Seasonal marine carbon system processes in an Arctic coastal landfast sea ice environment observed with an innovative underwater sensor platform

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Studying carbon dioxide in the ocean helps to understand how the ocean will be impacted by climate change and respond to increasing fossil fuel emissions. The marine carbonate system is not well characterized in the Arctic, where challenging logistics and extreme conditions limit observations of atmospheric CO2 flux and ocean acidification. Here, we present a high-resolution marine carbon system data set covering the complete cycle of sea-ice growth and melt in an Arctic estuary (Nunavut, Canada). This data set was collected through three consecutive yearlong deployments of sensors for pH and partial pressure of CO2 in seawater (pCO2sw) on a cabled underwater observatory. The sensors were remarkably stable compared to discrete samples: While corrections for offsets were required in some instances, we did not observe significant drift over the deployment periods. Our observations revealed a strong seasonality in this marine carbon system. Prior to sea-ice formation, air–sea gas exchange and respiration were the dominant processes, leading to increasing pCO2sw and reduced aragonite saturation state (ΩAr). During sea-ice growth, water column respiration and brine rejection (possibly enriched in dissolved inorganic carbon, relative to alkalinity, due to ikaite precipitation in sea ice) drove pCO2sw to supersaturation and lowered ΩAr to < 1. Shortly after polar sunrise, the ecosystem became net autotrophic, returning pCO2sw to undersaturation. The biological community responsible for this early switch to autotrophy (well before ice algae or phytoplankton blooms) requires further investigation. After sea-ice melt initiated, an under-ice phytoplankton bloom strongly reduced aqueous carbon (chlorophyll-a max of 2.4 μg L^{-1}), returning ΩAr to > 1 after 4.5 months of undersaturation. Based on simple extrapolations of anthropogenic carbon inventories, we suspect that this seasonal undersaturation would not have occurred naturally. At ice breakup, the sensor platform recorded low pCO2sw (230 μatm), suggesting a strong CO2 sink during the open water season.

Keywords: Biogeochemistry, Carbon cycle, Ocean acidification, Gas exchange, Sea ice, Chemical sensors

1. Introduction
As the Arctic warms at twice the rate of lower latitudes (Richter-Menge et al., 2019), the Arctic Ocean’s role as a significant sink for atmospheric CO2 (Bates and Mathis, 2009) is expected to be reduced, and its vulnerability to negative climate impacts, such as acidification, to increase (Arctic Monitoring and Assessment Programme [AMAP], 2018). However, the Arctic Ocean and associated shelf seas lack comprehensive monitoring to provide conclusive carbon budgets or observations of interannual, annual,
seasonal, or daily cycles. The scarcity of high-temporal resolution measurements presents a significant challenge for accurately constraining net carbon exchange and its future change in Arctic seas. The largest gap in observations occurs through the polar night, as the seasonal sea-ice cover limits access by research vessels (AMAP, 2018).

In the absence of high-resolution observations, conceptual models describing annual Arctic marine carbon cycling have needed to extrapolate between limited seasonal data sets. Yager et al. (1995) described polynya regions in the Arctic as strong annual sinks for atmospheric CO₂ because the seasonal cycle of the partial pressure of CO₂ in seawater (pCO₂sw) is in-phase with the seasonal cycle of sea-ice formation and melt. Yager et al. also suggested that if wind speeds are high over a seasonally ice-covered region before sea-ice formation in the fall, the region could act as major sink for atmospheric CO₂, replacing much of the inorganic carbon consumed by net production over the summer. The winter ice cover would then prevent outgassing as pCO₂sw reaches supersaturation because of net respiration, mixing with CO₂-rich deep water, and restricted air–sea gas exchange. In the spring, pCO₂sw will decrease to undersaturation before ice breakup due to net photosynthesis driven by ice-algal production. This model has been applied to interpretations of other seasonal ice zones, including flaw lead polynyas (Else et al., 2012; Shadwick et al., 2011) and landfast ice regions (Else et al., 2019). Indeed, the majority of studies examining seasonal ice zones near the time of ice breakup have found undersaturated pCO₂sw although Else et al. (2019) suggested that under-ice phytoplankton blooms, and not bottom-ice algal communities, are the most likely drivers of this undersaturation.

Similarly, seawater pH and carbonate mineral saturation state Ω, specifically calcite (ΩCa) and aragonite (ΩAr), important indicators for ocean acidification, also follow seasonal cycles. With the Arctic thought to be more vulnerable to acidification than any other ocean region (Shadwick et al., 2013), these seasonal cycles also warrant a deeper understanding. Through the winter, Ω in Arctic surface waters has been observed to decrease due to respiration and mixing with subsurface waters (Chierici et al., 2011). Over the spring and summer, photosynthetic uptake of carbon by phytoplankton in the surface layer decreases dissolved inorganic carbon (DIC), increasing pH and Ω (Shadwick et al., 2011). In the yearlong annual study described by Chierici et al. (2011) and Shadwick et al. (2011), prolonged periods of seasonal ΩAr undersaturation in the surface were not observed, with the only winter observation of undersaturation attributed to upwelling of Pacific origin waters. Observations of CaCO₃ undersaturation in spring or summer can be attributed to sea-ice meltwater and river runoff (Bates et al., 2009). Trends in the Western Arctic suggest that within a few decades, the entire upper water column may become undersaturated with respect to the CaCO₃ mineral aragonite (ΩAr) due to enhanced freshwater storage and atmospheric uptake of CO₂ (Qi et al., 2016). The highest rates of acidification are expected in the central Arctic, Canadian Basin, and Baffin Bay (AMAP, 2018). However, shallow nearshore waters that are seasonally covered by continuous landfast sea ice show the largest vulnerability (AMAP, 2013). These environments partially shut down CO₂ evasion during the winter while still permitting metabolism of terrigenous and marine organic carbon through respiration (Garneau et al., 2006), which leads to decreasing pH and Ω.

