

**Ocean acidification  
state in western  
Antarctic surface  
waters**

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# Ocean acidification state in western Antarctic surface waters: drivers and interannual variability

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## Abstract

Each December during four years from 2006 to 2010, the surface water carbonate system was measured and investigated in the Amundsen Sea and Ross Sea, western Antarctica as part of the Oden Southern Ocean expeditions (OSO). The I/B *Oden* started in Punta Arenas in Chile and sailed southwest, passing through different regimes such as, the marginal/seasonal ice zone, fronts, coastal shelves, and polynyas. Discrete surface water was sampled underway for analysis of total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ) and pH. Two of these parameters were used together with sea-surface temperature (SST), and salinity to obtain a full description of the surface water carbonate system, including pH in situ and calcium carbonate saturation state of aragonite ( $\Omega_{Ar}$ ) and calcite ( $\Omega_{Ca}$ ). Multivariate analysis was used to investigate interannual variability and the major controls (sea-ice concentration, SST, salinity and chlorophyll *a*) on the variability in the carbonate system and  $\Omega$ . This analysis showed that SST and chlorophyll *a* were the major drivers of the  $\Omega$  variability in both the Amundsen and Ross seas. In 2007, the sea-ice edge was located further south and the area of the open polynya was relatively small compared to 2010. We found the lowest pH in situ (7.932) and  $\Omega = 1$  values in the sea-ice zone and in the coastal Amundsen Sea, nearby marine out flowing glaciers. In 2010, the sea-ice coverage was the largest and the areas of the open polynyas were the largest for the whole period. This year we found the lowest salinity and  $A_T$ , coinciding with highest chl *a*. This implies that the highest  $\Omega_{Ar}$  in 2010 was likely an effect of biological  $CO_2$  drawdown, which out-competed the dilution of carbonate ion concentration due to large melt water volumes. We predict and discuss future  $\Omega$  values, using our data and reported rates of oceanic uptake of anthropogenic  $CO_2$ , suggesting that the Amundsen Sea will become undersaturated with regard to aragonite about 20 yr sooner than predicted by models.

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## 1 Introduction

The fast ocean uptake of anthropogenic CO<sub>2</sub> from the atmosphere has caused a shift in the marine carbonate system towards lower carbonate ion concentration, [CO<sub>3</sub><sup>2-</sup>], and lower pH, so called ocean acidification (OA). Since the start of the industrial era, pH in the surface water has decreased with 0.1 units (30 %), and the annual mean [CO<sub>3</sub><sup>2-</sup>] by 10 % (Feely et al., 2004; Sabine et al., 2004; Orr et al., 2005). OA is predicted to be a major threat to marine organisms at all trophic levels and may substantially alter the marine ecosystem functioning (e.g. Fabry et al., 2008).

Polar oceans are particularly vulnerable to ocean acidification due to the cold and relatively fresh surface waters that has great potential for CO<sub>2</sub> uptake. These regions are also naturally high in CO<sub>2</sub> concentration and low in pH and [CO<sub>3</sub><sup>2-</sup>] (Fransson et al., 2009; Steinacher et al., 2009). In steady-state, or during longtime changes (> 100 000 yr), the marine carbonate system is buffered by carbonate minerals that reduce the effect of acidic input. However, when changes occur over a short time interval (< 10 000 yr), such as the one we are facing now, the ocean pH becomes very sensitive to CO<sub>2</sub> input (e.g. Calderia and Wickett, 2003). Surface waters are generally supersaturated in calcium carbonate (CaCO<sub>3</sub>), but recent studies show undersaturated values of aragonite (the metastable form of CaCO<sub>3</sub>) in the Arctic Ocean during summer (Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009). Models of ocean-carbon cycles based on Business-as-usual scenario IS92a predict aragonite to be undersaturated in the surface waters of the Southern Polar Ocean by 2100 (Calderia and Wickett, 2003; Orr et al., 2005). However, there are few observations of the natural variability of the carbonate system in the area south of 60° S, which results in large uncertainties in the model calculations and projections.

The carbonate system and the CaCO<sub>3</sub> saturation state ( $\Omega$ ) are affected by biogeochemical processes such as air-sea CO<sub>2</sub> exchange, primary production and respiration, physical upwelling, temperature and salinity changes, and sea-ice dynamics. These processes will become affected in the case of climate change such as warming,

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increased freshwater addition, and changes in sea-ice cover and extent, which may all impose feedbacks on OA.

The Southern Polar Ocean is already facing dramatic changes from progressing global warming, which is particularly evident in the western Antarctica, such as increased glacier melt off. The mean Antarctic sea-ice cover shows a slight increase of the decadal sea ice extent of 1.2% (Jacobs and Comiso, 1997; Kwok and Comiso, 2002). However, the sea-ice cover in the Bellingshausen-Amundsen Sea area shows drastic decreased ice cover by 5.7% per decade. On the other hand, in the Ross Sea the sea-ice extent has increased by 4.2% per decade (Jacobs and Comiso, 1997; Comiso and Nishio, 2008). The contrasting sea-ice extent trend observed in the western Antarctic seas is explained by changes in the direction and intensity of the atmospheric pressure forcing such as the Southern Annual Mode (SAM) (e.g. Stammerjohn et al., 2008). The Amundsen Sea is part of the region identified as a climatologically anomalous region (Jacob and Comiso 1997). The areas comprise of the Western Antarctic Ice Sheet (WAIS), where substantial thinning and melting of glaciers (Pine Island, Getz, Dotz and Thwaites Glacier) have been observed over the last decades (e.g. Rignot et al., 2008). The largest melt from the Pine Island Glaciers drains along the coastline of the Amundsen Sea. Increased melting of the base of the floating ice sheets indicates that the forcing comes from the oceans. It is suggested that warm Circumpolar Deep Water (CDW) enters the continental shelf and drives the melting of floating terminus of the Pine Island Glacier (Jacobs et al., 1996; Thoma et al., 2008; Arneborg et al., 2012). If increased freshwater from sea-ice and glacier melt would lead to a decrease in  $\Omega$ , such as found in the Arctic Ocean, there is a large potential that further glacier melt off in this area has the potential to advance ocean acidification (Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009).

SAM also affects the westerly winds and model studies suggest that increased wind-induced upwelling driven by increased westerly winds, will lead to an increase of upwelling of CO<sub>2</sub>-rich subsurface water. This could result in a decreased oceanic CO<sub>2</sub>

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sink and perhaps shift the Southern Polar Ocean to act as an oceanic CO<sub>2</sub> source to the atmosphere (LeQuéré et al., 2007).

Biological processes has a large impact on the natural variability of carbonate system and calcium carbonate saturation state ( $\Omega$ ) in polar oceans (e.g. Chierici et al., 2011).

The Amundsen Polynya (AmP) and Ross Sea polynya (RSP) are among the most biologically productive areas in the Southern Ocean (Arrigo and van Dijken, 2003). A change in the primary production or in the efficiency of biological carbon uptake may have consequences for the OA and air-sea CO<sub>2</sub> exchange. In the Southern Polar Ocean, biological processes are closely connected to the sea-ice cover. Thus, it is likely that a change in sea-ice concentration and extent will affect both the carbonate system and the biological carbon uptake.

Calcite and aragonite are biogenically produced CaCO<sub>3</sub> and they are rarely formed inorganically. Calcite is the stable form and aragonite is the meta-stable form, which is given by their different solubility products,  $K_{sp}$ . The saturation state ( $\Omega$ ) is the thermodynamic potential to dissolve a mineral, when  $\Omega > 1$  the mineral will be kept in solid state, and when  $\Omega < 1$ , the mineral will dissolve.  $\Omega$  is expressed by the product of the concentrations of calcium ions [Ca<sup>2+</sup>] and [CO<sub>3</sub><sup>2-</sup>] in sea water divided by the  $K_{sp}$ , at a given temperature, salinity and pressure. [Ca<sup>2+</sup>] is linearly related to salinity and is generally in excess concentration in the ocean. The saturation state for CaCO<sub>3</sub> ( $\Omega$ ) is expressed in Eq. (1):

$$\Omega = [\text{CO}_3^{2-}] \cdot [\text{Ca}^{2+}] / K_{sp} \quad (1)$$

The carbonate-system parameters and  $\Omega$  are key variables to monitor the state of ocean acidification and give information on the dissolution state of shells and skeleton. In the polar oceans, attention has been drawn to aragonite-forming organisms, since aragonite is the least stable form of CaCO<sub>3</sub> and they may become the first organisms affected by ocean acidification (Lischka and Riebesell, 2012). Shelled pteropods are the dominating calcareous organism, which are important for the food web in the Southern Polar Ocean (SPO). Several reports show that the aragonite forming pteropod

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*Limacina helicina* is affected by both warming and high CO<sub>2</sub> levels. A study made by Bednarsek et al. (2012) showed that *Limacina helicina* was negatively affected by OA. Comeau et al. (2010) found that *L. helicina* was especially sensitive for low  $\Omega_{Ar}$  in combination with higher temperature and high CO<sub>2</sub>-levels. Except for calcification, experiments on non-calcifying organisms show effects due to a lower pH through changes in their enzymatic processes, and internal membrane functioning such as, ion-pump functioning, and protein synthesis (Gattuso and Hansson, 2009 and references therein). Changes in pH may also affect the bio-availability of important micro-nutrients such as iron and manganese (Breitbarth et al., 2010), which may have large consequences in the SPO where iron limitation controls primary production. To perform realistic experiments on the effects of OA on marine organisms it is important to have information on the organisms and their natural chemical environment with relevant pH and pCO<sub>2</sub> levels.

