

## Key Points:

- The Dalton Polynya was a weak net source of CO<sub>2</sub> to the atmosphere during summer observations
- Net community production estimates were 5–20 mmol C m<sup>-2</sup> day<sup>-1</sup> in ice-free and -4.0 mmol C m<sup>-2</sup> day<sup>-1</sup> in ice-covered regions
- Remotely sensed products reveal below average surface chlorophyll *a* and above average sea ice cover in contrast to long-term summer means

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# Summer Carbonate Chemistry in the Dalton Polynya, East Antarctica

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**Abstract** The carbonate chemistry in the Dalton Polynya in East Antarctica (115°–123°E) was investigated in summer 2014/2015 using high-frequency underway measurements of CO<sub>2</sub> fugacity (*f*CO<sub>2</sub>) and discrete water column measurements of total dissolved inorganic carbon (TCO<sub>2</sub>) and total alkalinity. Air-sea CO<sub>2</sub> fluxes indicate this region was a weak net source of CO<sub>2</sub> to the atmosphere ( $0.7 \pm 0.9$  mmol C m<sup>-2</sup> day<sup>-1</sup>) during the period of observation, with the largest degree of surface water supersaturation ( $\Delta f$ CO<sub>2</sub> = +45  $\mu$ atm) in ice-covered waters near the Totten Ice Shelf (TIS) as compared to the ice-free surface waters in the Dalton Polynya. The seasonal depletion of mixed-layer TCO<sub>2</sub> (6 to 51  $\mu$ mol/kg) in ice-free regions was primarily driven by sea ice melt and biological CO<sub>2</sub> uptake. Estimates of net community production (NCP) reveal net autotrophy in the ice-free Dalton Polynya (NCP = 5–20 mmol C m<sup>-2</sup> day<sup>-1</sup>) and weakly heterotrophic waters near the ice-covered TIS (NCP = -4–0 mmol C m<sup>-2</sup> day<sup>-1</sup>). Satellite-derived estimates of chlorophyll *a* (Chl *a*) and sea ice coverage suggest that the early summer season in 2014/2015 was anomalous relative to the long-term (1997–2017) record, with lower surface Chl *a* concentrations and a greater degree of sea ice cover during the period of observation; the implications for seasonal primary production and air-sea CO<sub>2</sub> exchange are discussed. This study highlights the importance of both physical and biological processes in controlling air-sea CO<sub>2</sub> fluxes and the significant interannual variability of the CO<sub>2</sub> system in Antarctic coastal regions.

**Plain Language Summary** Coastal polynyas in Antarctica are dynamic regions that play important roles in the global cycling of carbon. Polynyas are reoccurring areas of open water within sea ice and are often associated with enhanced rates of photosynthesis and exchange of carbon dioxide between the atmosphere and ocean surface. In this study, we use shipboard observations from the first oceanographic cruise in the Dalton Polynya near the Totten and Moscow University Ice Shelves in East Antarctica to characterize the inorganic carbon chemistry in the summertime. We find that the surface concentrations of total dissolved inorganic carbon are reduced in areas of open water mainly as a result of seasonal sea ice melt and the uptake of inorganic carbon by photosynthesis and less so due to air-sea exchange of carbon dioxide. Compared to other coastal polynyas in East Antarctica, our results show that the Dalton Polynya may have smaller rates of net photosynthesis and carbon dioxide exchange.

## 1. Introduction

The Southern Ocean plays an integral part in the global biogeochemical cycling of carbon, mediating the exchange of both natural and anthropogenic CO<sub>2</sub> between the upper ocean and atmosphere (Arrigo, van Dijken, & Long, 2008; Sabine et al., 2004; Takahashi et al., 2009). Although several global estimates of air-sea CO<sub>2</sub> exchange agree that the open Southern Ocean sustains one of the largest sinks of atmospheric CO<sub>2</sub> (Gruber et al., 2009; Khaliwala et al., 2009; Lenton et al., 2013), uncertainties remain regarding the magnitude of this CO<sub>2</sub> uptake along Antarctic continental shelves that are seasonally covered with sea ice (Lenton et al., 2013). Models are confounded in these regions by the limited number of direct observations and significant natural variability of the CO<sub>2</sub> system on both temporal and spatial scales (e.g., McNeil et al., 2011).

Polynyas are reoccurring areas of open water surrounded by sea ice that form along the coasts of the Antarctic icescape, typically in the lee of a fixed boundary, such as a grounded iceberg or a glacial tongue. In these regions, strong ocean currents and/or katabatic winds push newly formed sea ice away to sustain areas of open water or thin ice for much of the year (Massom et al., 1998; Morales Maqueda et al., 2004).

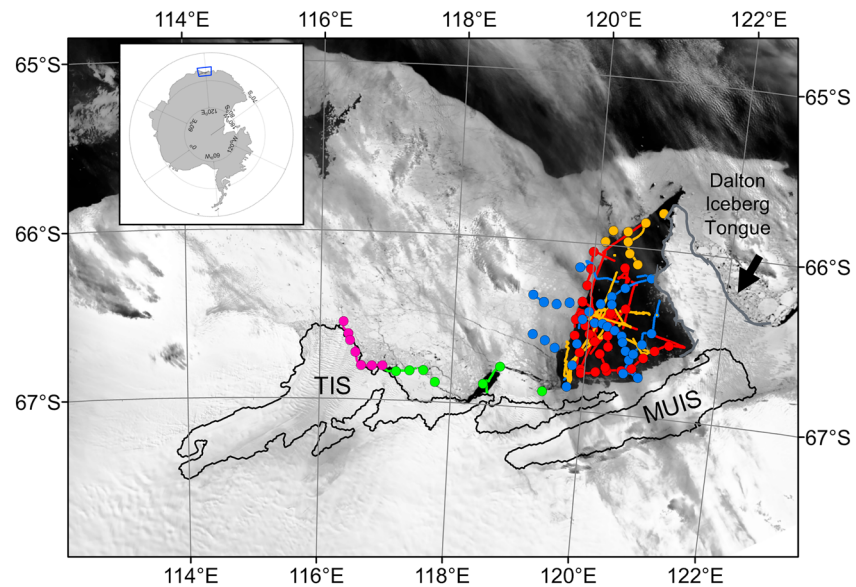
There is a growing understanding of the interactive physical and biological processes impacting CO<sub>2</sub> system dynamics in seasonally sea ice-covered regions such as the East Antarctic (Roden et al., 2016; Shadwick et al., 2014), the West Antarctic Peninsula (Jones et al., 2017; Legge et al., 2017), and the Amundsen (Mu et al., 2014; Yager et al., 2016) and Ross Seas (DeJong et al., 2015; DeJong & Dunbar, 2017). In the spring and summer, coastal polynyas often support intense biological activity relative to their small surface areas as reduced sea ice coverage exposes surface waters to incoming solar radiation (Arrigo & van Dijken, 2003), driving a dramatic undersaturation in CO<sub>2</sub> at the ocean surface. The timing and magnitude of surface biological CO<sub>2</sub> drawdown are strongly influenced by local sea ice dynamics that determine light and micro-nutrient (e.g., iron) availability, water column stratification, and the degree of open water. The organic matter that forms during the productive season can be recycled in the mixed layer or exported to depth where it will be subsequently remineralized back to CO<sub>2</sub>. In winter, deep convective mixing driven by brine rejection during sea ice formation reinjects CO<sub>2</sub>-rich waters to the surface layer where the presence of sea ice may act as a barrier for air-sea exchange and prevent the outgassing of CO<sub>2</sub> to the atmosphere (Loose et al., 2011; Yager et al., 1995). In some Antarctic polynyas, these CO<sub>2</sub>-rich waters may additionally be transported off the continental shelf with the formation of dense water (Shadwick et al., 2014). Their disproportionate roles in the air-sea exchange of CO<sub>2</sub> (e.g., Sweeney, 2003), primary production (e.g., Shadwick et al., 2017), and in some cases Dense Shelf Water and Antarctic Bottom Water formation (Orsi et al., 1999; Rintoul, 1998; Williams et al., 2008) make these coastal polynya systems important players in the biogeochemical cycles of the Southern Ocean.

Despite the importance of the continental shelf regions in global carbon cycling, few observational CO<sub>2</sub> system studies have been conducted in the coastal East Antarctic. The Dalton Polynya is a coastal polynya located on the Sabrina Coast in East Antarctica, forming in the lee of the Dalton Iceberg Tongue (Figure 1). The surrounding Totten and Moscow University Ice Shelves (TIS and MUIS, respectively), which terminate at the sea boundary in the Dalton Polynya, are among the fastest thinning on the East Antarctic Ice Sheet, with high rates of mass loss (Mohajerani et al., 2018) and basal ice shelf melting near their grounding lines over the past 15 years (Rignot et al., 2013). Basal melting of these ice shelves is driven by on shelf intrusions of relatively warm (>0 °C) modified Circumpolar Deep Water to ice shelf cavities (Li et al., 2015; Rintoul et al., 2016; Silvano et al., 2017) and is modulated by surface winds stress (Greene et al., 2017). These high basal melt rates (>4 m/year) are similar to those observed in the West Antarctic Ice Sheet near the Amundsen and Bellingshausen Seas, regions often thought of as more vulnerable to mass loss and glacial thinning (Rignot et al., 2013; Silvano et al., 2017). Meltwater input to the Dalton Polynya contributes to significant water column freshening, reducing the possibility for dense water formation in the region (Silvano et al., 2018). Previous studies in the coastal Antarctic suggest glacially derived meltwater may influence mixed-layer biogeochemistry and carbon cycling by stimulating high levels of primary production through the delivery of iron and other essential micronutrients to surface waters (e.g., Eveleth et al., 2017; Gerringa et al., 2012). The potential impacts of glacial mass loss and high rates of basal melting to the Dalton Polynya system may drive future changes in biological production and air-sea CO<sub>2</sub> flux that ultimately influence the carbonate chemistry.

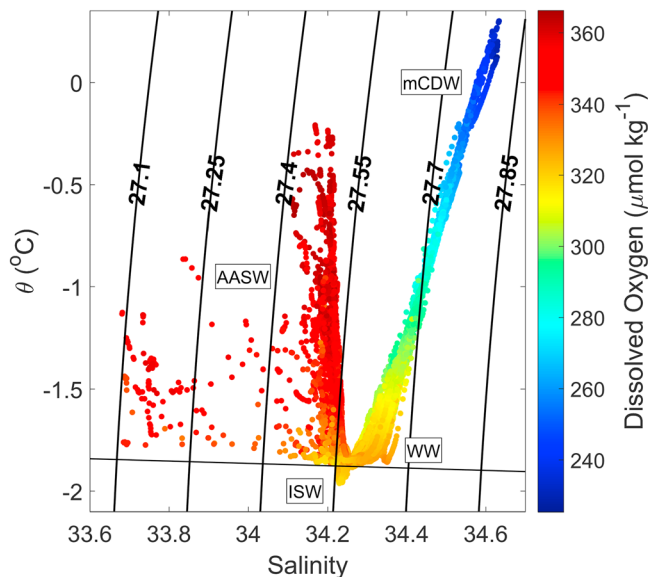
Here we present CO<sub>2</sub> system measurements from the Dalton Polynya in early summer (Figure 1). A combination of high-frequency underway measurements of sea surface CO<sub>2</sub> fugacity ( $f\text{CO}_2$ ) along the ship track and discrete samples of total dissolved inorganic carbon (TCO<sub>2</sub>) and total alkalinity (TA) is used to characterize the biogeochemistry of the region. The physical and biological processes responsible for observed distributions of mixed-layer TCO<sub>2</sub> are examined, and net community production is computed via seasonal deficits in TCO<sub>2</sub> concentration. Additionally, the spatial variability of air-sea CO<sub>2</sub> fluxes is evaluated. These new observations are also examined in comparison to the long-term (1997–2017) surface chlorophyll *a* concentration and sea ice coverage derived from remote sensing products to assess interannual variability. Results from the Dalton Polynya highlight the importance of both physical and biological processes in controlling the significant seasonality in the CO<sub>2</sub> system of Antarctic coastal waters.

