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**From ice covered
CO₂-rich waters to a
biological CO₂ sink**

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A rapid transition from ice covered CO₂-rich waters to a biologically mediated CO₂ sink in the eastern Weddell Gyre

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Abstract

Circumpolar Deep Water (CDW), locally called Warm Deep Water (WDW), enters the Weddell Gyre in the southeast, roughly at 25° E to 30° E. In December 2002 and January 2003 we studied the effect of entrainment of WDW on the fugacity of carbon dioxide ($f\text{CO}_2$) and dissolved inorganic carbon (DIC) in Weddell Sea surface waters. Ultimately the $f\text{CO}_2$ difference across the sea surface drives CO_2 air-sea fluxes. Deep CTD sections and surface transects of $f\text{CO}_2$ were made along the Prime Meridian, a northwest-southeast section, and along 17° E to 23° E during cruise ANT XX/2 on FS *Polarstern*. Upward movement and entrainment of WDW into the winter mixed layer had significantly increased DIC and $f\text{CO}_2$ below the sea ice along 0° W and 17° E to 23° E, notably in the southern Weddell Gyre. Nonetheless, the ice cover largely prevented outgassing of CO_2 to the atmosphere. During and upon melting of the ice, biological activity rapidly reduced surface water $f\text{CO}_2$ by up to 100 μatm , thus creating a sink for atmospheric CO_2 . Despite the tendency of the surfacing WDW to cause CO_2 supersaturation, the Weddell Gyre may well be a CO_2 sink on an annual basis due to this effective mechanism involving ice cover and ensuing biological $f\text{CO}_2$ reduction. Dissolution of calcium carbonate (CaCO_3) in melting sea ice may also play a role in this rapid reduction of surface water $f\text{CO}_2$. The CO_2 source tendency deriving from the upward movement of “pre-industrial” CDW is declining, as atmospheric CO_2 levels continue to increase, and thus the CO_2 sink of the Weddell Gyre will continue to increase as well (provided the upward movement of WDW does not change significantly).

1 Introduction

The Southern Ocean plays a pivotal role in the global carbon cycle. A considerable part of the global oceanic uptake of anthropogenic carbon dioxide (CO_2) occurs in this vast region (Sabine et al., 2004; McNeil et al., 2007). Recent observations and modelling suggest that the Southern Ocean is particularly sensitive to changes, be

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they anthropogenic or not (Stephens and Keeling, 2000; Hoppema, 2004; Lenton and Mearns, 2007; Le Quéré et al., 2007; Lovenduski et al., 2007; Zickfeld et al., 2007). Upwelling of CO₂-enriched deep water and its long-term trends play the major role in all these analyses.

5 The Weddell Gyre is an elongated, mainly wind-driven, cyclonic gyre (Gordon et al., 1981) in the Atlantic sector of the Southern Ocean, south of the Antarctic Circumpolar Current (ACC). Water flows westwards in the southern limb and eastwards in the northern limb of the gyre (Fig. 1). Due to its divergent nature, Ekman pump-
10 ing causes major upward transport of subsurface water in the gyre's interior. Formation of deep and bottom water occurs in the southern and western parts of the gyre (e.g. Carmack and Foster, 1975; Gordon et al., 1993; Foldvik et al., 2004); dense water originating here is found in most of the southern hemisphere as Antarctic Bottom Water (AABW). Surface water of the gyre is exchanged with the adjacent ACC along all of its northern and eastern boundaries. Subsurface water is supplied by the ACC,
15 where it is swept into the Weddell Gyre at its eastern boundary, i.e. 25° E to 30° E (Deacon, 1979; Gouretski and Danilov, 1993; Schröder and Fahrbach, 1999). There may be another subsurface water supply near 20° W (Bagrientsev et al., 1989). This subsurface water, known as Circumpolar Deep Water (CDW), but locally called Warm Deep Water (WDW), is recognized by its temperature maximum (T_{\max}) just underneath the
20 pycnocline. The highest T_{\max} are found in the southeastern Weddell Gyre, indicating that that region is the main recipient of CDW source water (Deacon, 1979; Gouretski and Danilov, 1993). On its course through the gyre, the T_{\max} is attenuated by mixing with waters above and below. As a result the temperature of T_{\max} in the southern limb is higher than in the northern limb of the gyre. The T_{\max} is accompanied by maxima
25 of salinity, dissolved inorganic carbon (DIC), and nutrients and by an oxygen minimum (Whitworth and Nowlin, 1987; Hoppema et al., 1997), although the exact depths of the extremes vary and may not be identical.