Despite progress, most of our understanding of the seasonal progression of the marine carbon system in Arctic environments is largely strung together by limited data, widely separated in space and time. The actual processes controlling this progression are not as straightforward as one conceptual model and are likely to be very different in different locations. One way of addressing this issue is to establish long-term time-series stations utilizing new autonomous sensor technology (Sastri et al., 2019).

Our goal here is to describe the seasonal marine carbon cycle in an Arctic continental shelf sea using an autonomous sensor platform. In pursuit of this primary goal, we also address the following objectives: (1) evaluation and correction of autonomous pH and pCO₂sw sensor measurements using discrete samples and (2) description of the oceanographic context for the autonomous measurements.

2. Study area
Cambridge Bay, Nunavut, Canada, was selected as the Arctic estuarine site for this experimental study (Figure 1). Herein, we refer to the marine region of Cambridge Bay as “CB,” to avoid confusion with the Hamlet of Cambridge Bay (also known as ᑲᑐᔾᔨᑦ ᓄᓇᕗᑦ, meaning “good fishing place”; Pitquhirnikkitilik Ulituktut, 2020). CB is a coastal inlet with a wide, shallow entrance that restricts exchange with the adjacent Dease Strait (a southern limb of the Northwest Passage). The bay has a maximum depth of approximately 85 m. CB is an outlet for a fairly large watershed (1,490 km²) on Victoria Island discharging to the ocean via Freshwater Creek (Figure 1), which typically starts flowing in early June, has a peak discharge of about 45 m³ s⁻¹ in late June or early July, and stops flowing in early November (Environment and Natural Resources Canada, 2019). CB experiences moderate tidal influence semi-diurnally with an average daily range of 0.4 m.

A landfast ice cover in the bay is typically established by mid-October, reaching an average maximum thickness in May of about 1.5 m (Oceans Networks Canada, 2017). In winter, the region experiences weak tides and minimal water movement beneath the sea-ice cover (Lewis and Walker, 1970). During much of winter, the sea ice is covered by snow of variable depths depending on the year but usually less than 0.3 m (Moon et al., 2019). Sea-ice thinning begins around June, and by the second half of July, CB is typically completely ice-free. The early summer water column experiences a pronounced two-step stratification, forced by a thin (<2 m) low-salinity layer caused by Freshwater Creek runoff and sea-ice melt (Lewis and Walker, 1970). Following an approximate 3-week period of two-step stratification, wind-driven mixing deepens the mixed layer to about 20-m depth, creating an isocline that persists through fall and winter.
3. Methods

3.1. Ocean Networks Canada (ONC) underwater platform

This study made use of the ONC Cambridge Bay Undersea Community Observatory (Figure 2). The platform was situated on the ocean floor at 7-m below the sea surface, approximately 120-m offshore (ONC; Figure 1). First installed in September 2011, the power and communications are provided to the platform via an underwater cable, enabling continuous real-time monitoring throughout the year. Data are streamed live over the open access ONC Ocean 2.0 data outlet (data.oceannetworks.ca). Wind speed data were retrieved from the nearby onshore ONC weather station.

Table 1 details deployment intervals and onboard sensors utilized by this study for the 2015, 2016, and 2017 deployments.

3.2. Carbonate system sensors

To measure $p$CO$_{2sw}$, Pro-Oceanus CO2-Pro CV sensors were deployed on the ONC platform, starting in 2015. The CO2-Pro uses a nondispersive infrared detector and executes an automatic zero point calibration every 12 h (Jiang et al., 2014). The CO2-Pro instrument was factory-calibrated by Pro-Oceanus using National Institute of Standards and Technology-traceable CO2 calibration gases prior to field deployment and after, when possible. Pro-Oceanus reports accuracy within 0.5% over the calibrated range (0–1,000 μatm) and drift restricted to less than 10 μatm year$^{-1}$, while measuring $p$CO$_{2sw}$ concentration with a precision of 0.01 μatm. CO2-Pro sensor deployments lasted approximately 1 year (Table 1) before recovery and redeployment of a freshly calibrated sensor.

Starting in 2016, Satlantic SeaFET instruments were used to measure pH on the ONC platform. The SeaFET utilizes two ion-sensitive field effect transistors, housed within both internal (FET|INT) and external (FET|EXT) potentiometric cells (Martz et al., 2010; Bresnahan et al., 2014). Both pH electrodes (pHINT and pHEXT) have demonstrated exceptional stability over a range of practical salinities (9–36) and temperatures (−1 °C to 35 °C; Martz et al., 2010; Bresnahan et al., 2014; Kapsenberg et al., 2017; Gonski et al., 2018; Miller et al., 2018). The SeaFET instruments were calibrated at Satlantic and tested prior to deployment in separate test tanks at ONC headquarters and the Institute of Ocean Sciences (IOS), both in Victoria, British Columbia. Satlantic reports that accuracy is within 0.05 pH, with a sensor precision of 0.0001 pH and stability of 0.06 pH year$^{-1}$. The SeaFET sensors were also exchanged every year (Table 1).

3.3. Discrete sampling for sensor evaluation and determining oceanographic context

Reference water samples were collected next to the sensor platform at the sensor depth and at 2 m, as well as at a secondary offshore site, for analysis of DIC and total alkalinity (TA). These samples were collected through holes.
drilled in the ice in winter or from small boats in summer (Text S1, Figure S1, and Table S1). Water was collected with 1.25-L Niskin bottles, followed by bottom-filling 125-mL borosilicate bottles with overflow of 3 volumes to prevent atmospheric contamination (Dickson et al., 2007). Samples were then poisoned with 50 μL of a saturated mercuric chloride (HgCl₂) solution to prevent biological activity. Depending on the time of year (Table S1), the lapsed time before sample poisoning varied between immediately (during the spring and summer) to an hour (during the winter). Following preservation, samples were capped using chlorobutyl-isoprene rubber stoppers and

