

# Calcium carbonate saturation states along the West Antarctic Peninsula

ELIZABETH M. JONES <sup>1,2</sup>, MARIO HOPPEMA <sup>3</sup>, KAREL BAKKER<sup>4,5</sup> and HEIN J.W. DE BAAR <sup>2,6</sup>

<sup>1</sup>Institute of Marine Research, Fram Centre, Hjalmar Johansens gate 14, 9007 Tromsø, Norway

<sup>2</sup>NIOZ, Royal Netherlands Institute for Sea Research, Den Burg, The Netherlands

<sup>3</sup>Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Climate Sciences Department, Postfach 120161, 27515 Bremerhaven, Germany

<sup>4</sup>NIOZ, Royal Netherlands Institute for Sea Research, Department of Ocean Systems (OCS), Den Burg, The Netherlands

<sup>5</sup>Utrecht University, PO Box 59, Den Burg 1790 AB, The Netherlands

<sup>6</sup>Ocean Ecosystems, University of Groningen, Nijenborgh 7, 9747 AG, Groningen, The Netherlands  
elizabeth.jones@hi.no

**Abstract:** The waters along the West Antarctic Peninsula (WAP) have experienced warming and increased freshwater inputs from melting sea ice and glaciers in recent decades. Challenges exist in understanding the consequences of these changes on the inorganic carbon system in this ecologically important and highly productive ecosystem. Distributions of dissolved inorganic carbon ( $C_T$ ), total alkalinity ( $A_T$ ) and nutrients revealed key physical, biological and biogeochemical controls of the calcium carbonate saturation state ( $\Omega_{\text{aragonite}}$ ) in different water masses across the WAP shelf during the summer. Biological production in spring and summer dominated changes in surface water  $\Omega_{\text{aragonite}}$  ( $\Delta\Omega_{\text{aragonite}}$  up to +1.39; ~90%) relative to underlying Winter Water. Sea-ice and glacial meltwater constituted a minor source of  $A_T$  that increased surface water  $\Omega_{\text{aragonite}}$  ( $\Delta\Omega_{\text{aragonite}}$  up to +0.07; ~13%). Remineralization of organic matter and an influx of carbon-rich brines led to cross-shelf decreases in  $\Omega_{\text{aragonite}}$  in Winter Water and Circumpolar Deep Water. A strong biological carbon pump over the shelf created  $\Omega_{\text{aragonite}}$  oversaturation in surface waters and suppression of  $\Omega_{\text{aragonite}}$  in subsurface waters. Undersaturation of aragonite occurred at  $< \sim 1000$  m. Ongoing changes along the WAP will impact the biologically driven and meltwater-driven processes that influence the vulnerability of shelf waters to calcium carbonate undersaturation in the future.

Received 23 October 2020, accepted 19 August 2021

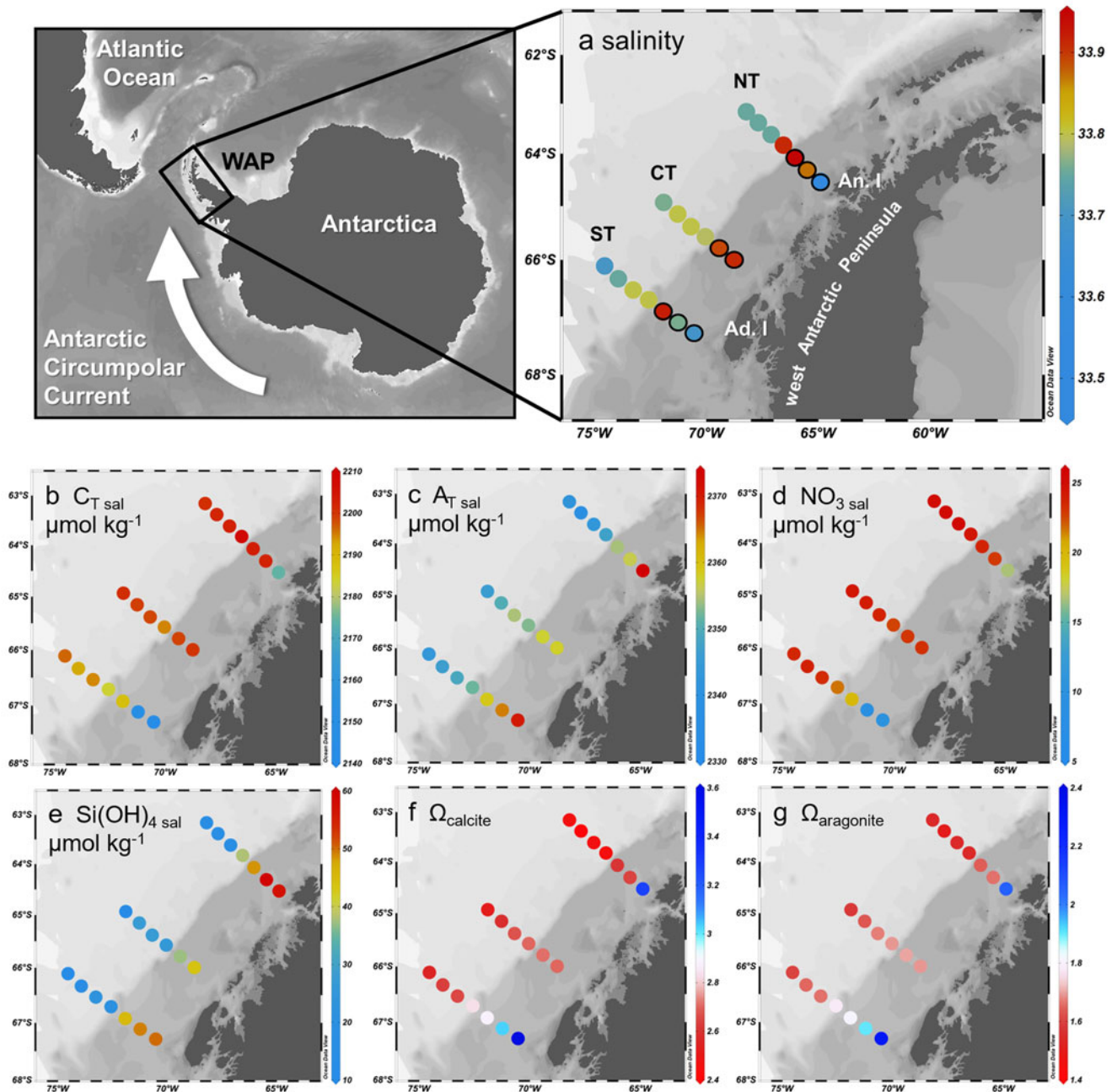
**Key words:** alkalinity, aragonite, Circumpolar Deep Water, inorganic carbon system, meltwater

## Introduction

The waters off the West Antarctic Peninsula (WAP) support some of the highest rates of phytoplankton primary production in the whole of the Southern Ocean and play a large role in biogeochemical cycling (Arrigo *et al.* 2008, Clarke *et al.* 2008). The marine environment of the WAP is strongly influenced by the offshore Antarctic Circumpolar Current (ACC; Fig. 1) that impacts the western shelf with intrusions of relatively warm upper Circumpolar Deep Water (uCDW; Fig. 2) across the shelf-break (Martinson *et al.* 2008). Along the shelf, glacial meltwater and melting sea ice stratify the water column to form relatively fresh Antarctic Surface Water (AASW) in the summer mixed layer overlying the permanent pycnocline that extends to the nutrient-rich and carbon-rich uCDW (Meredith *et al.* 2013). The AASW caps the cold and saline remnant of the winter mixed layer, called the Winter Water, which is identified by a minimum in potential temperature (Venables *et al.* 2013). The Winter Water in spring and summer reflects the (biogeochemical) signatures of the surface layer of

the preceding winter; however, some modification through advection, mixing and remineralization of organic matter is probable. Mixing of uCDW with overlying AASW and Winter Water forms modified CDW (mCDW) over the shelf, which is channelled into the coastal zone through numerous glacially eroded canyons (Smith *et al.* 1999, Martinson *et al.* 2008). Deep convective mixing during winter, following brine rejection from sea ice, cools and increases the salt content of the Winter Water (Venables *et al.* 2013).

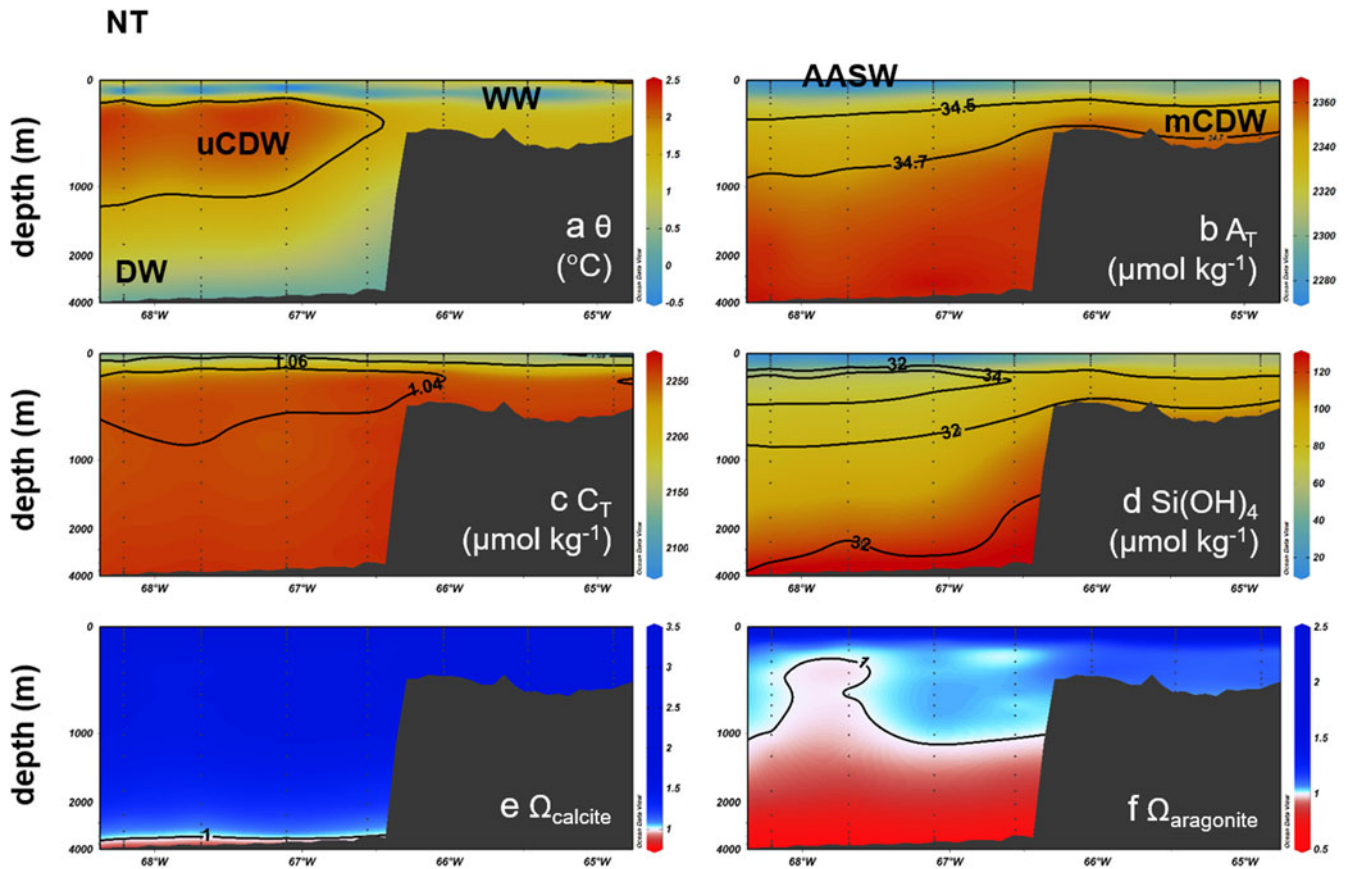
The WAP shelf is an ecologically important region (Clarke *et al.* 2008, Ducklow *et al.* 2013) with high primary productivity (Schofield *et al.* 2017) driving substantial oceanic uptake of carbon dioxide ( $\text{CO}_2$ ) from the atmosphere (Arrigo *et al.* 2008, Brown *et al.* 2019). The inorganic carbon system along the WAP is strongly regulated by meltwater inputs, primary production and respiration, sea-ice processes, mixing of different water masses and carbonate mineral formation and dissolution (e.g. Hauri *et al.* 2015, Tortell *et al.* 2015). The seasonal retreat of the ice pack exposes surface waters to increased light levels where freshwater from melting



**Fig. 1.** Map of Antarctica and the Southern Ocean showing the West Antarctic Peninsula (WAP) and general direction of flow of the Antarctic Circumpolar Current. Map sub-plots of the WAP showing sea surface **a.** salinity, **b.** salinity-normalized  $C_T$  ( $C_{T\text{ sal}}; \mu\text{mol kg}^{-1}$ ), **c.** salinity-normalized  $A_T$  ( $A_{T\text{ sal}}; \mu\text{mol kg}^{-1}$ ), **d.** salinity-normalized nitrate ( $\text{NO}_3\text{ sal}; \mu\text{mol kg}^{-1}$ ), **e.** salinity-normalized silicate ( $\text{Si(OH)}_4\text{ sal}; \mu\text{mol kg}^{-1}$ ), **f.** calcite saturation state ( $\Omega_{\text{calcite}}$ ) and **g.** aragonite saturation state ( $\Omega_{\text{aragonite}}$ ). The north (NT), central (CT) and south (ST) transects, shelf stations indicated by black-outlined circles and Anvers Island (An. I) and Adelaide Island (Ad. I) are marked in **a.**

glaciers, sea ice and snow stratifies the upper ocean across the WAP shelf (Meredith *et al.* 2013, Venables *et al.* 2013). Release of micronutrients, such as iron, and seeding by sea-ice algae promote the onset of phytoplankton blooms (Clarke *et al.* 2008, Vernet *et al.* 2008, Schofield

*et al.* 2017), driving intense uptake of inorganic carbon and nutrients. Phytoplankton blooms during spring and summer create hotspots of biological production and drawdown of atmospheric  $\text{CO}_2$  along the WAP shelf (Hauri *et al.* 2015, Tortell *et al.* 2015, Kerr *et al.* 2018).



**Fig. 2.** Vertical distribution along the north (NT; **a.–f.**), central (CT; **g.–l.**) and south (ST; **m.–r.**) transects of (**a., g., m.**) potential temperature ( $\theta$ , °C), (**b., h., n.**)  $A_T$  ( $\mu\text{mol kg}^{-1}$ ) including salinity contours, (**c., i., o.**)  $C_T$  ( $\mu\text{mol kg}^{-1}$ ) with  $A_T:C_T$  ratio contours, (**d., j., p.**)  $\text{Si(OH)}_4$  ( $\mu\text{mol kg}^{-1}$ ) with  $\text{NO}_3$  ( $\mu\text{mol kg}^{-1}$ ) contours, (**e., k., q.**) calcite saturation state ( $\Omega_{\text{calcite}}$ ) and (**f., l., r.**) aragonite saturation state ( $\Omega_{\text{aragonite}}$ ). Boundaries of Antarctic Surface Water (AASW), Winter Water (WW), upper Circumpolar Deep Water (uCDW), modified Circumpolar Deep Water (mCDW) and Deep Water (DW) are indicated. Contours for the calcium carbonate saturation horizon ( $\Omega = 1$ ) are included in **e., f., k., l., q.** and **r.**

Diatoms are key species in summertime phytoplankton communities, removing silicic acid (silicate) from the surface layer, and the subsequent export and dissolution of biogenic silica in subsurface waters is an important pathway in nutrient cycling in the region (Schofield *et al.* 2017, Henley *et al.* 2018, Tréguer *et al.* 2018). Coastal and shelf waters are typically iron-replete due to their proximity to glacial and sedimentary sources of iron, in addition to oceanic iron supply with transient periods of iron limitation during the growing season (Dinniman *et al.* 2020 and references cited therein). Macronutrients are replete over the WAP shelf, apart from exceptional episodic depletion in the surface layer that rarely occurs (and may not be subsequently captured and measured) following intense uptake in the spring and summer blooms (Henley *et al.* 2018). Remineralization of exported organic matter from productive surface waters and enrichment of the inorganic carbon and nutrient pools in subsurface waters is pronounced following the highly productive summer period (Jones *et al.* 2017,

Henley *et al.* 2018). Phytoplankton productivity decreases offshore as strong winds enhance mixing, removing phytoplankton from the surface layer, and, remote from topographical features, the supply and concentrations of iron can be limiting (e.g. Vernet *et al.* 2008, Trimborn *et al.* 2015). Episodic intrusions of CDW enrich the surface layer with inorganic carbon and, in the absence of efficient biological carbon drawdown, drive supersaturation of  $\text{CO}_2$  with respect to the atmosphere (Hauri *et al.* 2015, Jones *et al.* 2017, Kerr *et al.* 2018).