Here, we present four years of unique data of the carbonate system (pH,  $C_T$ ,  $A_T$ ) and estimates of  $\Omega$  in the surface water, from the nearly unexplored Amundsen Sea, and the more well studied Ross Sea. Data is discussed in relation to sea-ice concentration and melt water, salinity (S), sea-surface temperature (SST), and chlorophyll *a* levels (chl *a*). Main aims for the study is to: (1) present the current surface-water carbonate system and ocean acidification state in the Amundsen Sea and Ross Sea; (2) investigate the interannual variability of carbonate system parameters and  $\Omega$  during four years; and (3) use multivariate analysis to investigate the major processes affecting the variability in  $\Omega$ . Moreover, we use reported estimates of oceanic uptake of anthropogenic CO<sub>2</sub> to make preliminary estimates of the future projection of aragonite saturation in western Antarctic surface waters.

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## 2 Methods

### 2.1 Determination of the carbonate system

Discrete water samples were collected through stainless steel tubing from the ship's water intake ( $\sim 8$  m depth) for analysis of total alkalinity ( $A_T$ ), pH, and total dissolved inorganic carbon ( $C_T$ ).  $A_T$  and pH were measured onboard, on all four cruises, whereas  $C_T$  was only measured for samples collected in 2006 (Table 1). The methods for sampling and analysis of  $A_T$ , pH and  $C_T$  follow the state-of-the-art procedures fully described in Dickson et al. (2007). In 2006, seawater samples were preserved with mercuric chloride and stored dark at  $4^\circ\text{C}$  until  $C_T$  determination using extraction of acidified seawater and coulometric titration with photometric detection at the Department of Chemistry and Molecular Biology, University of Gothenburg, Göteborg, Sweden.

$A_T$  was determined by potentiometric titration in an open cell with 0.05 M hydrochloric acid (HCl), and the equilibrium point was determined by Gran evaluation as described in Haraldsson et al. (1997). The precision of  $A_T$  and  $C_T$  values were investigated at a daily basis from triplicate analysis of one sample, and was for  $A_T$  and  $C_T \pm 3 \mu\text{mol kg}^{-1}$  and  $\pm 2 \mu\text{mol kg}^{-1}$ , respectively. The accuracy of  $A_T$  and  $C_T$  were controlled using Certified Reference Material (CRM) supplied by A. Dickson (San Diego, USA). pH was determined spectrophotometrically (Diode-array spectrophotometer, HP8452 and HP8453 (from 2008) using a 2 mM solution of the sulphonaphtalein dye, m-cresol purple, as an indicator (Clayton and Byrne, 1993). Perturbation of indicator pH was corrected using the formulation described in Chierici et al. (1999).

$C_T$  was measured in 2006, and calculated from  $A_T$ , pH and SST and salinity for the other years. A pair of the parameters  $A_T$ ,  $C_T$ , and pH, salinity and temperature were used as input parameters in a  $\text{CO}_2$ -chemical speciation model (CO2SYS program, Pierrot et al., 2006) to calculate the full carbonate system including pH in situ, carbonate ion concentration ( $[\text{CO}_3^{2-}]$ ), and  $\text{CaCO}_3$  saturation of calcite and aragonite ( $\Omega_{\text{Ca}}$  and  $\Omega_{\text{Ar}}$ , respectively). We used the carbonate system dissolution constants from Roy

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et al. (1993, 1994), since they are well suited for polar surface waters (Chierici et al., 2004; Chierici and Fransson, 2009). The calculations were performed on the total hydrogen ion scale, and we used the  $\text{HSO}_4^-$  dissociation constant of Dickson (1990). The concentration of calcium,  $[\text{Ca}^{2+}]$  is assumed to be proportional to the salinity according to  $(10.28 \cdot S/35 \mu\text{mol kg}^{-1})$ . The thermodynamic solubility products for aragonite and calcite (Ksp) are from Mucci (1983).

## 2.2 Determination of continuous measurements of SST, salinity and chl *a*

Sensors for SST, salinity (thermosalinograph SBE-21, Seabird electronics Inc.) and chlorophyll *a* (chl *a*, MiniTracka II, Chelsea instruments) were connected to seawater intake for continuous measurements (1 min mean values). The calibration of the chl *a* sensor was performed in 2007/08 using conventional techniques for chl *a* determination, full details on the calibration of the chl *a* sensor are described in Chierici et al. (2012). A temperature sensor was placed at the seawater intake to record the temperature of the incoming surface water.

## 2.3 Statistical analysis on interannual variability and major drivers of $\Omega$

Multivariate analysis is a helpful tool to explore trends, outliers and to perform quality control in complex systems and data sets. Here we use the Simca P+ (Umetrics, I. Simca P+, vs: 12.0.1.0) to perform Principal Components Analysis (PCA) and Orthogonal Partial Least Squares (OPLS), which are projection methods that reduce dimensionality in data using the correlations in data. The information is given in two plots; score and loading, the score plot summarizes the observations and observe patterns, trends and clusters. The loading plot summarizes the variables and explain the position of the observations in the score plot. The PCA analysis was used to investigate the interannual variability in the whole data set. OPLS is a further development from PCA (Trygg and Wold, 2002). OPLS is a regression method that finds information in the *x*-data which is related to the *y*-data to make predictions. Here we use OPLS to

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investigate the major drivers explaining the variability in  $\Omega$ . The OPLS analysis was performed with  $\Omega_{Ar}$  as  $y$ -variable and one of  $A_T/C_T/pH^{15}/chl\ a/SST/salinity$  as  $x$ -variables. Two models were made; one for Amundsen Sea and one for Ross Sea.

### 3 Study area

This study uses data from measurements performed in the Pacific sector of the Southern Ocean, focusing on the western Antarctic surface water in the Amundsen Sea (65° S to 75° S; 90° W to 120° W, including Amundsen Sea Polynya) and Ross Sea (70° S to 78° S; 145° W to 180° W, including the Ross Sea Polynya). This data was obtained during four austral summers (December to January) onboard the Swedish icebreaker I/B *Oden* as part of the Swedish-USA collaboration on the Oden Southern Ocean (OSO) expeditions: OSO2006, OSO2007/2008, OSO2008/2009 and OSO2010/2011. Figure 1 shows the cruise tracks for the four expeditions, and Table 1 summarizes the expedition dates, start location, and the main scientific study area for each year. Typically, the OSO expeditions started in Punta Arenas, Chile in beginning of December. All expeditions ended in McMurdo Sound, Ross Sea, Antarctica. The expeditions passed through different regimes; permanently open ocean zone (POOZ), the seasonal ice zone (SIZ), and open polynyas. The SIZ is defined as the area between the maximum (usually in September) and the minimum sea-ice extent (usually in February) and covers the area from the Polar Front (APF) in the north to the Antarctic ice shelf in the south. This area is also referred to as the Antarctic Zone (AZ), and is the focus for this study. Several polynyas are found along the west coast of the Antarctic continent (Arrigo and van Dijken, 2003). Polynyas are areas of open water or reduced sea ice cover located in the sea ice. For all four expeditions we passed the Ross Sea Polynya (RSP) and, except for in 2006, we entered the Amundsen Polynya (AmP, Fig. 1). These polynyas are kept ice free by strong consistent katabatic winds (formed over inland glaciers) that transport newly formed frazil ice away from the ice edge (Arrigo, 2007) and are maintained by upwelling of relatively warm (up to  $\sim 1^\circ\text{C}$ ) modified

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Continental Deep Water (mCDW). In 2006, large part of the expedition was spent in at the northern extent of the sea-ice edge and in the SIZ, but did not enter the Amundsen Sea (AmS). In the three other years (2007/2008, 2008/2009 and 2010/2011), most of the scientific focus was in the sea ice in the Amundsen Sea and its polynya (AmP). In 2007/2008 substantial expedition time was spent in the open polynya and in coastal Amundsen Sea and Ross Sea. The Ross Sea and RSP were covered all four years.