**Table 1.** Onboard sensor details for the 2015, 2016, and 2017 Ocean Networks Canada platform deployments. DOI: https://doi.org/10.1525/elementa.2021.00103.t1

| Parameter                        | Deployment Year |
|----------------------------------|-----------------|
|                                  | 2015            | 2016            | 2017            |
| Deployment date                  | August 27, 2015 20:05 | August 25, 2016 22:24 | September 14, 2017 23:22 |
| Recovery date                    | August 24, 2016 03:21 | September 2, 2017 16:50 | July 24, 2018 22:06 |
| Carbon system sensors            |                 |                 |                 |
| pCO₂                             | Pro-Oceanus CO2-Pro CV (SN 35-250-75) | Pro-Oceanus CO2-Pro CV (SN 36-314-75) | Pro-Oceanus CO2-Pro CV (SN 35-250-75) |
| pH                               | (No sensor deployed) | Satlantic SeaFET Ocean pH Sensor (SN 246) | Satlantic SeaFET Ocean pH Sensor (SN 452) |
| Ancillary sensors                |                 |                 |                 |
| Oxygen                           | Sea-Bird SBE 63 Dissolved Oxygen Sensor (631008) | Sea-Bird SBE 63 Dissolved Oxygen Sensor (630834) | Sea-Bird SBE 63 Dissolved Oxygen Sensor (631008) |
| Ice draft                        | ASL Shallow Water Ice Profiler (53029) | ASL Shallow Water Ice Profiler (53029) | ASL Shallow Water Ice Profiler (53038) |
| Temperature, salinity, pressure  | Sea-Bird SeaCAT SBE19plus V2 (7589) | Sea-Bird SeaCAT SBE19plus V2 (7518) | Sea-Bird SeaCAT SBE19plus V2 (7589) |
| Photosynthetically active radiation (PAR) | WETLabs ECO-PARS (S/N 459) | WETLabs ECO-PARS (S/N 440) | WETLabs ECO-PARS (S/N 459) |
| Chlorophyll-a                    | WETLabs ECO-FLNTUS (3923) | WETLabs ECO-FLNTUS (3441) | WETLabs ECO-FLNTUS (3923) |

*All salinity values in this article are practical salinities.*
aluminum caps and stored in the dark at 4 °C until analysis (Jiang et al., 2008). During the 2015–2016 deployment, reference samples were collected using a 5-L Niskin bottle and 250-mL glass bottles with ground glass stoppers sealed with Apiezon M grease and electrical tape, according to standard sampling protocols (Dickson et al., 2007). Conductivity–temperature–depth (CTD) casts were deployed concurrently with all water sample collections, using an RBR Concerto calibrated by the manufacturer.

All 125-mL samples were analyzed at the University of Calgary. DIC was determined after acid extraction by quantifying the released CO2 by nondispersive infrared gas spectroscopy (AIRICA and LiCOR-7000); TA was measured by potentiometric titration using a semiautomated open-cell titration system (AS-ALK2 Apollo SciTech; Cai et al., 2010) with endpoint determination by modified Gran plots (Grasshoff et al., 1999). All 250-mL samples were analyzed for both DIC and TA at IOS. DIC was determined coulometrically (Dickson et al., 2007) using either a SOM-MA (Johnson et al., 1993) or VINDTA extraction system and UIC, Inc., model no. 5011 coulometers. TA was measured using a semiautomated open-cell potentiometric titration system, with end point determination by nonlinear least-squares fitting (Dickson et al., 2007). All measurements at the University of Calgary and IOS were calibrated against certified reference materials provided by Andrew Dickson from Scripps Institute of Oceanography. University of Calgary measurements had a precision better than 4 μmol kg⁻¹ for DIC and 3 μmol kg⁻¹ for TA. At IOS, precision, based on the average standard deviation between triplicate samples, was better than 2 μmol kg⁻¹ for DIC and 5 μmol kg⁻¹ for TA. Independent reference pH and pCO₂sw values used for sensor assessment were calculated from the measured DIC and TA at in situ temperature, salinity, and pressure (Table 1) using inorganic carbon dissociation constants from Lueker et al. (2000), the bisulfate ion acidity constant of Dickson (1990), and the boron-to-chlorinity ratio of Lee et al. (2010) in CO2SYS (Van Heuven et al., 2011).

In order to assess air–sea CO2 exchange and/or offshore ecological processes, ideally the in situ carbon sensors would have been positioned close to the surface and further offshore. To assess the spatial representativeness of the platform, we also collected water samples and deployed CTD casts regularly along a transect extending 0.65 km into the bay (Figure 1). Only CTD data were collected at sites between ONC and B1 (CTD-1, CTD-2, MB, CTD-3; Figure 1), whereas ancillary water samples were collected at depths of 2 m, 7 m (to match the platform), 30 m, and 70 m at station B1 (near maximum depth in CB). The rationale for the selection of these sites is described in the Supplemental Materials.

4. Instrument and sensor platform performance

4.1. pH sensor performance and correction

Some quality control and correction of the SeaFET sensor data were deemed necessary based on initial data.
inspection. Highly variable sensor values over the first 10 days of each deployment were observed due to SeaFET instability caused by sensor reconditioning as described by Bresnahan et al. (2014). These data were flagged and excluded. Discrepancies in uncorrected pH\textsubscript{INT} and pH\textsubscript{EXT} through both deployments also existed, as well as temperature discrepancies in the SeaFET thermistor response when compared to the co-located Sea-Bird SeaCAT (Table 1; Duke, 2019). New calibration coefficients were calculated for each reference point following Bresnahan et al. (2014), using measured FET\textsubscript{EXT} voltages, in situ temperature and salinity from the colocated Sea-Bird SeaCAT, and discrete sample pH. These single point coefficients were then averaged to give a multipoint calibration coefficient used to calculate pH from FET\textsubscript{EXT} voltage and the Nernst slope.