Sea-ice processes influence carbon cycling through the formation and dissolution of the abiotic calcium carbonate mineral ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) (Rysgaard *et al.* 2007, Dieckmann *et al.* 2008). These processes lead to shifts in dissolved inorganic carbon ( $C_T$ ; Eq. (1)) and total alkalinity ( $A_T$ ; Eq. (2)):

$$C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$



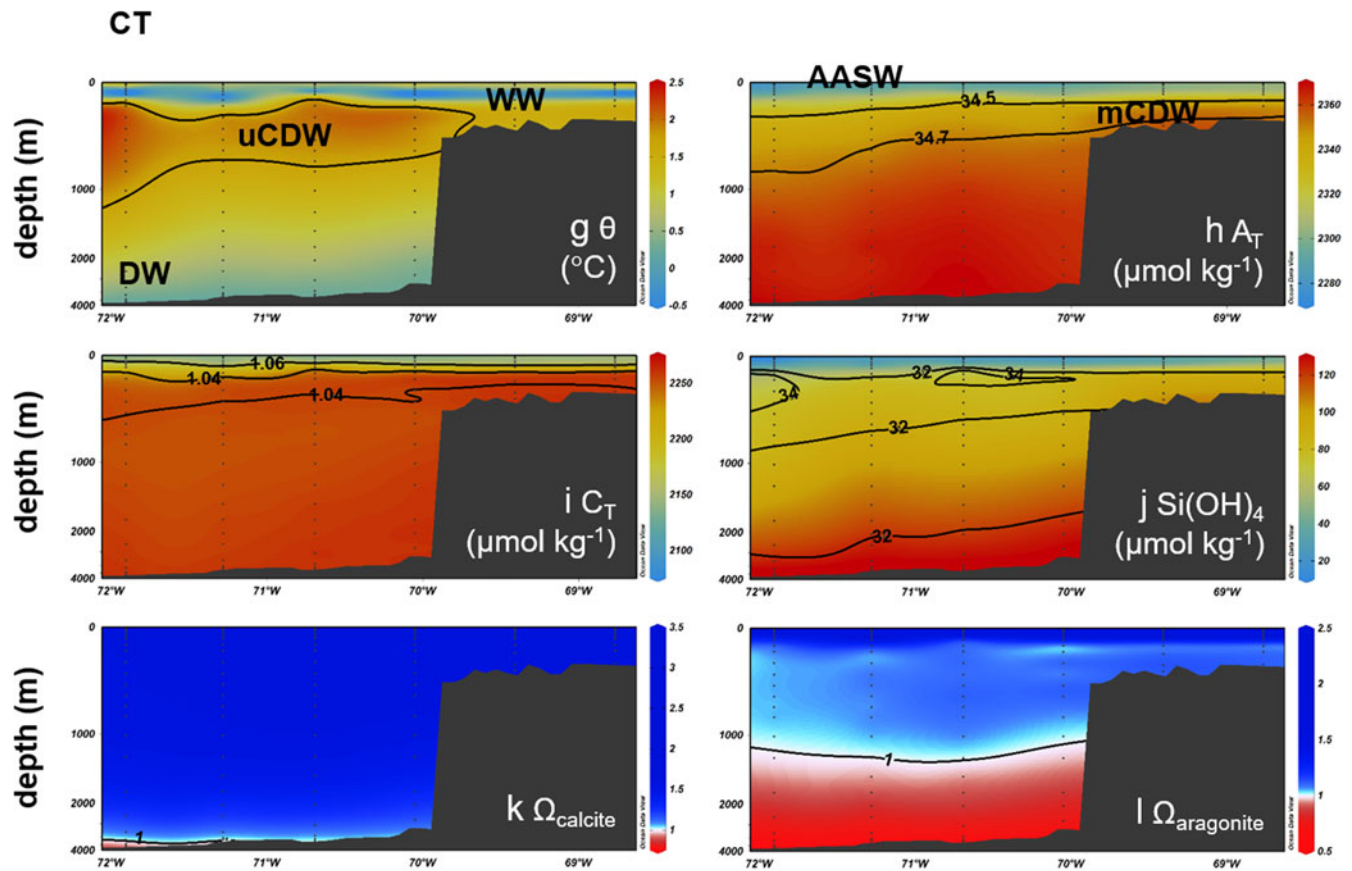


Fig. 2. Continued.

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] + \text{proton acceptors} - \text{proton donors} \quad (2)$$

where  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  are concentrations of bicarbonate and carbonate, respectively, and  $[\text{H}_2\text{CO}_3^*]$  comprises the concentrations of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and aqueous  $\text{CO}_2$ . The  $\text{H}_2\text{CO}_3$  content is negligible for practical purposes. The  $A_T$  is dominated by  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  representing  $\sim 76\%$  and  $\sim 19\%$ , respectively (when  $\text{pH} \approx 8.1$ ), and describes the capacity of seawater to buffer against acidic inputs (e.g.  $\text{CO}_2$ ) (Dickson 1981, Sarmiento & Gruber 2006). Ikaite crystals precipitate during sea-ice formation in autumn and winter where, due to the incorporation of calcium ions ( $\text{Ca}^{2+}$ ) and  $\text{CO}_3^{2-}$ , the  $A_T$  decreases by 2 for each ikaite molecule that is formed. These processes partition  $A_T$  within sea ice relative to the surrounding seawater as ikaite is retained within the brine channels and pockets in the sea ice (Dieckmann *et al.* 2008) and the  $\text{CO}_2$ -rich brines are rejected and increase the  $C_T$  content of the ice-covered upper ocean (Rysgaard *et al.* 2007). During sea-ice melt in spring and summer, meltwater inputs dilute  $A_T$ , hence lowering the buffer capacity of seawater; however, ikaite dissolution creates a small source of  $A_T$  that slightly

counteracts the dilution effects (Hauri *et al.* 2015, Jones *et al.* 2017, Legge *et al.* 2017).

Since the Industrial Revolution, the concentration of  $\text{CO}_2$  in the atmosphere has increased from  $\sim 280$  to  $\sim 410$  matm in 2019 ([https://www.esrl.noaa.gov/gmd/ccgg/trends/gl\\_data.html](https://www.esrl.noaa.gov/gmd/ccgg/trends/gl_data.html)), leading to invasion of atmospheric  $\text{CO}_2$  into the ocean through the solubility carbon pump. Increased oceanic uptake of  $\text{CO}_2$  increases the  $C_T$  in surface waters, resulting in increases in hydrogen ion concentrations ( $[\text{H}^+]$ ), reductions in  $[\text{CO}_3^{2-}]$  and lowering of seawater pH at a rate of  $\sim 0.02$  pH units per decade since the late 1980s (<https://www.ipcc.ch/srocc/chapter/chapter-5>). Declining pH and  $[\text{CO}_3^{2-}]$  are commonly referred to as ocean acidification (Feely *et al.* 2004, Orr *et al.* 2005); however, the seawater will remain basic, albeit a bit less basic (i.e.  $\text{pH} < 8.1\text{--}8.2$ ), rather than becoming acidic. The lowering of  $[\text{CO}_3^{2-}]$  leads to a reduction in the calcium carbonate ( $\text{CaCO}_3$ ) saturation states of the biominerals aragonite ( $\Omega_{\text{aragonite}}$ ) and calcite ( $\Omega_{\text{calcite}}$ ), defined for aragonite as follows:

$$\Omega_{\text{aragonite}} = ([\text{Ca}^{2+}]_{\text{sw}} \times [\text{CO}_3^{2-}]_{\text{sw}}) / K_{\text{SP}}^* \text{ aragonite} \quad (3)$$

where  $[\text{Ca}^{2+}]_{\text{sw}}$  and  $[\text{CO}_3^{2-}]_{\text{sw}}$  are the concentrations in ambient seawater and  $K_{\text{SP}}^* \text{ aragonite}$  is the solubility

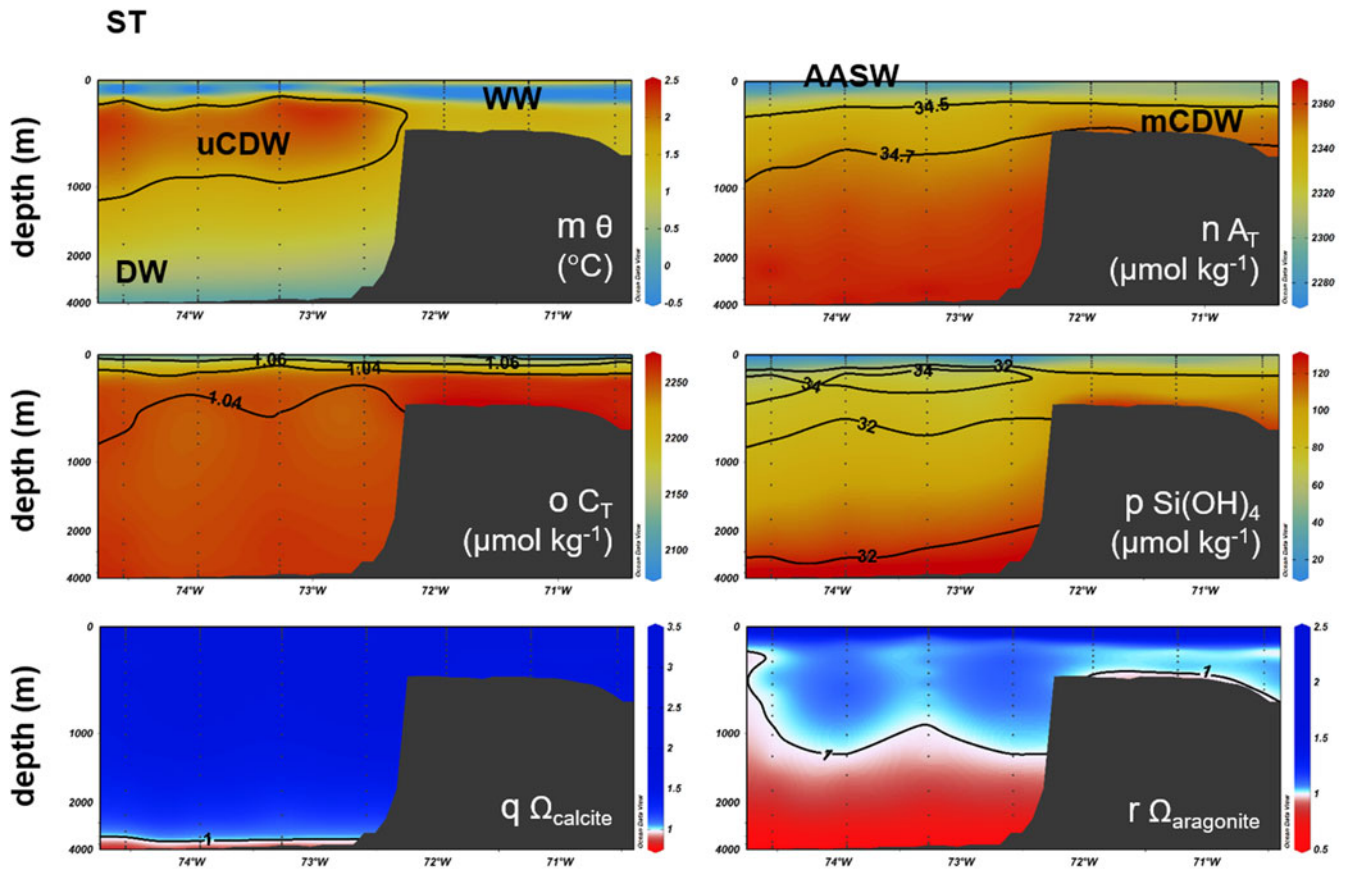


Fig. 2. Continued.

product of aragonite as a function of salinity, temperature and pressure (Broecker & Peng 1982, Sarmiento & Gruber 2006). The biotic  $\text{CaCO}_3$  minerals aragonite and calcite and the abiotic  $\text{CaCO}_3$  mineral ikaite have their own solubility properties (as a function of seawater temperature, salinity and pressure). Ikaite is extremely unstable and can only exist in crystalline form at low temperatures and high salinities (Dieckmann *et al.* 2008 and references cited therein). Aragonite is the less stable biomineral found in marine calcifiers due to its comparatively higher solubility relative to calcite. As such, aragonite is most vulnerable to dissolution and seawater is undersaturated when  $\Omega_{\text{aragonite}} < 1$ , whereby conditions can become energetically costly and potentially even corrosive for calcifiers (Feely *et al.* 2004, Orr *et al.* 2005).

The WAP marine environment has been routinely monitored through the US Palmer Long-Term Ecological Research (PAL-LTER) programme (Ducklow *et al.* 2013) and the British Antarctic Survey Rothera Time Series (RaTS) (Clark *et al.* 2008). High spatial variability and seasonality in inorganic carbon cycling is superimposed on decadal variations in ocean warming, intrusions of carbon-rich CDW onto the shelf, glacial melting and shortening of the sea-ice season (e.g.

Vaughan *et al.* 2003, Martinson *et al.* 2008). Increased and more southern upwelling of CDW in response to the El Niño Southern Oscillation and Southern Annular Mode (Hall & Visbeck 2002, Stammerjohn *et al.* 2008) further influences the seasonal sea-ice cover and oceanographic conditions along the WAP. Decadal enrichment of  $C_T$  and lowering of pH have already been reported in surface and subsurface waters along the WAP (Hauri *et al.* 2015, Kerr *et al.* 2018), and aragonite undersaturation has been found in the shallower water column closer to the coast (Jones *et al.* 2017). Encroaching  $\text{CaCO}_3$  undersaturation may have impacts on pelagic and benthic calcifiers such as pteropods that are important links between trophic levels and key contributors to organic and inorganic carbon cycling along the WAP (Feely *et al.* 2004, Bednaršek *et al.* 2012, Thibodeau *et al.* 2019). In addition, shifts in the inorganic carbon system may affect phytoplankton productivity and community composition (Trimborn *et al.* 2015 and references cited therein), which control the efficiency of atmospheric  $\text{CO}_2$  uptake, export of organic carbon and biogeochemical cycling (e.g. Arrigo *et al.* 2008). Understanding the collective effects of these processes that drive changes in calcium carbonate saturation states is key to better assessing future trends

in carbon cycling and potential impacts to the Antarctic ecosystem (Hauri *et al.* 2015, Kerr *et al.* 2018). This study, presenting new water column data along and across the WAP continental shelf, complements those from earlier campaigns with new insights into the role of 1) phytoplankton production, 2) the release of sea-ice and glacial meltwater containing dissolved minerals and 3) freshwater dilution and mixing of CDW, all of which drive spatial variability in calcium carbonate saturation in different water masses across the WAP shelf in summer.

## Methods

### *Sampling and hydrography*

Water samples were collected and hydrographic measurements were carried out in summer (9–31 January 2011) along the WAP (Fig. 1) during expedition ANT-XXVII/2 on board FS *Polarstern*. A total of 19 stations were occupied along three transects extending from the open ocean waters of the ACC (offshore, depth > 1000 m) to nearshore and coastal waters (shelf, depth < 750 m) of the WAP (Fig. 2). The area extended from 65°W (west of Anvers Island) to 75°W (west of Adelaide Island) and 63°S to 67°S. Depth profiles of potential temperature and salinity were obtained using a conductivity-temperature-depth (CTD) instrument (SBE 9/11plus) mounted onto a Seabird Carousel Water Sampler type SBE32 equipped with 121 Ocean Test Equipment bottles type SBE improved Model 110.

The definition of the mixed-layer depth (MLD) is taken as the depth where the potential density exceeds  $0.05 \text{ kg m}^{-3}$  relative to 10 m depth (Venables *et al.* 2013). The depth of the potential temperature minimum ( $\theta_{\min}$ ) is taken to represent the core of the Winter Water (remnant of the winter mixed layer). Salinity is reported on the practical salinity scale. Hydrographic data are available in the PANGAEA database (<https://doi.org/10.1594/PANGAEA.772244>). Ocean Data View 4 (<http://odv.awi.de>) was used for data visualization.

### *Inorganic carbon system*

Seawater samples for  $C_T$  and  $A_T$  were drawn from the Water Sampler bottles into 500 ml borosilicate glass bottles and analysed within 20 h on a VINDTA 3C instrument (Marianda, Kiel, Germany). Analyses for  $C_T$  were made through coulometric determination and  $A_T$  determination was carried out by automated potentiometric titration, following standard procedures (Dickson *et al.* 2007). Certified Reference Materials (CRM, batches 100 and 105) supplied by A.G. Dickson (Scripps Institution of Oceanography) were analysed to calibrate the measurements; the precision of these

analyses was  $1.0 \text{ } \mu\text{mol kg}^{-1}$  for  $C_T$  and  $1.5 \text{ } \mu\text{mol kg}^{-1}$  for  $A_T$ . The ranges of  $A_T$  (2342–2357  $\mu\text{mol kg}^{-1}$ ) and  $C_T$  (2253–2277  $\mu\text{mol kg}^{-1}$ ) in mCDW in this study are consistent with those previously reported for the wider WAP region (2350  $\mu\text{mol } A_T \text{ kg}^{-1}$  and 2253  $\mu\text{mol } C_T \text{ kg}^{-1}$ ; Hauri *et al.* 2015) and coastal waters on Adelaide Island ( $\sim 2340 \text{ } \mu\text{mol } A_T \text{ kg}^{-1}$  and  $\sim 2260 \text{ } \mu\text{mol } C_T \text{ kg}^{-1}$ ; Jones *et al.* 2017). The deep water observations correspond very well to previous measurements from the PAL-LTER 1998–2012 cruises ( $C_T = 2261 \pm 4 \text{ } \mu\text{mol kg}^{-1}$ ;  $A_T = 2365 \pm 7 \text{ } \mu\text{mol kg}^{-1}$ ), World Ocean Circulation Experiment (WOCE) and Climate and Ocean - Variability, Predictability, and Change (CLIVAR) cruises (1992, 2006, 2009, 2011) and accompanying calculated variables ( $C_T = 2262 \pm 3 \text{ } \mu\text{mol kg}^{-1}$ ;  $A_T = 2366 \pm 9 \text{ } \mu\text{mol kg}^{-1}$ ), as reported in Hauri *et al.* (2015).

