sampled on three occasions (FYI-1, FYI-2, and MYI-1; Table 2), while snow-ice slush was sampled opportunistically (stations FYI-1, FYI-2, FYI-6, FYI-8, and MYI-1). Samples of both snow and slush were collected using Ziplock bags for determination of salinity, \( \delta^{18}O \), TA, and DIC. Sea ice cores were collected using a MARK II coring system (internal diameter = 9 cm, Kovacs Enterprises, Roseburg, OR, USA) and analyzed for similar parameters as in snow and slush. Immediately after extraction of the cores, sea ice temperature was measured in situ using the same temperature probe inserted into predrilled holes (5-cm intervals), perpendicular to core sides. Cores were then cut into 5- to 10-cm sections and stored in sealed plastic containers. Samples were allowed to freeze during transit back to VRS. Opportunistically, we collected glacial ice samples for \( \delta^{18}O \) measurements. Due to low atmospheric temperatures, seawater samples were only collected during shorter sampling days to prevent samples from freezing during transit back to VRS. Seawater at the sea ice interface was collected through a core hole using a peristaltic pump (Cole Palmer, Masterflex...
Environmental Sampler). The water column was sampled at stations FYI-3, FYI-6, and MYI-1 at 3 m, 15 m, and bottom depths (50, 110, and 175 m, respectively) using a 5-L Niskin bottle for δ18O, TA, and DIC. Vertical profiles of water temperature and conductivity were measured with a calibrated SBE-19plus (Sea-Bird Scientific, Bellevue, WA, USA), accurate to ±0.005 °C and ±0.0005 S m⁻¹ (Dmitrenko et al., 2017). Air temperature data were taken from Greenland Survey (Asiaq) meteorological measurements collected at 5-min resolution from a height 9 m above ground at VRS (data available online at https://www2.dmu.dk/asiaqmet/Default.aspx).

Back at VRS, sea ice, glacial ice, snow, and slush samples were placed in gastight plastic bags (nylon/poly; Cabela’s, Sidney, NE, USA) and vacuum-sealed (Hu et al., 2018). Samples were then melted in the dark at <4 °C to minimize the possible dissolution of ikaite crystals. Once melted, meltwater and seawater samples were processed similarly by gently transferring meltwater to gastight vials (12-mL Exetainers, Labco High Wycombe, UK), leaving potential precipitates in the plastic bag. Samples were then poisoned with 12 mL of a solution of saturated HgCl₂ and stored in the dark at room temperature until analysis for TA and DIC. Water aliquots (2 mL) were also collected in glass vials without head space for the determination of δ18O.

2.3. Sample analysis

Salinity was calculated based on conductivity (Grasshoff et al., 1983) measured using a meter (Orion 3-star, Thermo Scientific, Waltham, MA, USA) coupled with a conductivity cell (Orion 013610MD, Thermo Scientific). TA was determined by Gran titration (Gran, 1952) using a TIM 840 titration system (Radiometer Analytical, A/S Scientific, Burlington, Ontario, Canada), consisting of a Ross sure-flow combination pH glass electrode (Orion 8172BNWP, Thermo Scientific) and a temperature probe (Radiometer Analytical, Lyon, France). A 12-mL sample was titrated with a standard 0.05 M HCl solution (Alfa Aesar, Haverhill, MA, USA). DIC was measured on a DIC analyzer (Apollo SciTech, Newark, DE, USA) by acidification of a 0.75-mL subsample with 1 mL of 10% H₃PO₄ (Sigma-Aldrich, Saint-Louis, MO, USA) and quantification of the released CO₂ with a nondispersive infrared CO₂ analyzer (LI-7000, LI-COR, Lincoln, NE). Results were then converted from μmol L⁻¹ to μmol kg⁻¹ based on sample density, which was estimated from salinity and temperature at the time of the analysis. Accuracies of ±3 and ±2 μmol kg⁻¹ were determined for TA and DIC, respectively, from routine analysis of certified reference materials (AG Dickson, Scripps Institution of Oceanography, San Diego, CA, USA). Brine volume was estimated from measurements of bulk ice salinity, temperature, and density according to Cox and Weeks (1983) for temperatures below −2 °C and according to Leppäranta and Manninen (1988) for ice temperatures between −2 °C and 0 °C. The δ18O was measured on an isotope analyzer (L2130-i, Picarro, Santa Clara, CA, USA) with a precision of 0.025 ‰, calculated as the standard deviation from 10 repeated measurements of standard materials.

3. Results

During May 2015, the air temperature ranged from −21.1 °C to −5.1 °C (Figure 3). Following a period of steady temperatures, warming started on May 12, reaching an average air temperature of −11.3 °C for the final sampling days.

