Carbonate saturation state of surface waters in the Ross Sea and Southern Ocean: controls and implications for the onset of aragonite undersaturation

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Abstract. Predicting when surface waters of the Ross Sea and Southern Ocean will become undersaturated with respect to biogenic carbonate minerals is challenging in part due to the lack of baseline high-resolution carbon system data. Here we present ∼1700 surface total alkalinity measurements from the Ross Sea and along a transect between the Ross Sea and southern Chile from the austral autumn (February–March 2013). We calculate the saturation state of aragonite (Ar) and calcite (Ca) using measured total alkalinity and pCO2. In the Ross Sea and south of the Polar Front, variability in carbonate saturation state (Ω) is mainly driven by algal photosynthesis. Freshwater dilution and calcification have minimal influence on variability. We estimate an early spring surface water Ar value of ∼1.2 for the Ross Sea using a total alkalinity–salinity relationship and historical pCO2 measurements. Our results suggest that the Ross Sea is not likely to become undersaturated with respect to aragonite until the year 2070.

1 Introduction

Atmospheric CO2 concentrations have increased by 40 % since preindustrial times to ∼400 ppm today and could reach 936 ppm by the year 2100 (IPCC AR5 WG1, 2013). Due to oceanic uptake of CO2, surface ocean pH is already 0.1 units lower than preindustrial values and is projected to decrease by another 0.3–0.4 units by the end of the century, equivalent to a 50 % decrease in carbonate ion (CO32−) concentrations (Orr et al., 2005). Even after CO2 emissions are halted, it will take thousands of years before the surface ocean pH returns to preindustrial levels (Caldeira and Wickett, 2003; Archer et al., 2009).

The saturation state (Ω) of seawater with respect to a specific calcium carbonate (CaCO3) mineral (aragonite, calcite, or magnesium calcite) is defined as

\[ \Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}, \]

where Ksp is the solubility product constant for the specific CaCO3 mineral and depends on salinity, temperature, and pressure (Mucci, 1983). Aragonite is ∼1.6 times more soluble than calcite at 0°C whereas the solubility of magnesium calcite varies depending on the mole fraction of magnesium ions (Dickson, 2010). ΩAr represents the saturation state of aragonite and ΩCa represents the saturation state of calcite. Ω < 1 represents undersaturation where dissolution is thermodynamically favorable and Ω > 1 represents supersaturation where precipitation is favorable. Most surface waters of the global oceans are currently supersaturated with respect to CaCO3 (Feely et al., 2009). However, for some species including coccolithophorids, foraminifera, and tropical corals, decreasing CO32− concentrations can decrease calcification rates even in supersaturated conditions (Riebesell et al., 2000; Moy et al, 2009; Andersson et al., 2011).

The Southern Ocean is especially vulnerable to ocean acidification (OA) due to its relatively low total alkalinity (TA) and because of increased CO2 solubility in cold water. In addition, Antarctic continental shelves have insignificant sedimentary CaCO3 to buffer against OA (Hauck et al., 2013). Modeling studies predict that surface waters in the Southern Ocean may start to become undersaturated with...
respect to aragonite by 2050 and be fully undersaturated by 2100 (Orr et al., 2005; Feely et al., 2009). McNeil and Matear (2008) have suggested that wintertime aragonite undersaturation in the Southern Ocean may begin as early as 2030.

OA-induced decreases in $\Omega$ have potentially serious consequences for Antarctic food webs. In the Ross Sea the aragonitic shelled pteropod *Limacina helicina* is a dominant zooplankton that can reach densities of 300 individuals m$^{-3}$ (Hopkins, 1987; Seibel and Dierissen, 2003; Hunt et al., 2008). Pteropods are important prey for nototheniid fish, which in turn are major prey for penguins, seals, and whales (Foster and Montgomery, 1992; La Mesa et al., 2000, 2004). Pteropods may also be important contributors to the biological pump (Collier et al., 2000; Acconnero et al. 2003; Manno et al., 2010). Orr et al. (2005) found that the shell of a subarctic pteropod started to dissolve within 48 h when placed in waters with the level of aragonite saturation expected to occur in the Southern Ocean by 2100. Severe dissolution pitting was observed on live pteropods that were collected from the upper 200 meters in the Atlantic sector of the Southern Ocean, from waters that were near undersaturation with respect to aragonite (Bednarsk et al., 2012).

Other organisms in the Southern Ocean may be negatively impacted by OA include krill (Kawaguchi et al., 2013), foraminifera (Moy et al., 2009), sea urchins (Sewell and Hofmann, 2011), deep sea hydrocorals (Shadwick et al., 2014), sea stars (Gonzalez-Bernat et al., 2013), bivalves (Cummings et al., 2011), and brittle stars (McCintosh et al., 2011). Conversely non-calcareous phytoplankton may benefit in the Ross Sea in a high $p$CO$_2$ world, especially the larger diatom *Chaetoceros lineola* (Tortell et al., 2008; Feng et al., 2010).

There are only a few surface carbon system data sets from the Ross Sea (Bates et al., 1998; Sweeney et al., 2000b; Sandrini et al., 2007; Long et al., 2011; Mattsdotter Björk et al., 2014; Rivaro et al., 2014; Kapsenberg et al., 2015) that can be used to establish baselines in order to understand the relative importance of physical, chemical, and biological processes that drive the large spatial and seasonal variability of $\Omega$. With no winter $\Omega$ measurements, it is challenging to predict when the Ross Sea will become undersaturated with respect to aragonite and calcite. A model by McNeil et al. (2010) suggests that winter surface waters in the Ross Sea will become undersaturated with respect to aragonite by the year 2045 since sea ice, upwelling of deep water, and short residence times prevent these surface waters from reaching equilibrium with the atmosphere. However, McNeil et al. (2010) indirectly estimated surface wintertime $\Omega_{\text{Ar}}$ values by using limited carbon system data from the spring (Sweeney et al., 2000b).