The  $\Omega_{\text{aragonite}}$  (Eq. (3)) and  $\Omega_{\text{calcite}}$  were calculated from  $C_T$  (Eq. (1)),  $A_T$  (Eq. (2)) and *in situ* temperature, salinity, pressure and concentrations of phosphate and silicic acid using the CO2SYS program (van Heuven *et al.* 2011). The carbonic acid dissociation constants  $K_1$  and  $K_2$  (Eqs (4) & (5)) determined in natural seawater by Mehrbach *et al.* (1973) as refitted by Dickson & Millero (1987) were selected. The constants  $K_1$  and  $K_2$  are functions of salinity ( $S$ ) and temperature ( $T$ ) in natural seawater and are derived from the equilibrium relationships between the inorganic carbon species (Eq. (1)):

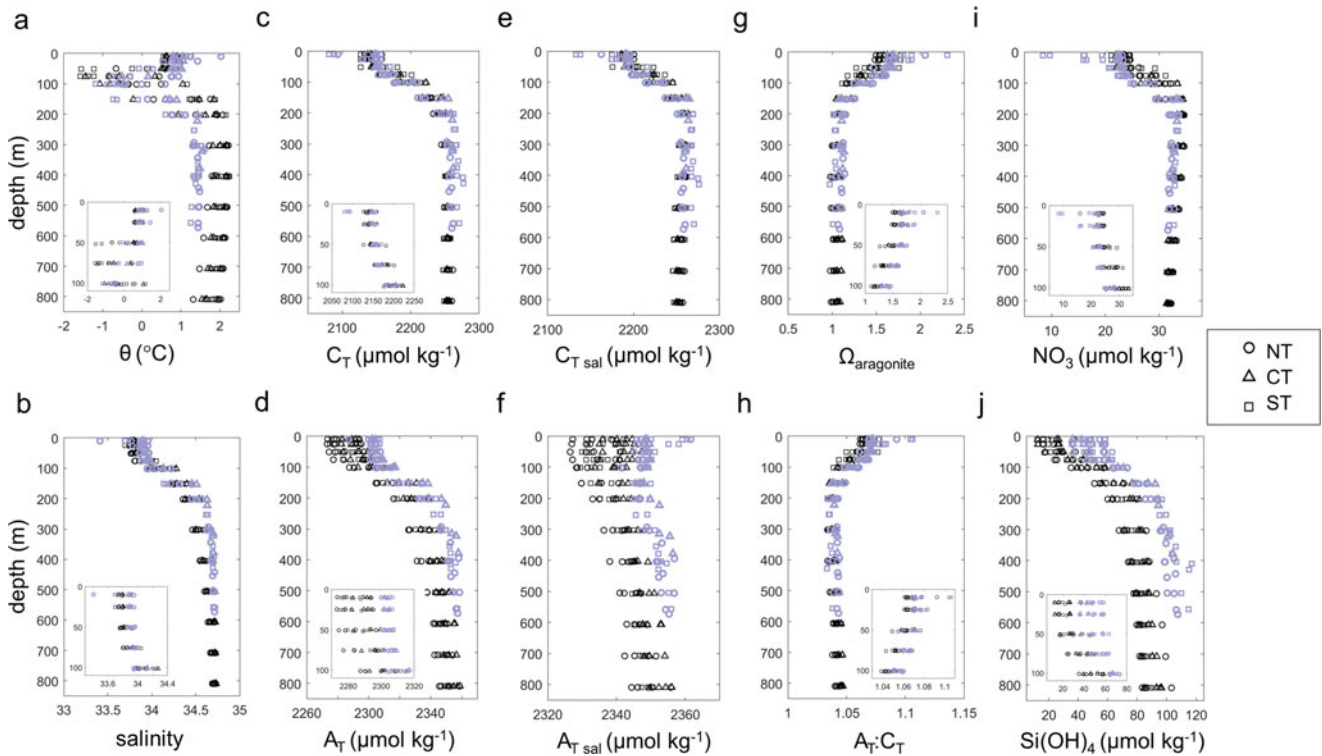
$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3^*] \quad (4)$$

and

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (5)$$

These constants were determined for  $19 \leq S \leq 43$  and  $2^\circ\text{C} \leq T \leq 35^\circ\text{C}$  and have been used in previous studies in the Southern Ocean and WAP regions where temperatures are frequently  $< 0^\circ\text{C}$  (e.g. Bednaršek *et al.* 2012, Hauri *et al.* 2015, Jones *et al.* 2017). More recent determinations of  $K_1$  and  $K_2$  in natural seawater by Mojica Prieto & Millero (2002) have been shown to be in excellent agreement with the values of Mehrbach *et al.* (1973), where the combined data have been fitted as functions of temperature (0–45°C) and salinity (5–42) by Mojica Prieto & Millero (2002). The values of  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  are used as indicators for changes in carbonate chemistry in relation to calcium carbonate saturation states and potential ocean acidification. When  $\Omega_{\text{aragonite}} < 1$ , the seawater is undersaturated with respect to aragonite, such that aragonite minerals become sensitive to dissolution and seawater becomes corrosive to organisms that produce aragonitic shells and skeletons (Feely *et al.* 2004, Orr *et al.* 2005). The  $\Omega_{\text{calcite}}$  remained positive (seawater was oversaturated with respect to calcite) in the upper  $\sim 2000 \text{ m}$





**Fig. 3.** Vertical profiles of **a.** potential temperature ( $\theta$ , °C), **b.** salinity, **c.**  $C_T$  ( $\mu\text{mol kg}^{-1}$ ), **d.**  $A_T$  ( $\mu\text{mol kg}^{-1}$ ), **e.**  $C_{T\text{sal}}$  ( $\mu\text{mol kg}^{-1}$ ), **f.**  $A_{T\text{sal}}$  ( $\mu\text{mol kg}^{-1}$ ), **g.** aragonite saturation state ( $\Omega_{\text{aragonite}}$ ), **h.** the  $A_T:C_T$  ratio, **i.**  $\text{NO}_3$  ( $\mu\text{mol kg}^{-1}$ ) and **j.**  $\text{Si(OH)}_4$  ( $\mu\text{mol kg}^{-1}$ ) in the upper 850 m (inserts showing upper 120 m) for offshore (black symbols) and shelf (blue symbols) for the north (NT, circles), central (CT, triangles) and south (ST, squares) transects.

of the water column. Therefore, this study is focused on  $\Omega_{\text{aragonite}}$  and its changes ( $\Delta\Omega_{\text{aragonite}}$ ) with respect to acidification in the contemporary and future marine environment along the WAP. The corresponding values for calcite ( $\Omega_{\text{calcite}}$ ) and its changes ( $\Delta\Omega_{\text{calcite}}$ ) are included as references.

#### Inorganic nutrients

For inorganic macronutrients silicic acid ( $\text{Si(OH)}_4$ , commonly referred to as silicate), phosphate ( $\text{PO}_4$ ), nitrate + nitrite ( $\text{NO}_3 + \text{NO}_2$ ) and nitrite ( $\text{NO}_2$ ), seawater was transferred from sample bottles into pre-rinsed 5 ml polyethylene vials and analysed with a Technicon TRAACS 800 Auto-analyzer. A freshly diluted home-made mixed nutrient standard containing Si ( $\text{OH}$ )<sub>4</sub>,  $\text{PO}_4$  and  $\text{NO}_3$  was measured daily in triplicate to monitor the performance of the analyser. Also measured was Reference Material for Nutrients in Seawater (RMNS; batch AZ from KANSO; [www.kanso.co.jp/eng/production](http://www.kanso.co.jp/eng/production)) for international consistency. The reported  $\text{NO}_3$  may in some samples comprise a very small amount of  $\text{NO}_2$  that is not distinguished and thus is incorporated into 'NO<sub>3</sub>' when described in the text. The precision values (expressed as the coefficient of variation) for  $\text{Si(OH)}_4$ ,  $\text{PO}_4$  and  $\text{NO}_3$  are estimated as

0.29%, 0.27% and 0.30%, respectively. The carbon and nutrient data are included in the GLODAPv2 data product (Olsen *et al.* 2019), which, according to stringent GLODAPv2 quality control measures, did not need any adjustments and thus are of high quality.

#### Seasonal changes

Seasonal changes in  $C_T$  and  $A_T$  were estimated from depth profiles (Fig. 3), using the difference between the average summer mixed-layer concentrations and the inferred winter concentrations from the observed concentrations at the depth of the temperature minimum, the latter taken to represent the remnant of the Winter Water (e.g. Jones *et al.* 2011, Tynan *et al.* 2016). The total seasonal change in  $C_T$  ( $\Delta C_T$ ) and  $A_T$  ( $\Delta A_T$ ) results from the influences of the main physical and biological processes, such as salinity changes ( $\Delta C_{T\text{sal}}$ ,  $\Delta A_{T\text{sal}}$ ) from freshwater inputs and mixing of different water masses, photosynthesis and respiration ( $\Delta C_{T\text{org}}$ ,  $\Delta A_{T\text{org}}$ ) and the formation and dissolution of biotic (aragonite, calcite) and abiotic (ikaite) calcium carbonate ( $\Delta C_{T\text{CaCO}_3}$ ,  $\Delta A_{T^*}$ ).

$$\Delta C_T = \Delta C_{T\text{sal}} + \Delta C_{T\text{org}} + \Delta C_{T\text{CaCO}_3} \quad (6)$$

$$\Delta A_T = \Delta A_{T\text{ sal}} + \Delta A_{T\text{ org}} + \Delta A_{T^*} \quad (7)$$

Salinity normalization of  $C_T$  and  $A_T$  ( $C_{T\text{ sal}}$  and  $A_{T\text{ sal}}$ ) was carried out using the normalization method that accounts for non-zero  $C_T$  and  $A_T$  freshwater endmembers and a reference salinity (34.68;  $S_{\text{ref}}$ ) of uCDW (Friis *et al.* 2003). The freshwater endmember for sea ice ( $C_T = 277 \pm 150 \mu\text{mol kg}^{-1}$ ;  $A_T = 328 \pm 150 \mu\text{mol kg}^{-1}$ ) from Legge *et al.* (2017), obtained from land-fast sea ice adjacent to Adelaide Island, was used. The values of  $\Delta C_{T\text{ sal}}$  and  $\Delta A_{T\text{ sal}}$  are determined from the difference between the total and salinity-normalized changes. It is assumed here that  $\Delta C_{T\text{ sal}}$  and  $\Delta A_{T\text{ sal}}$  integrate the signal from salinity changes due to freshwater inputs (e.g. meltwater) and advection, mixing and upwelling of different water masses.

Changes in  $C_T$  due to photosynthetic fixation of  $C_T$  and production of organic matter ( $\Delta C_{T\text{ org}}$ ) were determined from changes in salinity-normalized  $\text{NO}_3$  and the classical C/N Redfield ratio of 106/16 = 6.6 (Redfield 1958), which appears to be valid for the Southern Ocean (Hoppema & Goeyens 1999). Following Redfield stoichiometry (Redfield 1958), a decrease in  $C_T$  of  $1 \mu\text{mol kg}^{-1}$  due to phytoplankton uptake is accompanied by a decrease of  $16/106 = \sim 0.15 \mu\text{mol kg}^{-1}$  nitrate, which causes a  $\sim 0.15 \mu\text{mol kg}^{-1}$  increase in  $A_T$  (Dickson 1981, Sarmiento & Gruber 2006). The  $\Delta A_{T\text{ org}}$  is therefore estimated from  $\Delta C_{T\text{ org}}$  by applying  $0.15 \mu\text{mol } A_T \text{ kg}^{-1}$  per  $1 \mu\text{mol } C_T \text{ kg}^{-1}$  removed during photosynthetic production of organic matter. It has been argued that the uptake of the macronutrients of phosphorus (P) and sulphur (S) would also affect  $A_T$  (Wolf-Gladrow *et al.* 2007). This would lead to a higher uptake ratio of 21.8/106 and an ensuing increase in  $A_T$  of  $\sim 0.21 \mu\text{mol kg}^{-1}$  ( $\Delta A_{T\text{ org}}$ ) per  $1 \mu\text{mol kg}^{-1} \Delta C_{T\text{ org}}$ . The average difference between  $\Delta A_{T\text{ org}}$  determined from  $\Delta C_{T\text{ org}}$  using both ratios was  $2.7 \pm 1.7 \mu\text{mol kg}^{-1}$ . This would lead to average increases in  $\Delta \Omega_{\text{aragonite org}}$  of  $\sim 0.02$ , which is  $\sim 4\%$  of the total  $\Delta \Omega_{\text{aragonite org}}$  value and yields negligible difference from the result of this study. This is due to  $\Delta \Omega_{\text{aragonite org}}$  being dominated by  $\Delta C_{T\text{ org}}$ , so fractional adjustments in  $A_{T\text{ org}}$  have a very small effect on  $\Delta \Omega_{\text{aragonite org}}$ . Thereby, we adhere to the uptake ratio of 16 and the ensuing change of  $0.15 \mu\text{mol } A_T \text{ kg}^{-1}$  per  $1 \mu\text{mol } C_T \text{ kg}^{-1}$  removed during photosynthesis.

The  $\Delta C_{T\text{ CaCO}_3}$  accounts for any calcium carbonate mineral (biotic aragonite and calcite; abiotic ikaite) formation or dissolution that changes the  $A_T:C_T$  ratio by 2:1 (Dickson 1981, Broecker & Peng 1982, Sarmiento & Gruber 2006). This is determined from potential alkalinity ( $A_{T^*}$ ), which is the sum of salinity-normalized  $A_T$  and  $\text{NO}_3$  (Goldman & Brewer 1980 and references cited therein) following Jones *et al.* (2017). The  $A_{T^*}$  accounts for salinity changes and the increase (decrease)

in  $A_T$  of  $1 \mu\text{mol kg}^{-1}$  due to the uptake (release) of  $1 \mu\text{mol kg}^{-1} \text{NO}_3$  during photosynthesis (respiration), as described above (Broecker & Peng 1982, Sarmiento & Gruber 2006). Thus,  $\Delta C_{T\text{ CaCO}_3} = 0.5 \Delta A_{T^*}$ . It is acknowledged that from the dissolved constituents in seawater, and further calculated seawater tracers, the changes of such variables can be ascribed to the formation/dissolution of carbonate minerals but cannot define specifically which one, two or all three of the relevant minerals (aragonite, calcite or ikaite) is the carbonate source involved without the isolation and identification of such minerals. Hence, the role of other polymorphs, such as high-Mg calcite, and the identification of the carbonate source (e.g. aragonite, calcite or ikaite) with varying elemental ratios in solid  $\text{CaCO}_3$  is beyond the scope of this work.

The seasonal changes in  $C_T$  and  $A_T$  ( $\Delta C_T$  and  $\Delta A_T$ ) for each of the key processes were used to determine perturbations in summer mixed-layer  $\Omega$  ( $\Delta \Omega_{\text{aragonite}}$  and its partial constituents  $\Delta \Omega_{\text{aragonite sal}}$ ,  $\Delta \Omega_{\text{aragonite org}}$  and  $\Delta \Omega_{\text{aragonite CaCO}_3}$ ) alongside *in situ* temperature, salinity and macronutrient concentrations with the *CO2SYS* program. The different process-driven  $\Delta \Omega$  values are used alongside the  $A_T:C_T$  ratio as indicators of the buffering capacity of seawater to estimate the impacts of the changes on the aragonite saturation state.

#### *Uncertainties in analytical and calculation techniques*

Uncertainties associated with the analytical measurements of the total  $\Delta C_T$  (Eq. (6)) and  $\Delta A_T$  (Eq. (7)) were based on analytical precision ( $C_T \pm 1.0 \mu\text{mol kg}^{-1}$ ;  $A_T \pm 1.5 \mu\text{mol kg}^{-1}$ ) and estimated as  $\pm 2$  and  $\pm 3 \mu\text{mol kg}^{-1}$ , respectively. Uncertainties in  $\Delta C_{T\text{ sal}}$  and  $\Delta A_{T\text{ sal}}$  were estimated, by consideration of the uncertainty in the endmember ( $\pm 150 \mu\text{mol kg}^{-1}$ ; Legge *et al.* 2017) and by maximum difference between measured and salinity-normalized values ( $\pm 6 \mu\text{mol kg}^{-1}$ ), as  $\pm 8$  and  $\pm 9 \mu\text{mol kg}^{-1}$ , respectively. Uncertainties in  $\Delta C_{T\text{ org}}$  and  $\Delta A_{T\text{ org}}$  were estimated from the analytical precision of  $\text{NO}_3$ , where an upper bound of the error for  $\Delta \text{NO}_3\text{ sal}$  was set to  $\pm 0.11 \mu\text{mol kg}^{-1}$ ; thus, the equivalent for  $C_{T\text{ org}}$  was  $\pm 0.7 \mu\text{mol kg}^{-1}$  and for  $A_{T\text{ org}}$  was  $\pm 0.1 \mu\text{mol kg}^{-1}$ . By applying an uncertainty in the C/N ratio, which was set to  $\pm 1 \mu\text{mol kg}^{-1}$  to account for deviations in the ratio compared with Redfield stoichiometry (e.g. Hoppema & Goeyens 1999), the compound upper-bound uncertainty for  $\Delta C_{T\text{ org}}$  and  $\Delta A_{T\text{ org}}$  was  $\pm 1.7 \mu\text{mol kg}^{-1}$  and for  $A_{T\text{ org}}$  was  $\pm 1.1 \mu\text{mol kg}^{-1}$ . Upper-bound uncertainties in  $\Delta A_{T^*}$  and  $\Delta C_{T\text{ CaCO}_3}$  were estimated from the combined uncertainty of salinity-normalized  $A_T$  ( $\pm 6 \mu\text{mol kg}^{-1}$ ) and  $\text{NO}_3$  ( $\pm 0.09 \mu\text{mol kg}^{-1}$ ) as  $\pm 12 \mu\text{mol kg}^{-1}$ . Using the same approach, uncertainties associated with the  $\Delta \Omega_{\text{aragonite}}$  partial contributions were estimated from the



**Table 1.** Water mass classification and inorganic carbon system parameters  $C_T$  ( $\mu\text{mol kg}^{-1}$ ),  $A_T$  ( $\mu\text{mol kg}^{-1}$ ), calcite saturation state ( $\Omega_{\text{calcite}}$ ) and aragonite saturation state ( $\Omega_{\text{aragonite}}$ ) along the north transect (NT), central transect (CT) and south transect (ST) for Antarctic Surface Water (AASW), Winter Water (WW), upper Circumpolar Deep Water (uCDW), modified Circumpolar Deep Water (mCDW) and Deep Water (DW). Average values are shown per water mass per transect with the ( $\pm$ ) standard deviation in parentheses.