### 3.1 Hydrography

The area south of 60° S is marked by a sharp temperature gradient and salinity decrease (Fig. 2b), which denotes the Antarctic Polar Front (APF), and the entrance to the Polar Frontal Zone (PFZ, Fig. 2a). The APF marks the location where Antarctic surface water (AASW) meets subantarctic waters, sinks beneath it and creates a shallow mixed layer (Deacon, 1933). Further south, on the coastal shelves in western Antarctica, relatively warm Circumpolar Deep Water (CDW) enters the continental shelf through troughs and mixes with fresh and cold AASW becoming mCDW (i.e. Arneborg et al., 2012). Our main study area lies in the area south of 60° S, including the PFZ, the coastal shelves of Amundsen Sea and Ross Sea, and their polynyas.

SST and salinity varied between years to some extent due to different cruise tracks (Fig. 2a and b). Generally SST varied between 7.5 °C and -2 °C, with minimum SST in the AZ between 68° S and 70° S. SST increased entering the AmP and RSP. At approximately 60° S, the SST drastically decreased from ~3 °C to ~0.5 °C denoting the entrance to PFZ. In 2006, the PFZ was reached further south due to the more north-westerly cruise track (see Chierici et al., 2012 for details on 2006 expedition). After entering the PFZ and moving southward, SST continued to decrease (1 to -1.5 °C) and salinity varied between 33.7 and 34.0 (Fig. 2a and Fig. 2b). The sea-ice edge was reached at 67–69° S and the date and location of reaching the December ice edge for each year is summarized in Table 2. Here, SST was just above freezing point (-1.2 and -1.8 °C) and salinity varied between 33.6 and 34.0. Minimum salinity of 33.3 was found in 2010, between 66° S and 68° S (Fig. 2b). SST increased entering the AmP and RSP,

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and the warmest water ( $\geq 0^\circ\text{C}$ ) was found close to the coast and in the open polynyas. The coldest surface water was found in the AmS close to Pine Island Bay, where two of the largest glaciers found in Antarctica, Pine Island Glacier (PIG) and Thwaites Glacier (TG), drain melt water to the ocean. In AmS, salinity was the lowest to the east (33.6) and increased to the west coast ( $> 33.9$  at  $115^\circ\text{W}$ ) (Fig. 2b). The warmest and most saline water south of the December ice edge was found in RSP (Fig. 2a and Fig. 2b).

### 3.2 Sea ice extent and concentration

The seasonal and interannual variability of sea-ice extent and concentration were investigated using remotely sensed observations on the sea-ice distribution, and concentration from the Advanced Microwave Scanning Radiometer (AMSR-E) from University of Bremen (Spreen et al., 2008). The winter (September) sea-ice distribution was larger and extended further north in the Ross Sea, relative to the Amundsen Sea, and remained throughout December (Fig. 3a). The decrease in sea-ice concentration in the Ross Sea in December was due to the opening of the RSP. In the Amundsen Sea, sea-ice distribution showed larger seasonal and interannual variability than in the Ross Sea. For example, the December sea ice reached further north in 2010 than other years (Fig. 3b). In mid-February almost all sea ice has disappeared (not shown). It was obvious that the size of the open polynyas differed between years, particularly evident in the RSP (Fig. 4a to 4d). Generally, maximum December sea-ice concentration was found in 2010, and minimum in 2007 (Fig. 4b and 4d). However, the open areas of the RSP and AmP were the smallest in 2006 and 2007, and the largest in 2008 and 2010 (Fig. 4a to 4d). In December 2010, the coastal areas were completely open, connecting the two polynyas.

### 3.3 Chlorophyll *a*

Chlorophyll *a* (chl *a*) was used as to investigate the influence of primary production for the variability of the carbonate system and  $\Omega$ . During phytoplankton growth  $\text{CO}_2$  is

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consumed through photosynthesis and the  $[\text{CO}_2]$  in the surface water decreases. This leads to higher  $[\text{CO}_3^{2-}]$ , consequently higher  $\Omega$  in the surface layer during phytoplankton blooms.

Chl *a* peaked in the PFZ and at the ice edge, particularly evident in 2010, when chl *a* was up to six times higher than in the other areas (Fig. 5). Elevated chl *a* in 2010 at the ice edge, coincided with a drastic salinity decrease, indicating the influence of sea-ice melt water (Fig. 2b). Chl *a* drastically increased entering the AmP and RSP, and chl *a* exceeded  $10 \mu\text{L}^{-1}$ , which was the maximum range for chl *a* sensor. In the SIZ and at the coast of the Amundsen Sea chl *a* values were generally low ( $< 1 \mu\text{L}^{-1}$ , Fig. 5).

## 4 Results

### 4.1 Variability of the carbonate system and $\Omega$

Figure 6a–f shows the latitudinal surface water variability of  $A_T$ ,  $C_T$ , pH at  $15^\circ\text{C}$  ( $\text{pH}^{15}$ ), pH in situ,  $\Omega_{\text{Ar}}$ , and  $\Omega_{\text{Ca}}$  for all four years. Denotations show the location of the December sea-ice edge for each year, the zones and the polynyas in the Amundsen Sea (AmP) and Ross Sea (RSP) in each figure. All carbonate system parameters showed modest variability in the PFZ north of  $65^\circ\text{S}$  before reaching the ice edge, where  $A_T$ ,  $C_T$ , and  $\text{pH}^{15}$  values were approximately  $2290 \mu\text{mol kg}^{-1}$ ,  $2170 \mu\text{mol kg}^{-1}$ , and 7.82, respectively (Fig. 6a to 6c). At the ice edge,  $A_T$  dropped to the lowest value of  $2258 \mu\text{mol kg}^{-1}$  (in 2010, Fig. 6a), coinciding with a salinity decrease (Fig. 2b). Before the ice edge,  $\Omega_{\text{Ar}}$ , and  $\Omega_{\text{Ca}}$  were relatively stable of about 1.4 and 2.2, respectively (Fig. 6e and 6f). Between the PFZ and the AmS,  $A_T$  and  $C_T$  increased by approximately  $50 \mu\text{mol kg}^{-1}$  and  $100 \mu\text{mol kg}^{-1}$ , respectively. This coincided with decreased  $\text{pH}^{15}$  and pH in situ by approximately 0.25 and  $\Omega_{\text{Ar}}$  by the maximum of 0.6 units (Fig. 6c, 6d, and 6e). The carbonate system differed greatly between the two polynyas. Generally,  $A_T$  and  $\Omega_{\text{Ar}}$  was lower in the AmP relative to the RSP (Fig. 6e), likely related to the fresher

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water in the AmP. Entering the RSP,  $C_T$  decreased drastically in all years, reaching the minimum of  $1989 \mu\text{mol kg}^{-1}$  in 2010 (Fig. 6b, Table 3). This year, we observed the highest pH in situ of 8.47 (Fig. 6c, Table 3), and highest  $\Omega_{Ar}$  (3.3.) and  $\Omega_{Ca}$  (5.2), which was likely an effect of high phytoplankton production (i.e. high chl *a*, Fig. 5).

We calculated mean values for each year, which were compared to the four-year mean values to investigate the interannual variability, summarized in Table 3. In 2010, we observed the lowest  $A_T$  and  $C_T$ , about 40 and  $178 \mu\text{mol kg}^{-1}$  lower than the four-year mean values. This may be linked to the presence of low-salinity water, in combination with the high primary production in this year, relative to other years. In RSP, the values of all parameters, except  $C_T$ , increased for all years, most evident in 2006 and 2010 (Fig. 6a to 6f). The lowest pH in situ (7.932) and the lowest  $\Omega_{Ar}$  (1.0) and  $\Omega_{Ca}$  (1.6) were found in the AmP, most evident in 2007 (Fig. 6d to 6f). A close-up of the Amundsen Sea in 2007, show low pH and low  $\Omega_{Ar}$  in the sea-ice area and that values increase as approaching the coastal AmP, except for the lowest pH in situ and lowest  $\Omega_{Ar}$  value located close to the Thwaites glacier in the Pine Island Bay area (Fig. 7a and b). In 2010, the stations were located in the ice-covered part of AmP, where  $\Omega_{Ar}$  and pH in situ were higher than in 2007 (Fig. 8a and 8b). This was likely the result of  $\text{CO}_2$  decrease during phytoplankton production indicated by the high chl *a* in 2010, in the AmP (Fig. 5). The same trend was observed in the RSP, and pH in situ and  $\Omega_{Ar}$  was lower in 2007 than in 2010 (Fig. 9a and 9b). In 2010, the areas of the open AmP and RSP were larger than in 2007, which may have promoted primary production (Fig. 4b and 4d). In the AmP and coastal RSP,  $\Omega_{Ar}$  was between 1.0 and 1.5 in 2007, which was lower than in 2010 (Fig. 7a to Fig. 10a). The largest  $\Omega_{Ar}$  difference between the two years was found in the eastern RSP, where  $\Omega_{Ar}$  was about 1.2 units lower in 2007 relative to 2010 (Fig. 9 and Fig. 10a). This was likely due to the difference in the strength of biological production between the two years, as observed from the chl *a* variability.