Table 1. Sampling dates, locations, and thickness of associated sea ice, snow and slush. DOI: https://doi.org/10.1525/elementa.2021.00004.11

| Station | Day of May 2015 | Latitude (N) | Longitude (W) | Sea Ice Thickness (cm) | Snow Cover (cm) | Slush (cm) |
|---------|----------------|--------------|--------------|-----------------------|----------------|-----------|
| FYI-1   | 5              | 81°40.340    | 16°58.234    | 108                   | 104            | 10        |
| FYI-2   | 7              | 81°40.339    | 16°58.256    | 112                   | 90             | 19        |
| FYI-3   | 10             | 81°23.715    | 17°13.803    | 125                   | 79             | 0         |
| FYI-4   | 10             | 81°29.583    | 17°44.321    | 130                   | 72             | 0         |
| FYI-5   | 10             | 81°31.258    | 17°55.310    | 134                   | 65             | 0         |
| FYI-6   | 13             | 81°40.280    | 16°01.542    | 96                    | 92             | 12        |
| FYI-7   | 13             | 81°39.106    | 16°53.87     | 123                   | 86             | 0         |
| FYI-8   | 13             | 81°37.387    | 16°48.570    | 100                   | 90             | 5         |
| FYI-9   | 17             | 81°40.645    | 16°38.480    | 115                   | 93             | 0         |
| FYI-10  | 17             | 81°46.729    | 16°35.767    | 158                   | 72             | 0         |
| FYI-11  | 19             | 81°43.102    | 17°07.250    | 142                   | 98             | 0         |
| FYI-12  | 21             | 81°32.511    | 17°35.366    | 165                   | 55             | 0         |
| FYI-13  | 21             | 81°34.087    | 16°57.483    | 110                   | 92             | 0         |
| MYI-1   | 15             | 81°46.102    | 16°30.185    | 204                   | 138            | 10        |
| MYI-2   | 19             | 81°49.982    | 17°59.992    | 225                   | 125            | 10        |

FYI = first-year sea ice; MYI = multiyear sea ice.
3.1. Sea ice

The thickness of the ice cover ranged from 96 to 165 cm for FYI (Figure 4) and from 204 to 225 cm for MYI (Figure 5). Both FYI and MYI were nearly isothermal with an ice temperature of $-1.7 \pm 0.7$°C ($n = 140$; arithmetic mean ± standard deviation; same below) for FYI (Figure 4a) and $-0.8 \pm 0.2$°C ($n = 26$) for MYI (Figure 5a). Exceptions were observed for FYI-4 and FYI-5 where the surface ice temperature was considerably colder ($-5.3$°C and $-4.4$°C, respectively). Bulk ice salinity in FYI ranged from 0.8 to 7.2 and exhibited typical C-shaped profiles (Figure 4b; Eicken, 1992). However, averaged bulk ice salinities ($2.5 \pm 1.2, n = 140$) were lower than typical Arctic FYI ($S = 5$, Cox and Weeks, 1974; Carnat et al., 2013). Bulk ice salinity measured in MYI was lower than in FYI with values ranging from 0 to 0.6 ($0.2 \pm 0.2$, $n = 32$; Figure 5b), typical for MYI (Cox and Weeks, 1974).

Brine volume fraction in FYI had a similar C-shaped profile as for the bulk ice salinity (Figure 4c), with higher brine volume content (up to 17.5%) occurring in both the surface and bottom layer of the ice cover. Both surface and bottom layers of the ice cover had a brine volume content above the permeability threshold (i.e., 5%; Golden et al., 2007), except for FYI-4, FYI-5, and FYI-6 where a brine volume content below the permeability threshold was estimated for most of the ice.
column. This lower brine volume content was supported by lower ice salinity for FYI-4 and FYI-5 and the lower bulk ice salinity for FYI-6. In MYI, the low bulk ice salinities supported a brine volume content below the permeability threshold, with values ranging from 0 to 3.5% (Figure 5f).

FYI δ18O ranged from −21.5 to −8.0‰ (−11.9 ± 2.9‰, n = 137; Figure 4d), much lower than typical values (−8 to 2‰) reported for Arctic FYI (Carnat et al., 2013; Alkire et al., 2015). The lowest values were observed in the upper layer of the ice cover. The δ18O values increased downward throughout the ice cover and remained relatively constant toward the bottom of the cores, ranging from −11.4 to −8.0‰ (−9.6 ± 1.2‰, n = 55), except FYI-6 where the δ18O values remained low (mean = −15.0‰). MYI δ18O values ranged from −11.7 to −8.2‰ (−9.8 ± 0.9‰, n = 32). Profiles for MYI δ18O remained relatively constant throughout the entire ice thickness (Figure 5c).