Seasonal ice coverage is a prominent feature of the Weddell Gyre. In the far west perennial ice is found, while towards the east the vast ice field disappears rapidly in

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late spring and early summer. Two stages of ice disappearance in the central and eastern gyre are depicted for December 2002 (Fig. 2). By 17 December a transient polynya had formed within the melting ice pack northwest of Maud Rise (Fig. 2a), in a region, which has often been associated with ice melting events and polynyas (e.g. Martinson et al., 1981; Muench et al., 2001). On 24 December 2002, an ice-free intrusion from the east had combined with the initial polynya. Seasonal ice coverage strongly impacts on the cycling of chemical species and biological processes. For example, chlorofluorocarbons (CFCs) and oxygen (O₂) are strongly undersaturated, and CO₂ is oversaturated in ice-covered Weddell Gyre surface waters relative to their atmospheric contents (Gordon et al., 1984; Weiss et al., 1992; Bakker et al., 1997; Klatt et al., 2002), indicating that ice caps the water column, thus hindering air-sea gas exchange.

The southeastern Weddell Gyre appears to be vital for exchange processes with the ACC and for preconditioning water masses for their course through the Weddell Gyre. It is a highly dynamical and variable region with many eddies resulting from interactions of the ACC with topography (Gouretski and Danilov, 1993). Local deep-sea promontories, like Astrid Ridge and Maud Rise (Fig. 1), promote vertical mixing (Muench et al., 2001). Upward movement of the newly arriving CDW may well enhance vertical transport (Geibert et al., 2002). The relatively early break-up of the sea ice in the eastern Weddell Gyre (Fig. 2) may be related to the region's dynamic hydrography.

With major interaction between surface waters and CDW, the eastern Weddell Gyre is likely to be important from a biogeochemical point of view, but little is known about it. In spring the partial pressure of CO₂ (pCO₂) in surface water varied strongly with both over- and undersaturation relative to atmospheric CO₂ north of 60° S (Bakker et al., 1999), while in autumn surface water pCO₂ was undersaturated (Hoppema et al., 2000). Sparse chlorophyll and photosynthetic oxygen production data in December suggest low biological activity compared to adjacent regions (Odate et al., 2002). Satellite pigment data also point to low biological production (Sullivan et al., 1993; Moore and Abbott, 2000), while carbon export production is modelled to be among the lowest

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of the Southern Ocean (Schlitzer, 2002). By contrast, modelled opal export production is relatively high (Usbeck, 1999) and high densities of certain whales have been found in the eastern Weddell Gyre (Tynan, 1998). Further west around Maud Rise near 0° W, elevated densities of mammals, penguins and birds have been observed in mid-winter, which is thought to be related to wintering krill (Plötz et al., 1991).

It has been suggested that calcium carbonate (CaCO₃) precipitates along brine channels in sea ice (Jones and Coote, 1981; Rysgaard et al., 2007), thus reducing the alkalinity to DIC ratio and increasing fCO₂ in the brine. Any brine escaping from the ice would transfer these CO₂ characteristics to the winter mixed layer. Hydrated CaCO₃ crystals (ikaite, CaCO₃·6H₂O) have recently been detected in sea ice from the Weddell Sea (Dieckmann et al., 2008). During and upon ice melt, the dissolving CaCO₃ could increase the alkalinity to DIC ratio and decrease fCO₂ in surface water, at least if this CaCO₃ were to dissolve in the melting ice or in the surface mixed layer.

Thus, a biogeochemical study of the eastern Weddell Gyre is appropriate. We visited the eastern and central Weddell Gyre, as the ice pack was opening up in late spring and early summer, with the aim to assess the processes controlling surface layer carbon chemistry below the sea ice and upon the retreat of the sea ice. Our hypothesis is that both upwelling of WDW and ice cover exert a significant influence on the partial pressure of CO₂ and the DIC concentration in surface waters. In addition, we test whether the observations agree with the theory of the conversion of a pre-industrial CO₂ source to a present-day annual CO₂ sink in the Weddell Gyre (Hoppema, 2004). Furthermore, we look for evidence supporting the hypothesis of reduced ventilation of CO₂-rich, upwelled water by extensive sea ice coverage in the glacial Southern Ocean (Stephens and Keeling, 2000).

2 Methods

Inorganic carbon data were collected during cruise ANT XX/2 with the German ice breaker FS *Polarstern* starting and ending in Cape Town at 24 November 2002 and

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23 January 2003, respectively (Fütterer and Kattner, 2005). The ship made deep sections with stations at 0.5° latitude spacing along the Prime Meridian, along a northwest-southeast cross-transect and along 17° E to 23° E in the Weddell Gyre (Figs. 1, 3). High resolution vertical profiles of potential temperature and salinity were obtained during the downcasts of the ship's CTD (conductivity, temperature, depth) (type Seabird 911+), while samples for DIC and other biogeochemical parameters were taken from the CTD rosette during the upward casts. Atmospheric pressure, sea surface temperature and salinity were measured by the ship's sensors. While the ship was sailing, ice observations were made at almost hourly intervals from the bridge from 4 December 2002 to 3 January 2003, following the protocols by Worby et al. (1999).