## 2. Oceanographic Setting

We follow the water mass characterization of Silvano et al. (2017) to define the four major water masses in the Dalton Polynya (DP) during the summer season, constrained here by potential density anomaly surfaces



**Figure 1.** Map of the Dalton Polynya. Underway ship track (lines) and CTD stations (circles) on the *RV Aurora Australis* between 24 December 2014 and 8 January 2015 overlain on a MODIS-Terra satellite image from 10 January 2015. Observations were made within the polynya and near both the Moscow University Ice Shelf (MUIS) and the Totten Ice Shelf (TIS). Red indicates measurements between 24 and 29 December 2014 (DP1). Blue indicates measurements between 2 and 5 January 2015 and three CTD stations on 7 January (DP2). Yellow indicates measurements between 6 and 8 January 2015 (DP3). Measurements made near the TIS are indicated in magenta (West Totten; WT) and green (East Totten; ET) between 30 December 2014 and 1 January 2015.



**Figure 2.** Potential temperature ( $\theta$ ; °C) and salinity diagram, with contours of potential density anomaly ( $\sigma_\theta$ ; kg/m<sup>3</sup>), and colors for dissolved oxygen ( $\mu\text{mol/kg}$ ). The black thick solid line marks the surface freezing point of seawater. Water masses are labeled as Antarctic Surface Water (AASW), modified Circumpolar Deep Water (mCDW), Winter Water (WW), and Ice Shelf Water (ISW). See text and Table 1 for definitions.

referenced to surface pressure ( $\sigma_\theta$ , kg/m<sup>3</sup>) and potential temperature ( $\theta$ , °C; Figure 2 and Table 1). Antarctic Surface Water (AASW) is the lightest ( $\sigma_\theta < 27.55$  kg/m<sup>3</sup>) and is highly variable in surface temperature (between  $-1.86$  and  $-0.23$  °C) and salinity (between 33.6 and 34.2; Figure 2). AASW is relatively fresh, due to seasonal melting from both the surrounding sea ice and the ice shelves to the south. This water mass varies in thickness across the region: in the ice-free DP, AASW occupies the upper  $\sim 80$  m (Figure 3); near the TIS, signals of AASW virtually disappear, as Winter Water (WW) reaches the surface (Figure 4). WW ranges between  $27.55 < \sigma_\theta < 27.70$  kg/m<sup>3</sup> and  $-1.92 < \theta < -1.75$  °C and occupies most of the water column in summer as a product of vertical convection. The depth range of WW depends on its location within the polynya, as WW shoals nearly to the surface along the ice shelves.

Dense Shelf Water does not form in the DP. Instead, relatively warm, salty modified Circumpolar Deep Water (mCDW) floods the deep basin in summer ( $\sigma_\theta > 27.70$  kg/m<sup>3</sup>), bringing heat, nutrient, CO<sub>2</sub>-rich, and relatively O<sub>2</sub>-poor water onto the shelf. The inflow of mCDW through deep troughs in both the TIS and MUIS delivers a substantial amount of heat to drive rapid basal melt at the grounding line (Greenbaum et al., 2015; Rintoul et al., 2016; Silvano et al., 2017). At the MUIS ice front, the melting drives the formation of Ice Shelf Water (ISW), through the mixture of basal ice shelf meltwater and WW. ISW is supercooled due to pressure at  $\theta < -1.92$  °C within the same  $\sigma_\theta$  range as WW. The input of basal meltwater, particularly near the MUIS, also leads to a shoreward freshening of WW near the southern edge of the DP (Silvano et al., 2017).

**Table 1**  
*Water Mass Classifications*

Water mass	$\sigma_\theta$ (kg/m <sup>3</sup> )	$\theta$ (°C)
Antarctic Surface Water	$\sigma_\theta < 27.55$	
Winter Water	$27.55 < \sigma_\theta < 27.7$	$-1.92 < \theta < -1.75$
Ice Shelf Water	$27.55 < \sigma_\theta < 27.7$	$\theta < -1.92$
Modified Circumpolar Deep Water	$27.7 < \sigma_\theta$	

*Note.* Constraints of potential density anomaly ( $\sigma_\theta$ ; kg/m<sup>3</sup>) and potential temperature ( $\theta$ ; °C) follow definitions by Silvano et al. (2017).

### 3. Methods

Observations were made during a survey of the Dalton Polynya and surrounding ice shelves along the Sabrina Coast (116°–122°E) on board the *RV Aurora Australis* between 25 December 2014 and 8 January 2015 (Figure 1; Rosenberg & Rinoul, 2016). The ship occupied 68 stations in the DP and near the MUIS and 13 stations in a lead in front of the TIS. During each cast, continuous measurements of temperature (°C), salinity, pressure (dbar), and dissolved oxygen ( $\mu\text{mol/kg}$ ) were made using SeaBird instruments (SBE9plus and SBE43 models). Instruments were mounted onto a rosette frame with 22 10-L General Oceanics Niskin bottles for discrete seawater sampling; hydrographic property analysis of conductivity, temperature, and depth (CTD) data is described further in Silvano et al. (2017).

The shelf can be separated into two broad regions: DP refers to the region east of 119°E and TIS refers to the region west of 119°E. These regions are further partitioned into subregions illustrated in Figure 1. The DP includes measurements made between 24 and 29 December (DP1, blue), between 2 and 5 January and three CTD stations on 7 January (DP2, red), and between 6 and 8 January (DP3; yellow). The TIS region includes measurements between 30 December and 1 January and is divided into West Totten (WT; magenta) and East Totten (ET; green).

#### 3.1. Discrete CO<sub>2</sub> System and Biogeochemical Observations

Discrete samples of TCO<sub>2</sub> and TA were collected into 250-ml bottles at each station. Each sample was immediately fixed with a saturated solution of mercuric chloride to halt biological activity. TCO<sub>2</sub> and TA concentrations were measured on board by coulometric titration using a Single Operator Multiparameter Metabolic Analyzer (SOMMA) system and by automatic open-cell potentiometric titration with 0.1 M hydrochloric acid, respectively, following methods of Dickson et al. (2007). Routine analysis of Certified Reference Material (CRM Batch #137) from A. G. Dickson ensured that the analytical uncertainties (precision and accuracy) were better than  $\pm 1.4 \mu\text{mol/kg}$  for TCO<sub>2</sub> and  $\pm 1.5 \mu\text{mol/kg}$  for TA.

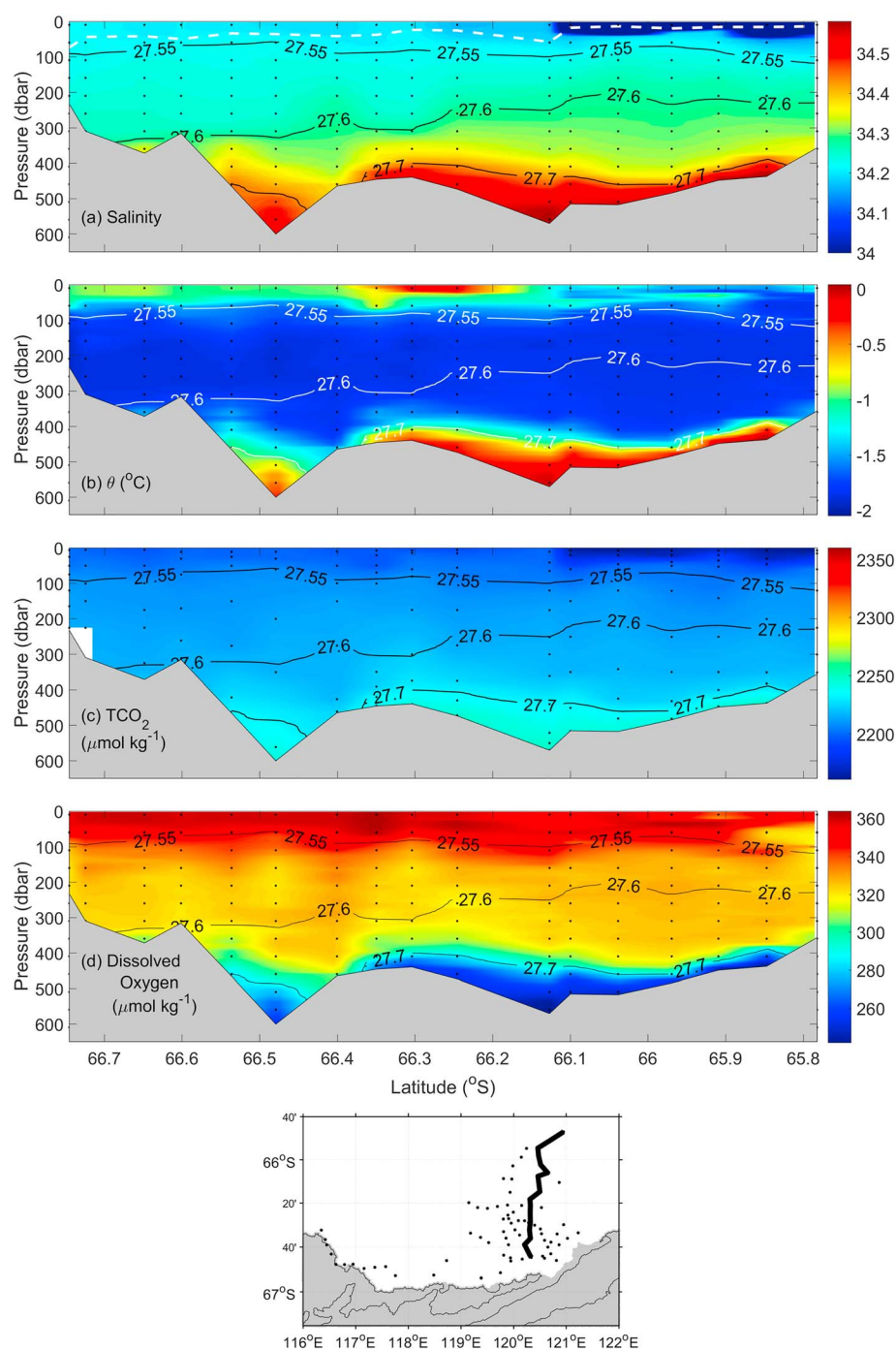
Samples of dissolved oxygen were collected in parallel to CO<sub>2</sub> system observations and analyzed on board by Winkler Titration following methods of Hood et al. (2010), with an uncertainty of <1%. Inorganic nutrient samples were collected for phosphate ( $\text{PO}_4^{3-}$ ) and silicic acid ( $\text{Si(OH)}_4$ ) and frozen until analysis at CSIRO in Hobart, Australia, following standard methods of Grasshoff et al. (2007). Uncertainties for  $\text{PO}_4^{3-}$  and  $\text{Si(OH)}_4$  were <5%.