TA and DIC concentration in FYI ranged from 116 to 595 μmol kg⁻¹ (236 ± 79 μmol kg⁻¹, n = 140) and from 108 to 515 μmol kg⁻¹ (221 ± 74 μmol kg⁻¹, n = 140), respectively (Figure 6). Both TA and DIC showed C-shaped profiles similar to that of bulk ice salinity, with maximum concentrations in the upper layer of the ice cover. Lower concentrations were found in MYI, ranging from 50 to 110 μmol kg⁻¹ (80 ± 13 μmol kg⁻¹, n = 31) for TA and from 56 to 106 μmol kg⁻¹ (75 ± 18 μmol kg⁻¹, n = 30) for DIC (Figure 5d and e).

3.2. Snow and slush
The snow cover over the ice ranged from 55 to 138 cm (90 ± 21 cm, n = 13) with thicker snow over MYI than over FYI (Table 1). The snow cover exhibited a strong temperature gradient with colder temperatures observed at the interface with the atmosphere (minimum = −16.8°C) and warmer temperatures, similar to those observed at the sea ice surface layer, at the snow-ice interface (data not shown). Averaged over the entire snow thickness (Table 2), snow was fresh (5 of approximately 0), had low TA and DIC (72 and 46 μmol kg⁻¹, respectively), and low δ18O (−26‰).

At a few stations (FYI-1, FYI-2, FYI-6, FYI-8, and MYI-1), a slush layer was visually observed at the base of the snow cover. Slush thickness ranged from 5 to 19 cm while salinity ranged from 30.9 to 515 μmol kg⁻¹, DIC from 542 to 2,167 μmol kg⁻¹, and heavy isotope depleted δ18O from −18.3 to −14.5‰ (Table 2).

3.3. Underlying seawater
Low sea surface salinities are associated with low TA (from 1,725 to 1,831 μmol kg⁻¹), DIC (from 1,639 to 1,737 μmol kg⁻¹), and δ18O (from −15.8 to −8.5‰; Figure 2). As the salinity increased with depth, TA, DIC, and δ18O increased as well. Temperature, salinity, TA, and DIC profiles appear homogeneous across the Wandel Sea, whereas δ18O profiles are more variable. FYI-3 and FYI-6

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Table 2. Snow and slush (when present) properties, averaged ± 1 standard deviation, over the entire thickness at the stations sampled. DOI: https://doi.org/10.1525/elementa.2021.00004.t2

| Sample | Station | Salinity | Total Alkalinity (μmol kg⁻¹) | Dissolved Inorganic Carbon (μmol kg⁻¹) | δ18O (%) |
|--------|---------|----------|------------------------------|---------------------------------------|----------|
| Snow   | FYI-1   | 0.1 ± 0.3 (n = 8) | NA°                         | NA°                                   | −26.7 ± 3.1 (n = 8) |
| FYI-2  | 0.0 ± 0.0 (n = 5) | 71 ± 5 (n = 5) | 46 ± 5 (n = 5) | −26.6 ± 2.7 (n = 5) |
| MYI-1  | 0.0 ± 0.0 (n = 9) | 73 ± 8 (n = 9) | 46 ± 3 (n = 9) | −24.5 ± 2.9 (n = 9) |
| Slush  | FYI-1   | 30.9      | 2,259                        | 2,167                                 | −15.0    |
| FYI-2  | 12      | 799      | 746                          | −14.5                                |
| FYI-6  | 15.5    | 1,095    | 1,053                        | −18.3                                |
| FYI-8  | 15.5    | 1,137    | 1,082                        | −15.3                                |
| MYI-1  | 6.6     | 561      | 542                          | −14.6                                |

FYI = first-year sea ice; MYI = multiyear sea ice.

°Parameters are not analyzed.
exhibited different profiles with more depleted $\delta^{18}O$ values at FYI-6 compared to FYI-3 (Figure 2d). Surface water from MYI-1 had similar $\delta^{18}O$ as FYI-6 ($-15.9$ and $-16.3\, ^{\circ}/oo\), respectively), which increased with depth to reach similar $\delta^{18}O$ values as in FYI-3. At depth, the presence of modified Atlantic Water was confirmed by the slightly enriched water ($\delta^{18}O = 0.6\, ^{\circ}/oo\) observed at MYI-1.