Water mass	Transect	$C_T$ ( $\mu\text{mol kg}^{-1}$ )		$A_T$ ( $\mu\text{mol kg}^{-1}$ )		$\Omega_{\text{calcite}}$		$\Omega_{\text{aragonite}}$		
		Offshore	Shelf	Offshore	Shelf	Offshore	Shelf	Offshore	Shelf	
AASW	$\sigma_0 \leq 27.4$	NT	2150 (9)	2150 (18)	2283 (9)	2302 (5)	2.38 (0.08)	2.65 (0.21)	1.49 (0.05)	1.66 (0.13)
		CT	2145 (8)	2154 (10)	2292 (6)	2305 (3)	2.58 (0.11)	2.63 (0.12)	1.62 (0.07)	1.65 (0.07)
		ST	2136 (11)	2144 (31)	2284 (6)	2305 (2)	2.60 (0.20)	2.78 (0.48)	1.63 (0.12)	1.74 (0.30)
WW	$\theta_{\text{min}}$ $\sigma_0 \leq 27.2\text{--}27.4$	NT	2190 (13)	2188 (19)	2296 (9)	2310 (5)	1.99 (0.11)	2.20 (0.19)	1.25 (0.07)	1.38 (0.12)
		CT	2181 (5)	2203 (2)	2298 (7)	2317 (1)	2.13 (0.05)	2.09 (0.02)	1.34 (0.03)	1.31 (0.01)
		ST	2181 (8)	2197 (18)	2291 (6)	2310 (3)	2.05 (0.03)	2.06 (0.20)	1.29 (0.02)	1.29 (0.13)
uCDW	$1.70 \leq \theta_{\text{max}} \leq 2.13^\circ\text{C}^a$ $34.54 \leq S \leq 34.75^a$ < 2000 m	NT	2255 (2)	-	2347 (5)	-	1.60 (0.05)	-	1.02 (0.03)	-
		CT	2254 (2)	-	2348 (5)	-	1.71 (0.05)	-	1.08 (0.03)	-
		ST	2252 (3)	-	2347 (4)	-	1.68 (0.07)	-	1.07 (0.04)	-
mCDW	$34.6 \leq S \leq 34.7^b$ < 750 m	NT	-	2253 (1)	-	2347 (0)	-	1.77 (0.01)	-	1.12 (0.00)
		CT	-	2261 (1)	-	2353 (5)	-	1.77 (0.02)	-	1.11 (0.01)
		ST	-	2270 (5)	-	2352 (5)	-	1.62 (0.04)	-	1.02 (0.03)
DW	$34.7 \leq S_{\text{max}}$ > 2000 m <sup>c</sup>	NT	2262 (2)	-	2366 (2)	-	1.01 (0.12)	-	0.66 (0.07)	-
		CT	2261 (2)	-	2369 (2)	-	1.08 (0.12)	-	0.70 (0.08)	-
		ST	2261 (3)	-	2366 (1)	-	0.99 (0.15)	-	0.65 (0.09)	-

<sup>a</sup>Martinson *et al.* (2008).

<sup>b</sup>Smith *et al.* (1999).

<sup>c</sup>Hauri *et al.* (2015).

'-' indicates no data.

associated errors for each  $\Delta C_T$  and  $\Delta A_T$  term in *CO2SYS*:  $\Delta\Omega_{\text{aragonite sal}} \pm 0.29$ ,  $\Delta\Omega_{\text{aragonite org}} \pm 0.05$  and  $\Delta\Omega_{\text{aragonite CaCO}_3} \pm 0.41$ . Uncertainties in  $\Omega_{\text{aragonite}}$  determined from the use of different equilibrium constants ( $K_1$  and  $K_2$ ; e.g. Mojica Prieto & Millero 2002, relative to those of Mehrbach *et al.* 1973 refit by Dickson & Millero 1987) were estimated in *CO2SYS* as  $\pm 0.04$ , which is of similar magnitude to the range of uncertainties determined above.

## Results

### Sea surface waters

The summer surface waters in the region were relatively warm and fresh (Fig. 3a & b), with salinities ranging from 33.41 to 33.95 and potential temperatures of 0.56–2.03°C. Warmer and more saline waters were observed on the shelf compared to offshore, with the exception of the freshest surface water that occurred closest to the coast near Anvers Island and Adelaide Island (Fig. 1a). The surface waters exhibited distinct changes in biogeochemical properties from north to south and between offshore and the shelf region (Fig. 1b–g). Values of  $C_T$  varied between 2080 and 2158  $\mu\text{mol kg}^{-1}$ , with lower concentrations in the south (Fig. 3c). Closest to the coast, lower  $C_T$  was coincident with low-salinity waters. Congruent with the distribution of salinity,  $A_T$  increased from 2273  $\mu\text{mol kg}^{-1}$  offshore to the highest values of 2305  $\mu\text{mol kg}^{-1}$  over the shelf (Fig. 3d). An exception was lower  $A_T$  (2287  $\mu\text{mol kg}^{-1}$ )

near Anvers Island. Salinity-normalized  $C_T$  ( $C_{T \text{ sal}}$ ) varied by  $\sim 60 \mu\text{mol kg}^{-1}$  and was lowest (2142  $\mu\text{mol kg}^{-1}$ ) on the southernmost transect as an indicator of the larger influence of biological carbon uptake in the south relative to the north (Fig. 1b). In contrast, salinity-normalized  $A_T$  ( $A_{T \text{ sal}}$ ) varied by  $\sim 30\text{--}40 \mu\text{mol kg}^{-1}$  from the lowest values offshore to higher values of 2375  $\mu\text{mol kg}^{-1}$  over the shelf where the impact of freshwater inputs was greatest in coastal waters (Fig. 1c). Low  $\text{NO}_3 \text{ sal}$  ( $< 10 \mu\text{mol kg}^{-1}$ ) occurred in the south and close to the coast as a result of biological drawdown (Fig. 1d), coinciding with low  $C_T$ . Closely following patterns in  $A_T$ , values of  $\text{Si(OH)}_4 \text{ sal}$  increased by  $> 30 \mu\text{mol kg}^{-1}$  from offshore surface waters to the highest value of 59.4  $\mu\text{mol kg}^{-1}$  over the shelf (Fig. 1e). The highest carbonate mineral saturation states were found over the shelf, with the highest values for  $\Omega_{\text{calcite}}$  (3.68) and  $\Omega_{\text{aragonite}}$  (2.31) closest to the coast (Fig. 1f & g). The degree of saturation in surface waters increased southwards from the lowest levels of  $\Omega_{\text{calcite}}$  (2.39) and  $\Omega_{\text{aragonite}}$  (1.50) offshore. The  $A_T:C_T$  ratio (Fig. 3h) ranged from 1.06, implying a reduced buffering capacity where  $A_T$  was lowest offshore, to 1.11 and an increased buffering capacity with higher  $A_T$  and lower  $C_T$  in the shelf region.

### Water masses of the West Antarctic Peninsula

The vertical distribution of potential temperature and salinity identified the fresher AASW, cold Winter Water

(with winter temperatures closer to freezing point) and warm core of uCDW in the ACC overlying cold, saline deep waters (Fig. 2 & Table I). Projections of uCDW that extended over the shelf mixed with Winter Water and formed the cooler and fresher variety of uCDW (i.e. mCDW). Water column  $A_T$ ,  $C_T$  and macronutrients showed reductions in the AASW and seasonal mixed layer as compared to the underlying Winter Water for both the shelf and offshore regions. The vertical distribution of  $A_T$  aligned well with that of salinity (Fig. 2b, h & n). The region was dominated by the  $C_T$ -rich CDW, with the lowest  $A_T:C_T$  ratios in the uCDW offshore (Fig. 2c, i & o). Macronutrients increased with depth and showed that the shelf region had generally lower  $NO_3$  and higher  $Si(OH)_4$  compared with offshore waters (Fig. 2d, j & p). The distribution of  $\Omega_{calcite}$  (Fig. 2e, k & q) and  $\Omega_{aragonite}$  (Fig. 2f, l & r) reflected the differences in  $C_T$  and  $A_T$ , with higher values (saturation) in the upper layers, especially over the shelf, and the lowest values (undersaturation) in deep waters.

#### Seasonal mixed layer

The AASW reflected seasonal warming (average  $\theta = 0.30$ – $1.04^\circ C$ ) and freshwater inputs (average  $S = 33.77$ – $33.92$ ) in the upper part of the water column compared to the Winter Water beneath (Fig. 3a & b & Table I). Summer MLDs (above the seasonal pycnocline) ranged between 7 and 107 m, being shallower and fresher over the shelf compared to offshore. The distribution of  $C_T$  (Fig. 3c) and  $NO_3$  revealed spatial variability with lower values over the shelf and averages of  $2136 \pm 11$  and  $19.1 \pm 5.2 \mu mol kg^{-1}$ , respectively, in the south transect (ST). In contrast, values of  $A_T$  (Fig. 3d) and  $Si(OH)_4$  exhibited notable cross-shelf variability and were higher at  $2305 \pm 3$  and at  $54.3 \pm 4.6 \mu mol kg^{-1}$ , respectively, over the shelf relative to offshore waters. Values of  $C_{T\ sal}$  were distinctly lower over the southern shelf region (ST) and  $A_{T\ sal}$  was elevated over the shelf, particularly in the north transect (NT). The AASW was most saturated with carbonate minerals with  $\Omega_{calcite}$  of  $2.78 \pm 0.48$  and  $\Omega_{aragonite}$  of  $1.74 \pm 0.30$  (Fig. 3g) over the shelf in the south. This was accompanied by the highest  $A_T:C_T$  ratio (Fig. 3h). Conversely, the lowest  $\Omega_{calcite}$ ,  $\Omega_{aragonite}$  and low  $A_T:C_T$  ratio values occurred in offshore AASW in the north.

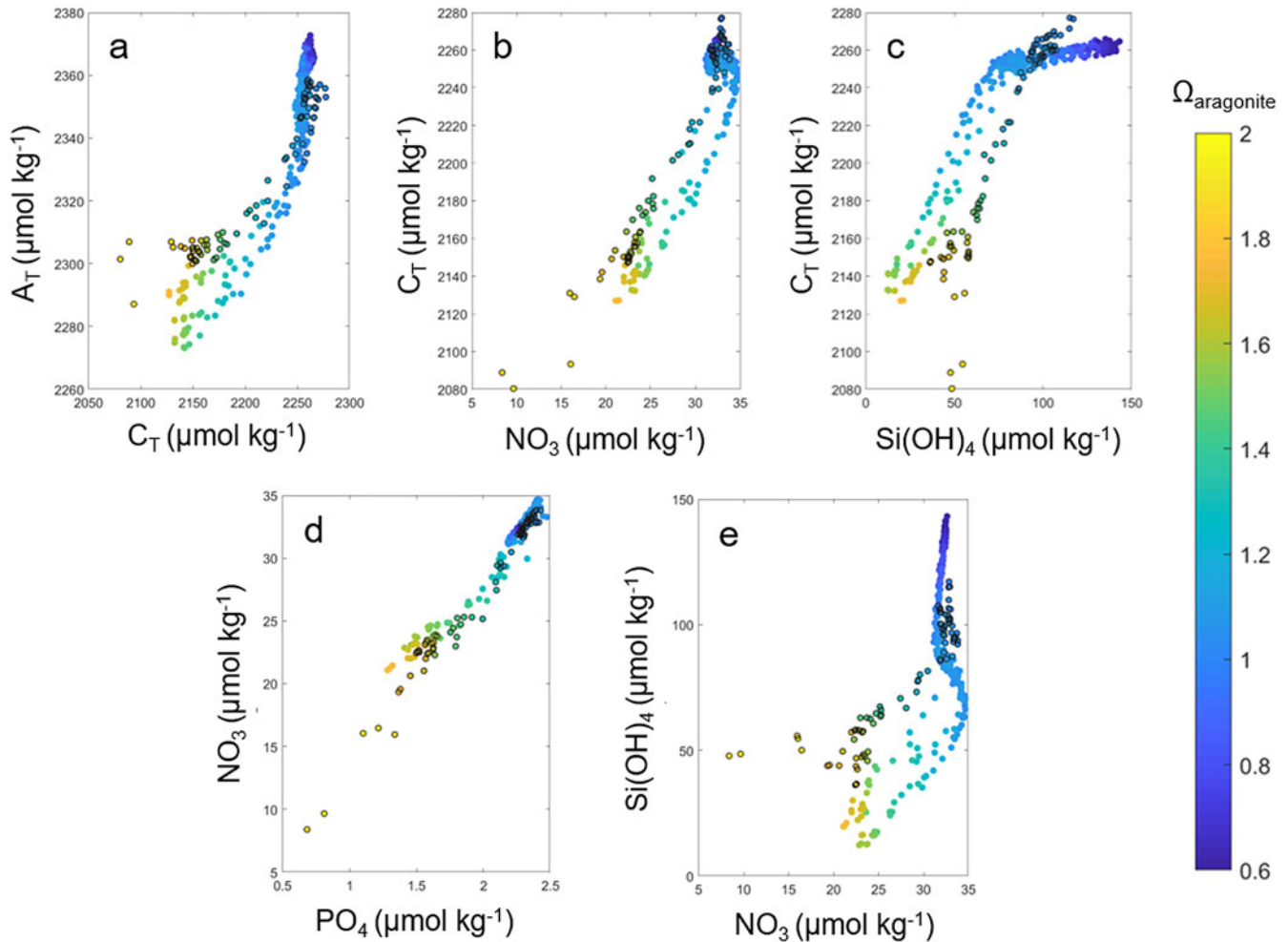
Deeper convective mixing during the previous winter was evident over the shelf as Winter Water depths increased up to 136 m depth compared with offshore waters. This was accompanied by warmer and saltier ( $-0.65 \pm 0.64^\circ C$ ,  $34.05 \pm 0.08$ ) Winter Water over the shelf (Fig. 3a & b) compared with offshore waters ( $-1.07 \pm 0.42^\circ C$ ,  $33.95 \pm 0.07$ ). Winter Water values of  $C_T$  and  $A_T$  over the shelf were  $2195 \pm 16$  and

$2311 \pm 5 \mu mol kg^{-1}$ , respectively, and there were higher than average offshore Winter Water values of  $C_T$  and  $A_T$  of  $2184 \pm 10$  and  $2295 \pm 8 \mu mol kg^{-1}$ , respectively (Fig. 3c & d). Winter Water  $C_{T\ sal}$  and  $A_{T\ sal}$  were slightly lower and higher, respectively, compared to  $C_T$  and  $A_T$  (Fig. 3e & f). Concentrations of  $NO_3$  were lower over the shelf ( $27.0 \pm 1.9 \mu mol kg^{-1}$ ) compared to offshore ( $29.0 \pm 1.1 \mu mol kg^{-1}$ ), and  $Si(OH)_4$  was clearly higher over the shelf ( $68.9 \pm 4.8 \mu mol kg^{-1}$ ) compared to offshore ( $44.1 \pm 7.8 \mu mol kg^{-1}$ ). A latitudinal gradient showed that the Winter Water potential temperature decreased by  $\sim 1^\circ C$  from the north (NT) to south (ST). Values of  $\Omega_{aragonite}$  varied between 1.15 and 1.46 (Fig. 3g), with the lowest values close to the coast near Adelaide Island. Values of  $\Omega_{calcite}$  varied between 1.83 and 2.33 in the upper mixed layer (not shown). The  $A_T:C_T$  ratio ranged from 1.04 to 1.06 (Fig. 3h).

#### Circumpolar Deep Water

The subsurface potential temperature maximum ( $1.70 \leq \theta \leq 2.13^\circ C$ ;  $34.54 \leq S \leq 34.75$ ) identified the offshore core of uCDW (Table I) in the ACC, which extended to the shelf break (Fig. 2). Concurrent potential temperature maxima over the shelf were cooler and fresher compared to the ACC-derived uCDW, which distinguished the mCDW (typically  $34.6 \leq S \leq 34.7$ ). Comparable increasing gradients in  $C_T$  and  $A_T$  were seen between the Winter Water and subsurface uCDW and mCDW (Fig. 3c & d). The variability in  $Si(OH)_4$  in the water column was similar to that of  $A_T$ , as shelf waters had higher concentrations, especially in the 400–600 m depth range compared with offshore waters. The average  $NO_3$  in both offshore and shelf regions was similar at  $\sim 33 \mu mol kg^{-1}$ . The mCDW was characterized by signatures of remineralization and upwelled deeper waters across the shelf break with higher  $C_T$  ( $2264 \pm 7 \mu mol kg^{-1}$ ),  $A_T$  ( $2350 \pm 5 \mu mol kg^{-1}$ ) and  $Si(OH)_4$  ( $102.8 \pm 7.8 \mu mol kg^{-1}$ ) compared with uCDW values of  $C_T$  ( $2253 \pm 3 \mu mol kg^{-1}$ ),  $A_T$  ( $2347 \pm 5 \mu mol kg^{-1}$ ) and  $Si(OH)_4$  ( $85.0 \pm 3.7 \mu mol kg^{-1}$ ). Within the uCDW and mCDW cores, the  $A_T:C_T$  ratio was lowest with values of 1.03–1.05. Subsurface concentrations of  $C_{T\ sal}$  and  $A_{T\ sal}$  on the shelf were  $\sim 5$ – $30 \mu mol kg^{-1}$  higher compared with those offshore ( $\sim 2253 \mu mol C_T kg^{-1}$ ,  $\sim 2347 \mu mol A_T kg^{-1}$ ). The highest  $C_{T\ sal}$  ( $2276 \mu mol kg^{-1}$ ) was found at 400 m depth in the south (ST).