The fugacity of CO₂ (fCO₂) was determined from the sailing ship quasi-continuously in surface water and marine air. Water was drawn from about 10 m depth at the keel of the ship, while air was sampled from the crow's nest. The fugacity of CO₂ is the partial pressure of CO₂ upon correction for non-ideal behaviour of CO₂ gas. The measurements were performed with an automated sampling system designed after Wanninkhof and Thoning (1993) based on a Li-COR 6262 infrared gas analyzer. Such a system has been used before during *Polarstern* cruises (e.g. Hoppema et al., 2000; Bellerby et al., 2004). Every three hours the measurements were calibrated by two out of three calibration gases, bracketing surface water fCO₂. The calibration gases of 250.53, 374.36, and 453.65 μmol mol⁻¹ had been calibrated to NOAA gas standards prior to the cruise. Warming of the water between the seawater intake and the equilibrator ranged from 0.43°C in subantarctic waters to 0.72°C near the ice (standard deviation of up to 0.2°C for 60 000 data points).

The DIC concentration was determined by coulometry following the method of Johnson et al. (1987). Samples were stored cold, were analysed within 24 h of collection and were not poisoned. Certified reference material (CRM) of batch 53 (DOE, 1994) was used for each CTD cast and for each coulometric cell.

Surface water fCO₂ has been co-located to CTD casts by taking the average of fCO₂ values determined within 20 min (or in a few cases within 30 min, 60 min or 120 min)

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of the CTD returning to the surface. Alkalinity has been calculated from surface water $f\text{CO}_2$ and DIC in the upper 25 m with the constants of Mehrbach et al. (1973), as revised by Dickson and Millero (1987).

3 Results

3.1 Sea ice cover and surface water CO_2 parameters

The ship first reached the ice edge at 4 December 2002 on the Prime Meridian at 56.5°S , roughly on the northern boundary of the Weddell Gyre (Fig. 3a). Over the next month FS *Polarstern* sailed through fully ice covered waters, areas with melting sea ice and open water in the Weddell Gyre. Two maps of the satellite-derived ice fraction give a picture of the rapidly disappearing ice pack and of high spatial variability between ice-covered waters and open water in December 2002 (Fig. 2). The ship finally left the ice pack in the eastern Weddell Gyre on 68.2°S 18.1°E on 3 January 2003 (Fig. 3a).

The $f\text{CO}_2$ difference between surface water and air, $\Delta f\text{CO}_2(w-a)$, varied from strong supersaturation to strong undersaturation along the cruise track in the Weddell Gyre (Fig. 3b). The distribution of DIC at 20 m depth showed a similar large spatial variability with a good correspondence between DIC and $\Delta f\text{CO}_2(w-a)$ (Fig. 3c). On the Prime Meridian the ice coverage, $\Delta f\text{CO}_2(w-a)$ and DIC were high in the northern Weddell Gyre. Significantly lower $\Delta f\text{CO}_2(w-a)$ and DIC were observed in a newly forming polynya at 62°S to 65°S northwest of Maud Rise. A repeat visit to 61°S to 64°S along 0°W highlights the reduction of surface water $f\text{CO}_2$ during sea ice melt over an 11 day period in this polynya (Fig. 4). On 8 to 10 December a significant fraction of the ice cover had disappeared, the remaining sea ice was melting rapidly, surface water $f\text{CO}_2$ was close to the atmospheric value and the sea surface temperature was -1.8 to -1.7°C . Eleven days later sea ice had disappeared along most of the section, surface water $f\text{CO}_2$ had been reduced by 10 to $25\ \mu\text{atm}$ and the water had warmed by 0 to 0.8°C . This translates into a rate of surface water $f\text{CO}_2$ decrease of 1.0 to $2.5\ \mu\text{atm d}^{-1}$

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or 1.0 to 3.4 $\mu\text{atm d}^{-1}$ upon correction to a constant temperature. The highest rates were found at 63° S to 64° S, where the ice melted first and a phytoplankton bloom was developing. These maximum rates were only just below the fCO_2 decrease of 3.8 $\mu\text{atm d}^{-1}$ by phytoplankton growing at a maximum growth rate in an iron-fertilised algal bloom at 61° S 139° W (Bakker et al., 2001). This suggests that iron was abundant and not limiting for phytoplankton growth in the Weddell surface layer during ice melt.

South of the polynya $\Delta\text{fCO}_2(\text{w-a})$ and DIC were high in an area with thick ice cover and melting sea ice (Figs. 2a, 3). Along the Antarctic coast $\Delta\text{fCO}_2(\text{w-a})$ values of below $-60 \mu\text{atm}$ were observed in a coastal polynya between 8° W and 0° W. In late December the southeastern Weddell Gyre at 17° E to 23° E was in a rapid transition from ice cover to open water (Fig. 2b), while fCO_2 varied from slight to strong supersaturation. All sea ice had vanished, by the time the ship sailed northwards north of 68.2° S 18.1° E on 3 January 2003. Within ice-free waters we observed undersaturation of fCO_2 and low DIC in phytoplankton blooms between 58.5° S and 62.5° S along 23° E.

