Calcium carbonate saturation states along the West Antarctic Peninsula

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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 (CT), total alkalinity (AT) and nutrients revealed key physical, biological and biogeochemical controls of the calcium carbonate saturation state (Ωaragonite) in different water masses across the WAP shelf during the summer. Biological production in spring and summer dominated changes in surface water Ωaragonite (ΔΩaragonite up to +1.39; ~90%) relative to underlying Winter Water. Sea-ice and glacial meltwater constituted a minor source of AT that increased surface water Ωaragonite (ΔΩaragonite up to +0.07; ~13%). Remineralization of organic matter and an influx of carbon-rich brines led to cross-shelf decreases in Ωaragonite in Winter Water and Circumpolar Deep Water. A strong biological carbon pump over the shelf created Ωaragonite oversaturation in surface waters and suppression of Ωaragonite in subsurface waters. Undersaturation of aragonite occurred at <~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.

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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 overlaying 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 (CO2) 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
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 CO$_2$ along the WAP shelf (Hauri et al. 2015, Tortell et al. 2015, Kerr et al. 2018).
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 CO₂ 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 (CaCO₃·6H₂O) (Rysgaard et al. 2007, Dieckmann et al. 2008). These processes lead to shifts in dissolved inorganic carbon (CT; Eq. (1)) and total alkalinity (AT; Eq. (2)):

\[
CT = [H_2CO_3^+] + [HCO_3^-] + [CO_3^{2-}]
\] (1)

\[
AT = [H_2CO_3^+] + [HCO_3^-] + [CO_3^{2-}]
\] (2)
\[ A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \]

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 \(\sim76\%\) and \(\sim19\%\), respectively (when \(pH \approx 8.1\)), 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 \(\sim280\) to \(\sim410\) ppm in 1991 (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 \(\sim0.02\) 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. \(pH < 8.1\)–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:

\[ \Omega_{\text{aragonite}} = ([\text{Ca}^{2+}]_{\text{sw}} \times [\text{CO}_3^{2-}]_{\text{sw}})/K_{\text{SP aragonite}}^{*} \]
product of aragonite as a function of salinity, temperature and pressure (Broecker & Peng 1982, Sarmiento & Gruber 2006). The biotic CaCO₃ minerals aragonite and calcite and the abiotic CaCO₃ 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 CT 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 CaCO₃ 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, Bednarsk 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 CO₂ 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-XVII/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 region (2350 μmol A_T kg^{-1} and 2253 μmol C_T kg^{-1}; Hauri et al. 2015) and coastal waters on Adelaide Island (~2340 μmol A_T kg^{-1} and ~2260 μmol C_T 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 ± 4 μmol kg^{-1}; A_T = 2365 ± 7 μmol 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 ± 3 μmol kg^{-1}; A_T = 2366 ± 9 μmol kg^{-1}), as reported in Hauri et al. (2015).

The Ω_{aragonite} (Eq. (3)) and Ω_{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)):

\[ K_1 = [H^+][HCO_3^-]/[H_2CO_3] \]  

and

\[ K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \]

These constants were determined for 19 ≤ S ≤ 43 and 2°C ≤ T ≤ 35°C and have been used in previous studies in the Southern Ocean and WAP regions where temperatures are frequently < 0°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 Ω_{aragonite} and Ω_{calcite} are used as indicators for changes in carbonate chemistry in relation to calcium carbonate saturation states and potential ocean acidification. When Ω_{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 Ω_{calcite} remained positive (seawater was oversaturated with respect to calcite) in the upper ~2000 m
of the water column. Therefore, this study is focused on Ω_{aragonite} and its changes (ΔΩ_{aragonite}) with respect to acidification in the contemporary and future marine environment along the WAP. The corresponding values for calcite (Ω_{calcite}) and its changes (ΔΩ_{calcite}) are included as references.