Carbonate mineral saturation showed a general latitudinal decrease from north to south with  $\Omega_{calcite}$  always above saturation. The  $\Omega_{aragonite}$  was close to saturation levels in uCDW ( $1.06 \pm 0.04$ ) and mCDW ( $1.07 \pm 0.05$ ). The aragonite saturation horizon ( $\Omega_{aragonite} = 1.0$ ) shoaled over the shelf where  $\Omega_{aragonite}$  was showing slight undersaturation at 0.97 at 430 m depth in the southern region.



**Fig. 4.** Relationships between **a.**  $A_T$  ( $\mu\text{mol kg}^{-1}$ ) and  $C_T$  ( $\mu\text{mol kg}^{-1}$ ), **b.**  $C_T$  ( $\mu\text{mol kg}^{-1}$ ) and  $\text{NO}_3$  ( $\mu\text{mol kg}^{-1}$ ), **c.**  $C_T$  ( $\mu\text{mol kg}^{-1}$ ) and  $\text{Si(OH)}_4$  ( $\mu\text{mol kg}^{-1}$ ), **d.**  $\text{NO}_3$  ( $\mu\text{mol kg}^{-1}$ ) and  $\text{PO}_4$  ( $\mu\text{mol kg}^{-1}$ ) and **e.**  $\text{Si(OH)}_4$  ( $\mu\text{mol kg}^{-1}$ ) and  $\text{NO}_3$  ( $\mu\text{mol kg}^{-1}$ ). Data are colour coded with respect to the aragonite saturation state ( $\Omega_{\text{aragonite}}$ ) and shelf waters are identified by black-outlined circles.

#### Deep waters offshore

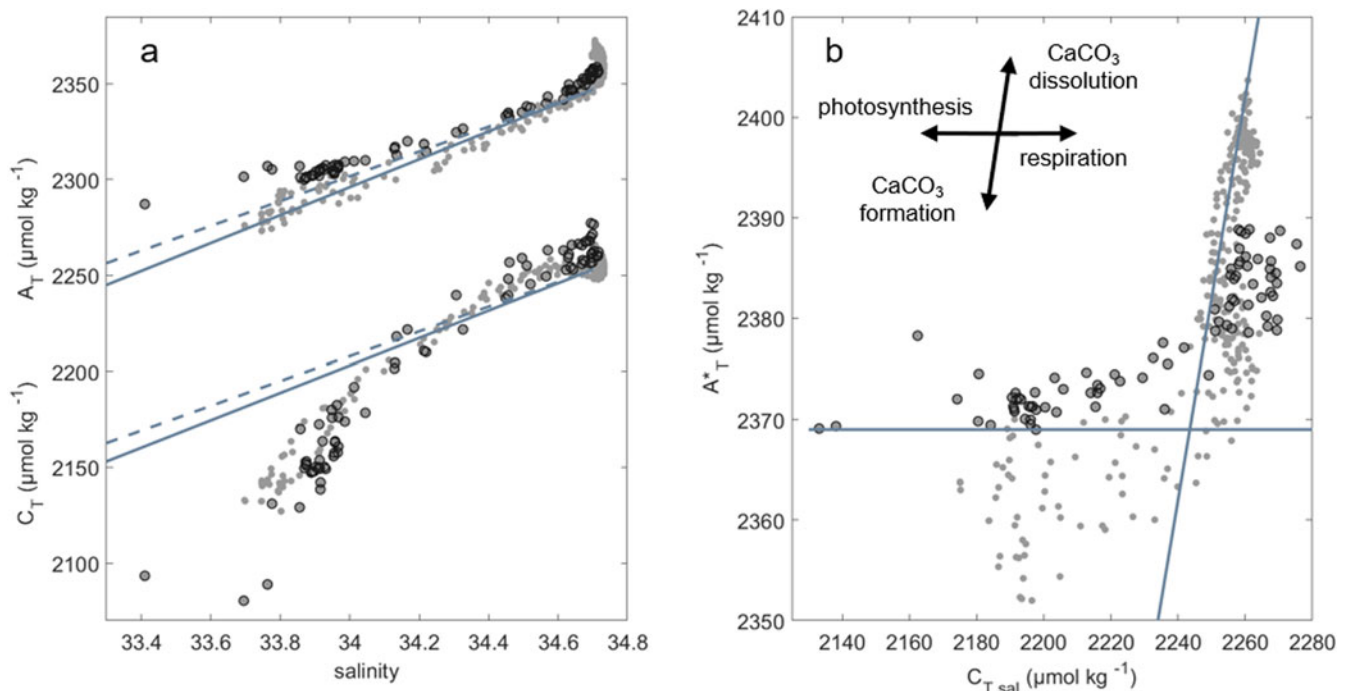
Deep waters (depths > 2000 m) in the ACC in the offshore region (Fig. 2), which included lower CDW, were characterized by  $C_T$  ( $2261 \pm 2 \mu\text{mol kg}^{-1}$ ),  $A_T$  ( $2367 \pm 2 \mu\text{mol kg}^{-1}$ ),  $\text{NO}_3$  ( $32.3 \pm 0.2 \mu\text{mol kg}^{-1}$ ) and  $\text{Si(OH)}_4$  ( $131.8 \pm 6.5 \mu\text{mol kg}^{-1}$ ). Deep waters were all undersaturated with respect to aragonite ( $\Omega_{\text{aragonite}}$  of 0.54–0.86), and the saturation horizon for calcite ( $\Omega_{\text{calcite}} = 1$ ) was found at  $\sim 3000$  m depth. The  $A_T:C_T$  ratio ranged between 1.04 and 1.05, showing a slightly higher buffering capacity compared with the overlying uCDW. The latitudinal distribution of deep water revealed variability as the isotherms were more steeply inclined towards the continental slope in the NT region, which is less apparent in the central transect (CT) region and almost absent in the ST region. This resulted in a southwards increase in the average potential temperature of waters in the 2000–2500 m depth range from  $0.68^\circ\text{C} \pm 0.25^\circ\text{C}$  to  $0.74^\circ\text{C} \pm 0.12^\circ\text{C}$ .

This was accompanied by a slight increase in salinity and reduction in  $C_T$  and  $\text{Si(OH)}_4$ .

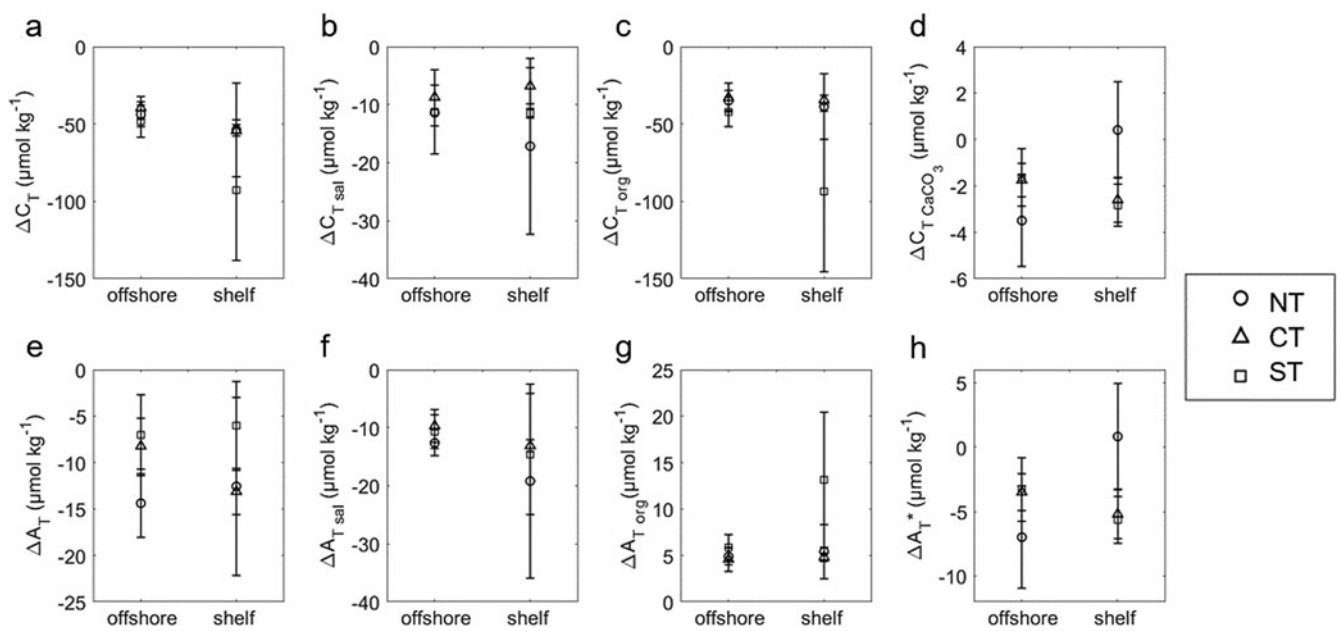
#### Inorganic carbon and nutrient cycling

The relationships between  $A_T$ ,  $C_T$  and macronutrients (Fig. 4) revealed different biogeochemical regimes in the different water masses and offshore and shelf regions. The highest  $A_T$ , high  $C_T$  and the lowest  $\Omega_{\text{aragonite}}$  at  $\sim 0.5$  distinguished the deep and bottom waters offshore (Fig. 4a). The highest  $C_T$  and near-undersaturation of aragonite ( $\Omega_{\text{aragonite}} \approx 1$ ) defined the shelf region. Aragonite supersaturation ( $\Omega_{\text{aragonite}} > 1.8$ ) was associated with the combination of the lowest  $C_T$  and elevated  $A_T$  over the shelf. The relationships between  $C_T$  and  $\text{NO}_3$  (Fig. 4b) and between  $C_T$  and  $\text{Si(OH)}_4$  (Fig. 4c) showed general trends with lowest concentrations co-occurring over the shelf and offshore, respectively, where  $\Omega_{\text{aragonite}}$  was in the 1.6–2.3 range. Regional differences were clearly

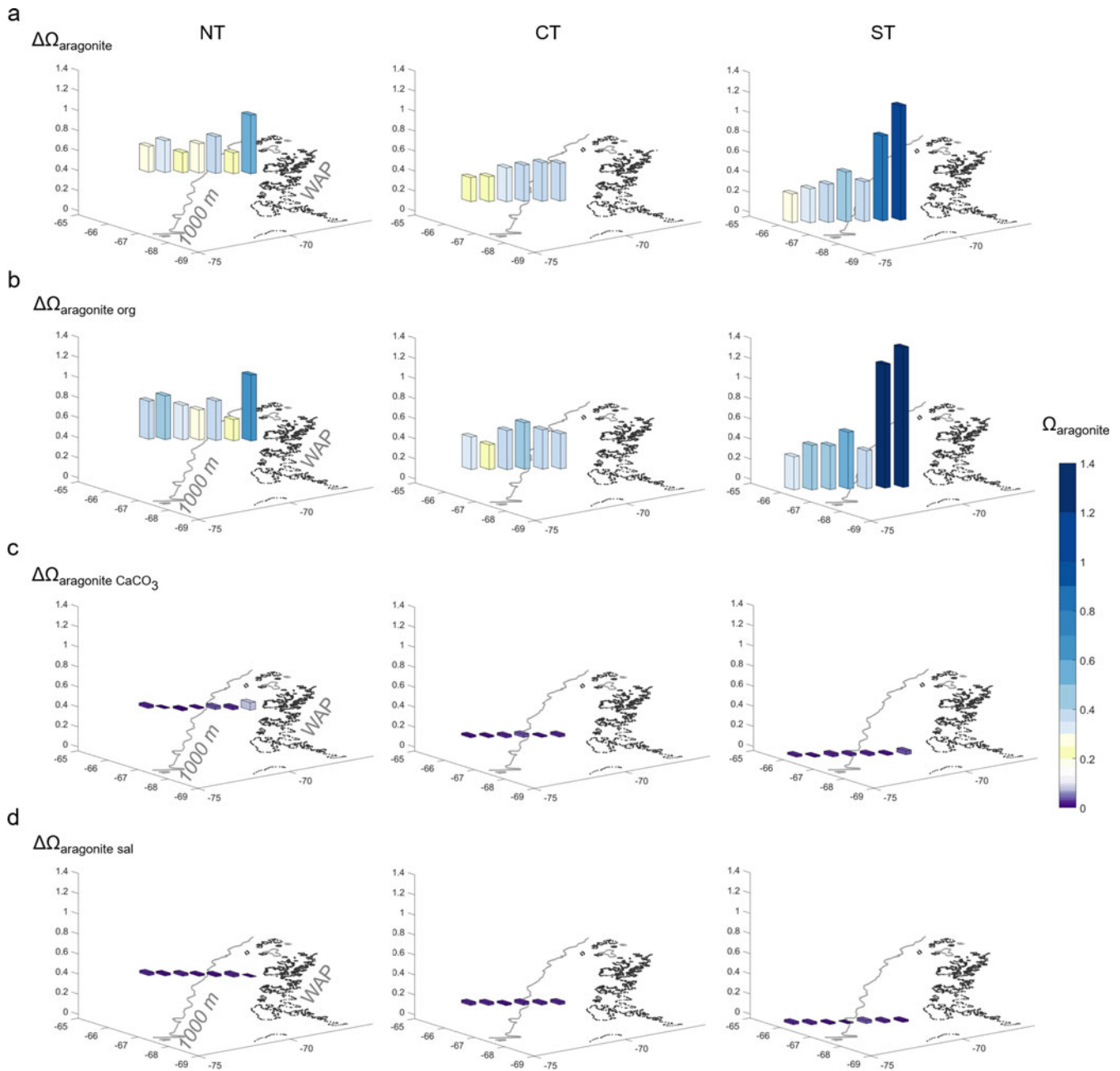




**Fig. 5.** Relationships between **a.** salinity and  $A_T$  ( $\mu\text{mol kg}^{-1}$ ) and salinity and  $C_T$  ( $\mu\text{mol kg}^{-1}$ ), and **b.** potential  $A_T$  ( $A_T^*$ ;  $\mu\text{mol kg}^{-1}$ ) and salinity-normalized  $C_T$  ( $C_{T\text{ sal}}$ ;  $\mu\text{mol kg}^{-1}$ ) for all data (grey dots) and the seasonal mixed layer (Antarctic Surface Water and Winter Water, black-outlined circles). Trend lines in **a.** represent the hypothetical dilution lines between endmembers for upper Circumpolar Deep Water with glacial ice (dashed lines) and sea ice (solid lines). Trend lines in **b.** represent the influence of photosynthesis/respiration and carbonate mineral formation/dissolution, as indicated by the insert.



**Fig. 6.** Deficits in  $C_T$  and  $A_T$  between the summer mixed layer and Winter Water ascribed to: **(a., e.)** total change in  $C_T$  ( $\Delta C_T$ ;  $\mu\text{mol kg}^{-1}$ ) and total change in  $A_T$  ( $\Delta A_T$ ;  $\mu\text{mol kg}^{-1}$ ); **(b., f.)** changes due to salinity ( $\Delta C_{T\text{ sal}}$ ,  $\Delta A_{T\text{ sal}}$ ;  $\mu\text{mol kg}^{-1}$ ); **(c., g.)** changes due to photosynthesis/respiration ( $\Delta C_{T\text{ org}}$ ,  $\Delta A_{T\text{ org}}$ ;  $\mu\text{mol kg}^{-1}$ ); and **(d., h.)** changes due to calcium carbonate mineral formation/dissolution ( $\Delta C_{T\text{ CaCO}_3}$ ,  $\Delta A_T^*$ ;  $\mu\text{mol kg}^{-1}$ ). Mean values with error bars ( $\pm 1$  SD) are shown for offshore and shelf waters for the north (NT, circles), central (CT, triangles) and south (ST, squares) transect.



**Fig. 7.** Changes in the aragonite saturation state ( $\Omega_{\text{aragonite}}$ ) between the summer mixed layer and Winter Water along the West Antarctic Peninsula ascribed to **a.** the total change ( $\Delta\Omega_{\text{aragonite}}$ ), **b.** changes due to photosynthesis/respiration ( $\Delta\Omega_{\text{aragonite org}}$ ), **c.** changes due to the formation/dissolution of any calcium carbonate minerals ( $\Delta\Omega_{\text{aragonite CaCO}_3}$ ) and **d.** changes due to salinity ( $\Delta\Omega_{\text{aragonite sal}}$ ) for each hydrographic station in the north transect (NT), central transect (CT) and south transect (ST). Uncertainties are  $\Delta\Omega_{\text{aragonite sal}} \pm 0.29$ ,  $\Delta\Omega_{\text{aragonite org}} \pm 0.05$  and  $\Delta\Omega_{\text{aragonite CaCO}_3} \pm 0.41$  (not taken into account is the  $\pm 0.04$  uncertainty in  $\Omega_{\text{aragonite}}$  from the use of different equilibrium constants  $K_1$  and  $K_2$ ).

identified; the highest  $\text{Si(OH)}_4$  and the highest  $\text{NO}_3$  occurred in undersaturated ( $\Omega_{\text{aragonite}} < 1$ ) deep and bottom waters offshore. The values of  $\text{NO}_3$  and  $\text{PO}_4$  (Fig. 4d) were closely coupled with the lowest values over the shelf associated with the highest  $\Omega_{\text{aragonite}}$  of  $\sim 2.3$ . The lowest  $\text{Si(OH)}_4$  (Fig. 4e) and reduced

$\text{NO}_3$  concentrations occurred offshore with  $\Omega_{\text{aragonite}}$  at  $\sim 1.8$ .