3.2 The vertical distribution of temperature and DIC

Contour plots of potential temperature in the upper 400 m along 0° W and 17° E to 23° E show the temperature maximum of the WDW, a temperature minimum above it and a shallow, relatively warm surface layer, where sea ice melting and subsequent warming had occurred (Fig. 5a, b). The stations closest to Antarctica are in the westward flowing Antarctic Coastal Current. The WDW had several local temperature maxima between 1.2°C and 1.5°C along both sections. Along 17° E to 23° E the core of WDW was shallower in the south than further to the north (Fig. 5b), while this lateral variation was less pronounced along 0° W (Fig. 5a). Effects due to the vicinity of Maud Rise are apparent in the temperature profiles along 0° W between 63° S and 66° S (Fig. 5a). The WDW is characterised by high DIC along both sections (Fig. 6a, b). The DIC maximum at 300 m depth between 59.5° S and 61.5° S along 0° W (Fig. 6a) is associated with the Central Intermediate Water (CIW) (Whitworth and Nowlin, 1987; Hoppema et al.,

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1997).

A temperature minimum, a remnant of the winter mixed layer, was evident above the pycnocline (Fig. 5a, b). The depth of the winter mixed layer (WML) is defined here as the depth below the temperature minimum, where potential temperature exceeded the temperature minimum by 0.02°C (Figs. 5, 7a, b). This 0.02°C increment has little effect on the WML depth at most stations, but improves its selection at stations with a broad temperature minimum. The temperature of the temperature minimum was higher in the southern Weddell Gyre (-1.7°C) than in the northern gyre (-1.8°C) (Fig. 7a) and was above the freezing temperature of seawater at -1.88°C . This slight temperature excess of the WML reflects the introduction of WDW heat into the mixed layer during winter (Gordon et al., 1984). Winter mixed layers depths were 30 to 80 m in the southern gyre (64.5°S to 69.0°S) and 50 to 130 m in the northern gyre (57.5°S to 64.0°S) along both sections (Fig. 7b). Stations at 66.8°S 17.0°E and 64.5°S 0°W had winter mixed layer depths shallower than 50 m and high DIC at 50 m depth (Fig. 7b, c), possibly reflecting recent upward movement of WDW.

Samples for DIC were systematically taken at 50 and 100 m depth. Here DIC at 50 m depth is taken as a proxy for DIC in the winter mixed layer for stations with a WML depth exceeding 50 m (Fig. 7b, c). Spring-time processes may have influenced DIC at 50 m depth at a few stations. The DIC concentration at 50 m depth was higher by about $5\ \mu\text{mol kg}^{-1}$ in the southern Weddell Gyre than further north along 0°W , if the station with a shallow winter mixed layer at 64.5°S is ignored (Fig. 7c). The northern Weddell Gyre along 23°E had low DIC and salinity (not shown) in the upper 50 m. This freshening cannot be explained by melting of sea ice alone and could reflect the presence of waters with an ACC origin, since surface waters in the ACC have lower salinity than in the Weddell Gyre.

The DIC difference between 50 m and 20 m depth is a measure for changes in surface water DIC from winter to spring and summer (Fig. 8). The DIC change due to ice melting and other fresh water inputs was calculated by correcting DIC at 50 m depth to the salinity at 20 m depth. The DIC change resulting from organic matter production

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was estimated from the change in nitrate from 50 m to 20 m, while assuming carbon to nitrogen uptake in a ratio of 117 moles to 16 moles (Anderson and Sarmiento, 1994). Residual DIC changes included the effects of dissolution or precipitation of calcium carbonate and CO₂ air-sea exchange.

5 The mixed layer became shallower than 50 m, as the sea ice started melting, such that absolute DIC changes between 50 m and 20 m increased along the cruise track from 0° W to the eastern gyre (Fig. 8). The DIC changes were small north of 62° S along 0° W below heavy ice cover in early December. Ice melt and other freshwater inputs locally reduced surface water DIC by 20 μmol kg⁻¹ along 0° W and by 40 μmol kg⁻¹ along 17° E to 23° E. The inflow of surface water from the ACC may have contributed to the large DIC reduction in the northeastern gyre. Organic matter production decreased DIC by 40–60 μmol kg⁻¹ in phytoplankton blooms in a polynya at 64.5° S 0° W and in open water in the northeastern Weddell Gyre. Residual DIC changes ranged from –15 to 12 μmol kg⁻¹.

15 4 Discussion

The processes affecting CO₂ chemistry in ice-covered waters and upon ice melt are further studied by comparing the behaviour of fCO₂, DIC and total alkalinity (TA) in surface water along the cruise track (Figs. 9, 10). The effect of ice melting on TA and DIC has been removed by normalisation to a salinity of 34.2. Freshening of surface water by ice melt barely affects fCO₂ as a result of compensating effects by lower DIC and alkalinity.