### 4. Discussion

#### 4.1. Meteoric water contribution to the water column

The coastal marine environment of the Wandel Sea shelf appears to be under strong influence of meteoric water as depleted $\delta^{18}O$ values were observed for both the water column (Figure 2d) and the ice cover (Figures 4d and 5c). As
sea ice mainly forms from freezing seawater, we first discuss the $\delta^{18}$O profiles observed within the water column. Measurements of $\delta^{18}$O, together with salinity, are used to estimate contribution of meteoric water (e.g., river input, glacial meltwater, and precipitation as snow or rain) and sea ice melt in the water body (Macdonald et al., 1995). As the study site is located in the northern Greenland (Figure 1), snow falling on the sea ice cover or making up glaciers is similarly depleted in $\delta^{18}$O relative to seawater. Therefore, we assume that any input of meteoric water will present similar $\delta^{18}$O and salinity, making it difficult to distinguish meteoric watersources from one another. We gather them under the term “meteoric water.” The water column can be viewed as a mixture of meteoric water (glacial meltwater, snow melt, and river input), sea ice melt, and saline seawater (Equation 1). These 3 primary water end-members require us to assign 2 conservative properties (salinity and $\delta^{18}$O) for each of the end-members to determine the water composition of our samples. Therefore, we use the following mass balance equations (Equations 2–4):

$$f_{si} + f_{mw} + f_{sw} = 1,$$  \(2\)

$$\left( S_{si} \times f_{si} \right) + \left( S_{mw} \times f_{mw} \right) + \left( S_{sw} \times f_{sw} \right) = S_{sample},$$  \(3\)

$$\left( \delta^{18}O_{si} \times f_{si} \right) + \left( \delta^{18}O_{mw} \times f_{mw} \right) + \left( \delta^{18}O_{sw} \times f_{sw} \right) = \delta^{18}O_{sample},$$  \(4\)

where the subscript refers to the three end-members, meteoric water (mw), sea ice melt (si), and unmodified seawater (sw); $f$ is the fraction of each water end-member; and $S$ and $\delta^{18}$O correspond to the salinity and $\delta^{18}$O, respectively, of the subscripted end-members. $S_{sample}$ and $\delta^{18}O_{sample}$ refer to the observed values (Figure 2). Based on the relationship between $\delta^{18}$O and salinity (Paren and Potter, 1984; Figure 7), we estimated the three end-member properties ($S$ and $\delta^{18}$O) contributing to the water budget in the area; using Equations 2–4, we

Figure 5. Multiyear sea ice (MYI) properties. Vertical profiles of (a) temperature ($^\circ$C), (b) bulk ice salinity, (c) $\delta^{18}$O (%o, the dashed line corresponds to the averaged surface seawater), (d) total alkalinity (μmol kg$^{-1}$), (e) dissolved inorganic carbon (μmol kg$^{-1}$), and (f) brine volume content (%) within MYI. DOI: https://doi.org/10.1525/elementa.2021.00004.f5
estimated the relative contribution of each of the 3 endmembers to the water budget, as illustrated in Figure 2. Melted sea ice and meteoric water end-members correspond to the averaged salinity and \( \delta^{18}O \) measured within FYI (\( S_{\text{si}} = 2.5 \) and \( \delta^{18}O_{\text{si}} = -12.9 \) ‰) and the snow cover (\( S_{\text{mw}} = 0, \delta^{18}O_{\text{mw}} = -25.8 \) ‰), respectively. The depleted \( \delta^{18}O \) observed in the water column (Figure 2) suggests a strong impact of meteoric water, except at 175-m depth at MYI-1 location where “unmodified” Atlantic Water with positive \( \delta^{18}O \) (0.6 ‰) was observed. Therefore, we chose to use the Atlantic Water mass properties (\( S_{\text{sw}} = 34.7, \delta^{18}O_{\text{sw}} = 0.6 \) ‰) for the seawater end-member. The mixing lines between sea ice, meteoric water, and seawater end-members (Figure 7, dotted lines) define a space where water samples would plot within, if they are a mixture of these three components.