Figure 3 shows a comparison of pH calculated from discrete DIC and TA samples (pH\textsubscript{DIC-TA}) with sensor values (pH\textsubscript{sensor}) with sensor values (pH\textsubscript{sensor}). A type II linear regression was used to assess sensitivity (c\textsubscript{1} or slope), and the root mean square error (RMSE) was calculated to assess uncertainty. In Figure 3, a sensor offset would be illustrated by separation between the regression lines and the 1:1 line. A slope significantly different than 1 would indicate a problem
with the sensor response over the range of measured values, and the systematic placement of points either above or below the 1:1 line as a function of time would indicate sensor drift. We saw none of these problems with the SeaFET sensor in either year. Even prior to correction, the raw regression line (blue dotted line) was close to the 1:1 line, with a slope not significantly different from 1. Sensor correction (red regression line) as described above did improve these metrics slightly. RMSE (around 0.03 pH units in both years) was higher than is typically desired, but this value includes uncertainty in both of the sensor measurements and in pH and $p\text{CO}_2$ values calculated from DIC and TA.

### 4.2. $p\text{CO}_2$sw sensor performance and correction

The CO2-pro $p\text{CO}_2$sw sensor ($p\text{CO}_2_{\text{final}}$) performance against discrete samples ($p\text{CO}_2_{\text{DIC-TA}}$) is shown in Figure 4. The initial calibration of the Pro-Oceanus sensors was not as robust as for the SeaFETs, as we observed offsets (separation of the blue dotted line from the 1:1 line) during all deployments. However, sensor drift was not apparent, as the distribution of points around the 1:1 line through time across all three deployments showed no discernable pattern. Also, the slopes of the regression lines were not significantly different ($P < .05$) from 1.

Correction of all $p\text{CO}_2$sw data sets therefore focused on reducing offsets. Correction of the 2015–2016 data used a postdeployment multipoint factory calibration from Pro-Oceanus of $-24.15$ µatm, the mean difference when compared to NIST-traceable CO2 calibration gases. This correction factor was used to increase sensor $p\text{CO}_2$sw by a constant throughout the deployment. For 2016–2017, no postdeployment factory calibration was available, as the infrared lamp failed before platform recovery. The calculated mean difference between raw sensor data and reference samples of 24.56 µatm was instead used as a correction factor throughout deployment. During the 2017–2018 deployment, the sensor quite significantly underestimated $p\text{CO}_2$sw through the entirety of the deployment with a mean difference relative to reference samples of 88.25 µatm. This calculated value was again used as a constant correction factor due to sensor failure prior to recovery. Regression lines for the corrected data (red lines, Figure 4) show that these calibration approaches were effective in removing the observed offsets. Final RMSE was highest in the 2017–2018 deployment ($+30$ µatm), but again this reflects uncertainty in both the sensor and the discrete samples. The final corrected sensor pH and $p\text{CO}_2$sw time series of ONC over all three deployments is shown in Figure 5. A more extensive analysis of the performance of $p\text{CO}_2$sw and pH sensors is available in Duke (2019).

Overall, discrete calibration samples appear to be needed in most cases only at deployment, following an appropriate conditioning period for the SeaFETs (Bresnahan et al., 2014; Duke, 2019), and at recovery. However, the CO2-Pro deployments indicate that collecting additional calibration samples mid-deployment, when possible, is still beneficial as a robust way to quality control the data.

### 4.3. Platform oceanographic setting

Figure 6 shows selected seasonal transects of temperature and salinity from the ONC platform to station B1, located at the deepest part of the Bay (Figure 1). The mixed layer depth was defined as the maximum depth at which the density is within 0.25 kg m$^{-3}$ of the shallowest measured density as identified in CTD profiles (Timmermans et al.,

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**Figure 5.** Time series of final corrected sensor $p\text{CO}_2$sw and pH over all three deployments. Depicted are final corrected values from (a) the SeaFET sensor pH and (b) CO2-Pro sensor $p\text{CO}_2$ over the 2015–2016, 2016–2017, and 2017–2018 deployments. Vertical dotted red lines denote deployment and recovery dates. Atmospheric $p\text{CO}_2$ is represented by the horizontal dashed black line on (b). DOI: https://doi.org/10.1525/elementa.2021.00103.f5
During winter (Figure 6a and b), we observed a relatively deep mixed layer, with constant temperature and salinity to a depth of about 25 m along the whole transect. During the ice melt/river runoff period, the water column above the sensor platform became stratified, with a salinity of 2 at the surface and 28 at 7-m depth (Figure 6c). During this period, the ONC platform (at 7-m depth) experienced much cooler and saltier water (\(-1.0^\circ C\), salinity of 27) than was at the surface (3 \(^\circ C\), 2–4). During summer (Figure 6e and f), open water and wind mixing resulted in mixed layer deepening (to approximately 10 m), reestablishing similar conditions between the platform depth and the surface. During sea-ice formation (Figure 6g and h), the ONC platform was well within the mixed layer (which had deepened to 25 m). Overall, water properties similar to the platform location were observed at B1 at a similar (7 m) depth, apart from slightly warmer water near shore in the fall.

We confirmed that the biogeochemical measurements at the ONC site are representative of the offshore during most seasons by comparing discrete DIC and TA samples collected at both 2 and 7 m at the ONC platform and B1 (Figure 7). As expected, values were similar at both depths on and offshore through the winter months and into the late spring. The data from 2 and 7 m at both ONC and B1 diverged in summer (July 3 and 10), as DIC, TA, and salinity values at the surface plummeted while temperature rose, likely due to a combination of river runoff from Freshwater Creek (Figure 1) and sea-ice melt. Following the melt/runoff period (after July 20), the surface stratification broke down, and the DIC, TA, salinity, and temperature values measured at the ONC platform depth were again representative of the surface mixed layer (Figure 7). Correlation coefficients (Pearson’s r) for ONC 7 m (the sensor depth) compared to ONC 2 m DIC values were strong all year (0.67) but improve when excluding July 3 and 10 (0.93). Comparing the sensor location to B1 7 m, DIC was strongly correlated year-round (0.88). Note that we observed warming at the ONC site about 2 weeks earlier than at B1 (May 16 vs. June 3; Figure 7c). Overall, the platform was chemically different from the surface for
about 2 weeks due to ice melt and runoff in spring but was thermally different from the surface layer for 8 weeks due to radiative forcing.