20 Normalised DIC and fCO₂ have a good correspondence (Fig. 9a), which is further improved by correcting fCO₂ to a constant temperature of –1.8°C (Fig. 9c). This relationship implies that processes affecting both parameters play a major role in the CO₂ chemistry of Weddell Sea surface waters. The narrow range of normalised alkalinity of 2305 to 2330 μmol kg⁻¹ (Fig. 9b) reflects the conservative behaviour of alkalinity in the Weddell Sea (Anderson et al., 1991).

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Normalised DIC and TA cluster together with a ‘tail’ for data from the northeastern Weddell Gyre (Fig. 10a). Lines with a slope of 2:1 delineate the cluster of points on the left and right. This ratio of 2:1 corresponds to changes in TA and DIC by calcification (negative changes) and CaCO₃ dissolution (positive changes). For example, the right line corresponds to increases in normalised TA and DIC of 24 and 12 μmol kg⁻¹, resulting in a decrease of surface water fCO₂ by 27 μatm. Points closest to the right line include the non-bloom stations along 0° W, some data from the cross-section and stations south of 64° S in the eastern gyre. Most stations with dense sea ice cover and high surface water salinity are close to the right line (red dots in Fig. 10b, d). If seasonal CaCO₃-ice processes from one year dominated the observed changes in TA and DIC, one would have expected these ‘ice’ stations to cluster together on the low end and nearby ice-free stations on the high end of the line, but this is not the case. Thus, the effect of CaCO₃ processes in ice on fCO₂ is consistent with our observations of high fCO₂ below the winter ice and a decrease in fCO₂ during and upon ice melt. However, we have failed to find any direct evidence for the CaCO₃-ice hypothesis in our data, other than the right line with a slope of 2:1 delineating the data.

Organic matter production would have changed DIC and TA in a ratio of -1 to +0.14 (Anderson and Sarmiento, 1994), as shown by the dashed line (Fig. 10c), which corresponds to a reduction in DIC and fCO₂ by 33 μmol kg⁻¹ and 90 μatm, respectively, and an alkalinity increase of 4.6 μmol kg⁻¹. The bloom stations at 0° W appear to the left of the right line with a 2:1 ratio, almost certainly reflecting organic matter production.

Data close to the left line (or “tail”) are from surface waters between 58.5° S and 62.5° S along 23° E, which have low TA and DIC, a possible ACC origin and are home to an intense phytoplankton bloom. Along the tail surface water fCO₂ increases by 38 μatm for decreases in TA and DIC of 46 and 23 μmol kg⁻¹, respectively. The 2:1 slope of the line is an indication that the phytoplankton bloom at 23° E may have been dominated by calcifying phytoplankton, but we have no further evidence for this.

High values of surface water fCO₂ and DIC were found below the sea ice in late

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spring in the Weddell Gyre (Fig. 3). Upward movement and entrainment of DIC-rich WDW into the winter mixed layer contributed strongly to these high values. Temperatures and DIC were higher at the temperature minimum, while winter mixed layers were shallower, in the southern than in the northern gyre (Fig. 7a–c). This suggests that the upward movement and entrainment of WDW into the winter mixed layer were stronger in the southern gyre than further north, both along 17° E to 23° E and along 0° W, as was previously suggested for waters near 0° W (Gordon and Huber, 1990). It is likely that upward movement and entrainment of WDW into the mixed layer continued below the sea ice, at least while air temperatures were cold enough (e.g. below –10°C) to remove the heat from the WDW input (Gordon and Huber, 1990).

While the ice and leads in the ice would have allowed heat to escape from the winter mixed layer to the atmosphere, the ice cover would have prevented release of CO₂ and other gases (Gordon et al., 1984; Klatt et al., 2002). Assuming that only insignificant gas exchange occurs through the ice itself (in contrast to some recent publications; e.g. Anderson et al., 2004), ice reduces the fetch of the wind and the gas transfer velocity in leads in the ice. In non-ice covered waters dissolved CO₂ takes many months to reach equilibrium with the atmospheric CO₂ content by air-sea gas exchange, as a consequence of the large carbonate buffer in seawater (Broecker and Peng, 1982). The bottom line is that we expect supersaturation of CO₂ under the sea-ice pack due to upwelling and entrainment of WDW into the winter mixed layer, in agreement with our measurements and with earlier observations in the wintertime Weddell Gyre (Weiss et al., 1992).