The saturation state of aragonite ( $\Omega_{\text{Ar}}$ ) and pH on the total scale were calculated from TCO<sub>2</sub> and TA using CO<sub>2</sub>SYS program by van Heuven et al. (2011), using the thermodynamic equilibrium constants by Mehrbach et al. (1973) refit by Dickson and Millero (1987). Average values of  $\text{PO}_4^{3-}$  ( $2.06 \pm 0.07 \mu\text{mol/kg}$ ) and  $\text{Si(OH)}_4$  ( $64 \pm 7 \mu\text{mol/kg}$ ) were used. Calcium ion concentration was assumed to be conservative with and calculated from salinity (Riley & Tongudai, 1967).

#### 3.2. Underway *f*CO<sub>2</sub> Measurements and Air-Sea CO<sub>2</sub> Flux Calculations

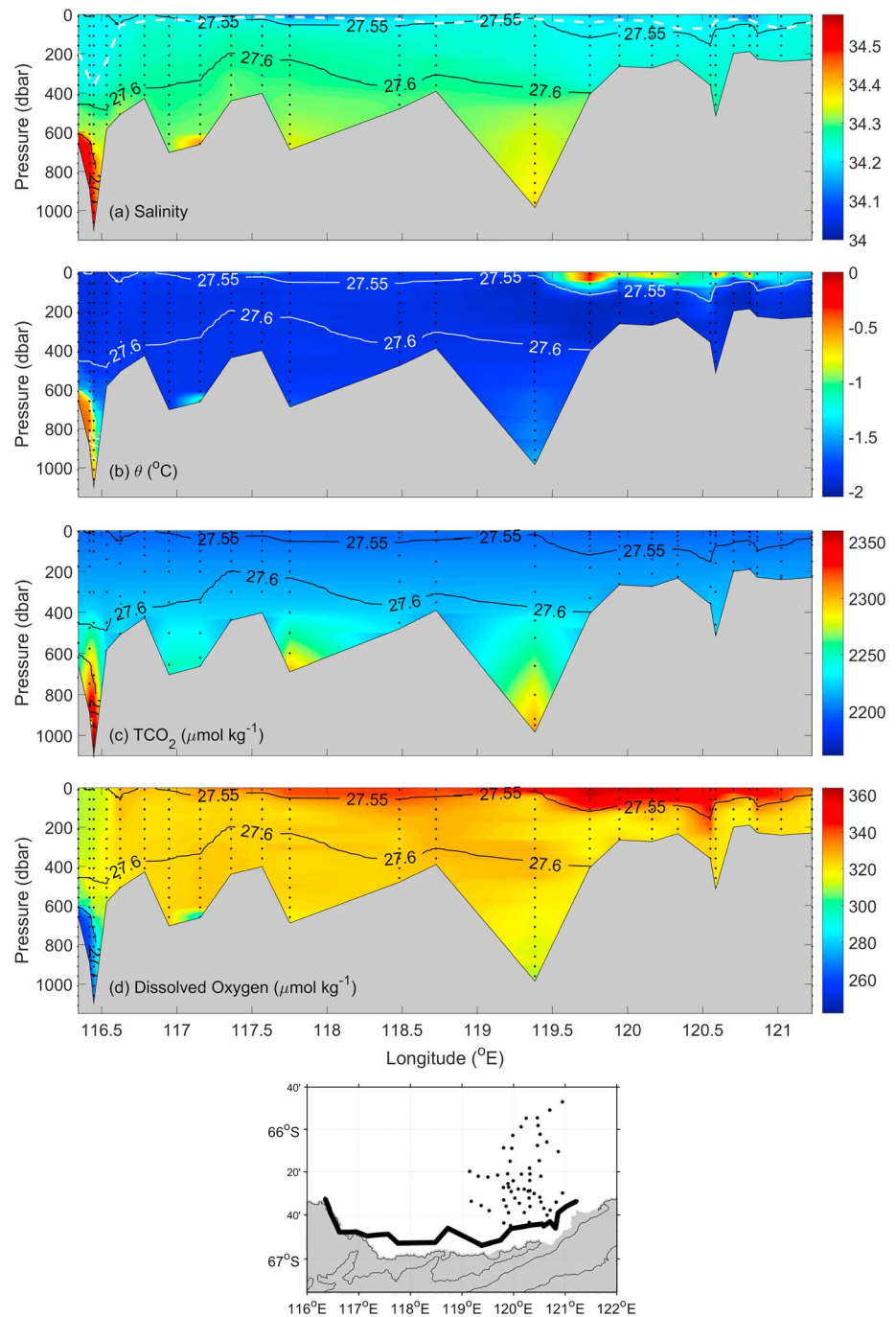
Continuous high-resolution underway measurements of the *f*CO<sub>2</sub>, sea surface salinity, and sea surface temperature were made from the seawater intake ~4 m below the ocean surface. The *f*CO<sub>2</sub> in seawater was measured via continuous flow equilibration using a nondispersive infrared spectrometer (LI-COR, LI7000; Pierrot et al., 2009). The underway *f*CO<sub>2</sub> system was calibrated every 4 hr with four standards: a CO<sub>2</sub>-free air and three CO<sub>2</sub> concentrations of 299.41, 354.00, and 402.15  $\mu\text{atm}$  in dry air on the WMO-X2007 mole





**Figure 3.** Offshore (north-south) section through the Dalton Polynya for (a) salinity, (b) potential temperature ( $\theta$ ;  $^{\circ}\text{C}$ ), (c)  $\text{TCO}_2$  ( $\mu\text{mol/kg}$ ), and (d) dissolved oxygen ( $\mu\text{mol/kg}$ ) with contours of potential density anomaly ( $\text{kg/m}^3$ ) and white dashed contour of calculated mixed layer depth in (a). The black dots indicate the station locations.

fraction scale. Approximately 70 s were needed for the seawater to pass from the ship intake to the  $\text{CO}_2$  system, warming by less than  $0.6^{\circ}\text{C}$ . All  $f\text{CO}_2$  measurements were corrected to in situ temperature and salinity and to 100% humidity. The atmospheric mole fraction of  $\text{CO}_2$  was also measured at roughly 16 m above sea level to calculate the atmospheric  $f\text{CO}_2$ . The mean atmospheric  $f\text{CO}_2$  was  $379 \pm 1.7 \mu\text{atm}$  throughout the voyage. The  $f\text{CO}_2$  measurement uncertainties are  $2 \mu\text{atm}$  in seawater and  $0.2 \mu\text{atm}$  in air at 350  $\mu\text{atm}$ .



**Figure 4.** Along-shore (west-east) section in front of the Totten and Moscow University Ice Shelves for (a) salinity, (b) potential temperature ( $\theta$ ; °C), (c)  $\text{TCO}_2$  ( $\mu\text{mol/kg}$ ), and (d) dissolved oxygen ( $\mu\text{mol/kg}$ ) with contours of potential density anomaly ( $\text{kg/m}^3$ ) and white dashed contour of calculated mixed layer depth in (a). The black dots indicate the station locations.

The air-sea flux of  $\text{CO}_2$  between the sea surface and the atmosphere was computed via the following equation:

$$F_{\text{CO}_2} = k \alpha \Delta f_{\text{CO}_2} \quad (1)$$

where  $F_{\text{CO}_2}$  is the flux ( $\text{mmol C m}^{-2} \text{ day}^{-1}$ ),  $k$  is the gas transfer velocity,  $\alpha$  is the solubility of  $\text{CO}_2$  (Weiss, 1974), and  $\Delta f_{\text{CO}_2}$  ( $\mu\text{atm}$ ) is the gradient in  $f_{\text{CO}_2}$  between the atmosphere and sea surface

( $\Delta f\text{CO}_2 = f\text{CO}_2^{\text{sea}} - f\text{CO}_2^{\text{air}}$ ). A positive flux indicates a net transfer from the ocean to the atmosphere (i.e., outgassing). The parametrization of Wanninkhof (2014) was used to compute  $k$  using daily averaged short-term winds, consistent with methodology from other polynya regions (e.g., Gibson & Trull, 1999; Shadwick et al., 2014, 2017), from the National Centers for Environmental Prediction and National Center for Atmospheric Research (NCEP/NCAR) Reanalysis product recorded at 10-m height above the sea surface (Kalnay et al., 1996). The exchange time of  $\text{CO}_2$  between the surface ocean and the atmosphere is on the order of months (Broecker & Peng, 1974) and air-sea  $\text{CO}_2$  fluxes were similarly computed using a long-term gas transfer velocity term to provide a broader context for instantaneous (short-term) fluxes. A long-term  $k$  was calculated from the average of the daily second moment of the wind speed ( $\langle \text{wind speed}^2 \rangle$ ) across eight NCEP/NCAR grid cells (within the spatial range of 65° - 68°S and 116° - 122°E) between December 2014 and January 2015 (Evans et al., 2015; Wanninkhof, et al. 2004). We estimate an uncertainty associated with the air-sea  $\text{CO}_2$  flux of 0.3 mmol C m<sup>-2</sup> day<sup>-1</sup> by comparing results obtained with several different gas transfer parameterizations (Edson et al., 2011; Ho et al., 2006; Sweeney et al., 2007; Wanninkhof, 1992).