Surface water at MYI-1 and FYI-6 exhibited highest meteoric water contribution (\( f_{\text{mw}} = 0.965 \) and 0.926, respectively), with lower contribution of unmodified seawater (\( f_{\text{sw}} = 0.697 \) and 0.626, respectively), and negative contribution of sea ice meltwater (\( f_{\text{si}} = -0.662 \) and \(-0.552 \), respectively; Figure 2). Therefore, surface water at MYI-1 and FYI-6 is made of a mixture meteoric water and unmodified seawater in a ratio 0.72 and 0.67, respectively, and 66–55% of this mixture is removed as ice. Both FYI-3 and FYI-6 seawater profiles are located in the vicinity of the Flade Isblink glacier outlets (Figure 1). However, their contrasting seawater properties illustrate the variable spatial and temporal influence of glacial discharge. The area northwest of Station Nord (e.g., FYI-6) has been suggested to be under strong influence of glacial inputs, even during winter when surface glacial runoff is negligible (Dmintrenko et al., 2017). Subglacial discharge, or submarine thawing glacial ice, has been suggested to affect both seawater temperature and salinity (Dmintrenko et al., 2017), resulting in the strongly depleted \( \delta^{18}O \) and high estimate of meteoric water. In contrast, the area west-southwest of Station Nord (e.g., FYI-3) has been suggested to be less impacted by glacial discharge and more representative of open water conditions (Dmintrenko et al., 2017). Less depleted \( \delta^{18}O \) observed in this area, associated with lower \( f_{\text{mw}} \) (0.18) and \( f_{\text{si}} \) (0.32) and higher \( f_{\text{sw}} \) (0.50), confirm these conclusions.
The water column at FYI-6 and surface seawater from MYI-1 exhibited strongly depleted δ18O values and high estimates of fmw (Figure 2). However, their salinities are higher than those expected from the mixing line between the unmodified seawater and meteoric water end-members (blue squares below mixing line in Figure 7). Therefore, we suggest that an additional process is responsible for decoupling the salinity from the δ18O values for these samples. Figure 7b and c illustrates how seawater freezing impacts both the salinity and δ18O of the residual seawater (Ssw,res and δ18Osw,res, respectively). From the mixing line between the unmodified seawater and meteoric water end-members, we selected 3 water masses at different salinity and δ18O values (Ssw,i = 15, 20, and 25; δ18Osw,i = –14.1, –10.3, and –6.6 ‰, respectively; Figure 7b and c). Assuming that 10, 20, 30, 40, and 50% of the water mass freezes (f), we estimated both the residual Ssw,res and δ18Osw,res as:

\[ S_{sw,\text{res}} = \frac{S_{sw,i} - (f \times S_{ice})}{1 - f} \]

\[ \delta^{18}O_{sw,\text{res}} = \frac{\delta^{18}O_{sw,i} - (f \times \delta^{18}O_{ice})}{1 - f} \]

To solve Equations 5 and 6, we need to estimate mean ice salinity and δ18O of the ice (Sice and δ18Oice, respectively). Therefore, either individual ice crystals, with no salt incorporation, form as frazil ice in the water column (Equation 7) or ice crystals form as part of a consolidated sea ice cover (Equation 8), with initial apparent salt fractionation (k) in the ice of 0.12 (Weeks and Ackley, 1982):

\[ S_{ice} = 0 \]

\[ S_{ice} = 0.12 \times S_{sw,i} \]

However, the latter would neglect further salinization of the water column through brine drainage processes. Regarding the δ18Oice, a fast freezing rate will induce a negligible apparent fractionation (eapp = 0), while a slow freezing rate will induce an apparent fractionation factor close to the equilibrium (eapp = 2.7; Eicken, 1998). Therefore,

\[ \delta^{18}O_{ice} = \delta^{18}O_{sw,i} + e_{app} \]

with the eapp ranging from 0 to 2.7 ‰. Figure 7b and c illustrates the case for platelet frazil at fast growth rates.
\( S_{\text{ice}} = 0, \theta_{\text{app}} = 0 \) and consolidated sea ice at slow growth rates \( S_{\text{ice}} = 0.12 \times S_{\text{sw,f}}, \theta_{\text{app}} = 2.7 \).

Clearly, the most modified waters indicate up to >0.40 \( ff \) at depth, which suggests, on the basis of mass balance, that platelet ice formation has to be the dominant (and very efficient) contribution in the decoupling. Platelet ice, up to 1.2 m thick, has been estimated at MYI-1 (Kirillov et al., 2018). However, \( ff \) and \( f_{\text{si}} \) (Figure 2) at FYI-6 are higher than other stations and remain high throughout the water column. Platelet ice production within the mixed water mass by supercooling or double diffusion would be an efficient way to quickly produce ice crystals (and therefore initiate the inferred decoupling) that will “spread out” under the preexisting sea ice cover or eventually be entrained “off-shore” by the currents. Platelet ice formation up to 350 m thick was estimated below the Filchner-Ronne Ice Shelf (Antarctica, Thyssen et al., 1993), while platelet ice has been observed at depths to 250 m in Antarctica (Gough et al., 2012). However, our values are in good agreement with estimated contribution of \( f_{\text{si}} \) to the water column where up to 66% of the mixture “unmodified” seawater and meteoric water was removed as ice (Figure 2) and illustrate the strong impact of meteoric water in the area.