**Inorganic nutrients**

For inorganic macronutrients silicic acid (Si(OH)₄, commonly referred to as silicate), phosphate (PO₄), nitrate + nitrite (NO₃ + NO₂) and nitrite (NO₂), 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(OH)₄, PO₄ and NO₃ 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) for international consistency. The reported NO₃ may in some samples comprise a very small amount of NO₂ that is not distinguished and thus is incorporated into 'NO₃' when described in the text. The precision values (expressed as the coefficient of variation) for Si(OH)₄, PO₄ and NO₃ 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 (ΔC_T) and A_T (ΔA_T) results from the influences of the main physical and biological processes, such as salinity changes (ΔC_T_{sal}, ΔA_T_{sal}) from freshwater inputs and mixing of different water masses, photosynthesis and respiration (ΔC_T_{org}, ΔA_T_{org}) and the formation and dissolution of biotic (aragonite, calcite) and abiotic (ikaite) calcium carbonate (ΔC_T_{CaCO3}, ΔA_T^{*}).

\[
\Delta C_T = \Delta C_T_{sal} + \Delta C_T_{org} + \Delta C_T_{CaCO3}
\]  

(6)
\[ \Delta A_T = \Delta A_{T\text{ sal}} + \Delta A_{T\text{ org}} + \Delta A_T^* \tag{7} \]

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; \( S_{ref} \)) 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 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 \( \Delta A_T \) org is therefore estimated from \( \Delta C_T\text{ org} \) by applying 0.15 \, \mu\text{mol kg}^{-1} per 1 \, \mu\text{mol kg}^{-1} \( C_T \) 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 \( C_T \) (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} \( C_T \text{ org} \)). 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 \( \Delta A_T\text{ org} \) 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 AT kg}^{-1} per 1 \, \mu\text{mol CT 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 \( \Delta A_T\text{ CaCO}_3 \) ratio by 0.1 (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 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} 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 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 \( \Omega_{\text{aragonite sal}} \) and \( \Omega_{\text{aragonite org}} \) and \( \Omega_{\text{aragonite CaCO}_3} \)) alongside in situ temperature, salinity and macronutrient concentrations with the CO2SYS program. The different process-driven \( \Delta \Omega \) values are used alongside the \( A_T\text{ CT} \) 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 NO\(_3\), where an upper bound of the error for NO\(_3\) 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 \( \pm 1.7 \, \mu\text{mol kg}^{-1} \); 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 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
associated errors for each $\Delta C_T$ and $\Delta A_T$ term in CO2SYS: $\Delta \Omega_{\text{aragonite}} \text{sal} \pm 0.29$, $\Delta \Omega_{\text{aragonite}} \text{org} \pm 0.05$ and $\Delta \Omega_{\text{aragonite}} \text{CaCO}_3 \pm 0.41$. 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 reft 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 μmol 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 μmol kg$^{-1}$ offshore to the highest values of 2305 μmol kg$^{-1}$ over the shelf (Fig. 3d). An exception was lower $A_T$ (2287 μmol kg$^{-1}$) near Anvers Island. Salinity-normalized $C_T$ ($C_T \text{sal}$) varied by ~60 μmol kg$^{-1}$ and was lowest (2142 μmol 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 ~30–40 μmol kg$^{-1}$ from the lowest values offshore to higher values of 2375 μmol kg$^{-1}$ over the shelf where the impact of freshwater inputs was greatest in coastal waters (Fig. 1c). Low NO$_3$ sal (< 10 μmol 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 Si(OH)$_4$ sal increased by > 30 μmol kg$^{-1}$ from offshore surface waters to the highest value of 59.4 μmol 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