We present ~1700 underway TA measurements from the surface waters of the Ross Sea and along a transect across the Southern Ocean from the Ross Sea to southern Chile. By combining the underway TA measurements with $p$CO$_2$ data we characterize the complete carbon system and describe patterns and controls on $\Omega$ variability. Finally, after establishing a relationship between salinity and TA, we use the Lamont Doherty Earth Observatory (LDEO) $p$CO$_2$ database (Takahashi et al., 2009) (available at http://www.ldeo.columbia.edu/res/pi/CO2) to provide an independent estimate of Ross Sea surface water $\Omega_{\text{Ar}}$ in early spring.

2 Study site

The Antarctic Circumpolar Current (ACC) flows from east to west around the entire Antarctic continent and is composed of multiple fronts that separate distinct water masses (Rintoul et al., 2001). There are three primary fronts – the southern ACC front (SACCF), the Antarctic Polar Front (PF), and the Subantarctic Front (SAF) (Orsi et al., 1995). Sokolov and Rintoul (2009) found that these primary fronts are composed of multiple jets that they label south (S), middle (M), and north (N). Convergent Ekman transport north of the westerly wind stress maximum (near the axis of the ACC) downwells surface water into the ocean interior. Circumpolar Deep Water (CDW) upwells south of the wind stress maximum where it becomes modified into Antarctic surface water (AASW) (Rintoul et al., 2001).

The cyclonic Ross Sea gyre is located south of the ACC (Smith et al., 2012). The southern portion of this gyre flows west along the Ross Sea continental slope and generates intrusions of CDW onto the Ross Shelf through the major troughs (Orsi et al., 2009; Dinniman et al., 2011; Kohut et al., 2013). In addition, AASW enters the Ross Sea in the east and flows westward along the Ross Ice Shelf (Orsi et al., 2009).

The Ross Sea is considered a biological hotspot supporting over 400 benthic species (Smith et al., 2012). During the winter the Ross Sea is mostly covered by sea ice, which begins to clear in November to form the largest polynya in Antarctica. There are two main phytoplankton blooms in the Ross Sea. The first bloom begins in late November in the Ross Sea polynya (Fig. 1a) and peaks in mid- to late December (Arrigo et al., 1999; Arrigo and van Dijken, 2004). In early January, sea ice melts in the western Ross Sea, lowering surface salinity and increasing stratification (Fig. 1b). As a result, a secondary diatom bloom forms in the west with productivity peaking in late January to early February (Arrigo et al., 1999; Arrigo and van Dijken, 2004) (Fig. 1c).

The Ross Sea phytoplankton blooms account for up to half of all primary production over the Antarctic continental shelf (Arrigo and McClain, 1994; Smith and Gordon, 1997; Arrigo and van Dijken, 2003). Photosynthesis reduces the concentration of nutrients and dissolved inorganic carbon (DIC) in the mixed layer, causing $\Omega$ to increase in surface waters (McNeil et al., 2010). Once the sea ice reforms during autumn and winter, remineralization of organic matter and deep convective mixing produces a relatively homogeneous water column, causing surface DIC concentrations to increase and $\Omega$ to decrease (Gordon et al., 2000; Sweeney et al., 2000b; Petty et al., 2014).

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3 Methods

3.1 Analytical methods

As part of the TRacing the fate of Algal Carbon Export in the Ross Sea (TRACERS) program, we undertook continuous measurements of surface water TA in the western Ross Sea aboard the Nathaniel B. Palmer (NBP13-02) from 13 February through 9 March 2013. In addition, from 19 March to 2 April 2013, we made continuous measurements of surface water TA in transit between the Ross Sea and southern Chile along the cruise track shown in Fig. 2. Underway TA measurements were conducted using the shipboard uncontaminated continuous flow system with an intake located at ~5 m depth. Seawater from the ship’s underway system was redirected to the bottom of a 250 mL free surface interface cup flowing at 2 L min⁻¹ and was drawn from the bottom of the cup for TA analysis without filtration. The entire system was automated and relatively unattended. The sampling cycle was every 24 min on a custom-configured Metrohm 905 Titirando equipped with three Metrohm 800 Dosino syringe pumps (two 50 mL units for sample handling and rinsing and one 5 mL unit for acid titration). Temperature was measured at the cup and in the titration cell. We used certified 0.1 N HCl provided by A. Dickson (Scripps Institution of Oceanography) for the potentiometric titrations and TA calculations following Dickson et al. (2003). Since we consumed the certified HCl after ~1000 measurements in the Ross Sea, we have no TA data from the eastern Ross Sea. For the transect to southern Chile, we mixed our own 0.1 N HCl solution (from 12.1 N HCl, laboratory grade NaCl, and deionized water). We calibrated TA measurements using certified reference materials (CRMs) Batch 122 provided by A. Dickson (Scripps Institution of Oceanography). Our estimated precision for the underway TA measurements from 68 CRM analyses is ±3 µmol kg⁻¹ (±1 SD).

Outlier TA analyses were identified by taking a running mean and standard deviation of nine consecutive measurements. A measurement was rejected if (1) the difference between the measurement and mean was greater than twice the standard deviation and (2) the difference between the measurement and mean was greater than 6 µmol kg⁻¹. A total of 65 measurements (out of 1716) were rejected.

We collected seawater samples for particulate organic carbon (POC) every 2 h from the ship’s continuous flow system between the Ross Sea and Chile. Following the protocols of Knap et al. (1996), we filtered 1 to 3 L of seawater through precombusted Whatman GFC filters and immediately rinsed these filters with 10 mL of 0.01 N HCl to remove carbonate. We air-dried the filters before sending them to Stanford University where they were analyzed on a Carlo Erba NA1500 Series 2 elemental analyzer.

Surface pCO₂ measurements were made every 3 min using the LDEO air–sea equilibrator permanently installed on the NBP (data available at http://www.ldeo.columbia.edu/res/pi/CO2). The estimated precision is ±1.5 µatm.
Underway salinity and sea surface temperature (SST) were measured continuously by the ship’s thermosalinograph (TSG) (Sea-Bird model SBE-45). These variables were binned into 1 min intervals.

We collected discrete water samples at 85 stations in the Ross Sea from 13 February through 18 March 2013 (Fig. 1a). We used a rosette sampler fitted with 24 Niskin bottles and a Sea-Bird model SBE-911+ conductivity, temperature, and depth sensor. We also measured salinity on discrete underway and hydrocast samples at 25 °C using a Guildline 8400 Autosal four-electrode salinometer. The difference between the Autosal measurements and salinity from the conductivity sensor was less than 0.02. In this paper we use the hydrocast samples to evaluate the controls of seasonal surface Ω_{Ar} variability. The water column data will be further analyzed in upcoming papers.