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## 4.2 Interannual variability based on multivariate analysis

Principal Component Analysis (PCA) was used to investigate interannual differences in the data set. A PCA analysis was performed on the full data set for all cruises and variables (SST, salinity, chl *a*,  $A_T$ ,  $\text{pH}^{15}$ ,  $C_T$  and pH in situ). The model was validated against the goodness of fit ( $R^2X$ ), and goodness of prediction ( $Q^2$ ). Observations and variables are summarized in a combined PCA score loading plot (Fig. 11). Loading vector ( $\boldsymbol{p}$ ) and score vector ( $\boldsymbol{t}$ ) are displayed correlation scaled as vector  $\boldsymbol{p}(\text{corr})$  and  $\boldsymbol{t}(\text{corr})$ . The PCA show little variability between years and there were no major clusters or obvious divergence between the four years (Fig. 11). However, the PCA identify that data from OSO2007/08 was mainly distributed towards high  $C_T$  and that data from OSO2010/11 was highly influenced by low salinity and low  $A_T$ . This agrees with the latitudinal distribution of salinity and  $A_T$  (Figs. 2b and Fig. 6a). The data points with large range, distributed to the far right in the PCA plot, were all located in the polynyas (Fig. 11).

## 5 Discussion

The latitudinal distribution and the multivariate analysis indicate interannual variability in the carbonate system and  $\Omega$ , which were likely linked to differences in sea-ice concentration, chl *a*, and salinity (i.e. freshwater). For example, the large winter ice extent and ice concentration in 2010 remained until December, in both AmS and RS, which may have caused large volumes of melt water resulting in a fresh, stratified summer surface layer. This also explains the low salinities and low  $A_T$  encountered in 2010, relative to the other years. Generally sea-ice melt water results in low  $\Omega$  due to dilution of  $\text{CO}_3^{2-}$ , as observed in the Arctic Ocean (Chierici and Fransson, 2009; Yamamoto-Kawai et al., 2009). This was not the case in our study, where we found the highest mean  $\Omega$  values in 2010, coinciding with high chl *a* levels and relatively low  $C_T$  (Table 3). Extremely high chl *a* ( $> 40 \mu\text{L}^{-1}$ , P. Yager, personal communication, 2011) was

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measured during a parallel expedition in the AmP in 2010 (ASPIRE-project, RV N.B. Palmer). This indicates that the positive effects on  $\Omega$  due to primary production (biological  $\text{CO}_2$  uptake) were out-competing the dilution of  $\text{CO}_3^{2-}$  from melt water in 2010. In 2007, the lowest  $\Omega$  in AmP may be due to less biological  $\text{CO}_2$  drawdown, also indicated by the high  $C_T$  values in the PCA analysis. The area of the open AmP was smaller in December 2007, and the low  $\Omega$  was perhaps more influenced by melt-water dilution, and less by primary production this year. The timing of the polynya opening may also play a large role affecting the  $\Omega$  variability. To investigate the main drivers and their contribution to the  $\Omega_{Ar}$  variability, we perform a multivariate statistics using an OPLS model (see method section for details). The results from this exercise show that pH and  $C_T$  have the strongest contribution, and  $A_T$  have low influence on the variability of  $\Omega$  (Fig. 12). This indicates that the processes, which directly affect  $\text{CO}_2$ , such as phytoplankton production and SST changes, have the largest effect on  $\Omega$ . This is also indicated by the large influence of chl *a* and SST, which have similar impact, and salinity has small contribution to  $\Omega$  variability (Fig. 12). According to the OPLS evaluation, salinity and  $A_T$  have stronger influence on  $\Omega$  in the AmS compared to the RS that was more influenced by SST and chl *a*. This is interesting since that implies that the  $\Omega$  in the AmS may be more sensitive to further freshening due to glacial and sea-ice melt than the RS. On the other hand, a change in the biological processes and temperature may have larger influence on the  $\text{CaCO}_3$  saturation state in the RS. However, there were no statistically significant differences between the drivers for the two regions.

As anthropogenic  $\text{CO}_2$  increases in the atmosphere, a corresponding increase in surface-water  $C_T$  may be expected. Sabine et al. (2008) determined the decadal increase of  $C_T$  due to oceanic uptake of anthropogenic  $\text{CO}_2$  to  $5\text{--}10\ \mu\text{mol kg}^{-1}\ \text{decade}^{-1}$  in the Pacific sector of the Southern Ocean ( $> 55^\circ\ \text{S}$ ) for the period from 1991 to 2006. Assuming a decadal increase of  $10\ \mu\text{mol kg}^{-1}$  and  $A_T$ , SST and salinity from our study, the sea-ice covered part of the Ross Sea and Amundsen Sea, and coastal AmS will experience  $\Omega_{Ar} < 1$  already by 2026–2030 (Fig. 13b). This is about 20 yr sooner than predicted by Orr et al. (2005). In additional 20 yr, almost all area will become

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undersaturated with regard to aragonite, except for coastal RSP (Fig. 13c). This estimate is based on steady-state and no changes in biological and physical processes. However, it is likely that these processes will change, possibly linked to changes in sea-ice extent and freshwater addition. During the last 30 yr, sea-ice duration has decreased in the Amundsen Sea and increased in the Ross Sea (e.g. Stammerjohn et al., 2008). The December anomalies from remotely sensed derived sea-ice concentration in the period 1979–2000 (Fetterer et al., 2002) show that except for year 2010, the sea-ice concentration was anomalously low in the Amundsen Sea and high in the Ross Sea in our study period (Fig. 14). Based on our study, we found the lowest  $\Omega$  in the Amundsen Sea in years of anomalously low sea-ice concentration (e.g. 2007). Assuming the 30 yr decreasing sea-ice trend, it is likely that  $\Omega$  will continue to decrease. On the other hand, increased sea-ice duration, similar to the situation in 2010, would probably result in increased primary production and increased  $\Omega$  values. In addition, reports show that the most significant losses in the marine glaciers have occurred across the AmS coastline, leading to increased discharge of glacier melt water due to increased upwelling of warm Circumpolar Deep Water (e.g. Thoma et al., 2008; Arneborg et al., 2012).

## 6 Conclusions

Our study indicates that increased freshwater (i.e. sea-ice melt water) may enhance biological  $\text{CO}_2$  drawdown leading to increased  $\Omega$  in summer. However, increased upwelling of  $\text{CO}_2$ -rich subsurface water may counteract the increased  $\Omega$  and advance ocean acidification in the Southern Polar Ocean. It is ultimately the net effect of increased freshening, sea-ice formation and melt, upwelling, and warming that will decide the direction and strength of continued air-sea  $\text{CO}_2$  uptake and the  $\text{CaCO}_3$  saturation state. Our study confirms the necessity of long-term monitoring in the polar areas, to deduce the carbonate system trends and the final effect of climate change driven feedbacks on the air-sea  $\text{CO}_2$  exchange and ocean acidification in polar oceans.

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**Table 1.** Summary of cruise dates, start location, measured carbonate system parameters, and the main study area for each year. All expeditions ended in McMurdo Sound, Ross Sea. Continuous surface water measurements of chlorophyll *a*, sea surface temperature (SST), and salinity (*S*) were performed during all four cruises. AmS denote the Amundsen Sea and SIZ refers to the seasonal ice zone.

Expedition	Cruise dates	Start location	Measured parameters	Main study area
OSO2006	12/12/2006–26/12/2006	P. Arenas (Chile)	$C_T$ , $A_T$ and pH	SIZ, Ross Sea
OSO2007/2008	1/12/2007–3/01/2008	P. Arenas (Chile)	$A_T$ and pH	AmS: open polynya and coastal AmS
OSO2008/2009	1/12/2008–8/01/2009	Montevideo (Uruguay), P. Arenas (Chile)	$A_T$ and pH	AmS, SIZ
OSO2010/2011	08/12/2010–11/01/2011	P. Arenas (Chile)	$A_T$ and pH	AmS, SIZ, coastal Ross Sea

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**Table 2.** Dates and positions for the arrival at the sea-ice edge, and the approximate date for the opening of the Amundsen Sea Polynya (AmP) and the Ross Sea Polynya (RSP), are summarized for each expedition.