### 3.3. Seasonal Partitioning of $\text{TCO}_2$ and Net Community Production Computations

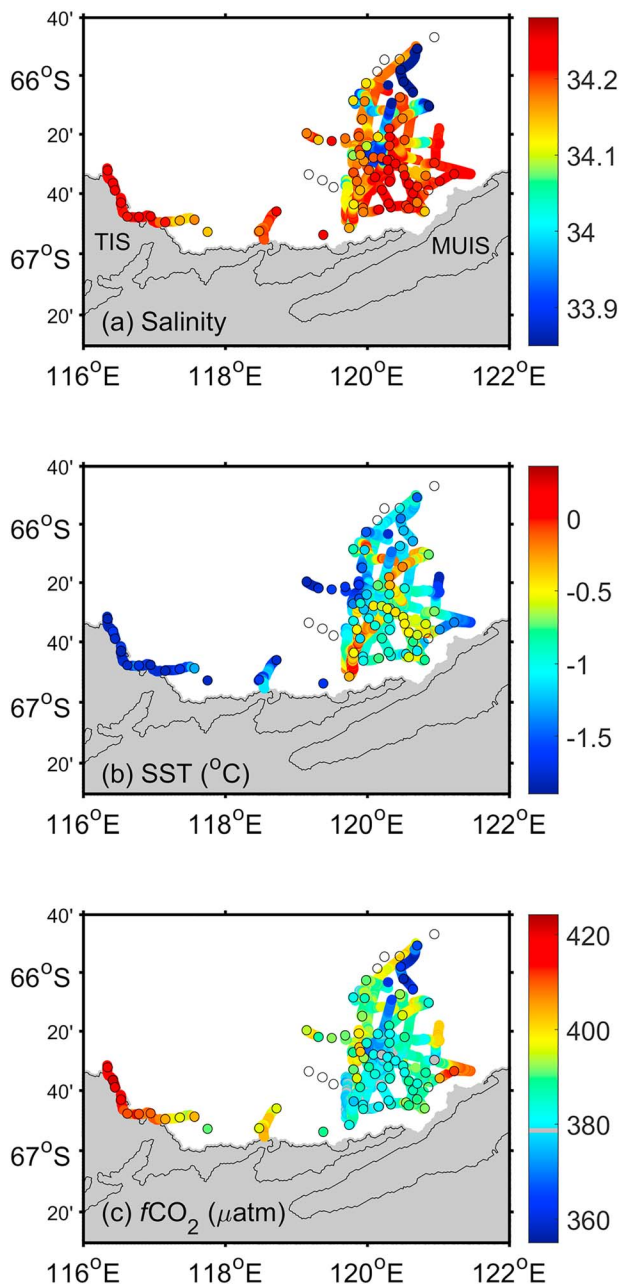
Seasonal changes of  $\text{TCO}_2$  in the summer mixed layer are influenced both by physical (e.g., air-sea  $\text{CO}_2$  exchange, mixing, and calcium carbonate dissolution) and biological (e.g., photosynthesis, respiration, and calcium carbonate formation) processes. The summer mixed layer depth (MLD) at each station is defined here as the depth at which the potential density exceeds that of a reference measurement at 10 m by a threshold 0.01 kg/m<sup>3</sup> (e.g., Shadwick et al., 2014) and was comparable to MLD expressed as the maximum of the buoyancy frequency (Carvalho et al., 2017). Although observed summer MLDs in the DP were typically <100 m, deeper vertical mixing earlier in the productive season (i.e., late winter, early spring) extends well below 100 m (Williams et al., 2011). Late-winter measurements in 2007 found the deepest winter mixed layer on the Sabrina Coast in the northern DP, reaching depths >350 m (Williams et al., 2011). Summer MLDs in front of the western TIS, however, were significantly deeper (MLDs >180 m) than in the open waters of the DP.

Wintertime  $\text{TCO}_2$  concentration in surface waters is often estimated using the value at the temperature minimum (e.g., Bates et al., 1998; Roden et al., 2016). However, on the Antarctic shelf, the temperature minimum is not well defined, for example in the areas in front of the MUIS where ISW is present (Silvano et al., 2017). Profiles of  $\text{TCO}_2$  indicate a consistent concentration at depths in the WW water mass ( $27.55 < \sigma_\theta < 27.70$  kg/m<sup>3</sup> and  $-1.92 < \theta < -1.75$  °C), roughly between 150 and 350 m. Thus, we estimate the surface wintertime  $\text{TCO}_2$  concentration as the average concentration at 150 m depth ( $\text{TCO}_2^{\text{winter}} = 2,216 \pm 2$  μmol/kg,  $n = 26$ ). Measurements of  $\text{TCO}_2$  and TA are normalized to the average regional salinity ( $S = 34.3$ ) to account for the seasonal variations in concentration due to changes in salinity from sea ice formation and melting, as well as mixing (e.g., Shadwick et al., 2014).

The seasonal change in  $\text{TCO}_2$  due to biological processes is expressed as the net community production (NCP), the difference between net primary production and heterotrophic respiration. NCP (mmol C m<sup>-2</sup> day<sup>-1</sup>) was computed at each station by the depth integrated seasonal deficit of salinity normalized  $\text{TCO}_2$  ( $n\text{TCO}_2$ ) via

$$\text{NCP} = \int_{z=0}^{z=100} [n\text{TCO}_2]^{\text{winter}} - [n\text{TCO}_2]^{\text{observations}} dz \quad (2)$$

where  $z$  is depth in meters. Although MLDs at each station were above 100 m within the open waters of the Dalton Polynya, we integrated to 100 m to account for deeper vertical mixing earlier in the productive season (Bates et al., 1998; Shadwick et al., 2014; Williams et al., 2011). The length of the productive season was defined as time since 1 November 2014 based on the increase in surface chlorophyll  $a$  (Chl  $a$ ) concentration relative to winter months (June, July, and August) inferred from Moderate Resolution Imaging Spectroradiometer (MODIS)-Aqua satellite imagery during the 2014/2015 summer season (see section 5.2). This estimation of NCP does not account for the contribution of seasonal air-sea  $\text{CO}_2$  exchange, although the contribution is small based on summer  $F_{\text{CO}_2}$  computations (see sections 4.2 and 5.1 for further discussion).



**Figure 5.** Underway surface measurements in the Dalton Polynya for (a) salinity, (b) sea surface temperature (SST; °C), and (c)  $f\text{CO}_2$  ( $\mu\text{atm}$ ). The mean atmospheric  $f\text{CO}_2$  (379  $\mu\text{atm}$ ) is indicated by the gray line in the color bar of (c). Colored circles correspond to the underway measurements taken at the time of CTD sampling. TIS = Totten Ice Shelf; MUIS = Moscow University Ice Shelf.

### 3.4. Satellite Remote Sensing Products

Satellite-derived sea surface Chl  $a$  concentrations were obtained from Level 3 processed, 9-km resolution measurements from SeaWiFS (Sea-viewing Wide Field-of-view Sensor) between July 1997 and June 2002 and from MODIS-Aqua between July 2002 and June 2017. Similarly, sea ice coverage estimates were obtained from the Special Sensor Microwave/Imager (SMM/I) and the Special Sensor Microwave Imager/Sounder (SMMIS) on the Defense Meteorological Satellite Program (DMSP) satellite from the National Snow and Ice Data Center (NSIDC) between July 1997 and June 2017 at 25-km resolution and Level 3 processing. All data presented here are monthly averaged values in the Dalton Polynya, within the region between 65.8 and 67.0°S and 119 and 121°E (see Figure 1).

## 4. Results

### 4.1. Hydrographic and Biogeochemical Properties

AASW ( $\sigma_\theta < 27.55 \text{ kg/m}^3$ ) in the DP was relatively warm and fresh, reflecting the summer conditions of surface warming and local sea ice melt (Figures 2 and 5 and Table 2). Sea surface salinity was between about 33.9 and 34.3 within the DP (east of 119°E). In the northern DP, minimum surface salinity ( $S < 33.9$ ) was observed toward the end of the voyage, likely driven by melting sea near the Dalton Iceberg Tongue. Sea surface temperatures were warmer in the central DP with values ranging from  $-1.2$  to  $+0.4$  °C, and colder near the outer edges of the polynya and near the TIS with a minimum of  $-1.8$  °C (Figure 5b). In front of the TIS, WW outcropped to the surface, and salinities of  $\sim 34.25$  were observed.

The mean concentration of dissolved oxygen ( $\sim 341 \mu\text{mol/kg}$ ) in AASW was greater than values found elsewhere in East Antarctica (Roden et al., 2016; Shadwick et al., 2014), with concentrations more comparable to saturated conditions ( $\sim 350$ – $360 \mu\text{mol/kg}$ ) though similar surface temperature and salinity was observed (Table 2). The percent saturation of dissolved oxygen at the sea surface was greatest ( $>99\%$ ) in the central, open waters of the Dalton Polynya (Figure 3d) and decreased toward and along the outer edges of the polynya and near the TIS (Figure 4d). In front of the TIS, surface dissolved oxygen reached a minimum concentration ( $305 \mu\text{mol/kg}$ , 85% saturation), coincident with the WW outcrop and entrainment of oxygen-poor subsurface waters. Dissolved oxygen concentration further decreased with depth below the surface mixed layer in WW (Figures 3d and 4d) to values ranging between 300 and 330  $\mu\text{mol/kg}$ , signaling the biological imprint of dissolved oxygen consumption. The cumulative influence of the remineralization of organic matter over longer time scales (i.e., years) is seen more dramatically in mCDW, where dissolved oxygen reaches as low as 220  $\mu\text{mol/kg}$  due to its isolation from the atmosphere.

### 4.2. Underway $f\text{CO}_2$ and Air-Sea $\text{CO}_2$ Exchange

The surface and mixed layer distribution of dissolved oxygen spatially mirrors the trends in underway  $f\text{CO}_2$  (Figures 3d, 4d, and 5c), where the lowest concentrations of dissolved oxygen are found in areas of high  $f\text{CO}_2$ . The sea surface  $f\text{CO}_2$  indicates that the region was mostly supersaturated or near equilibrium with respect to the average atmospheric value (379  $\mu\text{atm}$ ; Figures 5c and 6a) in both the DP and near the TIS. There was a distinct difference in surface  $f\text{CO}_2$  in areas with the absence (within DP) or presence (near TIS) of sea ice. In areas of open water in the DP,  $f\text{CO}_2$  ranged from 370 to 405  $\mu\text{atm}$ , extending to a



**Table 2**

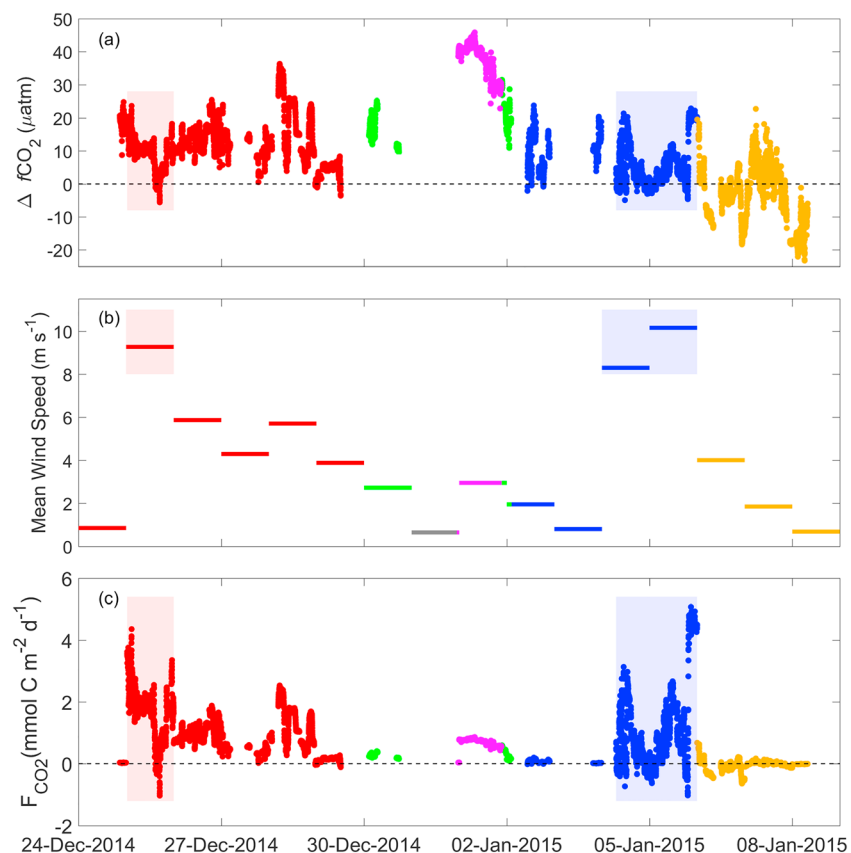
Characteristic Mean Values of Potential Density Anomaly ( $\sigma_\theta$ ;  $\text{kg/m}^3$ ), Potential Temperature ( $\theta$ ;  $^\circ\text{C}$ ), Salinity ( $S$ ), Dissolved Oxygen ( $\text{O}_2$ ;  $\mu\text{mol/kg}$ ), Total Dissolved Inorganic Carbon ( $\text{TCO}_2$ ;  $\mu\text{mol/kg}$ ), Total Alkalinity ( $\text{TA}$ ;  $\mu\text{mol/kg}$ ), pH, and Aragonite Saturation State ( $\Omega_{\text{Ar}}$ ) of Each Water Mass in the Dalton Polynya Region of East Antarctica