We collected hydrocast samples for TA and DIC following the protocols of Dickson et al. (2007) and immediately added saturated mercuric chloride (<0.1 % by volume). For TA, we ran each sample within 12 h of collection using a second potentiometric titrator, a Metrohm 855 Robotic Titrosampler equipped with two 800 Metrohm Dosino syringe pumps (one 50 mL unit for rinsing and sample handling and one 5 mL unit for acid titration). The samples were prefiltered through 0.45 µm polyvinylidene fluoride filters and the estimated prefiltration variability. The water column data will be further analyzed in upcoming papers.

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We measured DIC on hydrocast samples within ~ 4 h of collection without filtration. We acidified 1.25 mL of the sample using a custom-built injection system coupled to an infrared gas analyzer (LI-COR LI7000). As described by Long et al. (2011), the infrared absorption signal versus time is integrated for each stripped gas sample to yield a total mass of CO_{2}. Samples were run in triplicate or greater and were calibrated using CRMs between every 3–4 unknowns. Micro-bubbles regularly appeared within injected samples due to sample warming between acquisition and DIC analysis. Each integration curve was visually inspected and integration curves that exhibited evidence for bubbles were rejected. The estimated precision based upon unknowns (> 3500 runs) and CRM replicates (n = 855) for cruise NPB-1302 is ±3 µmol kg^{-1}.

### 3.2 Carbon system calculations and crosschecks

We calculate Ω and DIC (hereafter called DIC_{calc}) for underway samples with CO2SYS for MATLAB (Lewis and Wallace, 1998; van Heuven et al., 2011) with TA, pCO_{2}, SST, and salinity as input variables. Calculations are only conducted for pCO_{2} measured within 3 min of the TA measurement (n = 1034), the average cycle time for the automated pCO_{2} measurements. We use the equilibrium constants of Mehrback et al. (1973) as refit by Dickson and Millero (1987) since previous studies have found that they are the optimal choice, including for Antarctic waters (Lee et al., 2000; Millero et al., 2002; McNeil et al., 2007). For the hydrocast data, we calculate Ω using TA, DIC, temperature, and salinity as input variables.

As a means of internal quality control, we use the initial pH reading from the TA titration as a third carbon system parameter to crosscheck the accuracy of our Ω_{Ar} estimates. Ω_{Ar} calculated using TA and pCO_{2} is 0.02 ± 0.07 greater than Ω_{Ar} calculated using TA and pH. In addition, DIC_{calc} using TA and pCO_{2} is 2 ± 7 µmol kg^{-1} lower than DIC_{calc} using TA and pH. Finally, measured pCO_{2} is 4 ± 14 µatm lower than pCO_{2} calculated from TA and pH. These strong consistencies suggest that our pCO_{2} and TA measurements are accurate. Our surface TA and DIC_{calc} measurements versus latitude for the Southern Ocean are within the ranges of other studies (Metzl et al., 2006; McNeil et al., 2007; Matts-Jørgensen et al., 2014).

We compare the TA measurements from the surface hydrocasts (< 5 m deep) to the underway TA measurements made while the ship was still on station within ~ 15 min of when the surface samples were collected. The underway values are 3 ± 5 µmol kg^{-1} higher than the hydrocast TA values.

### 3.3 Ross Sea and Southern Ocean calculations

The Ω_{Ar} of surface waters in the Ross Sea increases during the austral summer months (McNeil et al., 2010). We use DIC, TA, SST, and salinity to determine the controls on the seasonal cycle of surface water Ω_{Ar}. We normalize DIC and TA to a salinity of 34.5, the average salinity of the Ross Sea (hereafter called sDIC and sTA). Due to the deep convective mixing during the winter, we use the average sDIC and sTA concentrations of hydrocast samples collected from 200 to 400 m to determine winter water values (sDIC_{calc} = 2221 ± 5 µmol kg^{-1}, sTA = 2338 ± 3 µmol kg^{-1}). While sDIC and sTA concentrations below 200 m are influenced by carbon export particularly in the summer and early autumn, observations show that sDIC and sTA concentrations are relatively uniform below 200 m across space and a given season (Table 1).

Following Hauri et al. (2013), the change in Ω_{Ar} of surface hydrocast samples (upper 10 m) from winter conditions can be expressed as

\[ \Delta \Omega_{Ar} = \frac{\partial \Omega}{\partial DIC} \Delta sDIC + \frac{\partial \Omega}{\partial TA} \Delta sTA + \frac{\partial \Omega}{\partial T} \Delta T + \Delta S_{\Omega} + \text{Residuals}, \]  

(2)

where

\[ \Delta S_{\Omega} = \frac{\partial \Omega}{\partial S} \Delta S + \frac{\partial \Omega}{\partial DIC} \Delta DIC + \frac{\partial \Omega}{\partial TA} \Delta TA. \]

\[ \Delta sDIC \text{ and } \Delta sTA \text{ are the difference in } sDIC \text{ and } sTA \text{ for each sample from the winter value. The term } \Delta T \text{ is calculated using a winter SST of } -1.89 \degree C \text{ (per Sweeney, 2003). } \Delta S_{\Omega} \text{ represents the total contribution of salinity changes to } \Delta \Omega_{Ar}. \]
Since salinity between 200 and 400 m is variable across the Ross Sea (Orsi and Wiederwohl, 2009), $\Delta S$ is calculated as the difference between the salinity of a surface sample and the average salinity for samples from that station that are between 200 and 400 m.

$\Delta$DIC and $\Delta$TA represent changes to DIC and TA due to dilution/concentration from freshwater input and sea-ice processes:

$$
\Delta \text{DIC} = \left[ \text{DIC}_{200-400} - \text{DIC}_{200-400} \right] - \left[ \text{DIC}_{200-400} - \text{DIC}_{200-400} \right]
$$

(4)

$$
\Delta \text{TA} = \left[ \text{TA}_{200-400} - \text{TA}_{200-400} \right] - \left[ \text{TA}_{200-400} - \text{TA}_{200-400} \right]
$$

(5)

DIC$_{200-400}$, TA$_{200-400}$, and Salinity$_{200-400}$ are the average values for samples collected from 200 to 400 m calculated at each station.