Relationships between inorganic carbon and nutrients in the seasonal mixed layer (AASW and Winter Water) for offshore waters were statistically significant and yielded ratio values (estimated from slopes of the linear

regression) for C/N of  $11.8 \pm 0.7$  ( $r^2 = 0.80$ ,  $P \ll 0.0001$ ,  $n = 72$ ), C/Si of  $1.0 \pm 0.1$  ( $r^2 = 0.76$ ,  $P \ll 0.0001$ ,  $n = 72$ ), N/P of  $12.9 \pm 0.2$  ( $r^2 = 0.98$ ,  $P \ll 0.0001$ ,  $n = 72$ ) and Si/N of  $7.3 \pm 1.1$  ( $r^2 = 0.39$ ,  $P < 0.001$ ,  $n = 72$ ). For the shelf region, nutrient uptake ratios were also estimated from statistically significant relationships with C/N of  $10.6 \pm 0.6$  ( $r^2 = 0.89$ ,  $P \ll 0.0001$ ,  $n = 48$ ), C/Si of  $1.2 \pm 0.1$  ( $r^2 = 0.68$ ,  $P < 0.0001$ ,  $n = 48$ ), N/P of  $13.8 \pm 0.3$  ( $r^2 = 0.98$ ,  $P \ll 0.0001$ ,  $n = 48$ ) and Si/N of  $4.8 \pm 0.9$  ( $r^2 = 0.40$ ,  $P < 0.001$ ,  $n = 48$ ). The carbon and nutrient ratio values in the shelf region were lower for C/N and Si/N and higher for C/Si and N/P compared with the offshore waters.

#### *Seasonal mixed-layer physical and biological processes*

Reductions in  $C_T$ ,  $A_T$  and macronutrients in surface water and the seasonal mixed layer compared to the Winter Water showed the impact of freshwater inputs in the shelf and offshore regions along the WAP (Fig. 2). Theoretical dilution lines between endmembers for uCDW, determined as average  $C_T$  and  $A_T$  in offshore CDW ( $S = 34.7$ ,  $C_T = 2253 \pm 3 \mu\text{mol kg}^{-1}$ ,  $A_T = 2347 \pm 3 \mu\text{mol kg}^{-1}$ ) and for sea ice ( $C_T = 277 \pm 150 \mu\text{mol kg}^{-1}$ ,  $A_T = 328 \pm 150 \mu\text{mol kg}^{-1}$ ) and glacial ice ( $C_T = 16 \pm 5 \mu\text{mol kg}^{-1}$ ,  $A_T = 100 \pm 5 \mu\text{mol kg}^{-1}$ ) showed the influence of salinity changes on  $C_T$  and  $A_T$  in the full water column (Fig. 5a). The relationships between  $C_T$  and  $A_T$  with salinity in the seasonal mixed layer (AASW and Winter Water) yielded  $C_T = 168S - 3530$  ( $r^2 = 0.90$ ,  $SE = 176 \mu\text{mol kg}^{-1}$ ,  $P \ll 0.0001$ ,  $n = 120$ ) and  $A_T = 58S + 333$  ( $r^2 = 0.71$ ,  $SE = 116 \mu\text{mol kg}^{-1}$ ,  $P \ll 0.0001$ ,  $n = 120$ ). The distribution of  $A_T$  closely followed the dilution lines, with deviations showing increased  $A_T$  in some of the fresher, upper-ocean waters and increased  $A_T$  in salty, deeper waters. Elevated  $A_T$  in the freshest waters over the shelf indicated an additional  $A_T$  source to surface waters with respect to sea ice- and glacial ice-derived  $A_T$ . Values of  $C_T$  showed greater variability relative to the dilution lines with strong deviations showing reduced  $C_T$  due to biological carbon uptake in fresher, upper-ocean waters and increased  $C_T$  largely from respiration in saltier, deeper waters. This is further explored by consideration of  $C_T$  sal and potential alkalinity ( $A_T^*$ ), where the seasonal mixed layer is strongly influenced by  $C_T$  uptake due to organic matter production with an imprint of  $\text{CaCO}_3$  formation/dissolution (Fig. 5b). Deep waters are distinguished by elevated  $A_T$  and  $C_T$  as a result of  $\text{CaCO}_3$  dissolution and respiration/remineralization, respectively.

The seasonal deficits in  $C_T$  and  $A_T$  (AASW vs Winter Water) for offshore and shelf waters were partitioned into the key driving physical and biological processes

(Fig. 6). Shelf waters had greater and variable  $C_T$  deficits with an average  $\Delta C_T$  of  $-69 \pm 35 \mu\text{mol kg}^{-1}$  in comparison to offshore waters with an average  $\Delta C_T$  of  $-44 \pm 9 \mu\text{mol kg}^{-1}$  (Fig. 6a). The largest  $\Delta C_T$  of  $-138 \mu\text{mol kg}^{-1}$  occurred closest to the coast (Adelaide Island) in the south, which was dominated by  $\Delta C_{T \text{ org}}$  of  $-132 \mu\text{mol kg}^{-1}$  (Fig. 6c). Values of  $\Delta A_T$  varied between  $-1$  and  $-23 \mu\text{mol kg}^{-1}$  (average  $\sim -10 \mu\text{mol kg}^{-1}$ ) across the region (Fig. 6e). Freshwater inputs were greatest in the shelf region with average  $\Delta C_{T \text{ sal}}$  and  $\Delta A_{T \text{ sal}}$  values of  $-12 \pm 9$  and  $-16 \pm 11 \mu\text{mol kg}^{-1}$ , respectively (Fig. 6b & f). The most notable freshwater impacts were closest to the coast in the north (Anvers Island), driving a maximum  $\Delta C_{T \text{ sal}}$  of  $-34 \mu\text{mol kg}^{-1}$  and  $\Delta A_{T \text{ sal}}$  of  $-37 \mu\text{mol kg}^{-1}$ . This was accompanied by the highest  $\Delta A_T^*$  of  $6 \mu\text{mol kg}^{-1}$  and an associated  $\Delta C_{T \text{ CaCO}_3}$  of  $3 \mu\text{mol kg}^{-1}$  (Fig. 6d & h). The average  $\Delta C_{T \text{ org}}$  over the shelf was  $-58 \pm 42 \mu\text{mol kg}^{-1}$ , which was generally larger and more variable compared with the average  $\Delta C_{T \text{ org}}$  of  $-37 \pm 9 \mu\text{mol kg}^{-1}$  offshore. The  $\Delta A_{T \text{ org}}$  followed similar spatial trends with a maximum  $\Delta A_{T \text{ org}}$  of  $19 \mu\text{mol kg}^{-1}$  coinciding with largest  $C_T$  deficits over the shelf (Fig. 6g). The  $\Delta A_T^*$  and  $\Delta C_{T \text{ CaCO}_3}$  were  $\leq 0 \mu\text{mol kg}^{-1}$  in offshore waters and were lowest at  $-12$  and  $-6 \mu\text{mol kg}^{-1}$ , respectively, in the north.

Changes in  $\Omega_{\text{aragonite}}$  between Winter Water and the summer mixed layer ( $\Delta\Omega_{\text{aragonite}}$ ) reflected the combined effects of  $\Delta C_T$  and  $\Delta A_T$  in the offshore and shelf regions and distinct latitudinal variability (Fig. 7). The  $\Delta\Omega_{\text{aragonite}}$  ranged between 0.20 in offshore waters in the north and as much as 1.15 over the shelf in the south (Fig. 7a). Salinity changes had minor effects on  $\Delta\Omega_{\text{aragonite}}$  across the region as  $\Delta\Omega_{\text{aragonite sal}}$  was  $0.02 \pm 0.01$  (Fig. 7b), indicating that dilution effects on  $A_T$  (reduced  $\Omega_{\text{aragonite}}$ ) were counteracted by concomitant reductions in  $C_T$  (increased  $\Omega_{\text{aragonite}}$ ). A higher average  $\Delta\Omega_{\text{aragonite}}$  ( $0.54 \pm 0.31$ ) in shelf waters was driven by biological carbon uptake, with the highest  $\Delta\Omega_{\text{aragonite org}}$  of 1.39 near Adelaide Island (Fig. 7c). Offshore waters had a lower average  $\Delta\Omega_{\text{aragonite}}$  ( $0.31 \pm 0.08$ ) as a result of decreases in mixed-layer carbonate (negative  $\Delta A_T^*$ ) as  $\Delta\Omega_{\text{aragonite CaCO}_3}$  (changes in  $\Omega_{\text{aragonite}}$  due to the processes of any  $\text{CaCO}_3$  mineral) was  $-0.02$  in the north (Fig. 7d). The lowest  $\Delta\Omega_{\text{aragonite sal}}$  ( $\sim 0$ ) occurred with the greatest freshening signal in shelf waters near Anvers Island and was accompanied by the highest  $\Delta\Omega_{\text{aragonite CaCO}_3}$  (0.07). Residual changes in  $\Delta\Omega_{\text{aragonite}}$ , determined from the difference in the total seasonal change and other contributing factors, were on average  $-0.12 \pm 0.09$  and represented a reduction in AASW  $\Omega_{\text{aragonite}}$  relative to Winter Water  $\Omega_{\text{aragonite}}$ . Changes in  $\Omega_{\text{calcite}}$  ( $\Delta\Omega_{\text{calcite}}$ ; not shown) exhibited the same spatial variations as  $\Delta\Omega_{\text{aragonite}}$  with a range of 0.32–1.83 and an average  $\Delta\Omega_{\text{calcite}}$  in the shelf (offshore) region of  $0.86 \pm 0.50$  ( $0.50 \pm 0.13$ ).



## Discussion

### *Meltwater influence on carbonate mineral saturation*

The seasonal changes in carbonate mineral saturation in the upper ocean reflected the spatial variability in  $C_T$  and  $A_T$  that created distinct gradients in  $\Omega_{\text{aragonite}}$  across the shelf from offshore and latitudinally along the WAP. The highest  $\Omega_{\text{aragonite}}$  in fresher surface waters close to the coast (Fig. 1) was accompanied by large salinity-driven seasonal deficits in  $A_T$  and  $C_T$  as a result of freshwater dilution of  $A_T$  and  $C_T$  over the shelf. The WAP shelf is influenced by numerous marine-terminating glaciers and is located in the seasonal sea-ice zone whereby glacial meltwater, snow and melting sea ice seasonally supply the continental shelf with freshwater (Meredith *et al.* 2013). The impacts of freshwater on  $A_T$  and  $C_T$  are revealed from the close relationships of both with salinity (Fig. 5). The variability of  $A_T$  was largely controlled by changes in salinity as driven by meltwater inputs (freshwater endmember) and mixing with uCDW (saline endmember). Deviations from theoretical mixing lines were most pronounced towards the two endmembers, where processes of photosynthesis/respiration and  $\text{CaCO}_3$  precipitation/dissolution were shown to play important roles in controlling  $A_T$ . The shelf region experienced a greater influence of freshwater as indicated by salinity-driven reductions in  $C_T$  and particularly  $A_T$  ( $\Delta C_{T \text{ sal shelf}} = -12 \pm 9 \mu\text{mol kg}^{-1}$ ;  $\Delta A_{T \text{ sal shelf}} = -16 \pm 11 \mu\text{mol kg}^{-1}$ ; Fig. 6) that exceeded those in offshore waters ( $\Delta C_{T \text{ sal offshore}}$  and  $\Delta A_{T \text{ sal offshore}} \approx -10 \mu\text{mol kg}^{-1}$ ). Mixing of seawater with sea-ice or glacial meltwater leads to a dilution of carbonate ions, with the potential to drive a decrease in  $\Omega_{\text{aragonite}}$  due to the lower  $A_T$  and  $C_T$  signatures in the fresh meltwater compared with seawater (Legge *et al.* 2017). However, surface waters were oversaturated with respect to aragonite, whereby reductions in surface-layer salinity actually contributed to an increased mixed-layer  $\Omega_{\text{aragonite}}$  of  $0.02 \pm 0.01$  (Fig. 7). These salinity-driven changes revealed the effects of combined  $A_T$  and  $C_T$  variability on  $\Omega_{\text{aragonite}}$  as the dilution and reduction of  $A_T$  (reducing  $\Omega_{\text{aragonite}}$ ) were counteracted by the parallel dilution and reduction of  $C_T$  (increasing  $\Omega_{\text{aragonite}}$ ). The seasonal meltwater release contributed to net increases in  $\Omega_{\text{aragonite}}$  to create spatial gradients in surface water calcium carbonate saturation during summer, which supports previous findings along the WAP (Hauri *et al.* 2015, Jones *et al.* 2017, Legge *et al.* 2017) and in the Southern Ocean region to the north-east of the WAP (e.g. Jones *et al.* 2011, Tynan *et al.* 2016).

### *Biological production drives carbonate mineral supersaturation*

Reductions in salinity-normalized  $C_T$  and  $\text{NO}_3$  occurred along the meltwater-influenced shelf, particularly in the

vicinity of Anvers Island and Adelaide Island (Fig. 1), indicating the stronger influence of biological carbon uptake and the production of organic matter in the nearshore region. Biological carbon uptake of up to  $132 \mu\text{mol kg}^{-1}$  dominated the seasonal changes in  $\Omega_{\text{aragonite}}$  (at least 93% of  $\Delta\Omega_{\text{aragonite}}$ ; Fig. 7) to counteract any meltwater-induced suppression of carbonate mineral saturation states ( $\Delta\Omega_{\text{aragonite bio}} > \Delta\Omega_{\text{aragonite sal}}$ ). Large phytoplankton blooms are known to occur along the WAP shelf during spring and summer (Vernet *et al.* 2008, Schofield *et al.* 2017), where enhanced productivity characterizes the coastal regions such as near Anvers Island and Adelaide Island (Clarke *et al.* 2008, Trimborn *et al.* 2015). The highest chlorophyll *a* concentrations of up to  $30 \mu\text{g l}^{-1}$  and elevated rates of primary production of  $98\text{--}183 \text{ mg C m}^{-3} \text{ day}^{-1}$  were found in diatom-dominated blooms that occurred in summer 2011 in the south near Adelaide Island (Trimborn *et al.* 2015). The enhanced nearshore phytoplankton production resulted in biologically driven decreases in  $C_T$  with  $\Delta C_{T \text{ org}} = -58 \pm 42 \mu\text{mol kg}^{-1}$  and associated increases in  $\Delta A_{T \text{ org}}$  (Fig. 6) and increased  $\Omega_{\text{aragonite}}$  by 1.39 (Fig. 7) despite the influence of freshwater along the shelf. These processes created substantial summertime sinks for atmospheric  $\text{CO}_2$  of  $> 40 \text{ mmol m}^{-2} \text{ day}^{-1}$  (Tortell *et al.* 2015). The shelf and coastal phytoplankton communities typically consist mainly of large diatoms, which was the case in summer 2011 as diatoms were dominant ( $> 70\%$ ) and accounted for most of the phytoplankton biomass and primary production (Trimborn *et al.* 2015). Enhanced productivity in this region is associated with glacial, sea-ice and snowmelt plumes that increase water column stratification, create favourable light conditions and supply nutrients to the surface layer (Vernet *et al.* 2008). As such, the combined effect of meltwater release and biological carbon uptake during the seasonal sea-ice melt period generated gradients in  $\Omega_{\text{aragonite}}$  in the AASW across the shelf from offshore (Fig. 1). These findings support previous observations of high  $\text{CaCO}_3$  saturation states in productive shelf and coastal waters during summer along the WAP (Hauri *et al.* 2015, Jones *et al.* 2017, Legge *et al.* 2017) and downstream of islands in the Southern Ocean (Tynan *et al.* 2016).

The distribution of  $\Delta\Omega_{\text{aragonite org}}$  for the shelf region (average  $\Delta\Omega_{\text{aragonite org}}$  on the shelf was  $0.62 \pm 0.44$ ) showed latitudinal variability ranging from  $0.42 \pm 0.22$  in the north to  $1.00 \pm 0.54$  in the south (Fig. 7). This reflects a temporal signal of summertime phytoplankton production with an earlier onset of blooms in the north, following increasing light levels at the lower latitude, compared to the south. This probably accounts for the wide range of  $\text{NO}_3$  concentrations that occurred in AASW ( $8.1\text{--}26.8 \mu\text{mol kg}^{-1}$ ; Fig. 3) in shelf waters, as the lowest concentrations in the south capture the more recent signal of biological drawdown *vs* the influence of

resupply from recycling and mixing with subsurface waters in the north (Henley *et al.* 2018). Nutrient concentrations were replete across the region between Anvers Island and Adelaide Island and showed that they were not limiting to primary production, as reported previously (Henley *et al.* 2018). Our observations do not preclude limiting conditions later in the austral growing season as the latter has not finished by the end of January.