Table I. Water mass classification and inorganic carbon system parameters $C_T$ (μmol kg$^{-1}$), $A_T$ (μmol 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 (±) standard deviation in parentheses.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>Transect</th>
<th>$C_T$ (μmol kg$^{-1}$)</th>
<th>$A_T$ (μmol kg$^{-1}$)</th>
<th>$\Omega_{\text{calcite}}$</th>
<th>$\Omega_{\text{aragonite}}$</th>
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</thead>
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<tr>
<td></td>
<td>Offshore</td>
<td>Shelf</td>
<td>Offshore</td>
<td>Shelf</td>
<td>Offshore</td>
</tr>
<tr>
<td>AASW</td>
<td>≤ 27.4</td>
<td>NT</td>
<td>2150 (9)</td>
<td>2150 (18)</td>
<td>2283 (9)</td>
</tr>
<tr>
<td>WW</td>
<td>≤ 27.2–27.4</td>
<td>NT</td>
<td>2190 (13)</td>
<td>2188 (19)</td>
<td>2296 (9)</td>
</tr>
<tr>
<td>uCDW</td>
<td>1.70 ≤ $\theta_{\text{max}}$ ≤ 2.13°C$^\text{a}$</td>
<td>NT</td>
<td>2255 (2)</td>
<td>-</td>
<td>2347 (5)</td>
</tr>
<tr>
<td>mCDW</td>
<td>34.54 ≤ $S$ ≤ 34.75$^b$</td>
<td>NT</td>
<td>2254 (2)</td>
<td>-</td>
<td>2348 (5)</td>
</tr>
<tr>
<td></td>
<td>≤ 2000 m</td>
<td>CT</td>
<td>2252 (3)</td>
<td>-</td>
<td>2347 (4)</td>
</tr>
<tr>
<td>DW</td>
<td>≤ 750 m</td>
<td>CT</td>
<td>-</td>
<td>2261 (1)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>&gt; 2000 m$^c$</td>
<td>CT</td>
<td>-</td>
<td>2261 (2)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST</td>
<td>-</td>
<td>2270 (5)</td>
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</tbody>
</table>

$^a$Mehrbach et al. (2008).

$^b$Smith et al. (1999).

$^c$Hauri et al. (2015).

$^d$ indicates no data.
(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 $\Delta_T$, $\Delta_S$ 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 $\Delta_T$ aligned well with that of salinity (Fig. 2b, h & n). The region was dominated by the $\Delta_S$-rich CDW, with the lowest $\Delta_T$:$\Delta_S$ 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 $\Delta_T$ and $\Delta_S$ 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°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 $\Delta_S$ (Fig. 3c) and NO$_3$ revealed spatial variability with lower values over the shelf and averages of 2136 ± 11 and 19.1 ± 5.2 μmol kg$^{-1}$, respectively, in the south transect (ST). In contrast, values of $\Delta_T$ (Fig. 3d) and Si(OH)$_4$ exhibited notable cross-shelf variability and were higher at 2305 ± 3 and at 54.3 ± 4.6 μmol kg$^{-1}$, respectively, over the shelf relative to offshore waters. Values of $\Delta_S$ were distinctly lower over the southern shelf region (ST) and $\Delta_T$ 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 ± 0.48 and $\Omega_{aragonite}$ of 1.74 ± 0.30 (Fig. 3g) over the shelf in the south. This was accompanied by the highest $\Delta_T$:$\Delta_S$ ratio (Fig. 3h). Conversely, the lowest $\Omega_{calcite}$ $\Omega_{aragonite}$ and low $\Delta_T$:$\Delta_S$ 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 ± 0.64°C, 34.05 ± 0.08) Winter Water over the shelf (Fig. 3a & b) compared with offshore waters (-1.07 ± 0.42°C, 33.95 ± 0.07). Winter Water values of $\Delta_T$ and $\Delta_S$ over the shelf were 2195 ± 16 and 2311 ± 5 μmol kg$^{-1}$, respectively, and there were higher than average offshore Winter Water values of $\Delta_T$ and $\Delta_S$ of 2184 ± 10 and 2295 ± 8 μmol kg$^{-1}$, respectively (Fig. 3c & d). Winter Water $\Delta_T$ sal and $\Delta_S$ sal were slightly lower and higher, respectively, compared to $\Delta_T$ and $\Delta_S$ (Fig. 3e & f). Concentrations of NO$_3$ were lower over the shelf (27.0 ± 1.9 μmol kg$^{-1}$) compared to offshore (29.0 ± 1.1 μmol kg$^{-1}$), and Si(OH)$_4$ was clearly higher over the shelf (68.9 ± 4.8 μmol kg$^{-1}$) compared to offshore (44.1 ± 7.8 μmol kg$^{-1}$). A latitudinal gradient showed that the Winter Water potential temperature decreased by ∼1°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 $\Delta_T$:$\Delta_S$ ratio ranged from 1.04 to 1.06 (Fig. 3h).