### 4.2. Meteoric water contribution to the sea ice cover

Contributions of meteoric water inputs can be observed throughout the water column, although the influence is most pronounced in surface seawater. During the melt season, sea ice and snow meltwater, combined with glacial discharge, has been shown to accumulate in the upper season, sea ice and snow meltwater, combined with glacial most pronounced in surface seawater. During the melt through the water column, although the influence is

\[ d_{\text{18O}} = \frac{1}{2} \ln \left( \frac{S_{\text{ice}}}{S_{\text{sw,f}}} \right) \]

\[ f_{\text{snow}} + f_{\text{si,msw}} = 1, \]

and the \( \delta^{18}O \) observed within sea ice \( \delta^{18}O_{\text{ice,obs}} \) should correspond to:

\[ (\delta^{18}O_{\text{snow,obs}} + \delta^{18}O_{\text{si,msw}}) = \delta^{18}O_{\text{ice,obs}}. \]
As sea ice $\delta^{18}O$ (here $\delta^{18}O_{\text{ice,obs}}$) relies on the surface seawater $\delta^{18}O$ ($\delta^{18}O_{\text{msw}}$) and the apparent fractionation factor ($e_{\text{app}}$), Equation 11 can be modified as:

$$
\delta^{18}O_{\text{snow}} \times f_{\text{snow}} + \left( \left( \delta^{18}O_{\text{msw}} + e_{\text{app}} \right) \times (1 - f_{\text{snow}}) \right) = \delta^{18}O_{\text{ice,obs}}.
$$

(12)

and $f_{\text{snow}}$ can be estimated as:

$$
f_{\text{snow}} = \frac{\left( \delta^{18}O_{\text{ice,obs}} - \delta^{18}O_{\text{msw}} - e_{\text{app}} \right)}{\left( \delta^{18}O_{\text{msw}} - \delta^{18}O_{\text{snow}} - e_{\text{app}} \right)}.
$$

(13)

Based on field observations, Eicken (1998) estimated an $e_{\text{app}}$ of 2.7 ‰ while Alkire et al. (2015) estimated an $e_{\text{app}}$ of 1.8 ‰. However, $e$ depends on sea ice growth rate (Souchez et al., 1988). Due to the lack of seawater samples from the ice-seawater interface, we estimated an $e_{\text{app}}$ of 2.5 ‰ based on the average $e_{\text{app}}$ estimated during an experimental sea ice growth experiment (Moore et al., 2017). Using the average $\delta^{18}O$ observed within all of the snow samples (~25.8 ‰) and all of the surface seawaters (~13.6 ‰), we computed $f_{\text{snow}}$ throughout the ice cover (Figure 8, thick black lines). This method relies on the estimation of the $\delta^{18}O$ of surface seawater and $e_{\text{app}}$. At the end of the melt season, we could expect the seawater surface to be more depleted in $\delta^{18}O$ compared to what was observed in early spring. In addition, brine migration could alter $\delta^{18}O_{\text{ice,obs}}$. Therefore, we assumed each ice section to be a closed system to neglect possible exchanges of liquid during sea ice formation or sampling (brine drainage during core extraction). That the estimated brine volume content was generally lower than the permeability threshold (5%; Golden et al., 2007) suggests a limited ability of brine to migrate throughout the ice thickness, isolating different sections of the ice (Figure 4).

Estimates of $f_{\text{snow}}$ (up to 0.68) in the upper section of the ice cover are high (Figure 8). With depth, $f_{\text{snow}}$ decreases, reaching negative values toward mid-depth (50–75 cm), except at FYI-3, FYI-6, FYI-12, and FYI-13 where $f_{\text{snow}}$ was positive throughout most of the ice thickness. The transition between positive and negative values of $f_{\text{snow}}$ occurred when the ice $\delta^{18}O$ reached similar $\delta^{18}O$ as surface seawater (Figure 4d). Positive estimates of $f_{\text{snow}}$ suggest the presence of additional meteoric water within sea ice, as snow ice formation, compared to the averaged surface water. Negative estimates are unrealistic and result from the use of the average modified seawater $\delta^{18}O$. Examining the sensitivity of $f_{\text{snow}}$ to more (~16.3 ‰) or less (~2.8‰) depleted surface water $\delta^{18}O$ observed in the system (Figure 2) reveals that a less modified surface seawater results in a positive $f_{\text{snow}}$ throughout the ice thickness (as shown by the gray area in Figure 8). High and positive estimates of $f_{\text{snow}}$ observed in FYI-3, FYI-6, FYI-12, and FYI-13 suggest a large contribution of snow throughout the ice thickness, making snow ice the predominant contributor to the ice thickness. This finding contrasts with all of the other stations where the contribution of snow was more restricted to the surface layer, which is consistent with thicker snow cover usually being observed in coastal areas and in downwind areas of ice shelf fronts and ice tongue walls.