The statistically significant correlation between inorganic carbon and nutrients in the seasonal mixed layer indicated that drawdown during primary production was a key process controlling concentrations during summer (Fig. 4). The observed C/N ratios of  $11.8 \pm 0.7$  and  $10.6 \pm 0.6$  for offshore and shelf waters, respectively, were higher than the Redfield ratios, probably due to the effect of air-sea CO<sub>2</sub> uptake and subsequent influx of C<sub>T</sub> in surface waters from strong summertime CO<sub>2</sub> sinks (Hauri *et al.* 2015, Tortell *et al.* 2015). The cycling of NO<sub>3</sub> and PO<sub>4</sub> was closely coupled with the lowest macronutrient concentrations over the shelf associated with a biologically driven high  $\Omega_{\text{aragonite}}$  value of  $\sim 2.3$  (Fig. 1). The observed N/P ratios of  $12.9 \pm 0.2$  for offshore waters and  $13.8 \pm 0.3$  for the shelf region indicate that the inorganic carbon and nutrient cycles depart from the Redfield stoichiometric value of 16 mol N (1 mol P)<sup>-1</sup> (Redfield 1958). The seasonal seawater N/P uptake ratios of  $\sim 13$ –14 probably result from the prevalence of diatoms along the WAP in summer 2011, which are known to exhibit lower N/P ratios compared with Redfield ratios and are consistent with previous findings (Clarke *et al.* 2008, Trimborn *et al.* 2015). The N/P uptake ratio values are within the range of those previously reported for the WAP region (N/P of 11.7–14.6; Hauri *et al.* 2015, Henley *et al.* 2018) and for the coastal waters of Adelaide Island (N/P of 11.1–15.3; Clarke *et al.* 2008).

Substantial decreases in concentrations of chlorophyll *a* to  $< 1 \mu\text{g l}^{-1}$  and lower rates of primary production of  $3$ – $9 \text{ mg C m}^{-3} \text{ day}^{-1}$  were observed in offshore waters (Trimborn *et al.* 2015). As for the shelf and coastal regions, diatoms were predominant in offshore waters ( $> 60\%$ ), whereas *Phaeocystis* accounted for  $\sim 20$ – $40\%$  of the biomass (Trimborn *et al.* 2015). The negative biological gradients across the WAP shelf are driven by concentrations of dissolved iron and reduced light levels from wind-driven deep mixing and the interaction between these two controlling factors (Dinniman *et al.* 2020 and references therein). The offshore phytoplankton communities during summer 2011 were exposed to lower dissolved iron concentrations compared with nearshore communities and exhibited physiological traits that indicate iron stress, perhaps coupled with light limitation in mixed layers up to 80 m deep (Trimborn *et al.* 2015). For this depth limit of offshore mixed layers, seawater N/P uptake ratios were reduced to  $9.6 \pm 0.4$

( $r^2 = 0.94$ ,  $P \ll 0.0001$ ,  $n = 48$ ) and provided a further indication of impeded nitrate assimilation induced by iron limitation during blooms of large diatoms in the Southern Ocean.

The Si/N uptake ratios that were greater than 1Si:1N are indicative of large bloom-forming Antarctic diatoms that tend to be very heavily silicified (e.g. Tréguer *et al.* 2018). The Si/N uptake ratios were much higher than expected for diatom production alone, reflecting the presence of other phytoplankton species (e.g. *Phaeocystis*) and that additional processes (e.g. terrestrial and sediment/porewater fluxes) had occurred and increased Si(OH)<sub>4</sub> relative to NO<sub>3</sub>. Lower dissolved Si(OH)<sub>4</sub> in the water column offshore is further evidence for strong biological drawdown in diatom blooms where assimilation processes exceeded Si(OH)<sub>4</sub> resupply processes, in contrast to conditions of elevated Si(OH)<sub>4</sub> in parallel to diatom-dominated production on the shelf (Fig. 3). The close coupling of C<sub>T</sub> and Si(OH)<sub>4</sub> (Fig. 4) indicates the key role of diatoms that drive intense oceanic CO<sub>2</sub> uptake in offshore and coastal areas of the WAP.

#### *Remineralization and lowering of carbonate mineral saturation in subsurface waters*

Subsurface values of C<sub>T</sub>, A<sub>T</sub>, Si(OH)<sub>4</sub> and, to a lesser extent, NO<sub>3</sub> increased across the shelf from offshore waters, which was most pronounced in the south (Fig. 2 & Table I). These features coincided with the steepest vertical gradients between productive surface waters to the underlying mCDW over the southern shelf (Fig. 3). Enhanced concentrations of macronutrients and C<sub>T</sub> in cross-shelf CDW has been previously reported for the southern WAP and attributed to organic matter remineralization and biogenic silica dissolution in the productive and diatom-dominated waters of the shelf and coastal areas (Jones *et al.* 2017, Henley *et al.* 2018). Enriched C<sub>T</sub> and low  $\Omega_{\text{aragonite}}$  distinguished the mCDW of the shelf region, resulting in a shoaling of the aragonite saturation horizon across the shelf break and aragonite undersaturation in the mCDW in the south (Fig. 2r). Compared with offshore waters, Winter Water on the shelf was generally located at greater depths, was more saline and was characterized by higher A<sub>T</sub> and Si(OH)<sub>4</sub> and generally higher C<sub>T</sub> concentrations. The elevated A<sub>T</sub>, Si(OH)<sub>4</sub> and C<sub>T</sub> of the Winter Water were indicative of mixing with underlying mCDW, where greater exchange between water masses probably takes place over the shallower shelf relative to offshore. This indicates that the upward mixing of mCDW into the seasonal mixed layer could also provide a supply of A<sub>T</sub> into the Winter Water layer. The concentrations of Si(OH)<sub>4</sub> also increased in the uCDW-mCDW layer across the shelf break (Fig. 2), indicating that upwelling and mixing of saline, A<sub>T</sub>-rich deeper waters may

contribute to this signal (higher  $A_T:C_T$  ratios). Therefore, the values of  $A_T$  in AASW and Winter Water may become decoupled from  $C_T$  concentrations (Fig. 4) through mixing of  $A_T$ -rich water into surface waters where biological  $C_T$  uptake occurs.

The relationship between salinity and  $A_T$  shows a mixing trend between  $A_T$ -rich subsurface waters and the fresher surface waters (Fig. 5), where the highest  $A_T$  at high salinities originates from the influence of  $\text{CaCO}_3$  dissolution in the deep and offshore bottom waters. Increases in potential  $A_T$  for a smaller range of  $C_T$  revealed the influence of  $\text{CaCO}_3$  dissolution in enriching  $A_T$  in subsurface waters overlying the shelf (Fig. 5b). For  $C_T$ , the mixing trend shows increasing subsurface  $C_T$  concentrations over the shelf as a result of remineralization and a contribution from  $\text{CaCO}_3$  mineral dissolution. The greater increase in subsurface  $C_T$  relative to increases in  $A_T$  with the cross-shelf modification of CDW drives lower  $A_T:C_T$  ratios and aragonite undersaturation in mCDW over the shelf (Fig. 2). Decoupling of Winter Water  $C_T$  and  $\text{NO}_3$  with more saline waters over the shelf suggests that not solely remineralization but also sea-ice processes contribute, with brine rejection transporting  $C_T$  into the underlying water column during ice formation. Increasing  $A_T$  (for a small range of  $C_T$ ) at salinities  $> 33.7$  indicated carbonate mineral dissolution in Winter Water and evidence of a sea-ice carbon pump (Rysgaard *et al.* 2007, Dieckmann *et al.* 2008) over the shelf.

The coupling of inorganic carbon and nutrients at high concentrations (Fig. 4) in mCDW is driven by remineralization of organic matter and dissolution of biogenic silica exported from the productive surface layer (Henley *et al.* 2018 and references cited therein). Remineralization enriched  $C_T$  (reduced  $A_T:C_T$  ratios) and suppressed  $\Omega_{\text{aragonite}}$  to yield a biologically induced acidification signal in subsurface water over the shelf (Fig. 2). Natural spatiotemporal variations in carbonate mineral saturation levels suggest that organisms of the WAP marine ecosystem are already exposed to low saturation states and as such may have evolved a degree of resilience to future acidification (Hauri *et al.* 2015, Legge *et al.* 2017). Enrichment of  $\text{Si(OH)}_4$  in water masses overlying the shelf (Fig. 3j) was probably due to dissolution of biogenic silica from the diatom communities that characterized the summer blooms along the WAP (Trimborn *et al.* 2015). In addition, dissolved  $\text{Si(OH)}_4$  from seafloor sediment resuspension and porewaters could contribute to elevated  $\text{Si(OH)}_4$  concentrations in bottom waters (Henley *et al.* 2018). Mechanisms for elevated  $A_T$  in subsurface waters could also result from seafloor fluxes that provide a source of  $A_T$  to the deep and bottom waters overlying the shelf. In addition, upwelling of salty,  $A_T$ -rich deep waters onto the shelf would also increase the  $A_T:C_T$  ratios in upper

shelf waters imprinted by the signal of biological  $C_T$  uptake.

Greater enhancements of the biogeochemical characteristics of mCDW in the southern shelf region relative to the north (Fig. 2) perhaps reflect 1) increases in  $C_T$ ,  $\text{NO}_3$  and  $\text{Si(OH)}_4$  as a result of temporal variability in the more recent summer production, organic matter export and subsequent remineralization, 2) greater signals of salt and  $C_T$  in rejected brine from sea-ice formation during the preceding winter and 3) contributions of  $A_T$  and  $\text{Si(OH)}_4$  from entrainment of deep waters, terrestrial minerals (e.g. dissolved minerals delivered in glacial meltwater plumes), porewater and sediment sources. As such, the passage of uCDW from the offshore waters of the ACC across the shelf break enabled enrichment of regenerated  $C_T$ , thus lowering  $A_T:C_T$  ratios and  $\Omega_{\text{aragonite}}$  in mCDW to drive a signal of biologically induced acidification over the WAP southern shelf.

#### *Buffering against acidification on the freshwater-influenced shelf*

Aragonite supersaturation ( $\Omega_{\text{aragonite}} > 1.8$ ) occurred as a result of low  $C_T$  and elevated  $A_T$  in fresher surface waters over the shelf (Fig. 1). The  $A_T$ -salinity relationship (Fig. 5a) indicated that freshwater in the region contained a minor source of  $A_T$ , the value of which agreed very well with sea-ice  $A_T$  from fast ice at Rothera Research Station, Adelaide Island (Legge *et al.* 2017). Glacial ice was found to contain very low concentrations of macronutrients,  $C_T$  and  $A_T$  in the southern WAP region (Legge *et al.* 2017). The freshwater-derived  $A_T$  would be supplied to surface seawater from sea-ice and glacial melt along the coast and, coupled with biological uptake of  $C_T$ , would act to increase the  $A_T:C_T$  ratio. Meltwater plumes have been identified as sources of dissolved iron (e.g. Dinniman *et al.* 2020) to coastal waters due to dissolution and transport of minerals from the surrounding bedrock. This geochemical meltwater enrichment is considered a main source of iron to the WAP shelf region (Dinniman *et al.* 2020 and references cited therein) and may be subsequently important for the Antarctic coastal marine environment (Trimborn *et al.* 2015). Particulate and dissolved minerals incorporated into meltwater probably enrich the plumes with  $A_T$  relative to  $C_T$ , and they also become transport mechanisms of terrestrially derived organic matter that yields  $C_T$  upon remineralization. These land-meltwater-ocean processes lead to variations in the  $A_T:C_T$  ratio in the meltwater and upper ocean (Fig. 3h) upon mixing with the plume.

Sea ice near Adelaide Island contained varying concentrations of macronutrients,  $C_T$  and  $A_T$  (Legge *et al.* 2017) that are delivered to surface waters during



the melt period, often with varying elemental stoichiometry compared with the source and surrounding seawater. Sea-ice processes play a key role in partitioning  $A_T$  and  $C_T$  differently within the ice and underlying water (Rysgaard *et al.* 2007, Dieckmann *et al.* 2008), and the variations in the  $A_T:C_T$  ratios exert geochemical control on  $\Omega_{\text{aragonite}}$  in the winter and summer mixed layers in the seasonally ice-covered regions. During sea-ice formation,  $\text{CO}_2$ -rich brines are rejected, reducing the  $A_T:C_T$  ratio in the underlying Winter Water. Upon sea-ice melt, any ikaite minerals that were formed are released and, upon dissolution, provide a source of  $A_T$  in the meltwater and increase the  $A_T:C_T$  ratio in the surrounding surface seawater during spring and summer (Rysgaard *et al.* 2007, Dieckmann *et al.* 2008). Dissolution of ikaite during sea-ice melt has also been suggested as a mechanism contributing to  $A_T$  variability in summer surface waters in Southern Ocean regions north of the WAP (Jones *et al.* 2011, Tynan *et al.* 2016).

As for biogeochemical modifications to uCDW, strong cross-shelf gradients relative to offshore in terms of  $A_T$  in AASW and Winter Water were observed as a result of mixing of low- $A_T$  meltwater and  $A_T$ -rich deep water (Fig. 2). The AASW with salinity of  $\sim 33.8$  found offshore is characteristic of ACC water and is accompanied by an  $A_{T \text{ sal}}$  value of  $\sim 2345 \mu\text{mol kg}^{-1}$ , which was typically compared to shelf waters (Fig. 3). Cross-shelf increases in AASW salinity, indicative of upwelling and mixing with subsurface mCDW, was evident in the vicinity of the shelf break and coincided with a higher  $A_{T \text{ sal}}$  value of  $\sim 2355 \mu\text{mol kg}^{-1}$  (Fig. 2). Exceptions were an elevated  $A_{T \text{ sal}}$  value of  $\sim 2370 \mu\text{mol kg}^{-1}$  in meltwater-influenced surface waters that became superimposed onto the upwelling signal at coastal locations (Fig. 1). The values of  $A_{T \text{ sal}}$  increased by up to  $40 \mu\text{mol kg}^{-1}$  in AASW overlying the shelf where the impact of meltwater was largest and dominated the seasonal change in  $A_T$  ( $\Delta A_T$ ; Fig. 6f) near Anvers Island and Adelaide Island. Variations in  $A_{T \text{ sal}}$  can be attributed to carbonate mineral processes in sea ice, terrestrially derived minerals in glacial meltwater plumes and runoff, benthic fluxes and a minor source during photosynthesis. Evaluating potential alkalinity ( $A_T^* = A_T + \text{NO}_3$ ; Goldman & Brewer 1980) allows the changes in  $A_T$  due to nitrate assimilation and inorganic nitrogen release to be accounted for, and remaining variations in  $A_T^*$  are due to carbonate mineral formation/dissolution (e.g. Jones *et al.* 2017). Elevated  $A_T^*$  (up to  $10 \mu\text{mol kg}^{-1}$ ; Fig. 5b) and increases in the  $A_T:C_T$  ratio in the coastal AASW (Fig. 3h) are consistent with a freshwater  $A_T$  source (e.g. terrestrially derived dissolved minerals in glacial meltwater, snowmelt and/or carbonate mineral dissolution in sea-ice meltwater).

Trends in  $A_T^*$  and salinity-normalized  $C_T$  (Fig. 5b) further indicated the role of carbonate mineral processes in controlling  $A_T$  in different water masses along the WAP. The shelf waters were biogeochemically distinct compared with offshore waters as a result of the greater contribution from calcium carbonate dissolution. This was reflected in the seasonal changes in calcium carbonate saturation states, with maximum increases in  $\Omega_{\text{aragonite}}$  from  $\text{CaCO}_3$  dissolution in the meltwater-influenced surface layers relative to Winter Water values (Fig. 7c). As the salinity normalization was carried out by considering the  $C_T$  and  $A_T$  signature of sea ice, the estimated increases in  $A_{T \text{ sal}}$  indicated that the contribution of  $A_T$  from the ice via the sea-ice carbon pump is probably variable within the ice and also varies with location (i.e. greater contributions over the southern shelf) and/or with contributions of  $A_T$  from terrestrial or benthic origin, as indicated previously by nutrient fluxes in the region (Henley *et al.* 2018). These processes make a small contribution to the seasonal changes in  $C_T$  (Fig. 6d). While surface water  $C_{T \text{ sal}}$  on the shelf was more depleted (higher  $A_T:C_T$  ratio) than in offshore waters (Fig. 1b), the  $A_{T \text{ sal}}$  in shelf waters (Fig. 1c) was elevated (higher  $A_T:C_T$  ratio). Both  $\text{CO}_2$  drawdown during photosynthesis and the release of excess  $A_T$  increase the geochemical buffering capacity of seawater and drive calcium carbonate supersaturation ( $\Omega_{\text{aragonite}} > 2.1$ ;  $\Omega_{\text{calcite}} > 3.1$ ) in the relatively fresh surface waters on the shelf (Fig. 1). These processes that counteracted any meltwater suppression of saturation states and increased  $\Omega_{\text{aragonite}}$  during the summer are consistent with other summer observations in coastal Antarctic waters (Jones *et al.* 2017, Legge *et al.* 2017).