Expedition	Date and position of Sea Ice Edge (Position, Date)	Opening of AmP	Opening of RSP
OSO2006	140° W; 68° S, 22/12/2006	10 October	1 November
OSO2007/2008	102° W; 68° S, 08/12/2007	15 October	12 November
OSO2008/2009	86° W; 69° S, 08/12/2008	10 October	5 November
OSO2010/2011	90° W; 67° S, 15/12/2010	1 October	3 November

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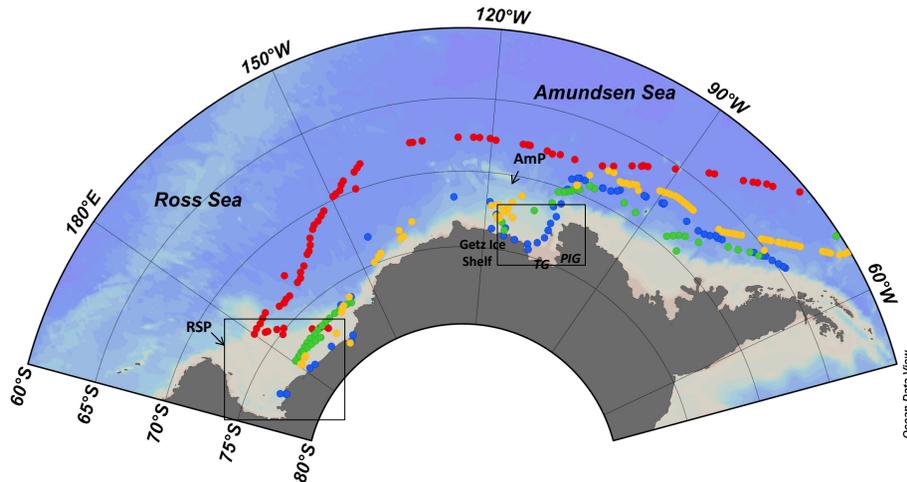
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**Table 3.** Summary of the mean values and variability of the carbonate system parameters, total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ), pH on total scale at 15 °C ( $\text{pH}^{15}$ ), pH on total scale at in situ temperature (pH in situ), aragonite saturation ( $\Omega_{Ar}$ ), and calcite saturation ( $\Omega_{Ca}$ ). N denotes number of data points used in the study for each year. Minimum and maximum values are denoted min and max, respectively.

Expedition	$A_T$ ( $\mu\text{mol kg}^{-1}$ )	min/ max	$C_T$ ( $\mu\text{mol kg}^{-1}$ )	min/ max	$\text{pH}^{15}$	min/ max	pH in situ	min/ max	$\Omega_{Ar}$	min/ max	$\Omega_{Ca}$	min/ max	N
OSO2006	2304 ± 16	2277/ 2353	2176 ± 23	2093/ 2216	7.829 ± 0.072	7.733/ 8.094	8.092 ± 0.070	8.004/ 8.376	1.50 ± 0.29	1.18/ 2.60	2.39 ± 0.46	1.89/ 4.16	48
OSO2007/08	2294 ± 15	2264/ 2343	2172 ± 30	2104/ 2225	7.813 ± 0.074	7.675/ 7.970	8.080 ± 0.077	7.932/ 8.244	1.44 ± 0.23	1.03/ 2.05	2.29 ± 0.38	1.64/ 3.27	56
OSO2008/09	2304 ± 19	2274/ 2344	2172 ± 37	2005/ 2210	7.836 ± 0.098	7.710/ 8.180	8.089 ± 0.098	7.976/ 8.443	1.54 ± 0.38	1.11/ 3.02	2.46 ± 0.60	1.77/ 4.82	53
OSO2010/11	2288 ± 15	2258/ 2326	2149 ± 44	1989/ 2211	7.857 ± 0.109	7.730/ 8.220	8.113 ± 0.110	7.968/ 8.471	1.61 ± 0.46	1.19/ 3.28	2.57 ± 0.74	1.90/ 5.23	64
Mean for all expeditions	2298		2167		7.834		8.094		1.52		2.43		

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**Fig. 1.** The cruise tracks and sampling locations (dots) for the Oden Southern Ocean expeditions in: 2006 (red), August 2007 (blue), September 2008 (green) and in November 2010 (yellow), respectively. The squares show the approximate locations of the polynyas in the Amundsen and Ross seas. TG and PIG denote Thwaites Glacier, Pine Island Glacier, respectively.

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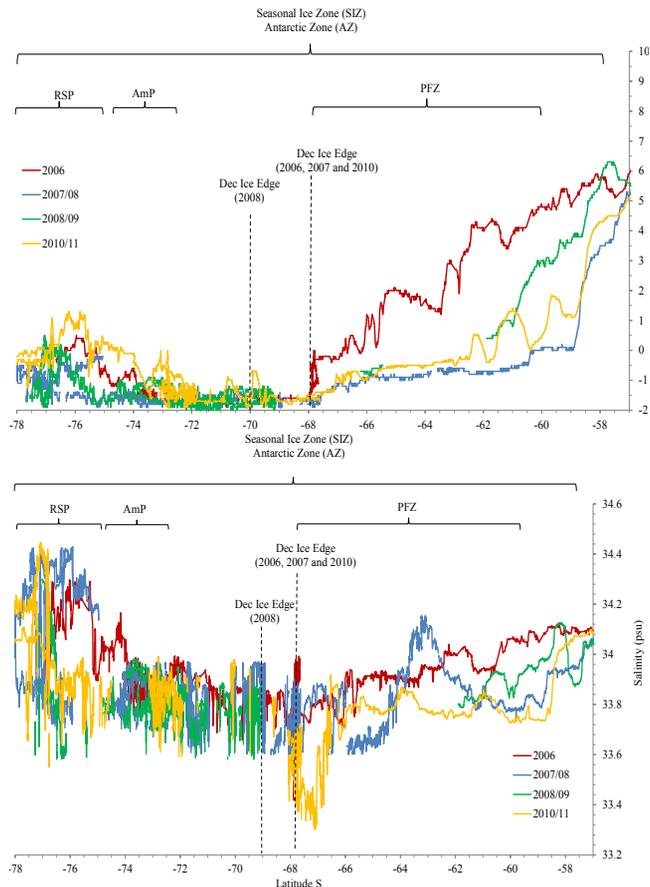
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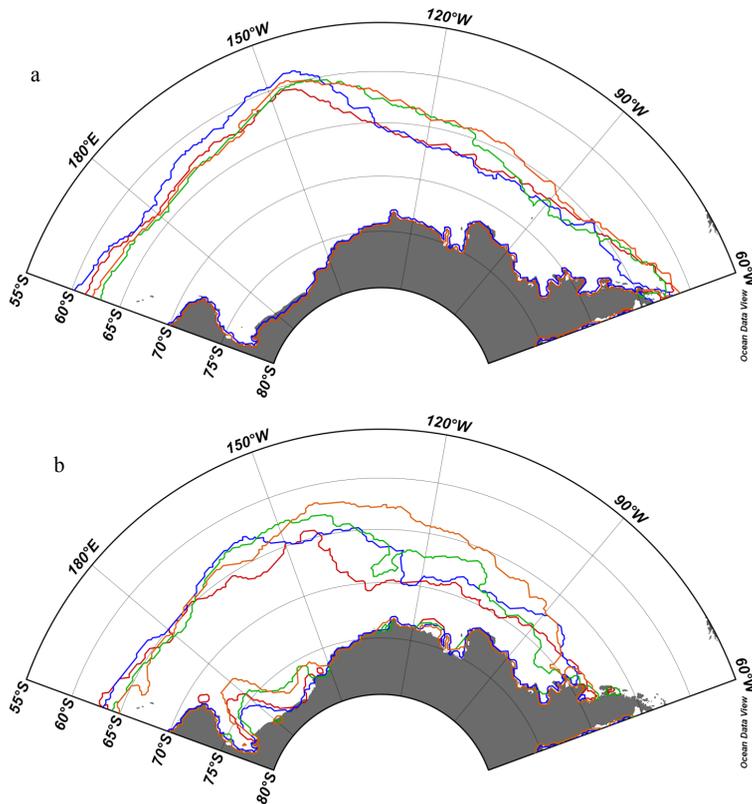
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**Fig. 2.** The variability of (a) sea surface temperature (SST, °C), and (b) salinity (S), versus latitude for the four OSO expeditions (2006: red; August 2007: blue; September 2008: green; November 2010: yellow). We indicate the location of the Seasonal Ice Zone (SIZ), the Polar Frontal Zone (PFZ), the polynyas in the Amundsen Sea (AmP) and the Ross Sea (RSP). The location of the sea-ice edge in December for each year is shown as a dashed line.