5. Biogeochemical cycles: Seasonal overview

Given the above results, the platform should be useful for understanding biogeochemical processes in this landfast ice region, at least from late summer to the beginning of ice breakup. Of all of the deployments, the data from 2016 to 2017 offer the most complete picture, when both the pH and $p$CO$_{2sw}$ sensors were operational and we collected most of our discrete samples (Table S1). In this section, we summarize the broad seasonal patterns observed in the biogeochemical and physical parameters (Figure 8). Our criteria for defining the seasonal intervals are described in Text S2.

Through the fall, $p$CO$_{2sw}$ was undersaturated with respect to the atmosphere and then continued to increase through the early winter until reaching a maximum on March 5 of 509 µatm. $p$CO$_{2sw}$ began to decrease shortly after (around the start of the “late winter” period) and continued to decrease at a steady rate as the ice continued to grow toward its maximum thickness on May 24. $p$CO$_{2sw}$ became undersaturated with respect to the atmosphere by May 5. The drawdown in $p$CO$_{2sw}$ accelerated at the end of May, as light penetration increased due to snow melt on the surface (Figure 8f, the period we have identified as “spring”) and as the sea ice began to thin, increasing primary production. $p$CO$_{2sw}$ reached a minimum of 223 µatm on June 23, and the site entered the open water season significantly undersaturated with respect to atmospheric $p$CO$_2$ (difference of −177 µatm).

Trends in pH and dissolved oxygen also showed a distinct seasonal cycle. Dissolved oxygen appeared to be inversely correlated to $p$CO$_{2sw}$ except during the fall season (Figure 8c), while pH was inversely correlated with $p$CO$_{2sw}$ throughout the entire study period (Figure 8d).
From freeze-up through spring, the correlation coefficients (Pearson’s $r$ value) between $O_2$ and both $pCO_{2sw}$ and pH were $>0.89$. Salinity (Figure 8g) was strongly correlated with sea-ice growth and decay, increasing from about 26 to a maximum of 29 as the ice thickened and then decreasing at the onset of ice melt. Chlorophyll fluorescence (Figure 8e) was low through most of the winter season but began to increase slightly in early April and then peaked rapidly after melt onset.

Carbonate system variables calculated from the sensor-based pH and $pCO_{2sw}$ observations using CO2SYS are shown in Figure 9. The DIC and TA results generally track the same seasonal pattern as $pCO_{2sw}$ (and inverse to pH), but we did observe seasonal changes in the DIC:TA ratio.
Conditions of aragonite undersaturation ($\Omega_{\text{Ar}} < 1$) were observed for 134 consecutive days through the winter into spring from January 17, 2017, through May 31, 2017 (Figure 9d).

5.1. Fall uptake
During the fall season, seawater temperatures were dropping (Figure 8h) leading to decreasing $pCO_{2\text{sw}}$ (Figure 8b). Yet during this time, DIC increased by approximately 150 $\mu$mol kg$^{-1}$ (Figure 9a). Given that open water conditions persisted during this time period (Figure 8a), we hypothesize that air–sea gas exchange and net respiration were providing a prominent source of DIC to our site through the fall. To calculate the magnitude of air–sea gas exchange during this period, we used the bulk parametrization:

$$F_{CO_2} = \alpha k \Delta pCO_2 (1-C_i),$$

where $\Omega$ is the solubility of CO$_2$ at in seawater as a function of temperature and salinity (Weiss, 1974), $k$ is the gas transfer velocity according to Wanninkhof (2014), $C_i$ is the fractional ice coverage, and $\Delta pCO_2$ is the gradient in $pCO_2$ between the platform and the atmosphere (constant value of 407 µatm from Butterworth and Else, 2018). Using this approach and wind speed from the onshore weather station, we calculated that air–sea gas exchange increased the DIC concentration by 11.9 $\mu$mol kg$^{-1}$ at the site. The majority of the DIC increase must therefore have been caused either by net respiration or potentially brine rejection later in the season (described in the next section). Fluxes varied from 0 to $-28.8$ mmol m$^{-2}$ day$^{-1}$ with an average flux of $-4.8$ mmol m$^{-2}$ day$^{-1}$ during this time, comparable to the open water average flux estimated in the region of $-5$ mmol m$^{-2}$ day$^{-1}$ (Ahmed and Else, 2019).

With the $pCO_2$ gradient between seawater and the atmosphere remaining relatively constant, variability in the exchange rate was driven by wind events. The largest fluxes coincided with wind speeds over 11 m s$^{-1}$. Consistent with observations in the Canadian Arctic Archipelago (Ahmed et al., 2019), the site acted as a net sink for atmospheric CO$_2$ in the fall, replacing inorganic carbon consumed by net production over the proceeding summer, with sea ice forming before the site reached equilibrium.

5.2. Sea-ice growth
Although the landfast ice cover was not firmly established at the site until October 19, the Canadian Ice Service...
reported drifting ice on October 9 (start of the “early winter” period). Figure 8d and g show that dissolved oxygen and salinity started increasing even earlier in October, while DIC (Figure 9a) began to increase at a similar time. These increases are all consistent with brine rejection, suggesting that ice formation may have started even earlier, perhaps as early as October 1.

By comparing DIC with dissolved oxygen and interpreting relationships within the context of the seasons, we can make inferences about which biogeochemical processes are dominant (Figure 10): Brine rejection (strongest when ice growth is fastest) should cause increases in both DIC and O₂. Net respiration (dominant under light-limited conditions) should cause an increase in DIC and a decrease in O₂, and net autotrophy (dominant when solar radiation is available) should cause DIC to decrease while O₂ increases. Figure 10 shows that through most of the month of October, a clear signal of brine rejection was present in both the DIC and O₂ data. During brine rejection, impurities are rejected from the sea ice, most notably salts (apparent in Figure 8g) but also dissolved gases (Tison et al., 2017). The positive correlation between DIC and O₂ through October is strong evidence for brine rejection being an important controlling process, which must have continued throughout the ice growth period.