**Circumpolar Deep Water**

The subsurface potential temperature maximum (1.70 ≤ $\theta$ ≤ 2.13°C; 34.54 ≤ $S$ ≤ 34.75) identified the offshore core of uCDW (Table I) 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 ≤ $S$ ≤ 34.7). Comparable increasing gradients in $\Delta_T$ and $\Delta_S$ 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 $\Delta_T$ 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 ∼33 μmol kg$^{-1}$. The mCDW was characterized by signatures of remineralization and upwelled deeper waters across the shelf break with higher $\Delta_T$ (2264 ± 7 μmol kg$^{-1}$), $\Delta_S$ (2350 ± 5 μmol kg$^{-1}$) and Si(OH)$_4$ (102.8 ± 7.8 μmol kg$^{-1}$) compared with uCDW values of $\Delta_T$ (2253 ± 3 μmol kg$^{-1}$), $\Delta_S$ (2347 ± 5 μmol kg$^{-1}$) and Si(OH)$_4$ (85.0 ± 3.7 μmol kg$^{-1}$). Within the uCDW and mCDW cores, the $\Delta_T$:$\Delta_S$ ratio was lowest with values of 1.03–1.05. Subsurface concentrations of $\Delta_T$ sal and $\Delta_S$ sal on the shelf were ∼5–30 μmol kg$^{-1}$ higher compared with those offshore (∼2253 μmol $\Delta_T$ kg$^{-1}$, ∼2347 μmol $\Delta_S$ kg$^{-1}$) and Si(OH)$_4$ (85.0 ± 3.7 μmol kg$^{-1}$). The highest $\Delta_T$ sal (2276 μmol 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 ± 0.04) and mCDW (1.07 ± 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.
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 ± 2 $\mu$mol kg$^{-1}$), $A_T$ (2367 ± 2 $\mu$mol kg$^{-1}$), NO$_3$ (32.3 ± 0.2 $\mu$mol kg$^{-1}$) and Si(OH)$_4$ (131.8 ± 6.5 $\mu$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 ~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°C ± 0.25°C to 0.74°C ± 0.12°C. This was accompanied by a slight increase in salinity and reduction in $C_T$ and 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 ~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 NO$_3$ (Fig. 4b) and between $C_T$ and 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. 4. Relationships between a. $A_T$ ($\mu$mol kg$^{-1}$) and $C_T$ ($\mu$mol kg$^{-1}$), b. $C_T$ ($\mu$mol kg$^{-1}$) and NO$_3$ ($\mu$mol kg$^{-1}$), c. $C_T$ ($\mu$mol kg$^{-1}$) and Si(OH)$_4$ ($\mu$mol kg$^{-1}$), d. NO$_3$ ($\mu$mol kg$^{-1}$) and PO$_4$ ($\mu$mol kg$^{-1}$) and e. Si(OH)$_4$ ($\mu$mol kg$^{-1}$) and NO$_3$ ($\mu$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.
Fig. 5. Relationships between a. salinity and $A_T$ ($\mu mol$ kg$^{-1}$) and salinity and $C_T$ ($\mu mol$ kg$^{-1}$), and b. potential $A_T$ ($A_T^*$; $\mu mol$ kg$^{-1}$) and salinity-normalized $C_T$ ($C_T_{sal}$; $\mu mol$ 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 $C_T$ ($\Delta C_T$; $\mu mol$ kg$^{-1}$) and total change in $A_T$ ($\Delta A_T$; $\mu mol$ kg$^{-1}$); (b, f.) changes due to salinity ($\Delta C_T_{sal}$, $\Delta A_T_{sal}$; $\mu mol$ kg$^{-1}$); (c, g.) changes due to photosynthesis/respiration ($\Delta C_T_{org}$, $\Delta A_T_{org}$; $\mu mol$ kg$^{-1}$); and (d, h.) changes due to calcium carbonate mineral formation/dissolution ($\Delta C_T_{CaCO_3}$, $\Delta A_T^*$; $\mu mol$ 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.