Over MYI, thicker snow cover was observed compared to FYI, leading to warmer sea ice temperature. However, bulk ice salinity and $\delta^{18}O$ profiles were nearly constant throughout the ice thickness, due to repetitive cycles of ice growth and melt where brine is typically flushed out of the ice during the first spring–summer (i.e., melted snow percolates through the ice cover, leaving the ice nearly fresh; Figure 5). The $\delta^{18}O$ observed within MYI is less depleted than observed in FYI, with values similar to those reported in the bottom section of FYI, and lower than the average surface seawater. Surface melt in summer could be responsible for removing the top 50 cm of the ice cover (Perovich and Richter-Menge, 2015), leaving the bottom section, with less depleted $\delta^{18}O$, to persist in the next winter. Therefore, estimates of $f_{\text{snow}}$ in MYI reach similar depleted values as for the bottom FYI (Figure 8).

Depicted $\delta^{18}O$ values observed in the water column suggest a strong input of glacial meltwater, while depleted $\delta^{18}O$ values within sea ice reflect both the formation of sea ice from surface water already depleted in $\delta^{18}O$ and the thick snow cover, promoting snow ice formation. Therefore, the marine environment of the Wandel Sea shelf is strongly affected by meteoric water, with estimates of $f_{\text{snow}}$ in the water column much higher than values (0–0.15) reported in sea ice from other regions of the Arctic, including the Beaufort Sea (Macdonald et al., 1995), Svalbard (Alkire et al., 2015), and the Arctic Ocean (Hendry et al., 2018).

4.3. Impact of glacial discharge on the carbonate system

Concentrations of TA and DIC in FYI and MYI (Figures 5 and 6) are at the low end of the range previously reported in the Arctic (Rysgaard et al., 2007; Miller et al., 2011; Fransson et al., 2015) and similar to those reported during sea ice melt, with low bulk ice salinity (Geiulfs et al., 2015). For both sea ice and the water column, observed TA and DIC were higher than expected from the dilution line calculated based on the seawater properties of the undisturbed seawater end-member ($S = 34.7$, $TA = 2,315 \, \mu mol \, kg^{-1}$, DIC = 2,179 \, \mu mol \, kg$^{-1}$; Figure 9a and c, black dashed line), which suggests a process was adding TA and DIC to our system. To identify the main processes affecting the carbonate system, we calculated the ratio of DIC:TA normalized to a salinity of 5 (noted as $n$DIC:nTA) to discard concentration and dilution effects. Based on the regression line calculated for both FYI (solid black line in Figure 9b and d) and seawater samples (solid black line in Figure 9a and c), we estimated their respective end-member ($S = 0$) for TA (83 and 916 \, \mu mol \, kg$^{-1}$) and DIC (71 and 890 \, \mu mol \, kg$^{-1}$). Values for nTA and nDIC were then calculated using the normalization from Friis et al. (2003).

In Figure 9e, the dotted lines represent the response of TA and DIC to different processes. While exchange of CO$_2(g)$ only affects DIC, precipitation and dissolution of calcium carbonate affect TA and DIC in a ratio of 2:1, and biological activity (photosynthesis/respiration) affects...
both TA and DIC in a ratio of –0.16 (Lazar and Loya, 1991). Most of the FYI data fall along the calcium carbonate dissolution line, with a slight offset toward CO₂ uptake and/or respiration; a similar slope is observed for the seawater data. The impact of biology appeared insignificant, consistent with the low chlorophyll-a concentrations (0.002 mg m⁻²) reported in FYI at the time of sampling (Hancke et al., 2018).

While precipitates of calcium carbonate, as ikaite, were not analyzed in our samples, ikaite was quantified within both FYI and MYI during fieldwork at VRS 3 weeks prior to this study. Estimates of ikaite concentrations within FYI and MYI ranged from 0.0 to 14.3 mol kg⁻¹ (Kyle et al., 2017). These concentrations are low compared to similar studies in both artificial (Rysgaard et al., 2014; Geilfus et al., 2016) and natural Arctic sea ice (Geilfus et al., 2013;
Rysgaard et al., 2013), which could be due to the relatively high sea ice temperature associated with the low bulk ice salinity. Using the regional concentrations estimated by Kyle et al. (2017) within sea ice, ikaite dissolution would contribute to an increase of TA and DIC up to 28.6 μmol kg⁻¹ and 14.3 μmol kg⁻¹, respectively. The difference between the observed TA and DIC in the water column and what is expected from the salinity (amount between sample and black dashed line in Figure 9a and c) averaged to 237 and 242 μmol kg⁻¹, respectively. Within sea ice, this difference averaged to 70 and 65 μmol kg⁻¹, respectively. However, using the averaged surface seawater properties ($S = 20.3$, $TA = 1,791$ μmol kg⁻¹, $DIC = 1,701$ μmol kg⁻¹), we calculated a dilution line specifically for sea ice (dotted black line in Figure 9b and d). Using this dilution line, the averaged difference between the observed and expected TA and DIC within sea ice decreased to 15 and 12 μmol kg⁻¹, respectively. This estimate is in the same order of magnitude as the amount of ikaite reported by Kyle et al. (2017).