The detail that this data set provides during the ice growth season allows for insights into two key paradigms of carbon cycling beneath sea ice (Figure 11). First is the “seasonal rectification” hypothesis (Yager et al., 1995), which predicts that pCO₂sw beneath sea ice likely becomes supersaturated due to net respiration and brine rejection. Our data seem to support this hypothesis, as pCO₂sw became supersaturated about 3 months after freeze-up. The second is the “sea-ice carbon pump” hypothesis (Rysgaard et al., 2007) which predicts that DIC should be rejected at higher rates than TA due to the formation of calcium carbonate (ikaite) crystals in the sea ice. Our data also appear to support this hypothesis, as we observed an increasing DIC:TA ratio in the winter surface mixed layer following freeze-up. Past studies using bottle measurements (summarized by Else et al., 2019) have not published time series of DIC:TA ratios under sea ice; using sensors may be the only way to resolve such subtle changes in the carbonate system.

Figure 11 shows key carbonate system parameters for the early winter period in greater detail. The increase in pCO₂sw to supersaturation is likely driven by a combination of net respiration and brine rejection, although a switch from positively correlated DIC/O₂ to negative correlation is apparent in Figure 10 beginning in early January, suggesting that net respiration became the dominant control in the second half of this season. An interesting feature of Figure 11a is the rapid increase in pCO₂sw that occurs throughout this time period. If simple brine rejection and net respiration were the key factors in the pCO₂sw increase, one would expect pCO₂sw to increase most rapidly earlier in winter, when ice formation is fastest and organic material from the summer season would be most available. The increase in the pCO₂sw accumulation rate in mid-December was likely tied to an increase in the Revelle factor as the DIC:TA ratio increased (Figure 11c and e). The Revelle factor is a measure of the relative increase in pCO₂sw with an increase in DIC as carbon speciation concentrations change. In this study, the Revelle factor increased from near 17 at the end of fall to a maximum of around 19 at the end of early winter, resulting in a more pronounced response in pCO₂sw to a change in DIC (Figure 11a). In turn, the increasing DIC:TA ratio was likely a result of ikaite precipitation and retention in the ice, as predicted by Rysgaard et al. (2007).

These findings suggest an interesting link between the sea-ice carbon pump and seasonal rectification paradigms. To our knowledge, winter supersaturation of pCO₂sw under a sea-ice cover has not actually been observed previously in the Arctic. The accumulation of dissolved CO₂ to near saturation has been observed (Else et al., 2019), and studies that began observations later in spring have noted undersaturation prior to ice breakup (Geilfus et al., 2012; Else et al., 2019). Initial chemical conditions, combined with the amount of ikaite precipitation, may play a possibly important role in pCO₂sw accumulation beneath ice. For example, a region with high initial Revelle factor and significant ikaite production would experience higher amplitude pCO₂sw changes than a region with low initial Revelle factor and minimal ikaite production.

The overall increase in the DIC:TA ratio and the Revelle factor over the early winter led to seasonal undersaturation of aragonite (Figures 9d and 11c). Previous studies reporting the annual cycle of O₂ sat in seasonally ice-covered Arctic waters did not report prolonged periods of undersaturation through the winter at the surface (Chierici et al., 2011; Shadwick et al., 2011). The prolonged
undersaturated winter waters we observed are potentially corrosive to calcifying benthic fauna (bivalves and echinoderms) found on the seafloor in CB (Vancouver Aquarium Marine Science Centre, 2016), implying that this area could be particularly vulnerable to future ocean acidification.

### 5.3. Polar sunrise

The maximum \( p\text{CO}_2 \) beneath the ice occurred on March 5, 2017, shortly after the first occurrence of a measurement of photosynthetically active radiation (PAR) \( \geq 2 \text{ \mu mol \cdot m}^{-2} \cdot \text{s}^{-1} \) at the platform depth on February 28 (Figure 12); 2 \text{ \mu mol \cdot m}^{-2} \cdot \text{s}^{-1} \) is described as the lower light limit of ice algae (Horner and Schrader, 1982; Gosselin et al., 1986). Following this “under-ice sunrise,” \( p\text{CO}_2 \) and \( \text{O}_2 \) patterns remain anticorrelated, suggesting that the observed drawdown was driven by an ecosystem switch toward net autotrophy at low light levels (average PAR values of 1.2 ± 0.7 \text{ \mu mol \cdot m}^{-2} \cdot \text{s}^{-1} through late winter; Figure 10). Chlorophyll-\( a \) concentrations steadily increased but remained very low through this period (Figure 12c). The observed DIC drawdown, with nearly no change in salinity or temperature during this time, was enough to drive \( p\text{CO}_2 \) to undersaturation with respect to the atmosphere after May 5 (Figure 12a). Our data confirm that photosynthetic drawdown of \( \text{CO}_2 \) starts earlier in the season than suggested by Leu et al. (2015), before surface melt allows substantial light penetration (by more than 60 days in the case of our study).