The partial derivatives quantify the change in $\Omega_{Ar}$ per unit change in DIC, TA, temperature, and salinity. To determine the partial derivatives, we calculate $\Omega_{Ar}$ for all hydrocast samples within the upper 10 m using DIC, TA, temperature, and salinity as input parameters. We recalculate $\Omega_{Ar}$ after independently increasing DIC, TA, temperature, and salinity by one unit. The partial derivatives are the average difference between the initial $\Omega_{Ar}$ and the recalculated $\Omega_{Ar}$.

We use the same equations to evaluate the relative importance of DIC, TA, temperature, and salinity on the variability of $\Omega_{Ar}$ from 75 to 55° S. For the $\Delta$ terms, we calculate the change in sDIC, sTA, temperature, and salinity from the mean of the first six underway measurements at 75° S. For Eqs. (4) and (5), instead of using DIC, TA, and salinity values from 200 to 400 m, we use the mean of the first six underway measurements at 75° S.

4 Results and discussion

4.1 $\Omega$ in the Ross Sea

Underway TA values range from 2268 to 2346 µmol kg$^{-1}$ (mean $= 2314 \pm 16$ µmol kg$^{-1}$). Since TA strongly covaries with salinity ($R^2 = 0.86$, residual $\pm 6$ µmol kg$^{-1}$), the lowest TA values are located in the west where the salinity is lowest (Fig. 1b). Values of sTA range from 2336 to 2386 µmol kg$^{-1}$ (mean $= 2360 \pm 7$ µmol kg$^{-1}$) and are influenced by calcification/dissolution as well as phytoplankton photosynthesis since one unit of nitrate drawdown increases TA by one unit (Brewer and Goldman, 1978) (Fig. 1d).

Surface $pCO_2$ values range from 162 to 354 µatm and are lower in the west due to late-season phytoplankton photosynthesis (Fig. 1e). Surface $\Omega_{Ar}$ ranges from 1.40 to 2.42 and $\Omega_{Ca}$ ranges from 2.24 to 3.89 (Fig. 2f). The highest $\Omega_{Ar}$ values are also located in the west. Phytoplankton photosynthesis increases $\Omega$ by both decreasing DIC and increasing TA.

Spatial and temporal variations in surface water $\Omega_{Ar}$ are mainly controlled by sDIC in the Ross Sea (Eq. 2, Fig. 3). The concentration of sDIC decreased by $58 \pm 20$ µmol kg$^{-1}$ from a winter value, causing $\Omega_{Ar}$ to increase by $0.5 \pm 0.2$. In addition, sTA increased by $11 \pm 7$ µmol kg$^{-1}$ during the preceding summer months, causing $\Omega_{Ar}$ to decrease by $0.1 \pm 0.1$. Although there was a significant reduction in salinity compared to winter values ($0.7 \pm 0.3$), $\Omega_{Ar}$ only decreased by $\sim 0.01$ due to this freshening since both DIC and TA concentrations were reduced. Lastly, the effect of temperature on $\Omega_{Ar}$ was negligible since the Ross Sea only experiences a 2°C seasonal change in SSTs (Sweeney, 2003).

Two processes can reduce sDIC, calcification, and phytoplankton photosynthesis. To evaluate the importance of calcification, we use time-dependent changes in potential alkalinity (PALK = sNitrate + sTA) from a winter value (2367 $\pm 3$ µmol kg$^{-1}$, defined as average value for all samples between 200 and 400 m). While TA will increase during photosynthesis due to nitrate drawdown, PALK will be conserved. Therefore, changes in PALK can be attributed to calcification and dissolution. The average $\Delta$PALK from a winter concentration is negligible ($0 \pm 5$ µmol kg$^{-1}$); therefore, calcification appears to be insignificant and the increase in sTA from winter conditions is largely driven by nitrate drawdown during photosynthesis. Earlier studies found that calcification contributed to only $\sim 5$% of the total seasonal DIC drawdown (Bates et al., 1998; Sweeney et al., 2000a). Therefore, we argue that photosynthesis exerts the dominant control on sDIC, sTA, and $\Omega_{Ar}$. While the highest $\Omega_{Ar}$ value that we observed was 2.4, values up to $\sim 4$ have been observed during December–January (McNeil et al., 2010).
the time we arrived in the Ross Sea, surface sDIC concentrations would have already increased relative to the summer due to enhanced air–sea CO$_2$ fluxes (Arrigo and van Dijken, 2007), deepening of the mixed layer (Sweeney, 2003), and remineralization of organic carbon (Sweeney et al., 2000b).

Mattsson and Björk et al. (2014) also argue that phytoplankton photosynthesis is the major control on surface water $\Omega_{Ar}$ variability between the Ross Sea and the Antarctic Peninsula based upon the covariance of $\Omega_{Ar}$ and chlorophyll a. The largest contributor to seasonal $\Omega_{Ar}$ change in the Chukchi Sea in the Arctic is also phytoplankton photosynthesis (Bates et al., 2013). However, unlike the Ross Sea, numerous studies have also demonstrated aragonite undersaturation of surface waters in parts of the Arctic due to sea-ice melt and river runoff (Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009; Robbins et al., 2013).

4.2 $\Omega$ in the Southern Ocean

The spatial changes in $\Omega_{Ar}$, SST, $pCO_2$, and POC between 75 and 55°S are shown in Fig. 4. We also include the mean location of the fronts from Sokolov and Rintoul (2009) as they intersect our cruise track. The lowest $\Omega_{Ar}$ value is 1.25 ($\Omega_{Ca} = 2.00$) at 75°S, corresponding with the highest $pCO_2$ of ~396 $\mu$atm. $\Omega_{Ar}$ increases along the transect to reach a maximum of 1.93 ($\Omega_{Ca} = 3.04$) at 55°S. The changes in $\Omega_{Ar}$ are not always monotonic. In two regions changes in $\Omega_{Ar}$ can be attributed to enhanced primary production. Between 74 and 73°S, $\Omega_{Ar}$ first increases and then decreases by ~0.1. This corresponds with a 40 $\mu$atm drop and then rise in $pCO_2$.