Parameter	AASW	WW	ISW	mCDW
$\sigma_\theta$	27.48	27.59	27.56	27.74
$\theta$	−1.24	−1.84	−1.94	−0.36
$S$	34.17	34.27	34.24	34.53
$\text{O}_2$	341	316	311	251
$\text{TCO}_2$	2,200	2,215	2,214	2,242
$\text{TA}$	2,310	2,315	2,313	2,335
pH	8.04	8.01	8.01	7.94
$\Omega_{\text{Ar}}$	1.30	1.17	1.17	1.03

maximum of  $410 \mu\text{atm}$  near the eastern MUIS. The largest  $f\text{CO}_2$  values were recorded near the TIS, with a maximum of  $424 \mu\text{atm}$  at the western edge, exhibiting the correspondingly greatest degree of supersaturation relative to the atmosphere ( $\Delta f\text{CO}_2 = +45 \mu\text{atm}$ ). In contrast, the northern DP showed the greatest degree of undersaturation with respect to the atmosphere ( $\Delta f\text{CO}_2 = -20 \mu\text{atm}$ ).

The Dalton Polynya was a net source of  $\text{CO}_2$  to the atmosphere during the sampling period as determined by both the long-term and instantaneous air-sea  $\text{CO}_2$  fluxes with means and standard deviations of  $0.5 \pm 0.6 \text{ mmol C m}^{-2} \text{ day}^{-1}$  and  $0.7 \pm 0.9 \text{ mmol C m}^{-2} \text{ day}^{-1}$ , respectively.  $F_{\text{CO}_2}$  values evaluated with a long-term  $k$  value reached a maximum of  $2.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$  in the most supersaturated waters near the TIS and a minimum of  $-1.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$  in the northern DP (DP3). Using short-term winds, values of instantaneous  $F_{\text{CO}_2}$  had a larger range, between a

maximum surface uptake of  $1.0 \text{ mmol C m}^{-2} \text{ day}^{-1}$  to a maximum surface outgassing of  $5.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$  from within the center of the DP (DP2) during the study period. Short-term wind speeds were locally variable throughout, ranging between near 0 to  $10 \text{ m/s}$  (Figure 6b); these fluctuations imposed a correspondingly large variation in flux. In particular, during periods of enhanced wind, defined here as wind speed  $>8 \text{ m/s}$ , and conditions with large  $\Delta f\text{CO}_2$ , there were correspondingly large fluxes of  $\text{CO}_2$  (Figure 6, shaded). We observed three high wind events: one at the beginning and two near the end of the study. In the first high wind event, the relatively large  $\Delta f\text{CO}_2$  resulted in an outgassing of roughly  $4.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$ . During



**Figure 6.** Underway measurements as a function of time between 24 December 2014 and 9 January 2015. (a)  $\Delta f\text{CO}_2$  ( $\mu\text{atm}$ ); (b) daily mean wind speed ( $\text{m/s}$ ). Wind speeds  $>8 \text{ m/s}$  are defined as high wind events and are indicated by the red shading in DP1 and blue shading in DP2. (c) Instantaneous  $F_{\text{CO}_2}$  ( $\text{mmol C m}^{-2} \text{ day}^{-1}$ ) where a positive flux indicates a net ocean source of  $\text{CO}_2$ . See Figure 1 for color references.

the second high wind event in the DP, a maximum  $F_{\text{CO}_2}$  of  $5.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$  was observed. Although both minimum and maximum  $\Delta f\text{CO}_2$  values were recorded near the northern DP and TIS, respectively, these gradients were observed during periods of much lower wind speeds ( $\sim 1$  to  $3 \text{ m/s}$ ) and were associated with correspondingly weaker  $\text{CO}_2$  fluxes on the order of  $\sim 0.02 \text{ mmol C m}^{-2} \text{ day}^{-1}$ .

#### 4.3. $\text{CO}_2$ System Properties in the Dalton Polynya

Vertical profiles of  $\text{TCO}_2$  and TA from stations in the DP during each sampling period (DP1, DP2, and DP3) were similar, reflecting the different properties within each water mass (Figure 7). Surface  $\text{TCO}_2$  concentrations ranged between 2,190 and 2,211  $\mu\text{mol/kg}$  in the central DP. Minimum surface  $\text{TCO}_2$  concentrations ( $\sim 2,170 \mu\text{mol/kg}$ ) were found in the northern polynya (yellow; DP3), corresponding with the surface salinity minimum. Similarly, surface TA values ranged between 2,303 and 2,314  $\mu\text{mol/kg}$  in the central DP, with a similar feature of minimum values of  $\sim 2,276 \mu\text{mol/kg}$  found in the northern DP. Subsurface parameters converge at a depth of approximately 150 m to an average  $\text{TCO}_2$  concentration of  $2,214 \pm 3 \mu\text{mol/kg}$  and TA concentration of  $2,315 \pm 2 \mu\text{mol/kg}$  in WW (Figures 7a and 7b), similar to other observations made in shelf waters in the East Antarctic (Table 2; Shadwick et al., 2014; Roden et al., 2016).

Profiles of pH and  $\Omega_{\text{Ar}}$  exhibit similar patterns with depth, reflecting the changes in  $\text{TCO}_2$  and TA concentrations. The surface pH and  $\Omega_{\text{Ar}}$  were elevated relative to subsurface values, enhanced by the biological drawdown of  $\text{TCO}_2$  by photosynthesis. We observed pH values ranging from 8.01 to 8.07 at the surface. Surface  $\Omega_{\text{Ar}}$  ranged from 1.22 and 1.38, with lower values near the western ice edge in the DP (not shown) coincident with regions of elevated surface  $\text{TCO}_2$ .  $\Omega_{\text{Ar}}$  was supersaturated throughout most of the water column, although undersaturated values of  $\Omega_{\text{Ar}}$  (i.e.,  $\Omega_{\text{Ar}} < 1$ ) were found at depth in the  $\text{TCO}_2$ -rich mCDW layer. Below  $\sim 400 \text{ m}$ ,  $\text{TCO}_2$  and TA continued to increase while pH and  $\Omega_{\text{Ar}}$  decrease with depth in the mCDW water mass.

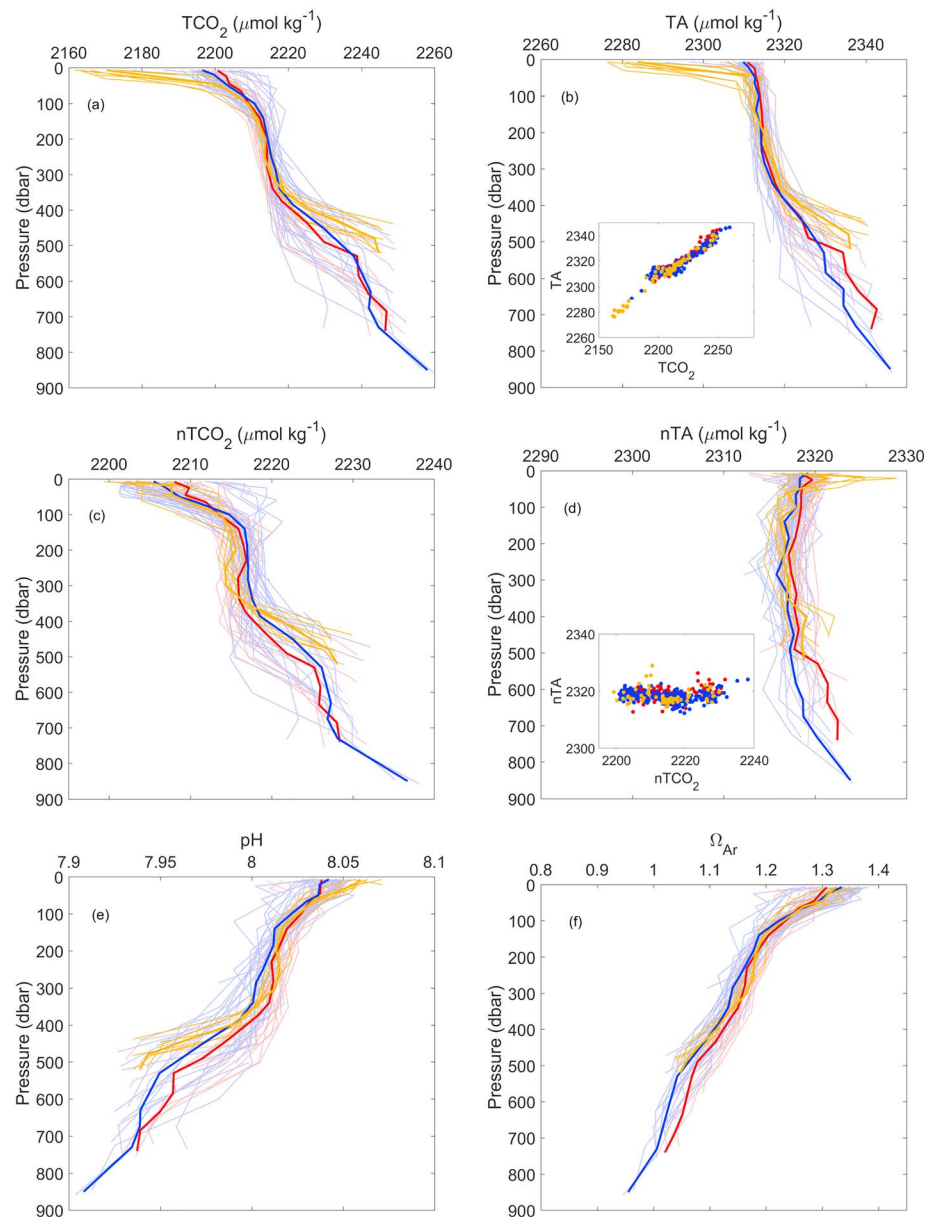
The precipitation of calcium carbonate (ikaite) during sea ice formation in the previous autumn and winter season may influence the  $\text{TCO}_2$  to TA ratio in both the newly formed sea ice and the underlying seawater (Dieckmann et al., 2008; Jones et al., 2010; Rysgaard et al., 2012; Shadwick et al., 2017). However, from our observations the conservative behaviors of the TA-salinity and the nTA-n $\text{TCO}_2$  relationships (Figure 7d inset) suggests that ikaite formation is not a dominant process in the Dalton Polynya.