Remote from freshwater influences, the lowest  $\Omega_{\text{aragonite}}$  of  $\sim 1.5$  occurred in AASW offshore north of  $64^\circ\text{S}$  (Fig. 1g). Concurrent high  $C_T$  ( $> 2140 \mu\text{mol kg}^{-1}$ ), salinity ( $> 33.7$ ) and temperature ( $> 1^\circ\text{C}$ ) indicated upwelling of uCDW in the region, with subsequent reduction of the  $A_T:C_T$  ratio and lowering of  $\Omega_{\text{aragonite}}$  (Fig. 3). Weaker signals of biological  $C_T$  uptake relative to coastal and southern waters and the absence of 'excess'  $A_T$  in offshore surface waters would result in comparatively low surface water  $\Omega_{\text{aragonite}}$ . Seasonal differences in  $A_T^*$  revealed an overall loss of  $A_T$  of up to  $10 \mu\text{mol kg}^{-1}$  (this being concomitant with decreases in  $C_T$ ) in surface waters relative to the Winter Water. This indicates either the formation of carbonate minerals or another mechanism removing (adding)  $A_T$  from surface waters (Winter Water) by late summer. Playing a role here may be the aragonitic pteropods, which are prevalent along the WAP and are frequently observed at elevated abundances offshore in the study region (Thibodeau *et al.* 2019). Pteropods remove  $A_T$  in the upper water column through the formation of aragonite

shells and release carbonate ions upon sinking and dissolution of the shells in deeper waters (Bednaršek *et al.* 2012). The 2:1 trend in  $A_T$  and  $C_T$  between Winter Water and AASW in the offshore region (Fig. 5b) could be due to the formation of calcium carbonate shells in the upper ocean and/or the supply of carbonates to the Winter Water from upwelling uCDW (with elevated carbonate from the dissolution of exported carbonate shells).

### Conclusions and future outlook

This study gives insight into the spatial variability in calcium carbonate saturation states along the WAP, specifically the patterns in different water masses from offshore and across the continental shelf. Biological production in diatom-dominated blooms generated high  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  with respect to the biotic minerals calcite and aragonite, respectively, along the WAP shelf in summer. Glacial meltwater and melting sea ice stratified the water column and facilitated the formation of phytoplankton blooms, accompanied by elevated  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  in surface waters close to the coast. The presence of excess  $A_T$  in the summer mixed layer indicates that dissolution of abiotic  $\text{CaCO}_3$  (ikaite) from sea ice and/or terrestrially derived minerals in glacial meltwater has contributed to the surface water variability in  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  during the seasonal thaw. The low  $A_T$  and  $C_T$  content of the meltwater dilutes the concentration of carbonate ions, thus tending to lower seawater  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  and inducing a freshwater-driven acidification signal. However, additional dissolved constituents that contribute  $A_T$  relative to  $C_T$  slightly counteract the dilution effects by enhancing the  $A_T:C_T$  ratios in the meltwater-influenced seawater. Thus, any meltwater-driven carbonate ion dilution (tending to decrease  $A_T$  and the seawater buffering capacity) was largely compensated by biologically driven  $C_T$  uptake and excess  $A_T$  from dissolved minerals resulting in increases in  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$ . These geochemical processes act as minor buffers against acidification and play a key role alongside the biological carbon uptake that drives increases in  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  in coastal waters around Antarctica. Remineralization of organic matter and export of  $\text{CO}_2$ -rich brines from forming winter sea ice drive low  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  in Winter Water and mCDW over the WAP shelf. A strong biological carbon pump in shelf waters and the coastal zone created surface water carbonate mineral supersaturation and biologically induced suppression of calcium carbonate saturation states in subsurface CDW. Mixing of water masses in the upper ocean suppresses surface water  $\Omega_{\text{aragonite}}$  and may enhance the vulnerability of the surface layer to acidification upon

further uptake of  $\text{CO}_2$  and freshwater discharge. Given the increased and southwards shift in the upwelling of CDW, changes in sea-ice cover and oceanographic conditions in response to the El Niño Southern Oscillation and Southern Annular Mode, the WAP marine system will be even more vulnerable in the future.

Enhanced  $\text{CO}_2$  drawdown in shelf waters may occur by 1) increased meltwater cooling of the surface layer that strengthens the solubility carbon pump, 2) releasing iron-rich terrigenous material in meltwater plumes to stimulate the biological carbon pump and 3) extended ice-free periods, enhanced water column stratification and favourable light environments that enhance the biological carbon pump. These processes have augmented the uptake of atmospheric  $\text{CO}_2$  and supply of inorganic carbon to surface waters along the WAP in recent decades. However, the future outlook is uncertain as a result of the large variability and shifts in phytoplankton species and primary production, ice-ocean dynamics and freshwater fluxes and biogeochemical cycling, with consequences for the biologically driven and meltwater-driven changes in  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  in the upper ocean. Our findings highlight the impact of high phytoplankton productivity, meltwater-derived mineral inputs and mixing of freshwater and CDW that regulate the spatial variability of calcium carbonate saturation states in the dynamic environment of the WAP. As such, the coastal zones of Antarctica are key regions for studying the response of marine ecosystems to impacts of ocean acidification. Spatiotemporal studies are therefore essential to elucidate the controls on calcium carbonate saturation states and to unravel the natural variability and long-term trends in order to better understand the impacts of future ocean acidification on marine ecosystems in the climatically vulnerable Antarctic coastal waters.

### Acknowledgements

The authors gratefully acknowledge the Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research for the opportunity to conduct fieldwork on board FS *Polarstern*. We acknowledge the leadership of the late E. Fahrback (AWI) as chief scientist. Extended thanks to G. Rohardt at AWI and P. Laan, L. Salt and S. van Heuven at Royal NIOZ for scientific and logistical support. We thank Dr Matthew Humphreys and an anonymous reviewer for their thorough and insightful comments, which have greatly improved the quality of the manuscript.

### Financial support

This work was part of postdoctoral research (E.M. Jones) at the Royal NIOZ supported through EU project CARBOCHANGE 'Changes in carbon uptake and

emissions by oceans in a changing climate', which received funding from the European Community's Seventh Framework Programme under grant agreement no. 264879.

### Author contributions

HJWdB and MH contributed to the conception and design of the study. EMJ, MH and KB contributed to the acquisition, analysis and interpretation of data. All authors drafted and/or revised the manuscript and approved the submitted version for publication.

### Details of data deposit

All hydrographical data are publicly available in the Pangaea database (<https://doi.org/10.1594/PANGAEA.772244>).

### References

- ARRIGO, K.R., VAN DIJKEN, G. & LONG, M. 2008. Coastal Southern Ocean: a strong anthropogenic CO<sub>2</sub> sink. *Geophysical Research Letters*, **35**, 10.1029/2008gl035624.
- BEDNARŠEK, N., TARLING, G., BAKKER, D., FIELDING, S., JONES, E.M., VENABLES, H.J., *et al.* 2012. Extensive dissolution of live pteropods in the Southern Ocean. *Nature Geoscience*, **5**, 10.1038/ngeo1635.
- BROECKER, W.S. & PENG, T.H. 1982. *Tracers in the sea*. Palisades, NY: Eldigio Press.
- BROWN, M.S., MUNRO, D.R., FEEHAN, C.J., SWEENEY, C., DUCKLOW, H.W. & SCHOFIELD, O.M. 2019. Enhanced oceanic CO<sub>2</sub> uptake along the rapidly changing West Antarctic Peninsula. *Nature Climate Change*, **9**, 10.1038/s41558-019-0552-3.
- CLARKE, A., MEREDITH, M.P., WALLACE, M.I., BRANDON, M.A. & THOMAS, D.N. 2008. Seasonal and interannual variability in temperature, chlorophyll and macronutrients in northern Marguerite Bay, Antarctica. *Deep-Sea Research II*, **55**, 10.1016/j.dsr2.2008.04.035.
- DICKSON, A.G. 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Research A*, **28**, 10.1016/0198-0149(81)90121-7.
- DICKSON, A.G. & MILLERO, F.J. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research A*, **34**, 10.1016/0198-0149(87)90021-5.
- DICKSON, A.G., SABINE, C. & CHRISTIAN, J.R. 2007. Guide to best practices for ocean CO<sub>2</sub> measurements. *PICES Special Publication*, No. 3, 1–191.
- DIECKMANN, G.S., NEHRKE, G., PAPADIMITRIOU, S., GÖTTLICHER, J., STEININGER, R., KENNEDY, H., *et al.* 2008. Calcium carbonate as ikaite crystals in Antarctic sea ice. *Geophysical Research Letters*, **35**, 10.1029/2008GL033540.
- DINNIMAN, M.S., ST-LAURENT, P., ARRIGO, K.R., HOFMANN, E.E. & VAN DIJKEN, G.L. 2020. Analysis of iron sources in Antarctic continental shelf waters. *Journal of Geophysical Research - Oceans*, **125**, e2019JC015736.
- DUCKLOW, H.W., FRASER, W., MEREDITH, M., STAMMERJOHN, S., DONEY, S., MARTINSON, D., *et al.* 2013. West Antarctic Peninsula: an ice-dependent coastal marine ecosystem in transition. *Oceanography*, **26**, 10.5670/oceanog.2013.62.
- FEELEY, R.A., SABINE, C.L., LEE, K., BERELSON, W., KLEYPAS, J., FABRY, V.J. & MILLERO, F.J. 2004. Impact of Anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> system in the oceans. *Science*, **305**, 10.1126/science.1097329.
- FRIIS, K., KÖRTZINGER, A. & WALLACE, D.W.R. 2003. The salinity normalization of marine inorganic carbon chemistry data. *Geophysical Research Letters*, **30**, 10.1029/2002GL015898.
- GOLDMAN, J. & BREWER, P. 1980. Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity. *Limnology and Oceanography*, **25**, 10.4319/l0.1980.25.2.0352.
- HALL, A. & VISBECK, M. 2002. Synchronous variability in the Southern Hemisphere atmosphere, sea ice, and ocean resulting from the Annular Mode. *Journal of Climate*, **15**, 10.1175/1520-0442(2002)015<3043:SVITSH>2.0.CO;2.
- HAURI, C., DONEY, S.C., TAKAHASHI, T., ERICKSON, M., JIANG, G. & DUCKLOW, H.W. 2015. Two decades of inorganic carbon dynamics along the West Antarctic Peninsula. *Biogeosciences*, **12**, 10.5194/bg-12-6761-2015.
- HENLEY, S.F., JONES, E.M., VENABLES, H.J., MEREDITH, M.P., FIRING, Y.L., DITTRICH, R., *et al.* 2018. Macronutrient and carbon supply, uptake and cycling across the Antarctic Peninsula shelf during summer. *Philosophical Transactions of the Royal Society*, **376**, 10.1098/rsta.2017.0168.
- HOPPEMA, M. & GOEYENS, L. 1999. Redfield behaviour of carbon, nitrogen and phosphorus depletions in Antarctic surface water. *Limnology and Oceanography*, **44**, 10.4319/l0.1999.44.1.0220.
- JONES, E.M., BAKKER, D.C.E., VENABLES, H.J., WHITEHOUSE, M.J., KORB, R.E. & WATSON, A.J. 2011. Rapid changes in surface water carbonate chemistry during Antarctic sea ice melt. *Tellus B*, **62**, 10.1111/j.1600-0889.2010.00496.x.
- JONES, E.M., FENTON, M., MEREDITH, M.P., CLARGO, N.M., OSSEBAAR, S., DUCKLOW, H.W., *et al.* 2017. Ocean acidification and calcium carbonate saturation states in the coastal zone of the West Antarctic Peninsula. *Deep-Sea Research II*, **139**, 10.1016/j.dsr2.2017.01.007.
- KERR, R., MATA, M.M., MENDES, C.R.B. & SECCHI, E.R. 2018. Northern Antarctic Peninsula: a marine climate hotspot of rapid changes on ecosystems and ocean dynamics. *Deep-Sea Research II*, **149**, 4–9.
- LEGGE, O.J., BAKKER, D.C.E., MEREDITH, M.P., VENABLES, H.J., BROWN, P.J., JONES, E.M. & JOHNSON, M.T. 2017. The seasonal cycle of carbonate system processes in Ryder Bay, West Antarctic Peninsula. *Deep-Sea Research II*, **139**, 167–180.
- MARTINSON, D.G., STAMMERJOHN, S.E., IANNUZZI, R.A., SMITH, R.C. & VERNET, M. 2008. Western Antarctic Peninsula physical oceanography and spatio-temporal variability. *Deep-Sea Research II*, **55**, 10.1016/j.dsr2.2008.04.038.
- MEHRBACH, C., CULBERSON, C.H., HAWLEY, J.E. & PYTKOWICZ, R.M. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, **18**, 897–907.
- MEREDITH, M.P., VENABLES, H.J., CLARKE, A., DUCKLOW, H.W., ERICKSON, M., LENG, M.J., *et al.* 2013. The freshwater system west of the Antarctic Peninsula: spatial and temporal changes. *Journal of Climate*, **26**, 10.1175/JCLI-D-25 12-00246.1.
- MOJICA PRIETO, F.J. & MILLERO, F.J. 2002. The values of pK<sub>1</sub> + pK<sub>2</sub> for the dissociation of carbonic acid in seawater. *Geochimica et Cosmochimica Acta*, **66**, 10.1016/S0016-7037(02)00855-4.
- OLSEN, A., LANGE, N., KEY, R.M., TANHUA, T., ÁLVAREZ, M., BECKER, S., *et al.* 2019. GLODAPv2.2019 - an update of GLODAPv2. *Earth System Science Data*, **11**, 10.5194/essd-11-1437-2019.
- ORR, J.C., FABRY, V.J., AUMONT, O., BOPP, L., DONEY, S.C., FEELY, R.A., *et al.* 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, **437**, 10.1038/nature04095.
- REDFIELD, A. 1958. The biological control of chemical factors in the environment. *American Scientist*, **3**, 205–221.
- RYSGAARD, S., GLUD, R.N., SEJR, M.K., BENDTSEN, J. & CHRISTENSEN, P.B. 2007. Inorganic carbon transport during sea ice growth and decay: a carbon pump in polar seas. *Journal of Geophysical Research*, **112**, 10.1029/2006JC003572.



- SARMIENTO, J.L. & GRUBER, N. 2006. *Ocean biogeochemical dynamics*. Princeton, NJ: Princeton University Press.
- SCHOFIELD, O., SABA, G., COLEMAN, K., CARVALHO, F., COUTO, N., DUCKLOW, H., *et al.* 2017. Decadal variability in coastal phytoplankton community composition in a changing West Antarctic Peninsula. *Deep-Sea Research I*, **124**, 42–54.
- SMITH, D.A., HOFMANN, E.E., KLINCK, J.M. & LASCARA, C.M. 1999. Hydrography and circulation of the West Antarctic Peninsula continental shelf. *Deep-Sea Research I*, **46**, 10.1016/S0967-0637(98)00103-4.
- STAMMERJOHN, S.E., MARTINSON, D.G., SMITH, R.C., YUAN, X. & RIND, D. 2008. Trends in Antarctic annual sea ice retreat and advance and their relation to El Niño-Southern Oscillation and Southern Annular Mode variability. *Journal of Geophysical Research*, **113**, 10.1029/2007JC004269.
- THIBODEAU, P.S., STEINBERG, D.K., STAMMERJOHN, S.E. & HAURI, C. 2019. Environmental controls on pteropod biogeography along the Western Antarctic Peninsula. *Limnology and Oceanography*, **64**, 10.1002/lno.11041.
- TORTELL, P.D., BITTIG, H.C., KÖRTZINGER, A., JONES, E.M. & HOPPEMA, M. 2015. Biological and physical controls on N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> distributions in contrasting Southern Ocean surface waters. *Global Biogeochemical Cycles*, **29**, 10.1002/2014GB004975.
- TRÉGUER, P., BOWLER, C., MORICEAU, B., DUTKIEWICZ, S., GEHLEN, M., AUMONT, O., *et al.* 2018. Influence of diatom diversity on the ocean biological carbon pump. *Nature Geoscience*, **11**, 27–37.
- TRIMBORN, S., HOPPE, C.J., TAYLOR, B.B., BRACHER, A. & HASSLER, C. 2015. Physiological characteristics of open ocean and coastal phytoplankton communities of Western Antarctic Peninsula and Drake Passage waters. *Deep-Sea Research I*, **98**, 115–124.
- TYNAN, E., CLARKE, J.S., HUMPHREYS, M.P., RIBAS-RIBAS, M., ESPOSITO, M., RÉROLLE, V.M.C., *et al.* 2016. Physical and biogeochemical controls on the variability in surface pH and calcium carbonate saturation states in the Atlantic sectors of the Arctic and Southern Oceans. *Deep-Sea Research II*, **127**, 10.1016/j.dsr2.2016.01.001.
- VAN HEUVEN, S., PIERROT, D., RAE, J., LEWIS, E. & WALLACE, D. 2011. *MATLAB program developed for CO<sub>2</sub> system calculations. ORNL/CDIAC-105b*. Oak Ridge, TN: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, 10.3334/CDIAC/otg.CO2SYS.
- VAUGHAN, D.G., MARSHALL, G.J., CONNOLLEY, W.M., PARKINSON, C., MULVANEY, R., HODGSON, D.A., *et al.* 2003. Recent rapid regional climate warming on the Antarctic Peninsula. *Climatic Change*, **60**, 10.1023/A:1026021217991.
- VENABLES, H.J., CLARKE, A. & MEREDITH, M.P. 2013. Wintertime controls on summer stratification and productivity at the Western Antarctic Peninsula. *Limnology and Oceanography*, **58**, 10.4319/lo.2013.58.3.1035.
- VERNET, M., MARTINSON, D., IANNUZZI, R., STAMMERJOHN, S., KOZLOWSKI, W., SINES, K., *et al.* 2008. Primary production within the sea-ice zone west of the Antarctic Peninsula: sea ice, summer mixed layer, and irradiance. *Deep-Sea Research II*, **55**, 10.1016/j.dsr2.2008.05.021.
- WOLF-GLADROW, D.A., ZEEBE, R.E., KLAAS, C., KÖRTZINGER, A. & DICKSON, A.G. 2007. Total alkalinity: the explicit conservative expression and its application to biogeochemical processes. *Marine Chemistry*, **106**, 10.1016/j.marchem.2007.01.006.