Given that SST is constant, this localized increase in $\Omega_{Ar}$ is likely due to phytoplankton photosynthesis. This region may be along the Antarctic Slope Front that is known for higher biological activity (Jacobs, 1991). There is another step in $\Omega_{Ar}$ from ~1.4 to ~1.55 between 68 and 66°S across the SACCF-N. This step also corresponds with a decrease in $pCO_2$ from ~370 to ~340 $\mu$atm. Elevated POC concentrations between the SACCF-N and the PF-M correspond with these lower $pCO_2$ values and again indicate enhanced phytoplankton photosynthesis. Rubin (2003) also found that $pCO_2$ is reduced south of the PF (170°W) due to primary production.

To further gain insight into why $\Omega_{Ar}$ increases along our transect, we quantify the contribution of changing sDIC (calculated from TA and $pCO_2$), sTA, SST, and salinity to changing $\Omega_{Ar}$ (Fig. 5a). The dominant control is declining sDIC$_{calc}$ from ~2240 to ~2140 $\mu$mol kg$^{-1}$ between 75 and 55°S, which causes $\Omega_{Ar}$ to increase by 0.87 if sTA, SST, and salinity are held constant (Fig. 6). Declining sTA from ~2340 to ~2310 $\mu$mol kg$^{-1}$ partially counters the influence of sDIC$_{calc}$ and reduces $\Omega_{Ar}$ by 0.28. The influences of SST and salinity on $\Omega_{Ar}$ are minimal.

$\Omega_{Ar}$ variability is driven almost entirely by changes in sDIC$_{calc}$ from 75°S to the PF-S. Between the PF-S and the SAF-N, variability in $\Omega_{Ar}$ is influenced by the opposing effects of sDIC$_{calc}$ and sTA. The $TA: DIC_{calc}$ ratio and $\Omega_{Ar}$ are constant between the PF-S and the SAF-S since both sDIC$_{calc}$ and sTA decrease at the same rate (Fig. 5b).
Between the SAF-S and the SAF-N, $\Omega_{\mathrm{Ar}}$ increases since $\Delta$DIC$_{\text{calc}}$ declines faster than $\Delta$TA. North of the SAF-N, $\Omega_{\mathrm{Ar}}$ variability is again driven by $\Delta$DIC$_{\text{calc}}$. $\Omega_{\mathrm{Ar}}$ increases due to a decrease in $\Delta$DIC$_{\text{calc}}$ while $\Delta$TA remains constant.

We examine possible controls on $\Delta$DIC$_{\text{calc}}$ along the transect. The concentration of $\Delta$DIC$_{\text{calc}}$ is highest south of the PF-S due to upwelling of CDW (Fig. 6a). To evaluate the properties of CDW, we use data from the 2011 Repeat Hydrography Cruise SO4P, which is part of the US Climate Variability and Predictability (CLIVAR) program (Swift and Orsi, 2012) (available at: http://www.clivar.org/resources/data/hydrographic). We only use data from hydrocasts located between 168°E and 73°W where the bottom depth is > 1000 m (Fig. 2b). We reject the data from hydrocast 46(B) where the deep DIC data below 200 m are $\sim 30 \mu$mol kg$^{-1}$ higher than the rest of the stations. Following Sweeney (2003), CDW is defined as centered on the level of maximum temperature below 150 m.

From this CLIVAR data set, CDW has a DIC value of 2243 ± 3 $\mu$mol kg$^{-1}$. Between 75 and 74°S, sDIC$_{\text{calc}}$ concentration of surface water is also 2243 ± 5 $\mu$mol kg$^{-1}$, indicating little modification to CDW and consistent with the observation that this region was covered by sea ice even during the summer of 2013. At 74°S sDIC$_{\text{calc}}$ drops to $\sim 2220 \mu$mol kg$^{-1}$ and by 66°S, across the SACCFF-N, sDIC$_{\text{calc}}$ drops to $\sim 2200 \mu$mol kg$^{-1}$. This 40 $\mu$mol kg$^{-1}$ decrease in sDIC$_{\text{calc}}$ between Antarctica and the PF-S is consistent with the observed drops in $p$CO$_2$ that we attributed to photosynthesis. Rubin et al. (1998) also observed a 30–50 $\mu$mol kg$^{-1}$ decrease in DIC at 67°S in Pacific Antarctic waters between winter and summer that they attribute to primary productivity.

sDIC$_{\text{calc}}$ continues to drop from $\sim 2220 \mu$mol kg$^{-1}$ at the PF-S to $\sim 2140 \mu$mol kg$^{-1}$ at 55°S, consistent with surface DIC measurements between 70 and 40°S compiled by McNeil et al. (2007). There are multiple factors likely responsible for this decrease in sDIC$_{\text{calc}}$. Both satellite (Arrigo et al., 2008) and in situ measurements (Reuer et al., 2007) show that annual primary productivity increases from south to north in the Southern Ocean. In addition, surface waters north of the PF advect northwards and accumulate a DIC deficit. Finally, warmer water holds less DIC while in equilibrium with the atmosphere. There is little net air–sea CO$_2$ flux between 5% and 55°S (except for net efflux at 60°S) since warming and increased biological production compensate each other (Takahashi et al., 2012).

We also examine possible controls on $\Delta$TA concentrations along the transect. The concentration of $\Delta$TA is also highest south of the PF-S due to upwelling of CDW. Based off the CLIVAR data set, the $\Delta$TA of CDW is 2334 ± 3 $\mu$mol kg$^{-1}$. The $\Delta$TA of surface water between 74°S and the PF-S is $\sim 2340 \mu$mol kg$^{-1}$, slightly higher than its CDW source (Fig. 6b). Nitrate drawdown during photosynthesis may explain the elevated $\Delta$TA. Between 75 and 74°S, $\Delta$TA exceeds 2360 $\mu$mol kg$^{-1}$. One possible explanation is that ikaite (CaCO$_3$·6H$_2$O), a mineral that has been observed directly and indirectly to precipitate in Antarctic sea ice (Dieckmann et al., 2008; Fransson et al., 2011), dissolved into surface waters during the summer causing $\Delta$TA concentrations to increase. Between the PF-S and SAF-N, $\Delta$TA drops to 2310 $\mu$mol kg$^{-1}$ where the concentrations level off. This drop appears to be in part due to the mixing of two end member water masses, AASW south of the PF-S and subantarctic surface water north of the SAF-N. The decreasing $\Delta$TA is consistent with the suggestion of Millero et al. (1998) that a negative linear relationship between $\Delta$TA and SST is due to colder water being indicative of greater upwelling of TA rich water.