Salinity-normalizing  $\text{TCO}_2$  and TA values accounts for the freshwater dilution of sea ice melt in the Dalton Polynya on surface concentrations; surface to subsurface gradients in n $\text{TCO}_2$  and nTA are thus much weaker than in the in-situ observations (Figures 7c and 7d). Surface n $\text{TCO}_2$  values ranged between 2,200 and 2,216  $\mu\text{mol/kg}$  and surface nTA to between 2,315 and 2,323  $\mu\text{mol/kg}$ . Higher surface n $\text{TCO}_2$  values were found along the western sea ice edges in the DP as compared to the center of the DP (not shown). At 150 m depth, mean n $\text{TCO}_2$  concentration was  $2,216 \pm 2 \mu\text{mol/kg}$ , which is assumed to represent the winter concentration of n $\text{TCO}_2$  at the surface (see section 3.3).

#### 4.4. $\text{CO}_2$ System Properties Near the Totten Ice Shelf

Profiles of  $\text{CO}_2$  system parameters show somewhat different properties near the TIS than those described above (Figure 8). Here, WW outcrops to the surface near the TIS, particularly in the western edge (see Figure 4) where MLDs extended over 360 m. The stations occupied in the east TIS (magenta) show a similar pattern with depth as those in the DP, where AASW is present at the surface and MLDs ranged between 12 and 46 m. Surface  $\text{TCO}_2$  in the eastern TIS stations show a mean value of 2,205  $\mu\text{mol/kg}$ , similar to the DP, whereas surface  $\text{TCO}_2$  in the western TIS show higher values with an average of 2,213  $\mu\text{mol/kg}$  (Figure 8a). Surface n $\text{TCO}_2$  was more depleted in the east ( $\sim 2,212 \mu\text{mol/kg}$ ) than in the west ( $\sim 2,218 \mu\text{mol/kg}$ ). In WW, the n $\text{TCO}_2$  in stations near the TIS converged to  $2,217 \pm 2 \mu\text{mol/kg}$ . In stations in the western TIS, n $\text{TCO}_2$  at the surface was modestly elevated (between 0 and 4  $\mu\text{mol/kg}$ ) relative to the subsurface winter value.

Mean surface pH ( $\sim 8.02$ ) and  $\Omega_{\text{Ar}}$  ( $\sim 1.24$ ) near the TIS were lower as compared to the DP. Surface pH and  $\Omega_{\text{Ar}}$  values also increased from west to east spatially in front of the TIS, corresponding to higher concentration of  $\text{TCO}_2$  in the west.  $\Omega_{\text{Ar}}$  reached undersaturation ( $\Omega_{\text{Ar}} < 1$ ) at depths  $> 750 \text{ m}$ .

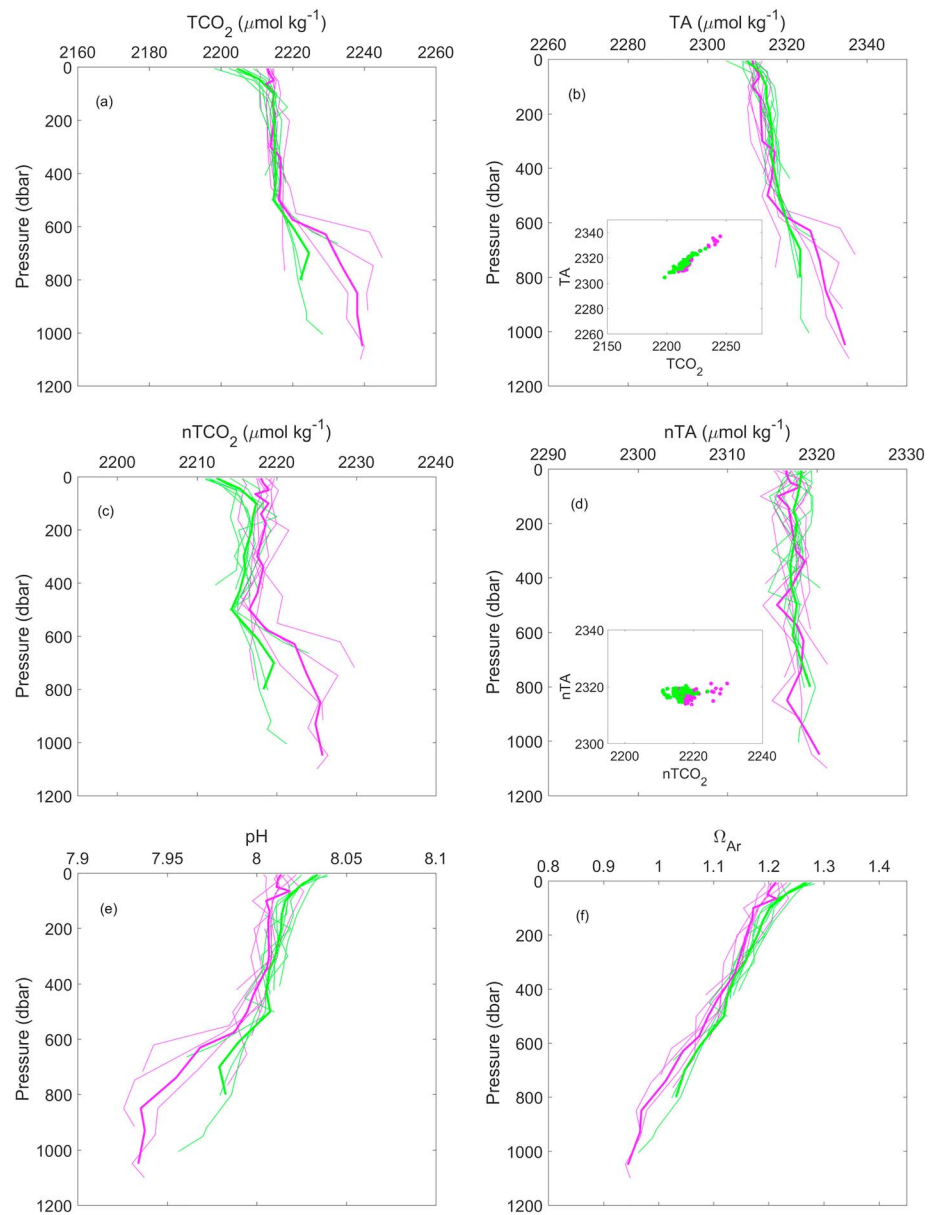


**Figure 7.** Profiles of CO<sub>2</sub> system properties in the Dalton Polynya. (a) TCO<sub>2</sub> (μmol/kg), (b) TA (μmol/kg) with TA versus TCO<sub>2</sub> inset, (c) nTCO<sub>2</sub> (μmol/kg), (d) nTA (μmol/kg) with nTA vs. nTCO<sub>2</sub> inset, (e) pH, and (f) saturation state of aragonite ( $\Omega_{Ar}$ ). Bin-averaged profiles are indicated in each with a bold line.

## 5. Discussion

### 5.1. Net Community Production

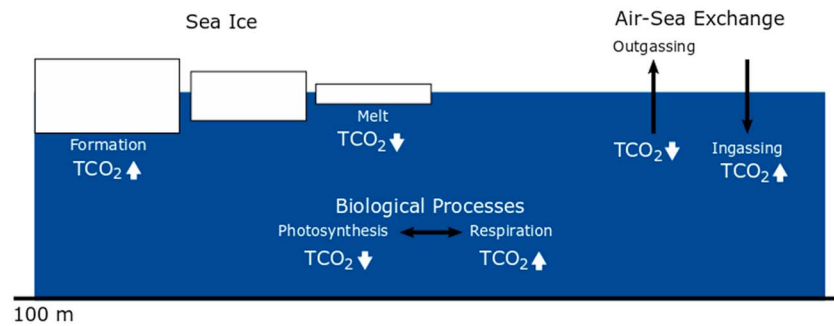
Seasonal depletions of TCO<sub>2</sub> in the upper 100 m were determined and attributed to a combination of physical and biological processes in both waters in the ice-free DP and ice-covered TIS (Figure 9 and Table 3). Processes such as sea ice melt (formation), CO<sub>2</sub> outgassing (ingassing) and photosynthesis (respiration) will decrease (increase) the concentration of TCO<sub>2</sub>. Total integrated deficits of TCO<sub>2</sub> ( $\Delta\text{TCO}_2^{\text{total}}$ ; Table 3) were larger in ice-free regions as compared to areas with greater sea ice coverage. In the DP, the contribution from the seasonal melting of sea ice accounted for less than half of the total change in TCO<sub>2</sub> in DP1 and DP2 but was more significant in DP3. Observations of surface salinity and temperature in DP3 suggest that sea ice melt was ongoing near the Dalton Iceberg Tongue (section 4.1). At all stations in the Dalton Polynya, NCP was positive, ranging between 1 and 21 mmol C m<sup>-2</sup> day<sup>-1</sup> (Figure 10a; see section 3.3), indicating



**Figure 8.** Profiles of CO<sub>2</sub> system properties in front of the Totten Ice Shelf. (a) TCO<sub>2</sub> (μmol/kg), (b) TA (μmol/kg) with TA versus TCO<sub>2</sub> inset, (c) nTCO<sub>2</sub> (μmol/kg), (d) nTA (μmol/kg) with nTA versus nTCO<sub>2</sub> inset, (e) pH, and (f) saturation state of aragonite ( $\Omega_{Ar}$ ). Binned-averaged values are indicated in each with a bold line.

net autotrophy or the dominance of primary production over respiration (Table 3). Both the nTCO<sub>2</sub> deficits and the resulting NCP values were greatest in the center of the DP and lower near the western boundary and the sea ice edge. Estimates of NCP are on the order of 10 to 20 mmol C m<sup>-2</sup> day<sup>-1</sup> within the ice-free regions in the polynya and increase over the duration of the of the cruise, from DP1 to DP3, in parallel with decreasing mixed layer nTCO<sub>2</sub> concentrations (Figure 10). In the northernmost stations of the polynya (DP3), sea ice melt locally enhanced stratification and stabilized the mixed layer (MLDs = ~12 m), increasing light availability and contributing to enhanced biological activity and greater NCP. This is consistent with observations of decreased *f*CO<sub>2</sub> in the region (Figure 4a). By contrast, the nTCO<sub>2</sub> deficits and NCP are lower in front of the TIS (Table 3), ranging from -3.8 to a maximum of 6.6 mmol C m<sup>-2</sup> day<sup>-1</sup>, increasing spatially from west to east in parallel to decreasing MLDs and the increasing dominance of AASW at the surface (Figure 4). In the eastern edge of the TIS (ET), deficits of TCO<sub>2</sub> are dominated by changes in salinity with smaller contributions from biological CO<sub>2</sub> uptake resulting in weakly autotrophic





**Figure 9.** Schematic representing the physical and biological processes driving the changes in TCO<sub>2</sub> concentration in the upper 100 m from the transition from winter to summer in the Dalton Polynya. Physical processes such as sea ice formation and ingassing of atmospheric CO<sub>2</sub> increase TCO<sub>2</sub> concentrations while sea ice melt and outgassing of CO<sub>2</sub> decrease TCO<sub>2</sub> concentrations. Biological photosynthesis reduces TCO<sub>2</sub> concentration through the formation of organic matter, while respiration and the remineralization of this organic matter increases TCO<sub>2</sub> concentration.

conditions. At stations of the western TIS (WT), NCP was negative ranging from  $-3.8$  to  $0$  mmol C m<sup>-2</sup> day<sup>-1</sup>, suggesting the region may be weakly heterotrophic in the summer season, consistent with highly supersaturated  $f$ CO<sub>2</sub> in the surface waters of the region (Figure 5c).