Ice melting first occurred northwest of Maud Rise in the first half of December 2002, creating a transient polynya (Fig. 2). Relatively early ice melting at 60° S to 61° S and 66° S to 67° S along 17° E to 23° E in mid-December coincided with the presence of warm WDW cores below the winter mixed layer (Figs. 2, 5b). Ice melting itself reduced surface water DIC by up to 40 μmol kg⁻¹ through dilution (Fig. 8), but did not significantly affect fCO₂, as a result of compensating effects of lower DIC and alkalinity on fCO₂. During and upon ice melting, net community production rapidly reduced fCO₂

and DIC by up to $100 \mu\text{atm}$ and $60 \mu\text{mol kg}^{-1}$, respectively (Figs. 3, 8), thus converting a potential oceanic CO_2 source into a sink for atmospheric CO_2 . This reduction of fCO_2 from supersaturation to undersaturation already started during ice melt, as is shown by fCO_2 close to the atmospheric value on the repeat section along 0°W on 8 to 10 December (Fig. 4). Zemmeling et al. (2008) have demonstrated that biological activity occurs in leads in Weddell Sea ice in early spring.

Sea ice in regions with ice melt frequently had a brown layer of about 5 cm thick, indicative of ice algae, somewhat above the ice-water interface. It is probable that the ice algae had taken up DIC from the surrounding brine and that mixing in of this brine contributed to the rapid reduction of surface water fCO_2 and DIC during ice melt. We have found no direct evidence of the effects of CaCO_3 processes in sea ice on CO_2 chemistry in surface water other than an overall change in TA and DIC in a ratio of 2:1 (Fig. 10). Surface water fCO_2 decreased at a rate of 1.0 to $2.5 \mu\text{atm d}^{-1}$ in a phytoplankton bloom on the repeat section at 0°W (Fig. 4). Since surface water fCO_2 was close to the atmospheric CO_2 value during our first visit, biological CO_2 uptake for 11 days sufficed to create a small CO_2 sink, by which time the ice had almost completely disappeared.

Our observations of high wintertime CO_2 values below the ice with rapid transition to a biologically-mediated CO_2 sink during and upon ice melt fit well with other data from the region. Notably supersaturation of fCO_2 by 0 to $40 \mu\text{atm}$ was determined in the southeastern Weddell Gyre in June–November 1986 during ANT V/2 and V/3 (Weiss et al., 1992), while strong undersaturation of fCO_2 by 60 to $130 \mu\text{atm}$, was found along the Prime Meridian in January to February 1984 during Ajax 2 (Weiss et al., 1992).

Past cruises along 0°W hint at an opposite shift from fCO_2 undersaturation to supersaturation in autumn. In 1996 modest supersaturation by $10 \mu\text{atm}$ and undersaturation by $15 \mu\text{atm}$ and were observed north and south of about 60°S , respectively (Hoppema et al., 2000). By contrast, in April to May 1998 surface water fCO_2 was supersaturated by 20 to $30 \mu\text{atm}$ south of 64°S , while mixed layers were significantly deeper and more saline in autumn 1998 than in April 1996 (Bellerby et al., 2004). This suggested that

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(more) entrainment of WDW into the mixed layer had occurred in 1998 than in 1996 (Bellerby et al., 2004). Further north $f\text{CO}_2$ was similar in autumn 1996 and 1998. High $f\text{CO}_2$ values in autumn before the formation of the sea ice pack would provide a short window for CO_2 outgassing to the atmosphere.

5 Thus, high biological carbon uptake during and upon melting of the sea ice in late spring and summer creates a seasonal and annual CO_2 sink, as ice impedes outgassing of CO_2 from upwelled CO_2 -rich waters below the winter ice. It is possible that dissolution of CaCO_3 during ice melt plays a role in the reduction of $f\text{CO}_2$. These findings are in agreement with the Weddell Sea as a CO_2 sink (Hoppema et al., 1999; Stoll
10 et al., 1999). A similar mechanism has been proposed for the seasonally ice-covered Northeast Water Polynya off Greenland (Yager et al., 1995), where waters below the winter ice are supersaturated in CO_2 due to strong remineralisation of organic matter, but where rapid biological carbon uptake creates an annual CO_2 sink upon melting of the sea ice.

15 The modern Weddell Gyre CO_2 sink is thus pre-conditioned by upwelling of CO_2 -charged WDW and rapid biological carbon uptake during and upon ice melt. In pre-industrial times the relative CO_2 source from the upwelled water would have been stronger by about $100 \mu\text{atm}$, thus creating an overall, annual CO_2 source (Hoppema, 2004) with biologically mediated, summertime supersaturation of surface water $f\text{CO}_2$
20 by $50 \mu\text{atm}$, assuming that biological carbon uptake did not change much.

Gordon and Huber (1990) estimated the residence time of Weddell Sea surface water as 2.5 years, based on an average annual upwelling of WDW of 45 m close to the Prime Meridian with higher upwelling of 50 to 75 m in the southern gyre. Hoppema et al. (1995) derived an annual upwelling of 30 m for the western Weddell Gyre at
25 $65^\circ \text{S } 40^\circ \text{W}$. Surface water leaves the Weddell Gyre as surface water flowing into the ACC along the northern boundary of the gyre or as AABW, which is formed along the southern and southwestern margins of the gyre. The above suggests that upwelled WDW in the southern Weddell Gyre, with its high upwelling rates and short ice free periods (5 months per year), has little opportunity for exchanging gases with the atmo-

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sphere, before some of it becomes part of AABW. This fits well with observations of low CFC concentrations in the surface water source of AABW (Klatt et al., 2002) and estimates of a low anthropogenic CO₂ content in AABW (Poisson and Chen, 1987; Hoppema et al., 2001).