**Fig. 3.** The monthly average sea-ice extent from AMSR-E in **(a)** September, and in **(b)** December for the four years: 2006 (red line), 2007 (blue), 2008 (green), and 2010 (orange). The monthly average sea-ice charts were downloaded from the Webpage of the University of Bremen, <http://iup.physik.uni-bremen.de/iuppage/psa/2001/amsrop.html> (Spreen et al., 2008).

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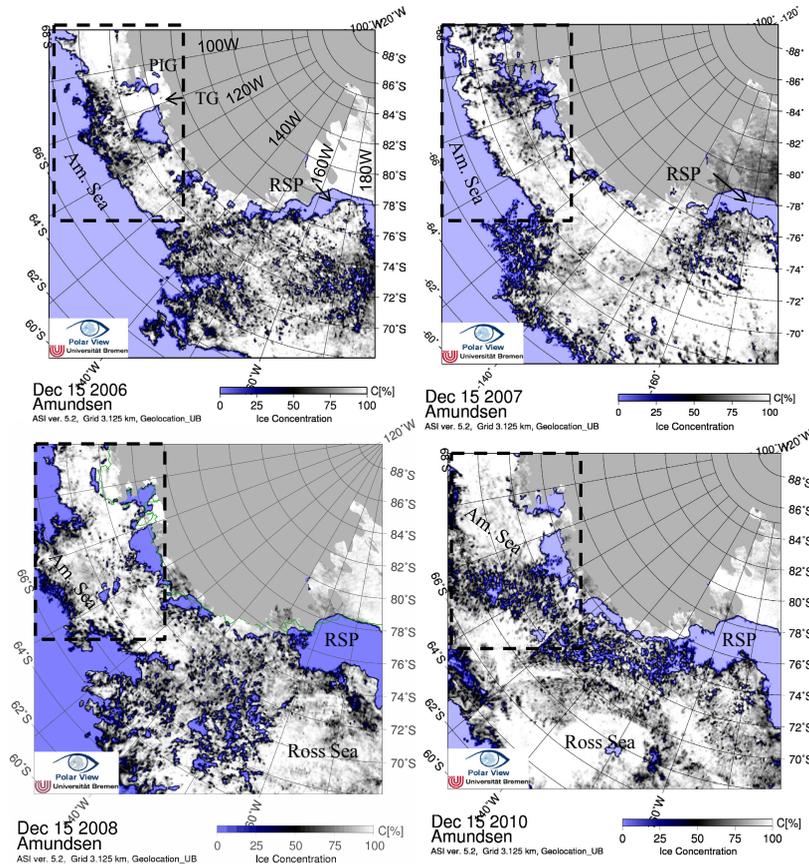
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**Fig. 4.** The sea-ice concentration in 15 December for year, **(a)** 2006, **(b)** 2007, **(c)** 2008, and **(d)** 2010, downloaded from the Webpage of the University of Bremen, <http://iup.physik.uni-bremen.de/iuppage/psa/2001/amsrop.html> (Spren et al., 2008). The dashed box indicates the approximate boundaries of the Amundsen Sea, RSP denotes Ross Sea Polynya. Blue areas indicate open water, and white is 100 % sea-ice concentration.

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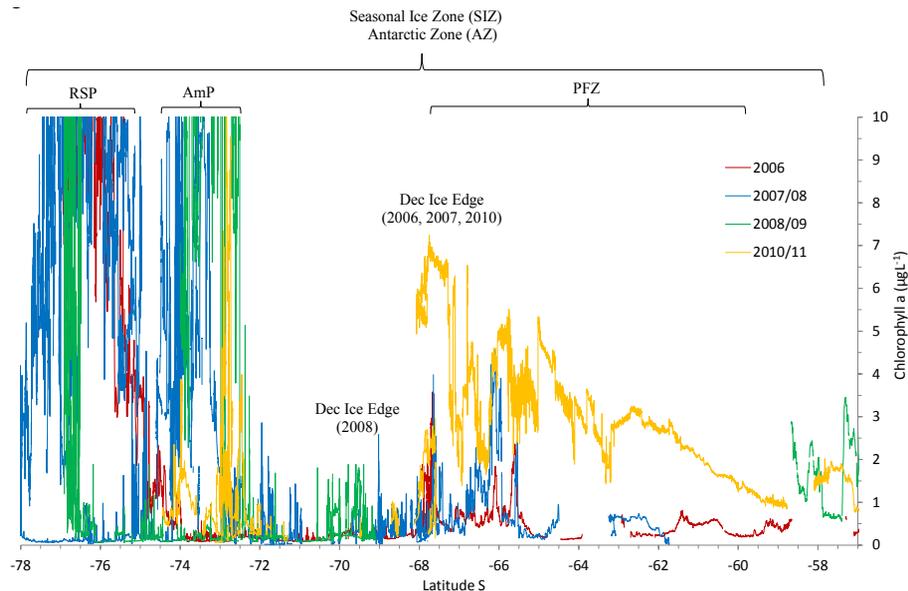
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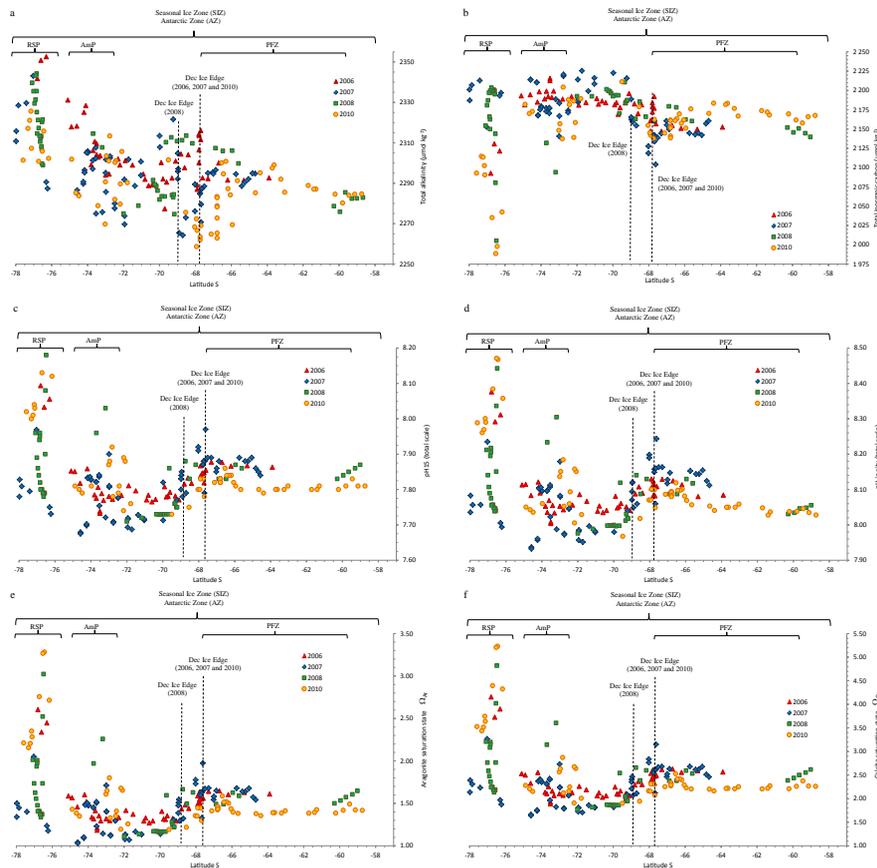


**Fig. 5.** Surface water chlorophyll *a* concentrations for all years (2006: red; August 2007: blue; September 2008: green; November 2010: yellow), along the latitude ( $^{\circ}$  S). Note that the chl *a* sensor range is between  $0.1$  to  $10 \mu\text{L}^{-1}$ . We indicate the location of the Seasonal Ice Zone (SIZ), the Polar Frontal Zone (PFZ), the polynyas in the Amundsen Sea (AmP) and the Ross Sea (RSP). The dashed line show the location of the sea-ice edge in December for each year. Note that the expedition in 2006 did not enter the AmP.