This data set supports the argument that increased upwelling of CDW from strengthening westerly winds will increase OA in the Southern Ocean (Lenton et al., 2009). While the TA:DIC ratio for CDW is 1.040 ± 0.002, the TA:DIC$_{\text{calc}}$ ratio for surface waters between 75°S and the PF-S ranges from 1.046 to 1.064 (Fig. 5b). Therefore increased upwelling will lower the TA:DIC ratio and cause $\Omega_{\mathrm{Ar}}$ to decrease.

### 4.3 Estimate of wintertime surface $\Omega_{\mathrm{Ar}}$ values in the Ross Sea

Efforts to predict winter $\Omega_{\mathrm{Ar}}$ undersaturation in the Ross Sea are complicated by the complete lack of carbon system measurements from the winter months in the Ross Sea. McNeil et al. (2010) estimated winter surface water $\Omega_{\mathrm{Ar}}$ by using the lowest observed $\Omega_{\mathrm{Ar}}$ value from early spring when the Ross Sea is still covered by sea ice. They used mid-
October and early November carbon system measurements from the Joint Global Ocean Flux Study (JGOFS) (Sweeney et al., 2000b). Although sea-ice algae productivity peaks in November, its impact on water column DIC concentrations is likely to be negligible (Saenz and Arrigo, 2014). McNeil et al. (2010) found that early spring surface water $\Omega_{Ar}$ was $\sim 1.2$. There was a single $\Omega_{Ar}$ value < 1.1 that they used as an initial condition along with the IPCC US92a scenario to predict that surface waters of the Ross Sea could begin to experience seasonally undersaturated conditions with respect to aragonite as early as 2015 if full equilibrium with rising atmospheric CO$_2$ is achieved. Based on a three-dimensional coupled ice, atmosphere, and ocean model (Arrigo et al., 2003, Tagliabue and Arrigo, 2005), McNeil et al. (2010) argued that only 35 % of the atmospheric CO$_2$ signal equilibrates with Ross Sea surface waters due to sea ice, upwelling of CDW, and short residence times, thereby delaying the onset of aragonite undersaturation until 2045. Decadal wintertime surface carbon system measurements do not exist to directly validate this disequilibrium assumption. In addition, McNeil et al. (2010) would inaccurately predict when the Ross Sea would become undersaturated with respect to aragonite if the minimum wintertime surface $\Omega_{Ar}$ value used was low due to measurement error.

To independently calculate $\Omega_{Ar}$ from early spring surface waters, we use the LDEO pCO$_2$ measurements from November 1994, 1997, 2005, and 2006 that are from the Ross Shelf (defined by the 1000 m isopleth) and are south of 74° S (Fig. 7a). The earliest pCO$_2$ measurements are from 16 November 1994, 17 November 1997, 6 November 2005, and 13 November 2006 when much of the Ross Sea is still covered in sea ice. The earliest measurements from 2005/06 are more likely to represent winter conditions since they are from 74° S as the NBP entered the Ross Sea. Conversely, the earliest measurements from 1994/97 are from the 76.5° S line, close to where the Ross Sea polynya opens up from.

We calculate wintertime TA in the Ross Sea by establishing a salinity–TA relationship using data from Bates et al. (1998), Sweeney et al. (2000b), and our own hydrocast TA measurements from the upper 10 m (Fig. A1 in the Appendix). Since one unit of nitrate drawdown increases TA by one unit, the TA measurements are adjusted to winter nitrate concentrations of 29 µmol kg$^{-1}$ (the mean nitrate concentration between 200 and 400 m from our cruise). The relationship between TA and salinity is consistent among these independent data sets and the standard deviation of the residuals for TA is $\pm 5$ µmol kg$^{-1}$.

We calculate historical $\Omega_{Ar}$ using historical pCO$_2$ measurements, salinity-derived TA, SST, and salinity. Phosphate and silicate are set to the winter values of 2.1 and 79 µmol kg$^{-1}$, respectively. The TSG salinity data from the historical pCO$_2$ measurements appear reasonable and are uncalibrated. While the largest offset in TSG salinity compared with Autosal measurements is 0.3, such error is not typical. To test the possible impact of a poor salinity calibration, we recalculate $\Omega_{Ar}$ for all pCO$_2$ measurements after increasing salinity by 0.3. TA calculated from the observed TA–salinity relationship increases by $\sim 21$ µmol kg$^{-1}$ and $\Omega_{Ar}$ increases by 0.024 ± 0.003.

The lowest $\Omega_{Ar}$ measurements are 1.24 in 1994, 1.25 in 1997, 1.22 in 2005, and 1.20 in 2006 (Fig. 7b). Although $\Omega_{Ar}$ declines from 1994 to 2006, we have low confidence in any trend due to spatial–temporal sampling biases. The lowest $\Omega_{Ar}$ values are consistently between 1.2 and 1.3 as the ship crossed sea-ice-covered regions and open water that had experienced DIC drawdown. With the exception of a single measurement, the lowest 1996/97 $\Omega_{Ar}$ values from McNeil et al. (2010) are also $\sim 1.2$. The similarity between the $\Omega_{Ar}$ values reported by McNeil et al. (2010) from 1996/97 and our 2005/06 values is consistent with their delayed acidification hypothesis.