These late winter observations led us to ask what photosynthetic community might be responsible for a drawdown of 152.8 \text{ \mu mol \cdot kg}^{-1} of DIC between polar sunrise and the onset of melt. In the nearby Dease Strait, Campbell et al. (2017) reported particulate organic carbon in ice algae equal to approximately 2,000 mg \text{ \cdot m}^{-2} on May 25, 2014. Using this value and applying a simple calculation discussed in Else et al. (2019), the total calculated uptake of DIC by ice algae would equate to only 6.3 \text{ \mu mol \cdot kg}^{-1} over the CB surface mixed layer. Similarly, using observed chlorophyll-\( a \) concentrations (Figure 12c) and a carbon:chlorophyll-\( a \) ratio of 60:1, we can infer pelagic biomass...
fixation of only 0.26 μmol kg⁻¹ of DIC. As carbon:chlorophyll ratios can be quite variable (Jakobsen and Markager, 2016), we tried varying the ratio by an order of magnitude in either direction (i.e., 6:1 to 600:1), but this only produced a DIC fixation of 0.02–2.6 μmol kg⁻¹. However, the relative magnitudes of the calculated sympagic (i.e., ice-associated) and pelagic algal communities during this period are consistent with previously reported values (Gradinger, 2009). Inclusive of the uncertainty, the production in these communities is not even of the same order of magnitude as the drawdown we report. Benthic algal production is another process that could potentially be responsible, given the proximity of the platform to the seafloor, but benthic production in a similar environment at this time of year was barely detectable (Horner and Schrader, 1982). The prokaryotic process of nitrification that involves CO₂ fixation might have contributed to DIC drawdown, but reported rates have been very low (Firth et al., 2016). Having ruled out ice algae, phytoplankton, benthic microalgae, and bacterial nitrifiers as possible communities contributing significantly to the sunrise drawdown, another possible explanation for DIC drawdown without a matching increase in chlorophyll concentration may be tied to a different component of the microbial ecosystem. Despite harsh conditions through the polar night, virtually all taxonomic groups of Arctic microbes are sustained under the ice (Weslawski et al., 1999; Sherr and Sherr, 2003; Terrado et al., 2009; Iversen and Seuthe, 2011; Niemi et al., 2011). One possibility is that under low temperatures, large quantities of EPS are being produced without producing chlorophyll (as in winter sea ice; Krembs et al., 2002). Another possibility is that a tight coupling between primary production and grazing keeps chlorophyll levels low. Significant grazing of sea-ice algae during this period is unlikely; past studies have shown that grazing by micro- and meiofauna within the sea ice is negligible (Michel et al., 2002) and that grazing of ice algae by amphipods does not become significant until ice melt (Michel et al., 1996; Gradinger and Bluhm, 2010). However, Seuthe et al. (2007) found that common Arctic copepod species rapidly become active under the ice at polar sunrise and may consume enough phytoplankton to control standing stocks. Thus, grazing within the water column is a viable hypothesis to explain carbon drawdown during this time period. Without direct observations of the microbial community or grazing activity over the deployment interval, we cannot definitively attribute the sunrise DIC drawdown to a specific community, but understanding these pathways should be a priority for future research.

Figure 12. Key parameters capturing the sunrise carbon drawdown in late winter 2017. Depicted are data for (a) pCO₂, (b) O₂, (c) chlorophyll-a, and (d) photosynthetically active radiation (PAR). Atmospheric pCO₂ is represented by the horizontal dashed black line in (a). Sunrise under the ice, when PAR first measured 2 μmol m⁻² s⁻¹, is denoted by the vertical dashed black line on February 28, 2017. DOI: https://doi.org/10.1525/elementa.2021.00103.f12
We also considered this late-winter period in the context of the sea-ice pump hypothesis. While the retention of ikaite in sea ice during freezing constitutes one lever of the pump (Section 5.2), the other lever is the release of ikaite during ice melt. The release of ikaite and its subsequent dissolution in the water column will increase both DIC and TA, but at a 1:2 (DIC:TA) ratio which in turn lowers $p$CO$_2$ (Rysgaard et al., 2007). Indeed, we did observe a decrease in the DIC:TA ratio at this time (Figure 9c), coincident with the strong decrease in $p$CO$_2$ (Figure 8b). Although sea ice was still growing slowly at this time, Geilfus et al. (2016) showed that ikaite release from sea ice can occur before melt onset. We plan to investigate the potential to draw inferences about ikaite precipitation and dissolution from this data set in future work, but a strong biological drawdown in the late winter period is still required to explain observed decreases in DIC and TA (Figure 9a and b).

5.4. Spring bloom
At the onset of snowmelt (May 24, 2017), PAR transmission increased by two orders of magnitude, followed by a rapid increase in water column chlorophyll and decline in $p$CO$_{2sw}$ (Figure 13). The evolution of the carbon system during this period can be explained as the result of an under-ice phytoplankton bloom, consistent with observations under similar landfast ice conditions (Fortier et al., 2002; Mundy et al., 2009, 2014; Arrigo et al., 2012). However, the bloom we recorded at our site, with maximum chlorophyll-\(a\) of 2.4 $\mu$g L$^{-1}$, was significantly lower than observed elsewhere, for example, 12 $\mu$g L$^{-1}$ in Fortier et al. (2002), 25 $\mu$g L$^{-1}$ in Mundy et al. (2009), 18 $\mu$g L$^{-1}$ in Arrigo et al. (2012), and 11 $\mu$g L$^{-1}$ in Mundy et al. (2014). An interesting feature revealed by the high-temporal resolution data is the obvious diurnal pattern in chlorophyll-\(a\) (Figure 13c), with a similar (although less pronounced) pattern in $p$CO$_{2sw}$. Under-ice biological communities are well-adapted to low-light conditions (Mundy et al., 2009), and sudden increases in light availability may lead these communities to use a photoacclimation strategy such as nonphotochemical quenching (Falkowski and LaRoche, 1991; Macintyre et al., 2000). During this time period, the chlorophyll-\(a\) signal was visibly anti-correlated with PAR on a diurnal time scale, likely due to fluorescence quenching (Figure 13c and d). Nonetheless, diurnal $p$CO$_{2sw}$ minima appeared to occur at midday along with O$_2$ maxima, suggesting that primary production was still more efficient during periods of higher irradiance.

Figure 13. Key parameters capturing the vernal bloom of under-ice phytoplankton during spring 2017. Depicted are data for (a) $p$CO$_2$, (b) $\Omega_{AR}$, (c) chlorophyll-$a$, and (d) photosynthetically active radiation. Seawater $p$CO$_2$ (a) is undersaturated with respect to the atmosphere throughout the entire period. Saturation of $\Omega_{AR}$ is given by the horizontal dashed black line in (b). DOI: https://doi.org/10.1525/elementa.2021.00103.f13
During this under-ice phytoplankton bloom, the water once again became supersaturated with respect to aragonite (Figure 13b). Our site appears to follow a seasonal trend in CaCO₃ saturation states similar to those reported from other Arctic regions, where high rates of phytoplankton primary production and net ecosystem production act to decrease both DIC and pCO₂sw in summer, increasing CaCO₃ saturation states (Bates et al., 2009). On the other hand, freshwater from either river runoff or sea-ice melt can decrease saturation states in surface waters (Yamamoto-Kawai et al., 2009), but the shallow stratification at our site during spring (Figure 6) precluded observation of that phenomenon from the ONC platform at 7-m depth.