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**Fig. 6.** Latitudinal variability of surface water, **(a)** total alkalinity,  $A_T$ ,  $\mu\text{mol kg}^{-1}$ ; **(b)** total dissolved inorganic carbon ( $C_T$ ,  $\mu\text{mol kg}^{-1}$ ), **(c)** pH at 15°C ( $\text{pH}^{15}$ ); **(d)** pH in situ; **(e)** aragonite saturation state ( $\Omega_{Ar}$ ), and **(f)** calcite saturation state ( $\Omega_{Ca}$ ) for all years (2006: red triangle; August 2007: blue diamond; September 2008: green square; November 2010: yellow circle). We indicate the location of the Seasonal Ice Zone (SIZ), the Polar Frontal Zone (PFZ), the polynyas in the Amundsen Sea (AmP) and the Ross Sea (RSP). The location of the sea-ice edge in December for each year is shown as a dashed line. Note that the expedition in 2006 did not enter the AmP.

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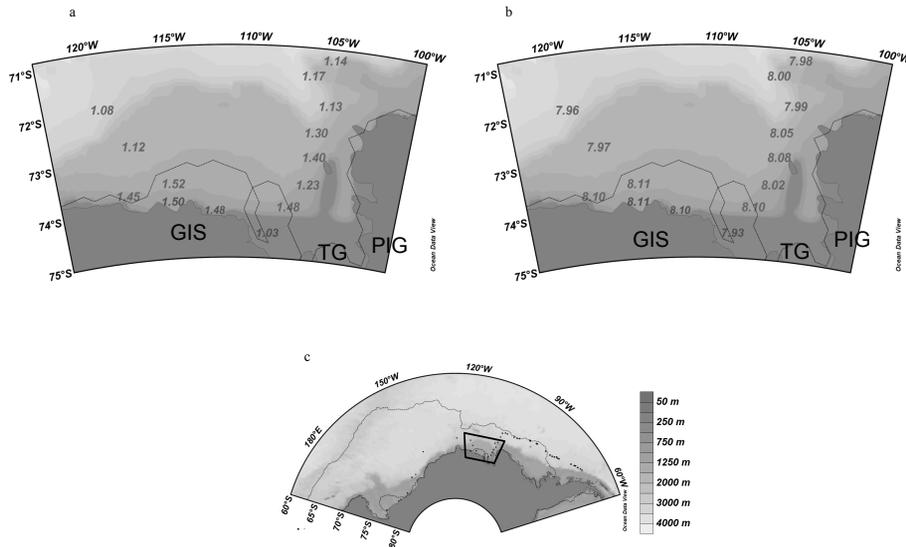
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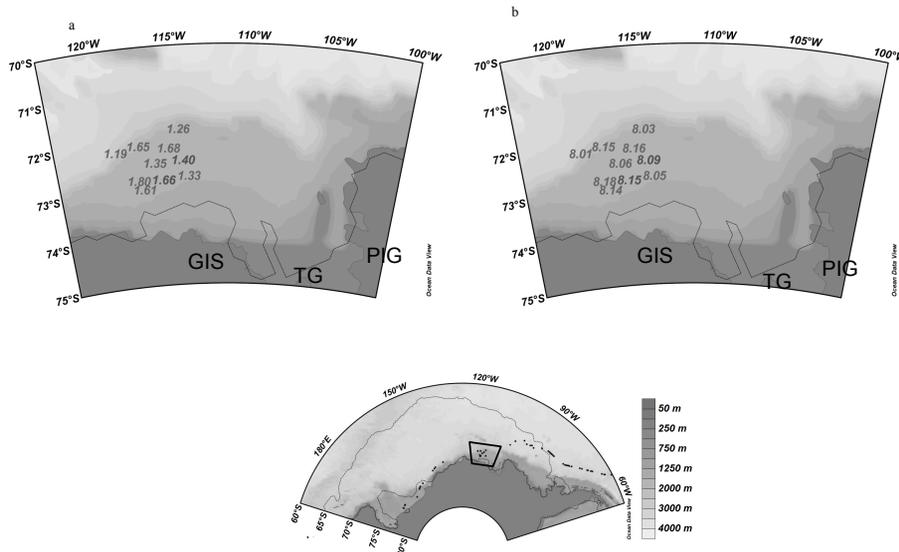


**Fig. 7.** The variability of **(a)** Aragonite saturation ( $\Omega_{Ar}$ ), and **(b)** pH in situ in the Amundsen Sea Polynya (station locations on map below) in 2007. GIS, TG and PIG denote Getz Ice Shelf, Thwaites Glacier, Pine Island Glacier, respectively.

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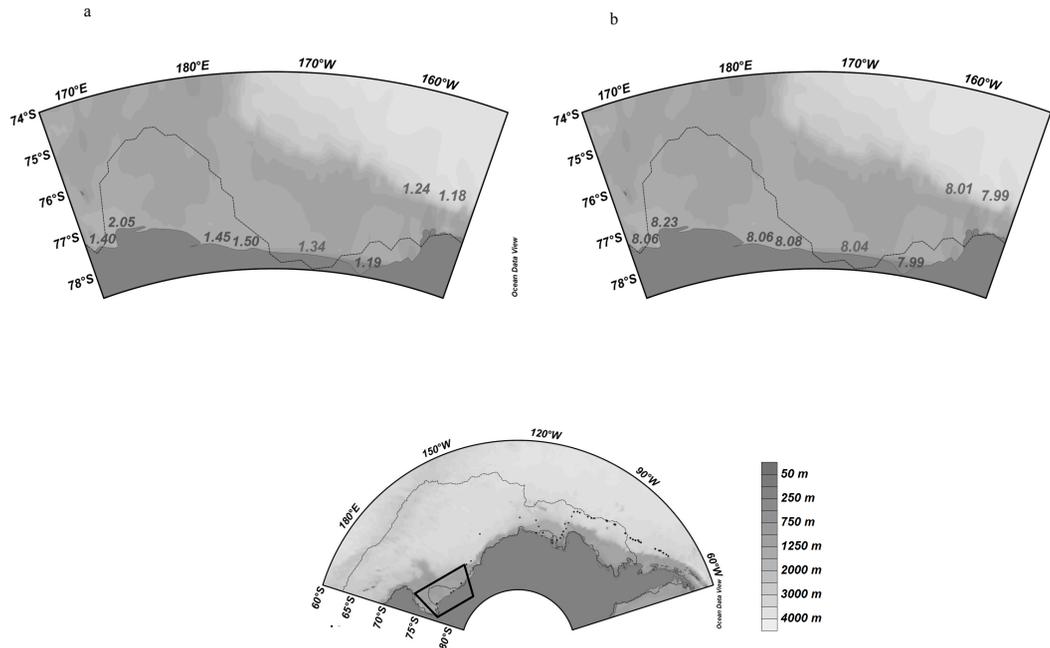


**Fig. 8.** The variability of (a) Aragonite saturation ( $\Omega_{Ar}$ ), and (b) pH in situ in the Amundsen Sea Polynya (c, station locations on map below) in 2010. GIS, TG and PIG denote Getz Ice Shelf, Thwaites Glacier, Pine Island Glacier, respectively.

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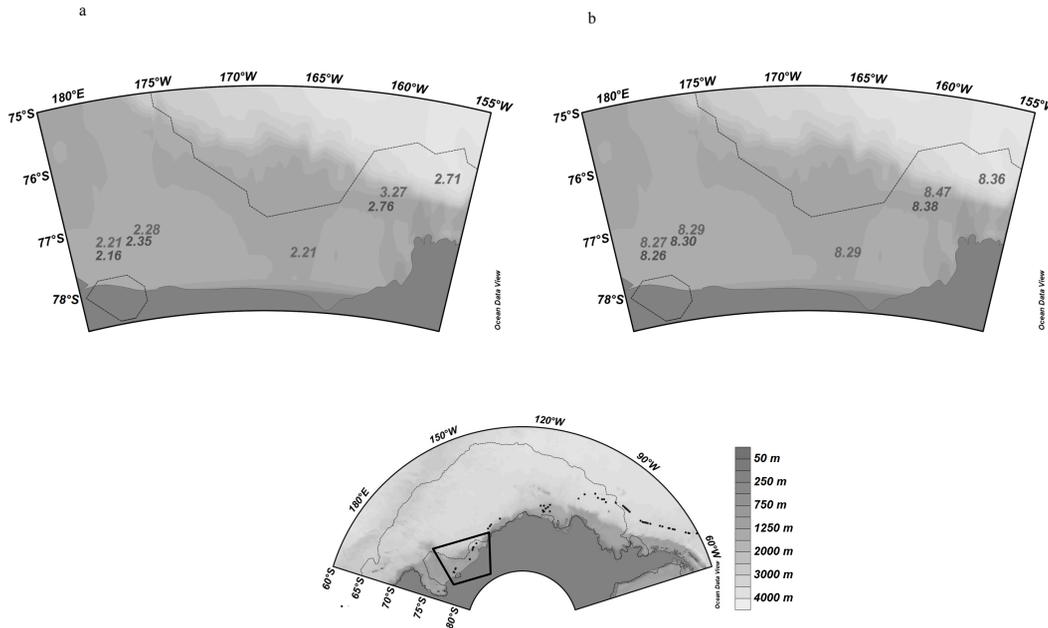


**Fig. 9.** The variability of **(a)** Aragonite saturation ( $\Omega_{Ar}$ ), and **(b)** pH in situ in the coastal Ross Sea and the Ross Sea Polynya (station locations on map below) in 2007.