These estimates of NCP include uncertainties associated with the analytical determination of TCO<sub>2</sub> concentrations as well as the assumptions regarding winter TCO<sub>2</sub> concentrations. Vertical transport processes that may influence mixed-layer TCO<sub>2</sub> have not been explicitly accounted for, although it is assumed the integration to 100 m accounts for deeper mixing (e.g., Sweeney et al., 2000). In addition, both CaCO<sub>3</sub> precipitation/dissolution and the air-sea exchange of CO<sub>2</sub> are not explicitly included in the seasonal deficit approach, although the former has been shown to be a negligible process during the period of observation (section 4.3). The mean instantaneous  $F_{CO_2}$  computed from our shipboard observations was  $0.7 \pm 0.9$  mmol C m<sup>-2</sup> day<sup>-1</sup>. If this mean flux were to persist since 1 November (defined as the beginning of the productive season), then this would lead to an additional nTCO<sub>2</sub> concentration of  $0.4$  μmol/kg in the upper 100 m from the air-sea exchange of CO<sub>2</sub>, which is small (<2%), relative to the integrated deficits.

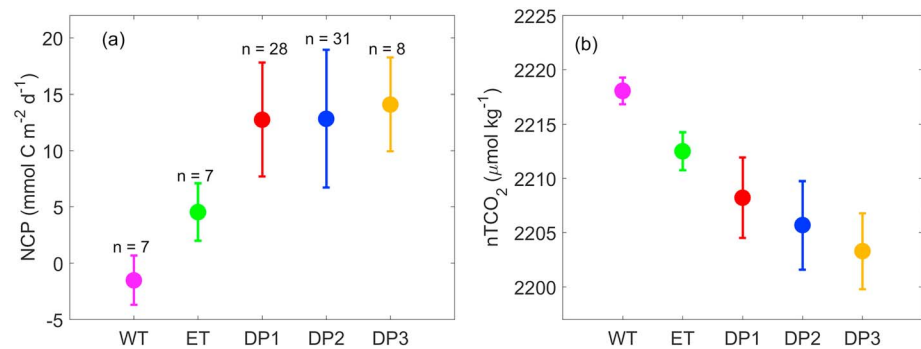
The onset of biological activity in the coastal Antarctic is generally thought to occur when MLDs <40 m (Smith et al., 2000). As most MLD in the open waters of the DP are <40 m, photosynthesis dominates respiration, associated with positive values of NCP. It is likely we observed the beginning of the productive season when NCP rates were relatively low, capturing conditions consistent with the transition from winter to summer. In this period, the biological driver of  $f$ CO<sub>2</sub> drawdown has not yet fully compensated for the increased winter  $f$ CO<sub>2</sub> due to remineralization (and small seasonal warming of surface waters); thus, surface waters remain supersaturated in  $f$ CO<sub>2</sub> despite the positive NCP (i.e., autotrophic conditions). Similarly, dissolved oxygen concentration in AASW within the open waters of the DP was still slightly undersaturated (~1–12%) during the period of observation, suggesting the autotrophic community has not yet fully compensated for loss of dissolved oxygen during the predominating winter heterotrophy. The continuation of summer surface productivity beyond the period of shipboard observation is supported by satellite Chl  $a$  and discussed in more detail below.

**Table 3**

The Total Deficit in Surface TCO<sub>2</sub> ( $\Delta$ TCO<sub>2</sub><sup>total</sup>, μmol/kg), With Contributions From Seasonal Sea Ice Melt ( $\Delta$ TCO<sub>2</sub><sup>salinity</sup>, μmol/kg) and Biological Processes and CO<sub>2</sub> Gas Exchange ( $\Delta$ TCO<sub>2</sub><sup>bio+gas</sup>, μmol/kg) and Estimates of Net Community Production (NCP; mmol C m<sup>-2</sup> day<sup>-1</sup>) for Each Region During Observations

Variable	DP1	DP2	DP3	WT	ET
$\Delta$ TCO <sub>2</sub> <sup>total</sup>	8.2	9.5	19.6	-0.9	3.4
$\Delta$ TCO <sub>2</sub> <sup>salinity</sup>	3.5	3.6	12.6	2.3	3.0
$\Delta$ TCO <sub>2</sub> <sup>bio+gas</sup>	4.7	5.9	7.0	-3.2	0.4
NCP	12.7	12.9	14.1	-1.5	4.5

The negative NCP that was observed near the TIS may be fueled by the remineralization of allochthonous organic material, which can include production remaining from previous years, assuming the particulate and dissolved organic carbon is labile or semilabile. Upwelling and mixing of TCO<sub>2</sub>-rich waters could also be associated with accumulated signals of biological remineralization (rather than the accumulation of organic matter) from distant sources. The MLDs near the western end of the TIS were relatively deep, reaching over 300 m in certain areas, extending well below the depth of our definition for winter TCO<sub>2</sub> concentration and seasonal integration (100 m). This deep mixing could entrain TCO<sub>2</sub>-rich



**Figure 10.** Mean (a) NCP ( $\text{mmol C m}^{-2} \text{ day}^{-1}$ ) and (b) nTCO<sub>2</sub> ( $\mu\text{mol/kg}$ ) in the mixed layer for each region. Error bars represent the standard deviation.

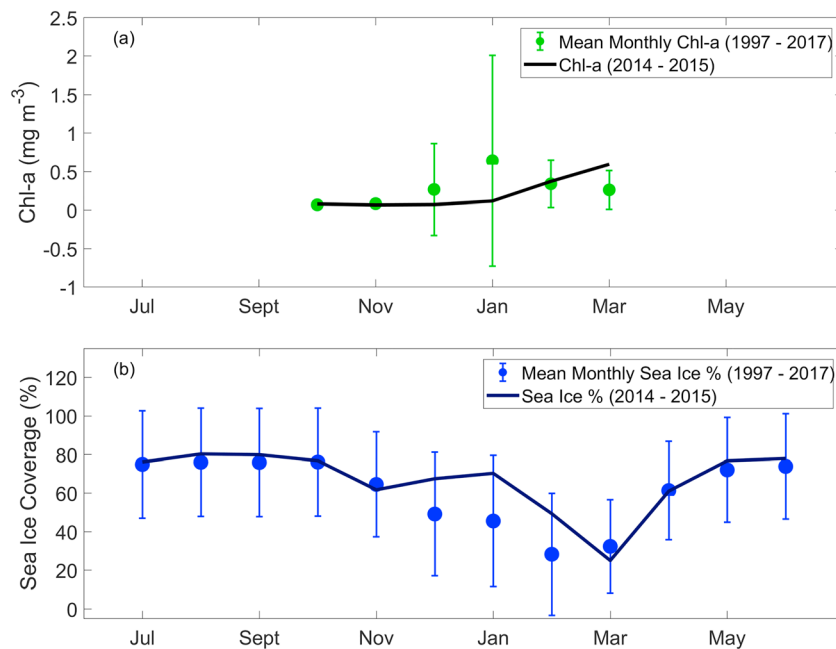
subsurface water into the summer mixed layer; if these deeper waters have sufficiently high TCO<sub>2</sub> concentrations (from the remineralization of organic matter over timescales that exceed a season), the resulting deficit would indicate net heterotrophic conditions. Finally, since the ice-covered waters near the TIS appear to be significantly less productive than those in the ice-free Dalton Polynya (inferred from the degree of  $f\text{CO}_2$  undersaturation), these early summer observations may represent pre-bloom conditions in the TIS perhaps due in part to light limitation associated with sea ice coverage. If the observations had been made later in the season, it is possible that greater surface TCO<sub>2</sub> depletions in a more open TIS region would result in positive NCP (i.e., net autotrophy), similar to conditions observed in the ice-free regions of the adjacent Dalton Polynya. This potential bias due to the timing of observations with respect to ice melt and the onset of open water biological production will be discussed in more detail in the next section.

## 5.2. Interannual Variability

Coastal shelf waters are known to exhibit significant variability that is difficult to diagnose with shipboard observations (Kaufman et al., 2014; Roden et al., 2013). Fortunately, satellite remote sensing products allow this variability to be assessed over seasonal and interannual timescales in regions where direct biogeochemical observations do not exist. Surface Chl *a* concentrations and sea ice coverage can serve as proxies to assess the variability in biological productivity and the physical environment, respectively, allowing long-term trends in regions with sparse in-situ observations to be evaluated.

Climatological estimates of Chl *a* ( $\text{mg/m}^3$ ) and percent sea ice coverage (%) between 1997 and 2017 (Figure 11) reveal significant interannual variability in the Dalton Polynya. The average seasonal cycle of Chl *a* indicates that the onset of productive season can begin as early as October, when light returns in the austral spring, and suggests that the productive season was underway at the time of observations in early summer. Maximum concentrations of Chl *a* typically peak in January, with an average maximum concentration of  $2 \text{ mg/m}^3$  when sea ice coverage is below 50%. In winter (between May and October), there is little and/or nondetectable surface Chl *a* and sea ice coverage is on the order of 70%. Sea ice retreat typically begins in November.

In contrast to the long-term average Chl *a* concentration, the 2014/2015 surface Chl *a* concentrations remained relatively low until February, roughly 1 month after then end of the voyage (black line; Figure 11a). Assuming that Chl *a* can be considered as reliable proxy for biomass, it is likely that increased  $f\text{CO}_2$  undersaturation coincided with maximum surface Chl *a* concentrations due to biological drawdown by photosynthesis. During the period of observations in early January, areas of the Dalton Polynya exhibited  $f\text{CO}_2$  supersaturation and low surface Chl *a* concentrations. Thus, during the 2014/2015 season, our sampling preceded the height of the open-water productive season, and we observed the early spring-to-summer transition when the surface waters were still supersaturated with respect to atmospheric CO<sub>2</sub>. If the growing season persisted through March of the sampling year, as the satellite record suggests, it is likely that the open surface waters would have become undersaturated in the region as a whole and may have transitioned to a sink for atmospheric CO<sub>2</sub> in the late summer and early autumn seasons. This suggests that our seasonal estimates of NCP in the Dalton Polynya may be underestimated, and these values cannot be extrapolated over



**Figure 11.** Satellite record of mean monthly (a) surface Chl *a* concentration ( $\text{mg m}^{-3}$ ) from SeaWiFS (July 1997–June 2002) and MODIS-Aqua (July 2002–June 2017) and (b) percent sea ice coverage (%) from NSIDC (July 1997–June 2017) in the Dalton Polynya. Error bars represent the monthly standard deviations. The black line in each represents the Chl *a* or percent sea ice coverage between July 2014 and June 2015. The absence of points and black line in (a) represents no data.

longer time scales. Similarly, as sea ice coverage near the TIS continued to decline in February, the region may also have transitioned to net autotrophic conditions.