identified; the highest Si(OH)₄ and the highest NO₃ occurred in undersaturated (Ω_aragonite < 1) deep and bottom waters offshore. The values of NO₃ and PO₄ (Fig. 4d) were closely coupled with the lowest values over the shelf associated with the highest Ω_aragonite of ∼2.3. The lowest Si(OH)₄ (Fig. 4c) and reduced NO₃ concentrations occurred offshore with Ω_aragonite at ∼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 ± 0.7 ($r^2 = 0.80$, $P << 0.0001$, $n = 72$), C/Si of 1.0 ± 0.1 ($r^2 = 0.76$, $P << 0.0001$, $n = 72$), N/P of 12.9 ± 0.2 ($r^2 = 0.98$, $P << 0.0001$, $n = 72$) and Si/N of 7.3 ± 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 ± 0.6 ($r^2 = 0.89$, $P << 0.0001$, $n = 48$), C/Si of 1.2 ± 0.1 ($r^2 = 0.68$, $P < 0.0001$, $n = 48$), N/P of 13.8 ± 0.3 ($r^2 = 0.98$, $P << 0.0001$, $n = 48$) and Si/N of 4.8 ± 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 ($S = 34.7$, $C_T = 2253 ± 3 \text{ mol kg}^{-1}$, $A_T = 2347 ± 3 \text{ mol kg}^{-1}$) and for sea ice ($C_T = 277 ± 150 \text{ mol kg}^{-1}$, $A_T = 328 ± 150 \text{ mol kg}^{-1}$) and glacial ice ($C_T = 16 ± 5 \text{ mol kg}^{-1}$, $A_T = 100 ± 5 \text{ mol kg}^{-1}$) 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 $C_T = 168S - 3530$ ($r^2 = 0.90$, $SE = 176 \text{ mol kg}^{-1}$, $P << 0.0001$, $n = 120$) and $A_T = 58S + 333$ ($r^2 = 0.71$, $SE = 116 \text{ mol kg}^{-1}$, $P << 0.0001$, $n = 120$). 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 CaCO$_3$ formation/dissolution (Fig. 5b). Deep waters are distinguished by elevated $A_T$ and $C_T$ as a result of 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 ± 35 mol kg$^{-1}$ in comparison to offshore waters with an average $\Delta C_T$ of -44 ± 21 mol kg$^{-1}$ (Fig. 6a). The largest $\Delta C_T$ of -138 mol kg$^{-1}$ occurred closest to the coast (Adelaide Island) in the south, which was dominated by $\Delta C_T$ of -132 mol kg$^{-1}$ (Fig. 6c). Values of $\Delta A_T$ varied between -1 and -23 mol kg$^{-1}$ (average ~10 mol kg$^{-1}$) across the region (Fig. 6e). Freshwater inputs were greatest in the shelf region with average $\Delta C_T$ sal and $\Delta A_T$ sal values of -12 ± 9 and -16 ± 11 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 $\Delta C_T$ sal of -34 mol kg$^{-1}$ and $\Delta A_T$ sal of -37 mol kg$^{-1}$. This was accompanied by the highest $\Delta A_T^*$ of 6 mol kg$^{-1}$ and an associated $\Delta C_T$ CaCO$_3$ of 3 mol kg$^{-1}$ (Fig. 6d & h). The average $\Delta C_T$ org over the shelf was -58 ± 42 mol kg$^{-1}$, which was generally larger and more variable compared with the average $\Delta C_T$ org of -37 ± 9 mol kg$^{-1}$ offshore. The $\Delta A_T$ org followed similar spatial trends with a maximum $\Delta A_T$ org of 19 mol kg$^{-1}$, coinciding with largest $C_T$ deficits over the shelf (Fig. 6g). The $\Delta A_T^*$ and $\Delta C_T$ CaCO$_3$ were ≤ 0 mol kg$^{-1}$ in offshore waters and were lowest at -12 and -6 mol kg$^{-1}$, respectively, in the north.