Therefore, while the dissolution of calcium carbonate is indicated as the main process affecting the carbonate system in the water column, the small amount of ikaite precipitation within the local sea ice. Dmintrenko et al. (2017) reported an increase in seawater turbidity in the vicinity of FYI-6 and attributed this increase to either a subglacial discharge or melt of ice-releasing sediments. Although no samples were collected.

Figure 9. Relationships between total alkalinity, dissolved inorganic carbon, and salinity. Panels a and c present the relationship between salinity and total alkalinity (TA, μmol kg⁻¹) and dissolved inorganic carbon (DIC, μmol kg⁻¹), respectively, for first- (FYI) and multiyear sea ice, seawater, slush, and snow samples. Panels b and d show the same relationship focusing on sea ice (note x-axis scale differences). The dashed line represents the dilution line calculated based on the seawater properties of the undisturbed seawater end-member ($S = 34.7$, $TA = 2,315$ μmol kg⁻¹, $DIC = 2,179$ μmol kg⁻¹). The dotted line represents the dilution line calculated based on the mean surface seawater properties ($S = 20.3$, $TA = 1,791$ μmol kg⁻¹, $DIC = 1,701$ μmol kg⁻¹). The solid black line represents the respective regression line between $S$, TA, and DIC for seawater in Panels a and c and for FYI in Panels b and d. Their respective equation and $R^2$ value is noted in each panel. The ratios of normalized TA and DIC ($nDIC:nTA$, $S = 5$) for FYI, seawater and slush samples are presented in Panel e. Dotted lines represent the theoretical changes following precipitation/dissolution of calcium carbonate, release/uptake of CO₂(g), and biological activity (photosynthesis/respiration). DOI: https://doi.org/10.1525/elementa.2021.00004.f9
to potentially identify the type of sediments released by the glacier, the carbonate nature of the bedrock has been reported previously by Håkansson and Pedersen (2001). The bedrock composition therefore has the potential to affect the carbonate system in the host water environment, most notably those fed by proglacial streams draining land-terminating glaciers (Anderson et al., 2000). Due to physical erosion from the bedrock through glacial-water action (scouring and transport resulting from friction and lubrication; Benn et al., 2007), chemical components are accumulated at the base of the glacier and added to the water body (Fransson et al., 2015). Therefore, the input of enriched carbonate glacial meltwater into the water column could provide additional TA and DIC to the marine environment (Fransson et al., 2015). The presence of glacial sediment and its role in marine biogeochemical processes need to be investigated further in future studies.

5. Conclusions
Depleted δ18O values observed in the water column on the Wandel Sea shelf, northeastern Greenland, suggest a strong input of glacial meltwater. Within sea ice, depleted δ18O values reflect both the formation of sea ice from the already depleted surface water and the snow ice formation initiated by the thick snow cover observed in the area. The result is an ice cover with low salinity and relatively warm temperature due to insulation from the snow cover. These conditions result in low ikaite precipitation within sea ice (Kyle et al., 2017) where low concentrations of both TA and DIC were observed. However, the TA:DIC ratios in both sea ice and the water column indicate that calcium carbonate dissolution is the main process affecting the carbonate system. Therefore, we suggest that carbonate minerals from glacial bedrock are exported along with glacial drainage into the marine environment. Their dissolution would largely overcompensate for the small amount of ikaite precipitated within the sea ice cover. Our study thus suggests that increasing inputs of glacial meltwater may counteract the lack of ikaite by increasing glacier-derived sediments (carbonate minerals) to the coastal marine system, where their dissolution will increase TA and carbonate ions, potentially mitigating the effects of ocean acidification.

Data accessibility statement
Data used in this study are available at https://doi.org/10.4211/hs.51e0247d059c473dab9418390c7a4b67. Air temperature data (Figure 2) are available at https://www2.dmu.dk/asiaqmet/Default.aspx.

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Competing interests
The authors declare no competing interests.

Author contributions
Field sampling was performed by N-XG, laboratory and data analyses were performed by N-XG, KM, ML, and J-LT, and the article was written by N-XG, KM, FW, J-LT, and SR. All authors have reviewed and approved the submitted version for publication.

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