A simple calculation also suggests that wintertime $\Omega_{Ar}$ values may be closer to 1.2 than 1.1. If salinity is 34.5, approximately the mean salinity of the water column, TA would be 2339 µmol kg$^{-1}$ based on the observed TA–salinity linear relationship. Sweeney (2003) estimates winter pCO$_2$ values of $\sim 425$ µatm based on deep pCO$_2$ measurements made during early spring. Setting salinity to 34.5, TA to 2339 µmol kg$^{-1}$, pCO$_2$ to 425 µatm, temperature to $-1.89$, silicate to 79 µmol kg$^{-1}$, and phosphate to 2.1 µmol kg$^{-1}$ yields a $\Omega_{Ar}$ value of 1.22.

Although pCO$_2$ measurements of surface waters colder than $-1.75$ °C south of 60° S typically reach $\sim 410$ µatm by September, Takahashi et al. (2009) present a few measurements of $\sim 450$ µatm. Even if pCO$_2$ reaches 450 µatm during winter in the Ross Sea, $\Omega_{Ar}$ would be 1.16 (with salinity at 34.5 and TA at 2339 µmol kg$^{-1}$). In order to obtain $\Omega_{Ar}$ of 1.1, pCO$_2$ would need to be $\sim 480$ µatm, a value that appears unreasonably high given the available data sets from the Ross Sea.
McNeil et al. (2010) calculated the \( \Omega_{\text{Ar}} \) of water arriving onto the Ross Shelf following the recipes of Jacobs et al. (1985): 50 % CDW, 25 % \( \text{Tmin} \) water (minimum temperature in upper 100 m), and 25 % AASW. To calculate the \( \Omega_{\text{Ar}} \) of these three source water masses, they used hydrocast temperature, salinity, and DIC data collected during the austral winter of 1994 from north of the Ross Shelf as described in Sweeney (2003). They calculated that the average \( \Omega_{\text{Ar}} \) of incoming water would be 1.08.

We independently calculate \( \Omega_{\text{Ar}} \) of incoming water using the 2011 CLIVAR hydrocast data from north of the Ross Shelf between 168°E and 73°W as described earlier (Fig. 2b). The \( \Omega_{\text{Ar}} \) of water in the upper 100 m (AASW and \( \text{Tmin} \)) from the CLIVAR data set is 1.36 ± 0.13 and the \( \Omega_{\text{Ar}} \) of CDW (maximum temperature below 150 m) is 1.18 ± 0.03 (Fig. A2 in the Appendix). Even if 100 % of the incoming water onto the Ross Shelf is CDW, the \( \Omega_{\text{Ar}} \) of this incoming water would be greater than 1.08. While most properties of CDW are similar between the 2011 CLIVAR data and the 1994 data used by McNeil et al. (2010), the TA of CDW from the CLIVAR data set is 18 \( \mu \text{mol kg}^{-1} \) higher (Table 2).

Another approach to estimate the \( \Omega_{\text{Ar}} \) of winter surface waters is to use the properties of water below 200 m. For the TRACERS data, sTA below 200 m is 2338 ± 2 \( \mu \text{mol kg}^{-1} \). For the JGOFS autumn cruise (NBP 97-3) sTA below 200 m is 2339 ± 2 \( \mu \text{mol kg}^{-1} \). Using the CLIVAR data set, sTA of CDW from off the Ross Shelf is 2334 ± 3 \( \mu \text{mol kg}^{-1} \). This consistency between independent data sets suggests that we can accurately estimate winter TA in the Ross Sea.

The range in sDIC below 200 m is much greater than that for sTA (Table 2). The lowest value is 2220 ± 5 \( \mu \text{mol kg}^{-1} \) from our cruise and the highest is 2237 ± 3 \( \mu \text{mol kg}^{-1} \) from the summer JGOFS cruise (NBP 97-01). This range in sDIC concentrations below 200 m is not surprising given that sDIC concentrations vary across the input water masses. In addition, sDIC concentrations below 200 m will be influenced by carbon export particularly in summer and early autumn and over multiple seasons’ air-to-sea flux of \( \text{CO}_2 \).

Assuming that deep water concentrations of TA and DIC are relatively unmodified following wintertime deep convective mixing, we estimate the \( \Omega_{\text{Ar}} \) of winter surface water by setting TA to 2338 \( \mu \text{mol kg}^{-1} \), salinity to 34.5, temperature to −1.89 °C, phosphate to 2.1 \( \mu \text{mol kg}^{-1} \), and silicate to 79 \( \mu \text{mol kg}^{-1} \). If DIC concentrations are 2220 \( \mu \text{mol kg}^{-1} \), \( \Omega_{\text{Ar}} \) would be 1.37. If sDIC concentrations are 2237 \( \mu \text{mol kg}^{-1} \), \( \Omega_{\text{Ar}} \) would be 1.24 and \( p\text{CO}_2 \) would be 417 \( \mu \text{atm} \).

These results are consistent with a study by Matson et al. (2014) where early spring \( \Omega_{\text{Ar}} \) at 20 m depth calculated using pH and salinity-derived TA was 1.2–1.3 from Hut Point (bottom depth > 200 m) and Cape Evans (bottom depth < 30 m) in McMurdo Sound. In Prydz Bay, the lowest measured winter surface \( \Omega_{\text{Ar}} \) values were also ~1.2 for both 1993–1995 (Gibson and Trull, 1999; McNeil et al., 2011) and 2010–2011 (Roden et al., 2013). Weeber et al. (2015) using hydrocast data estimated that the \( \Omega_{\text{Ar}} \) of winter water in the Weddell Sea was ~1.3. In the Mertz Polynya, the lowest \( \Omega_{\text{Ar}} \) value at 100 m (below the mixed layer) was 1.2 (Shadwick et al., 2013). In Arthur Harbor on the western Antarctic Peninsula the lowest winter surface \( \Omega_{\text{Ar}} \) value was 1.31 (Schram et al., 2015).