Changes in $\Omega_{aragonite}$ between Winter Water and the summer mixed layer ($\Delta \Omega_{aragonite}$) 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 $\Delta \Omega_{aragonite}$ 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 $\Omega_{aragonite}$ across the region as $\Delta \Omega_{aragonite}$ sal was 0.02 ± 0.01 (Fig. 7b), indicating that dilution effects on $A_T$ (reduced $\Omega_{aragonite}$) were counteracted by concomitant reductions in $C_T$ (increased $\Omega_{aragonite}$). A higher average $\Delta \Omega_{aragonite}$ (0.54 ± 0.31) in shelf waters was driven by biological carbon uptake, with the highest $\Delta \Omega_{aragonite}$ org of 1.39 near Adelaide Island (Fig. 7c). Offshore waters had a lower average $\Delta \Omega_{aragonite}$ (0.31 ± 0.08) as a result of decreases in mixed-layer carbonate (negative $\Delta A_T^*$) as $\Delta \Omega_{aragonite}$ CaCO$_3$ (changes in $\Omega_{aragonite}$ due to the processes of any CaCO$_3$ mineral) was -0.02 in the north (Fig. 7d). The lowest $\Delta \Omega_{aragonite}$ sal (-0) occurred with the greatest freshening signal in shelf waters near Anvers Island and was accompanied by the highest $\Delta \Omega_{aragonite}$ CaCO$_3$ (0.07). Residual changes in $\Delta \Omega_{aragonite}$ determined from the difference in the total seasonal change and other contributing factors, were on average -0.12 ± 0.09 and represented a reduction in AASW $\Omega_{aragonite}$ relative to Winter Water $\Omega_{aragonite}$. Changes in $\Omega_{calcite}$ (not shown) exhibited the same spatial variations as $\Delta \Omega_{aragonite}$ with a range of 0.32–1.83 and an average $\Delta \Omega_{calcite}$ in the shelf (offshore) region of 0.86 ± 0.50 (0.50 ± 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 $\Omega_{aragonite}$ across the shelf from offshore and latitudinally along the WAP. The highest $\Omega_{aragonite}$ 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 CaCO$_3$ precipitation/sedimentation 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$C_T$ sal shelf = -12 ± 9 $\mu$mol kg$^{-1}$; $\Delta$A$_T$ sal shelf = -16 ± 11 $\mu$mol kg$^{-1}$; Fig. 6) that exceeded those in offshore waters (\Delta$C_T$ sal offshore and $\Delta$A$_T$ sal offshore $\approx$ -10 $\mu$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 $\Omega_{aragonite}$ 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 $\Omega_{aragonite}$ of 0.02 ± 0.01 (Fig. 7). These salinity-driven changes revealed the effects of combined $A_T$ and $C_T$ variability on $\Omega_{aragonite}$ as the dilution and reduction of $A_T$ (reducing $\Omega_{aragonite}$) were counteracted by the parallel dilution and reduction of $C_T$ (increasing $\Omega_{aragonite}$). The seasonal meltwater release contributed to net increases in $\Omega_{aragonite}$ 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 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 $\mu$mol kg$^{-1}$ dominated the seasonal changes in $\Omega_{aragonite}$ (at least 93% of $\Omega_{aragonite}$ Fig. 7) to counteract any meltwater-induced suppression of carbonate mineral saturation states ($\Delta\Omega_{aragonite}$ bio > $\Delta\Omega_{aragonite}$ sal). Large phytoplankton blooms are known to occur along the WAP shelf during spring and summer (Vernet et al. 2008, Schofield et al. 2017), when 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 $\mu$g l$^{-1}$ and elevated rates of primary production of 98–183 $mg$ C m$^{-3}$ 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 $\Delta C_T$ org of -58 ± 42 $\mu$mol kg$^{-1}$ and associated increases in $\Delta\Omega_{aragonite}$ org (Fig. 6) and increased $\Omega_{aragonite}$ org by 1.39 (Fig. 7) despite the influence of freshwater along the shelf. These processes created substantial summertime sinks for atmospheric CO$_2$ of > 40 mmol m$^{-2}$ 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 $\Omega_{aragonite}$ in the AASW across the shelf from offshore (Fig. 1). These findings support previous observations of high 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 $\Delta\Omega_{aragonite}$ org for the shelf region (average $\Delta\Omega_{aragonite}$ org on the shelf was 0.62 ± 0.44) showed latitudinal variability ranging from 0.42 ± 0.22 in the north to 1.00 ± 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 NO$_3$ concentrations that occurred in AASW (8.1–26.8 $\mu$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 ± 0.7 and 10.6 ± 0.6 for offshore and shelf waters, respectively, were higher than the Redfield ratios, probably due to the effect of air-sea CO2 uptake and subsequent influx of C_T in surface waters from strong summertime CO2 sinks (Hauri et al. 2015, Tortell et al. 2015). The cycling of NO3 and PO4 was closely coupled with the lowest macronutrient concentrations over the shelf associated with a biologically driven high Ω_aragonite value of ~2.3 (Fig. 1). The observed N/P ratios of 12.9 ± 0.2 for offshore waters and 13.8 ± 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)^1 (Redfield 1958). The seasonal seawater N/P uptake ratios of ~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 < 1µg m^3^1^ 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 ~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 ± 0.4 (r^2 = 0.94, P << 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)4 relative to NO3. Lower dissolved Si(OH)4 in the water column offshore is further evidence for strong biological drawdown in diatom blooms where assimilation processes exceeded Si(OH)4 resupply processes, in contrast to conditions of elevated Si(OH)4 in parallel to diatom-dominated production on the shelf (Fig. 3). The close coupling of C_T and Si(OH)4 (Fig. 4) indicates the key role of diatoms that drive intense oceanic CO2 uptake in offshore and coastal areas of the WAP.