5 The distribution of O₂ at 100 m depth shows a distinct minimum between 65° S and 69° S in the eastern and central Weddell Gyre (Olbers et al., 1992; this study), reflecting the upwelling of O₂-poor (and CO₂-rich) WDW. The O₂ minimum is particularly deep at 10° W to 10° E in and extends into the western gyre (Olbers et al., 1992). The O₂ minimum is found in a discontinuous, circumpolar band around Antarctica, which suggests that upwelling of CDW at a short distance off Antarctica also occurs in the ACC, rather than in the Weddell Gyre alone. It remains to be seen whether seasonal sea ice coverage and rapid summertime biological carbon uptake equally prevent ventilation of the CO₂ from this discontinuous ring of upwelled CDW around Antarctica.

10 Our observations of a rapid transition from ice-covered CO₂-rich waters to a biologically mediated CO₂ sink during and upon ice melt support the hypothesis by Stephens and Keeling (2000) that more winter-time sea ice cover in glacial periods would have reduced wintertime ventilation of CO₂ in the Southern Ocean, thus contributing to the observed decrease in atmospheric CO₂. Even if the Antarctic sea ice would have melted back in glacial summer, rapid biological CO₂ uptake during and upon ice melt would have prevented outgassing of CO₂.

5 Conclusions

The observations demonstrate high DIC in the winter mixed layer by upwelling and entrainment of WDW in the eastern Weddell Gyre. Seasonal sea ice cover prevents outgassing from these CO₂-rich waters. Rapid biological CO₂ uptake during and upon ice melt creates a summertime CO₂ sink. Despite the tendency of the surfacing of WDW to cause CO₂ supersaturation, the Weddell Gyre may well be a CO₂ sink on an annual basis due to this effective fCO₂ reduction mechanism, as suggested by Hoppema (2004).

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The CO₂ source tendency deriving from the upward movement of ‘pre-industrial’ CDW is currently declining, as atmospheric CO₂ levels continue to increase. Thus, the CO₂ sink of the Weddell Gyre will continue to increase (provided the upward movement of WDW does not change much). Our observations seem to support the hypothesis that an increase in sea ice coverage contributed to the decrease of atmospheric CO₂ in glacial periods (Stephens and Keeling, 2000).

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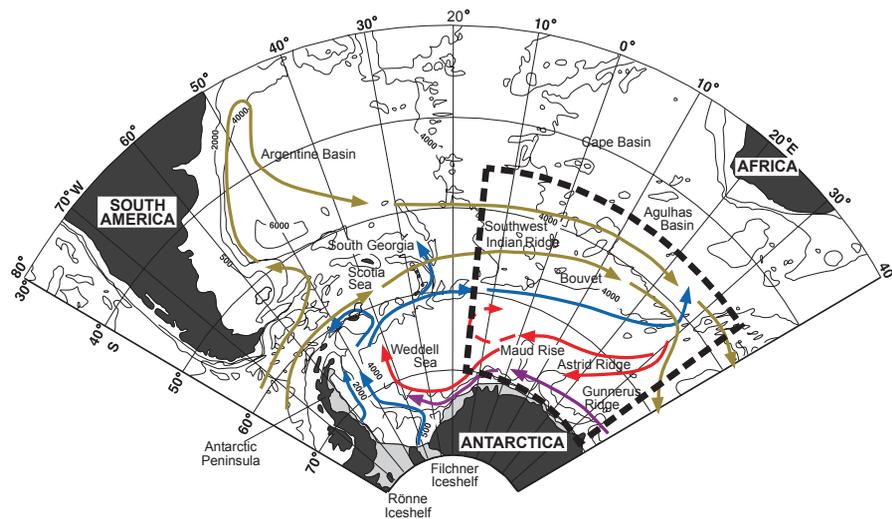


Fig. 1. Map of the Weddell Sea with schematically the deep inflow of Circumpolar Deep Water (CDW) (red) at 25° E to 30° E, the Antarctic Coastal Current (purple), and the formation and outflow of Weddell Sea Bottom Water and Antarctic Bottom Water (blue). The Antarctic Circumpolar Current (ACC) is in green. The research area is within the dashed frame.