6. Carbon drawdown
Our study site in Cambridge Bay is likely a net annual sink for atmospheric CO₂. Through the fall, the site acted as a prominent sink for atmospheric carbon, with an average air–sea gas flux of −4.8 mmol m⁻² day⁻¹. Entering the open water season at the end of spring pCO₂sw at the platform depth was again undersaturated, and although the platform was isolated from the surface by stratification for 3 weeks in early July, discrete samples collected at the surface through that time (Figure 7) indicated that surface pCO₂sw remained undersaturated.

The observed period of 134 days of Ω₄ underline undersaturation during winter and spring of the 2016–2017 deployment is, to the best of our knowledge, the longest period of under-ice Arctic surface water Ω₄ underline undersaturation yet reported. Based on the assumption that surface waters in CB share similar exposure to anthropogenic emissions as surface waters of the Canada Basin, we can estimate the anthropogenic contribution to the DIC load in Cambridge Bay (Tanhua et al., 2009). Given the typical inorganic carbon properties in CB, if the anthropogenic CO₂ component of DIC (40 ± 5 μmol kg⁻¹, from Tanhua et al., 2009) were subtracted from our calculated DIC values, then Ω₄ would be 0.33 ± 0.02 higher. This higher value means that during preindustrial times, Ω₄ underline undersaturation would not likely have occurred in CB, assuming that all other environmental conditions were the same (e.g., temperature, salinity, net ecosystem production, sea-ice thickness, and growth duration). Therefore, we conclude that the observed seasonal Ω₄ underline undersaturation is likely caused by the biologically induced seasonality of Ω₄ underline, superimposed on a decline in Ω₄ due to long-term ocean acidification similar to the findings of Bates et al. (2009).

As is often the case, the location of the sensor platform was a compromise between logistics and scientific objectives. Nonetheless, our results show that the site is representative of the greater sea-surface mixed layer in the bay after sea-ice formation and development of the winter mixed layer. Stratification in the spring isolated the platform from the air–sea interface, and therefore, the platform did not provide information on surface conditions for approximately 3 weeks during 2017. Manning et al. (2020) showed how important this period can be for methane fluxes in CB, but the platform’s current location limited it from resolving air–sea gas fluxes for CO₂ during this time. However, the platform was still representative of offshore conditions at similar depths year-round. Future users of physical and biogeochemical data produced at bottom-moored observatories, even in shallow waters, should be aware of such seasonal constraints when interpreting data.

Our seasonal analyses showed that through the fall, pCO₂sw was undersaturated with respect to the atmosphere, acting as a net sink for air–sea gas exchange. Following sea-ice freeze-up, brine rejection and respiration drove pCO₂sw to supersaturation with respect to the atmosphere, and aragonite to undersaturation. These are the first observations of prolonged (130 day) seasonal aragonite undersaturation in surface waters of the Arctic. Shortly after light availability under the ice began to increase yet was still very low, the ecosystem at the platform changed from net heterotrophic to net autotrophic, driving pCO₂sw back to undersaturation well before sea ice had begun to melt. During this late winter period, reported growth in ice algae, observed water column chlorophyll-a used to infer phytoplankton production, and assumed benthic microalgal production were insufficient to explain the sunrise DIC drawdown. A likely possibility is that grazing within the water column kept pelagic phytoplankton stocks low, while production decreased DIC. The lack of under-ice ecosystem observations during this time period highlights the need for further investigation. As the sea ice melted in the spring and light availability increased in the underlying water column, an under-ice phytoplankton bloom was able to draw down a significant amount of carbon before the open water season, effectively increasing pH and restoring aragonite supersaturation. Although the sensor platform could not measure surface pCO₂sw shortly after ice melt, it provided strong evidence that this region is a significant sink for atmospheric CO₂ through-out the open water season.

Data accessibility statement
Ocean Networks Canada platform data: data.oceannetworks.ca.
Discrete sample data: Duke (2019).
Supplemental files
The supplemental files for this article can be found as follows:
Text S1–S3.docx
Table S1–S3.docx
Figure S1.png
Acknowledgments
Thanks to the Hamlet and residents of Cambridge Bay for allowing us to conduct research on the traditional territory of the Inuit people. Thanks to Ocean Networks Canada for operating the sensor platform from deployment and recovery to data streaming and to the Ekalutktiak Hunters and Trappers Organization, and all the guides that helped in the field, especially C. Amegainik. Polar Knowledge Canada and staff at the Canadian High Arctic Research Station, particularly A. Pedersen, made this study possible by providing logistical support. Special thanks to F. Emingak for additional field support. We also thank M. Davelaar for DIC and TA sample analyses. The Arctic Research Foundation, Polar Knowledge Canada, and the Nunavut Arctic College provided logistical support. A portion of the data used in this work were provided by Ocean Networks Canada.

Funding
Funding for this project was provided by NSERC Discovery, NSERC Northern Research Supplement, and Canada Foundation for Innovation Grants to B. Else. This project also received significant financial support from the MEOPAR, the ArcticNet Network of Centres of Excellence, and Fisheries and Oceans Canada. H. Thomas acknowledges support by the German Academic Exchange Service (DAAD, MOPGA-GRI, #57429828) supported by funds of the German Federal Ministry of Education and Research (BMBF).

Competing interests
The authors declare that they have no conflicts of interest.

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Substantial contributions to conception and design: PJD, BGTE, SFJ, SM, RD, AS, LAM, HT.

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Analysis and interpretation of data: PJD, BGTE, MMMA, VN, BB, LAM.

Drafting the article or revising it critically for important intellectual content: PJD, BGTE, MMMA, VN, BB, LAM.

Final approval of the version to be published: PJD, BGTE, SFJ, SM, MMMA, VN, BB, SFG, RD, AS, LAM, KGS, HT.

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