A few studies find Antarctic winter \( \Omega_{\text{Ar}} \) values for surface water below 1.2. Hauri et al. (2015) used LDEO \( p\text{CO}_2 \) measurements and predicted TA from salinity to estimate winter \( \Omega_{\text{Ar}} \) values of surface water in the western Antarctic Peninsula. They found that 20 % of \( \Omega_{\text{Ar}} \) values were below 1.2 during the spring and winter, with a few winter values near undersaturation. It is not surprising that winter surface \( \Omega_{\text{Ar}} \) values are lower in the Antarctic Peninsula than the Ross Sea given less sea ice in the Peninsula. In another study, Kapsenberg et al. (2015) report \( \Omega_{\text{Ar}} \) at 18 m depth (bottom depth < 30 m) at two coastal sites in McMurdo Sound, the Jetty, and Cape Evans, for December–May and November–June, respectively, using pH and salinity-derived TA as input variables. The lowest \( \Omega_{\text{Ar}} \) observations were from May at both sites and were 1.22 and 0.96 at the Jetty and Cape Evans. The maximum calculated \( p\text{CO}_2 \) was 559 at Cape Evans. The low \( \Omega_{\text{Ar}} \) and high calculated \( p\text{CO}_2 \) values measured by Kapsenberg et al. (2015) may represent differences between coastal and open ocean systems – there may be a coastal amplification signal when sinking organic matter hits a shallow bed. Another possibility is that their carbon system time series, particularly at Cape Evans, is inaccurate. After conditioning and calibrating their pH measurements using discrete water samples, for logistical reasons Kapsenberg et al. (2015) could not collect additional validation samples during deployment or measure multiple carbon system parameters for crosscheck. Although the SeaFET pH sensors that they used are generally stable, they can drift (Bresnahan et al., 2014). Kapsenberg et al. (2015) have no means to assess possible pH sensor drift.

Following McNeil et al. (2010) and a Representative Concentration Pathway (RCP8.5) scenario (Meinshausen et al., 2011), we use the lowest \( \Omega_{\text{Ar}} \) values from 2006 (\( \Omega_{\text{Ar}} = 1.20\).
that while echinoid larvae can maintain calcification in high long term, especially for larvae. Stumpp et al. (2012) shows associated energy costs may be difficult to maintain over the 

Laternula elliptica

that the Antarctic bivalve tock et al., 2009). For instance, Cummings et al. (2011) showisms may be able to compensate for this dissolution (McClintock et al., 2014). In addition, the shells of post-mortem bivalves and pteropod larvae develop during the winter/spring (Gannefors et al., 2010) and could have dramatic ecological effects up the food web.

If the Ross Sea experiences aragonite undersaturation during winter in the future, live pteropod shells would start dissolving, making them more vulnerable to predation and bacterial infection (Bednaršek et al., 2012, 2014). In particular, pteropod larvae develop during the winter/spring (Gannefors et al., 2005; Hunt et al., 2008) and their shells have been shown to completely dissolve within weeks of exposure to aragonite undersaturation (Comeau et al., 2010). Declines in pteropod populations may reduce carbon export (Manno et al., 2010) and could have dramatic ecological effects up the food web.

Antarctic deep sea hydrocorals may also decline or disappear at the onset of aragonite undersaturation (Shadwick et al., 2014). In addition, the shells of post-mortem bivalves and brachiopods show significant dissolution within 2 months of exposure to undersaturated conditions, although live organisms may be able to compensate for this dissolution (McCintock et al., 2009). For instance, Cummings et al. (2011) show that the Antarctic bivalve Laternula elliptica can increase calcification in undersaturated conditions. However, the associated energy costs may be difficult to maintain over the long term, especially for larvae. Stumpp et al. (2012) shows that while echinoid larvae can maintain calcification in high pCO₂ treatments, increased energetic costs reduce growth rates and ultimately increase mortality. Larvae of the Antarctic sea urchin Sterechinus neumayeri and sea star Odontaster validus are smaller and exhibit abnormal development under elevated pCO₂ treatments (Byrne et al., 2013; Gonzalez-Bernat et al., 2013; Yu et al., 2013). In addition, the synergistic effects of warming and OA could impact echinoderm fertilization and embryo development (Ericson et al., 2012). Although it is not clear to what extent species may acclimatize or adapt (e.g., Suckling et al., 2015), the onset of aragonite undersaturation during winter months may have profound impacts on the Ross Sea ecosystem.

5 Conclusions

Our study demonstrates the possibility of setting up underway TA measurement systems. Although our system was relatively unattended, carbon system crosschecks and comparisons between hydrocast and underway data indicate that our measurements were accurate. Similar underway TA systems could be set up on scientific vessels and ships of opportunity in undersampled regions of the world’s oceans.

We find that the seasonal increase in OA in the Ross Sea by early autumn is driven almost entirely by phytoplankton photosynthesis. In the Southern Ocean between the Ross Sea and Chile we find that OA also increases mainly due to declining DIC-calc although declining TA partially counters the influence of declining DIC-calc. The influences of SST and salinity on OA are minimal in the Ross Sea and on our Southern Ocean transect.

We establish a salinity–TA relationship for the winter that is consistent across independent data sets. Using historical pCO₂ measurements from early spring along with TA predicted from salinity, we argue that it is unlikely that the Ross Sea actually experienced winter surface OA values of ~1.1 during 1996 (as per McNeil et al., 2010) and that a OA value of ~1.2 may more accurately represent current winter conditions.

Since predictions are sensitive to current surface winter-time OA values as well as the extent of disequilibrium, highly accurate carbon system measurements from the winter are crucial. It is also essential to measure more than two carbon system parameters for crosscheck. For instance, pH and pCO₂ sensors on moorings and floats could be used with TA predicted from salinity to calculate during the winter.

Our analysis indicates that the Ross Sea will not experience aragonite undersaturation until the year 2070 following RCP8.5. In some CO₂ stabilization scenarios, including RCP4.5 (Meinshausen et al., 2011), the Ross Sea may avoid becoming corrosive to aragonite.
Appendix A

Figure A1. Linear regression between TA and salinity with surface data from February to March 2013 (blue; this study), November to December 1994 (green; Bates et al., 1998), December to January 1995/1996 (red; Bates et al., 1998), and April 1997 (magenta; Sweeney et al., 2000a). TA has been corrected to a nitrate concentration of 29 µmol kg$^{-1}$ to account for the effects of nitrate drawdown on TA (Brewer and Goldman, 1976).

Figure A2. Profiles of aragonite saturation state ($\Omega_{\text{Ar}}$) from off the Ross Shelf (see Fig. 2b) from the CLIVAR program (NBP 11-02) calculated from TA, DIC, temperature, and salinity at surface pressures.
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