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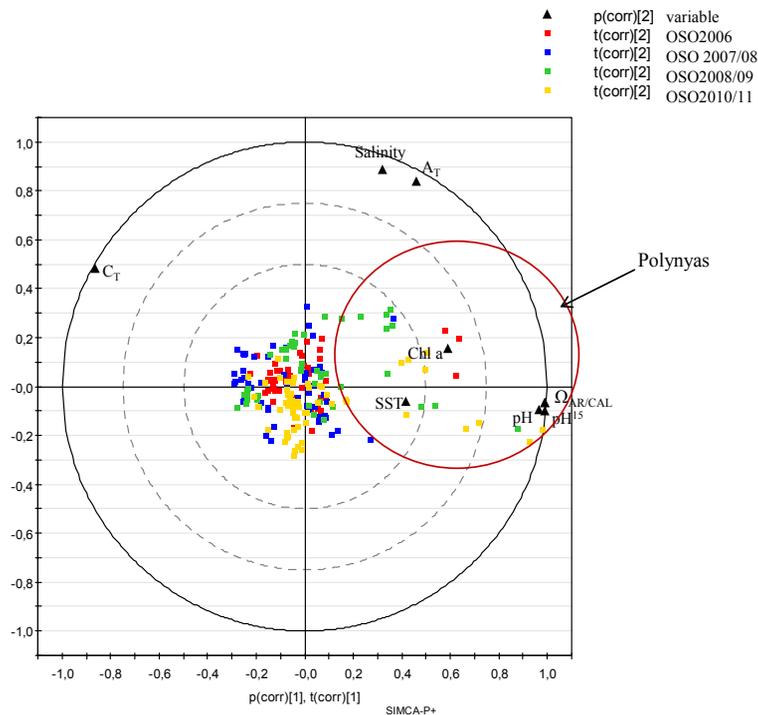


**Fig. 10.** The variability of **(a)** Aragonite saturation ( $\Omega_{Ar}$ ), and **(b)** pH in situ in the coastal Ross Sea and the Ross Sea Polynya (station locations on map below) in 2010.

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**Fig. 11.** A combined PCA score loading plot of observations and variables of SST, Salinity, chl a,  $A_T$ ,  $pH^{15}$ ,  $C_T$  and pH in situ. Loading vector ( $p$ ) and score vector ( $t$ ) are displayed correlation scaled as vector  $p(\text{corr})$  and  $t(\text{corr})$ . All points are distributed inside the correlation circle of radius 1 (black circle). The markings denote observations from cruise OSO2006 (red), OSO2007/08 (blue), OSO2008/09 (green) and OSO2010/11 (yellow), respectively. The black pyramids denote the location of variables in the loading plot. Data points encircled (burgundy) are located in the polynyas.

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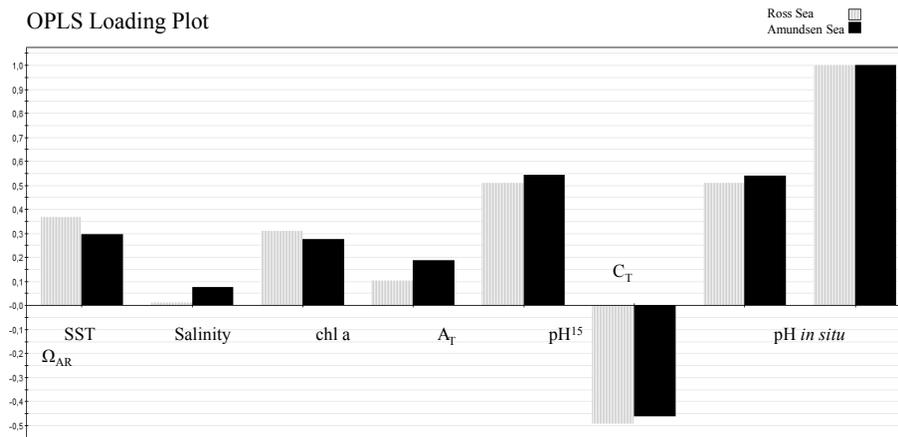
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**Fig. 12.** OPLS Loading Plot for Amundsen Sea (black) and Ross Sea (grey) including polynyas for OSO2007/08, OSO2008/09 and OSO2010/11. OSO2006 is excluded from the analysis due to lack of data in the Amundsen Sea from this year. The plot shows the correlation of each  $x$ -variable (SST, salinity, chl  $a$ ,  $A_T$ ,  $pH^{15}$ ,  $C_T$  and  $pH$  in situ) to the aragonite saturation ( $\Omega_{AR}$ ,  $y$ -variable).

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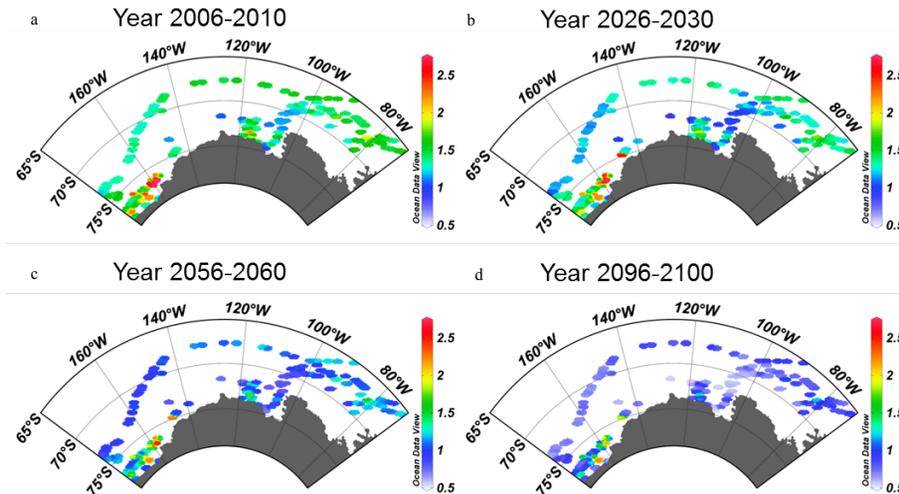
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**Fig. 13.** Current and projected surface water  $\Omega_{Ar}$  for the period: **(a)** 2006–2010, **(b)** 2026–2030, **(c)** 2056–2060, and **(d)** 2096–2100, based on a  $C_T$  increase of  $10 \mu\text{mol kg}^{-1} \text{decade}^{-1}$  (Sabine et al., 2008), and current  $A_T$ ,  $SS_T$ , and salinity.

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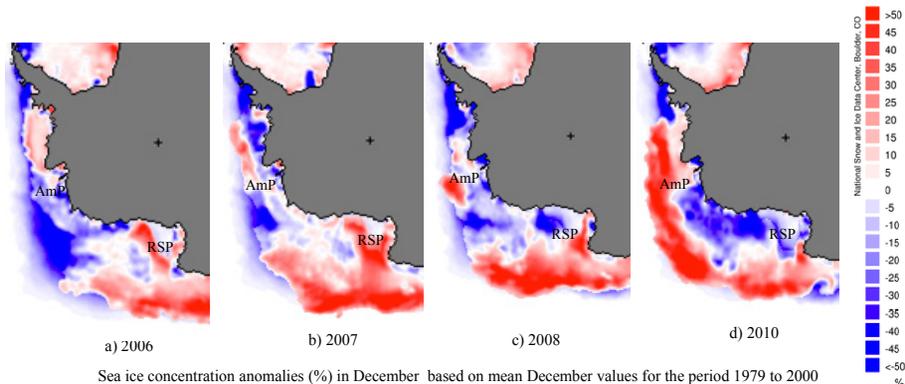
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**Fig. 14.** Sea ice concentration anomalies in December as percentage difference (%) for year: **(a)** 2006, **(b)** 2007, **(c)** 2008, and **(d)** 2010, from the mean December sea-ice concentration in the period 1979 to 2000. The AmP and RSP refer to the Amundsen Sea polynya and Ross Sea polynya, respectively. Note: appearances of large anomalies near the ice edge are often simply artifacts of the movement of the ice edge (Fetterer et al., 2002).

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