Remineralization and lowering of carbonate mineral saturation in subsurface waters

Subsurface values of C_T, A_T, Si(OH)4 and, to a lesser extent, NO3 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_T 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_T and low Ω_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_T and Si(OH)4 and generally higher C_T concentrations. The elevated A_T, Si(OH)4 and C_T 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_T into the Winter Water layer. The concentrations of Si(OH)4 also increased in the uCDW-mCDW layer across the shelf break (Fig. 2), indicating that upwelling and mixing of saline, A_T-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 CaCO$_3$ dissolution in the deep and offshore bottom waters. Increases in potential $A_T$ for a smaller range of $C_T$ sal revealed the influence of 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 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 $A_T$:CT ratios and aragonite undersaturation in mCDW over the shelf (Fig. 2). Decoupling of Winter Water $C_T$ and 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 carbonic 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 $A_T$:CT 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 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 Si(OH)$_4$ from seafloor sediment resuspension and porewaters could contribute to elevated 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 $C_T$, NO$_3$ and 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 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 $A_T$:CT 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 $C_T$ sal and elevated $A_T$ sal 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, 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 $A_T$ sal value of $\sim$2345 μmol kg$^{-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 $A_T$ sal value of $\sim$2355 μmol kg$^{-1}$ (Fig. 2). Exceptions were an elevated $A_T$ sal value of $\sim$2370 μmol kg$^{-1}$ in meltwater-influenced surface waters that became superimposed on the upwelling signal at coastal locations (Fig. 1). The values of $A_T$ sal increased by up to 40 μmol 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 $A_T$ 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 ($A_T^* = A_T + NO_3^-$; 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 μmol 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 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 $A_T$ 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 $C_T$ sal on the shelf was more depleted (higher $A_T:C_T$ ratio) than in offshore waters (Fig. 1b), the $A_T$ sal in shelf waters (Fig. 1c) was elevated (higher $A_T:C_T$ ratio). Both 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°S (Fig. 1g). Concurrent high $C_T$ (> 2140 μmol kg$^{-1}$), salinity (> 33.7) and temperature (> 1°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 μmol 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 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 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 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 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 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.

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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).

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CALCIUM CARBONATE SATURATION STATES ALONG THE WEST ANTARCTIC PENINSULA