In addition to the role of sea ice in light limitation, sea ice provides a source of dissolved iron to the surface waters during the seasonal melt (Lannuzel et al., 2007), which may stimulate biological productivity (e.g., Sedwick & Ditullio, 1997). During the 2014/2015 season, the onset of sea ice melt in October is in line with the long-term mean (Figure 11b). However, there was an increase in sea ice coverage in December and January, resulting in a greater degree of coverage than the long-term average. This late season sea ice growth would have impeded light penetration, limiting biological productivity and may have restricted the delivery of iron to the surface waters via sea ice melt in early summer.

### 5.3. Comparison of the Dalton Polynya With Other Coastal Antarctic Systems

Coastal polynyas range widely in their physical icescapes, formation mechanisms, seasonal sea ice dynamics, and wind and current regimes, which ultimately influence spring and summer biological production and  $\text{CO}_2$  system properties (e.g., Arrigo et al., 2015). Of the 13 major Antarctic coastal polynyas identified by Nihashi and Ohshima (2015) and Ohshima et al. (2016), the Dalton Polynya ranks eleventh in terms of average wintertime polynya area ( $3.7 \pm 2.0 \times 10^3 \text{ km}^2/\text{year}$  with daily standard deviation) and twelfth in terms of its mean annual sea ice production ( $31 \pm 3 \text{ km}^3/\text{year}$ ) between 2003 and 2011.

The Dalton Polynya has a substantially lower seasonal NCP and summer air-sea  $\text{CO}_2$  flux than the majority of observed coastal polynyas and bays in the East Antarctic (Table 4). NCP from this study in the Dalton Polynya was similar to values reported in the Mertz Polynya (Adélie and George V Land region of East Antarctica,  $143\text{--}148^\circ\text{E}$ ) in January 2001 and January 2008, before the calving of the Mertz Glacier Tongue (MGT) in 2010 (Sambrotto et al., 2003; Shadwick et al., 2014). Precalving air-sea  $\text{CO}_2$  fluxes in the Mertz Polynya were also slightly greater ( $-15 \text{ mmol C m}^{-2} \text{ day}^{-1}$ ) than the instantaneous fluxes in the Dalton Polynya reported here due to larger degrees of surface  $f\text{CO}_2$  undersaturation (Shadwick et al., 2014). However, NCP and air-sea  $\text{CO}_2$  exchange rates in the Dalton Polynya stand in contrast to rates from the post-calving configuration of the Mertz Polynya. The MGT calving event substantially reduced Mertz Polynya size and sea ice production in the subsequent years (Nihashi & Ohshima, 2015; Tamura et al., 2012), yet postcalving deficits in mixed-layer  $\text{TCO}_2$  concentrations and the rates of NCP and air-to-sea flux of  $\text{CO}_2$  in the Mertz

**Table 4**  
*Estimates of Net Community Production (NCP) and Air-Sea CO<sub>2</sub> Exchange From Coastal Regions in East Antarctica*

Region	Location	NCP	Air-Sea CO <sub>2</sub> Exchange	Year	Reference
Dalton Polynya	66.5 °S 120 °E	10 – 20	–1 to 5	2015	This study
Mertz Polynya	66.5 °S 145 °E	26 – 70	–30 to –5	2013	Shadwick et al. (2017)
		35 – 76		2012	Shadwick et al. (2017)
		25 – 78		2011	Shadwick et al. (2017)
		13 – 27		2008	Sambrotto et al. (2003)
		11 – 19		2001	Shadwick et al. (2014)
Terra Nova Bay, Ross Sea	68.5 °S 75 °E	425 ± 204		2013	DeJong et al. (2017)
			–72 ± 32	2013	DeJong & Dunbar (2017)
Prydz Bay	75.0 °S 165 °E	15 ± 3	–15 to 2	2011	Roden et al. (2013)
			–28.4	1995	Gibson & Trull (1999)
			–37.2	1994	Gibson & Trull (1999)

Note. All units are mmol C m<sup>–2</sup> day<sup>–1</sup>.

Polynya dramatically increased in following summers (Shadwick et al., 2017). These corresponding impacts to the CO<sub>2</sub> system have been primarily attributed to an enhancement in biological production as a result of large increases in sea ice meltwater, potentially delivering a source of dissolved iron to the mixed layers (Shadwick et al., 2013). A recent analysis by Moreau et al. (2019) concluded that a larger volume of sea ice meltwater in the Mertz Polynya and neighboring Ninnis Polynya best explained their enhanced biological productivities relative to the Dalton Polynya. The calving of the MGT in the Mertz Polynya set up an interesting natural experiment to assess how changes to the Antarctic icescape impact polynya productivity. As the Dalton Polynya is sustained by the Dalton Iceberg Tongue to the east, a natural calving or shift in the sea ice regime near the Dalton Polynya could potentially lead to changes in the CO<sub>2</sub> system as similarly experienced in the Mertz Polynya system.

NCP and FCO<sub>2</sub> are significantly smaller in the Dalton Polynya than continental shelf waters of the Ross Sea, where annual rates of primary production can reach up to 180 g C m<sup>–2</sup> year<sup>–1</sup>, among the most productive in the Southern Ocean (Arrigo, van Dijken, & Bushinsky, 2008; Smith & Gordon, 1997). Rates of seasonal NCP exhibit a large range of variability in space and time (Peloquin & Smith, 2007; Smith et al., 2006), though they are several times greater than those observed in the Dalton Polynya (Table 4). In the Terra Nova Bay (TNB) polynya in the western Ross Sea (163–167°E), late summer NCP is an order of magnitude larger than the Dalton polynya at roughly 425 mmol C m<sup>–2</sup> day<sup>–1</sup> (Table 4; DeJong et al., 2017). Biological production in TNB is typically dominated by diatoms in summer when stratification is stronger and mixed layers are shallower (Arrigo et al., 2000; Tortell et al., 2011), in contrast to the *Phaeocystis antarctica* communities in the Dalton Polynya (Moreau et al., 2019). Polynya formation in TNB is primarily driven by intense offshore katabatic winds (Bromwich & Kurtz, 1984) that prevent a consolidated sea ice pack from forming in the lee of the Drygalski Ice Tongue, with wind speeds often ranging between 10 and 30 m/s (Bromwich, 1989). DeJong et al. (2017) hypothesize these katabatic winds create ideal conditions for the formation of Langmuir circulation cells that encourage frazil ice formation, concentrate algal biomass in the surface, and potentially introduce micronutrient- (e.g., iron-) rich subsurface waters to boost productivity in late summer. The coupling between enhanced late season primary production and the corresponding undersaturation of surface fCO<sub>2</sub> and strong wind speeds results in extremely high CO<sub>2</sub> uptake rates in TNB surface waters (–75 ± 32 mmol C m<sup>–2</sup> day<sup>–1</sup>; Table 4). An analysis of environmental controls on coastal Antarctic productivity by Arrigo et al. (2015) revealed that continental shelf width plays an important role in controlling hot spots of productivity. Wider continental shelves, such as in TNB in the Ross Sea, increase the contact time of bottom waters with iron-rich sediments. Advection of iron-rich subsurface waters to the upper sunlit layers could play a role in driving the late summer TNB productivity (DeJong et al., 2017). This mechanism of iron delivery is less likely on the narrower continental shelf waters in the Dalton Polynya.

In Prydz Bay, located in the Indian Ocean sector of the Antarctic (70–80°E), NCP rates on the order of 15 ± 3 mmol C m<sup>–2</sup> day<sup>–1</sup> (1.8 ± 0.4 mol C/m<sup>2</sup> over a 4-month period) have been reported (Roden et al., 2013). Seasonal deficits in mixed-layer TCO<sub>2</sub> were attributed to a combination of sea ice melt and



biological production (Roden et al., 2013), similar to the drivers of TCO<sub>2</sub> depletion in the Dalton Polynya, resulting in low surface water  $f\text{CO}_2$  and an air-to-sea flux of CO<sub>2</sub>. Recent studies in Prydz Bay propose that glacial meltwater from the nearby Amery Ice Shelf may bring a large, bioavailable source of dissolved iron from marine-accredited ice beneath the ice shelf, locally enhancing primary productivity (Herraiz-Borreguero et al., 2016). In contrast to the glacial meltwaters introduced by the intrusions of mCDW beneath the TIS and MUIS (warm-regime) to Dalton Polynya, the glacial meltwaters introduced into Prydz Bay are the result of intrusions of cold Dense Shelf Water beneath the Amery Ice Shelf (cold regime; Silvano et al., 2016). The resulting outflow of supercooled ISW can entrain subglacial dissolved iron into the marine ice layer beneath the ice shelf and, upon basal melting, can deliver dissolved iron onto the continental shelf in concentrations up to 4 orders of magnitude higher than typical Southern Ocean waters (Herraiz-Borreguero et al., 2016). In the analysis by Arrigo et al. (2015), the input of basal meltwater by nearby ice shelves can explain almost 60% of the variance in mean Chl *a* concentrations in Antarctic polynyas. The ongoing input of glacial meltwater from the basal melting of the TIS and MUIS may drive future changes to the biological productivity and carbonate chemistry in the adjacent Dalton Polynya waters.

## 6. Conclusions

New shipboard observations from the Dalton Polynya were used to assess the biological and physical controls on the CO<sub>2</sub> system during the early summer season between December 2014 and January 2015. Profiles of TCO<sub>2</sub> concentration allowed the seasonal NCP to be estimated. The Dalton Polynya is found to be net autotrophic in ice-free areas, though the rates are lower than those observed elsewhere in the East Antarctic. The surface waters near the Totten Ice Shelf show relatively little TCO<sub>2</sub> drawdown, likely due to the ice coverage impeding light penetration to support photosynthesis. NCP near the TIS suggest weakly heterotrophic conditions, with a surplus of organic matter to fuel remineralization potentially coming from the TCO<sub>2</sub>-rich winter water during deep mixing. Because polynyas are open or have reduced sea ice cover year-round, they are often thought of as areas of intense biological production leading to enhanced air-sea CO<sub>2</sub> exchange and uptake of atmospheric CO<sub>2</sub>. The observations presented here provide an alternative view of Dalton Polynya, with midsummer outgassing of CO<sub>2</sub> to the atmosphere. However, satellite derived Chl *a* concentrations suggest that late-summer productivity increased in parallel with declining sea ice coverage after the completion of the voyage. Long-term remote sensing data indicate interannual variability in surface productivity in the Dalton Polynya and neighboring areas is significant. Improved understanding of CO<sub>2</sub> system dynamics in the coastal Southern Ocean will require more observations to accurately assess the status of these systems as CO<sub>2</sub> sources or sinks.

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