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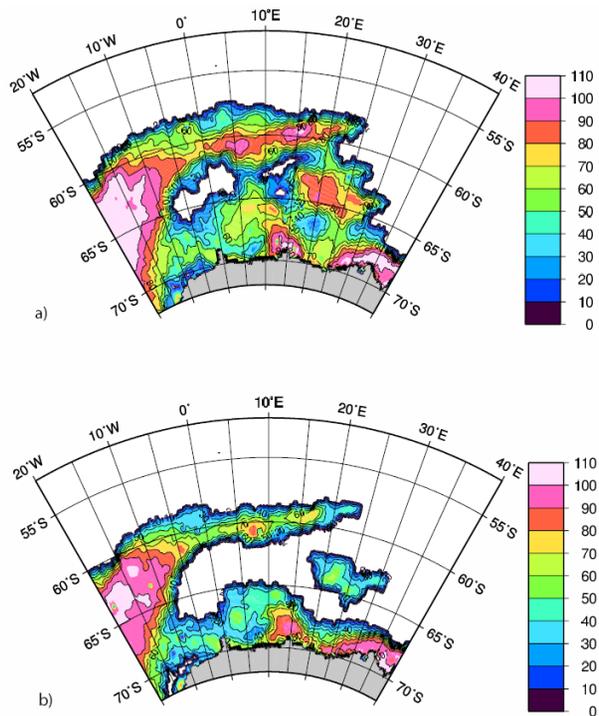


Fig. 2. Maps of the distribution of sea ice (%) in the central and eastern Weddell Gyre for (a) 17 and (b) 24 December 2002 (data from Comiso, 1999; updated 2007).

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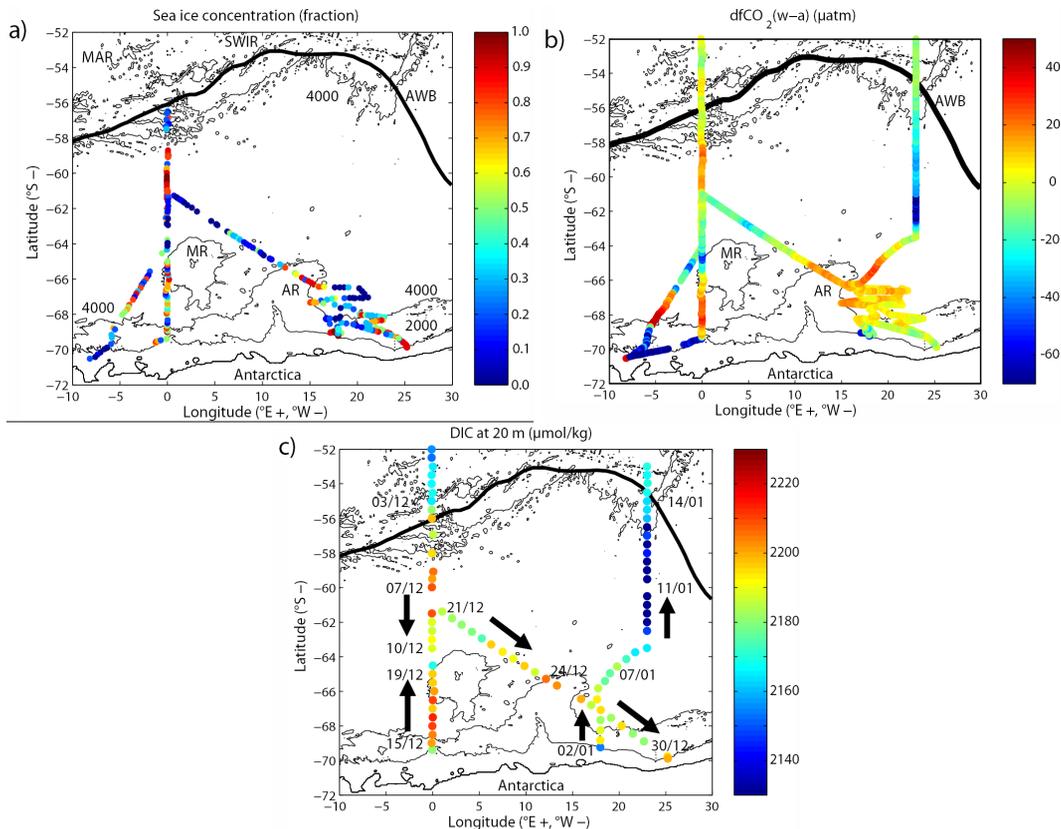


Fig. 3. (a) Sea ice concentration (fraction), (b) the difference of $f\text{CO}_2$ between surface water and marine air, $\Delta f\text{CO}_2(w-a)$, and (c) DIC at 20 m depth with the timing of the sampling along the cruise track in December 2002 and January 2003. The Antarctic coast line (ETOPO 5, 1988) and depth contours at 2000 m and 4000 m (Smith and Sandwell, 1997, version 8.2) have been indicated. The average position of the ACC-Weddell Boundary (AWB) is given (thick black line) (Orsi et al., 1995). Topographic features are Maud Rise (MR), Astrid Ridge (AR), the Mid-Atlantic Ridge (MAR), and the Southwest Indian Ridge (SWIR).

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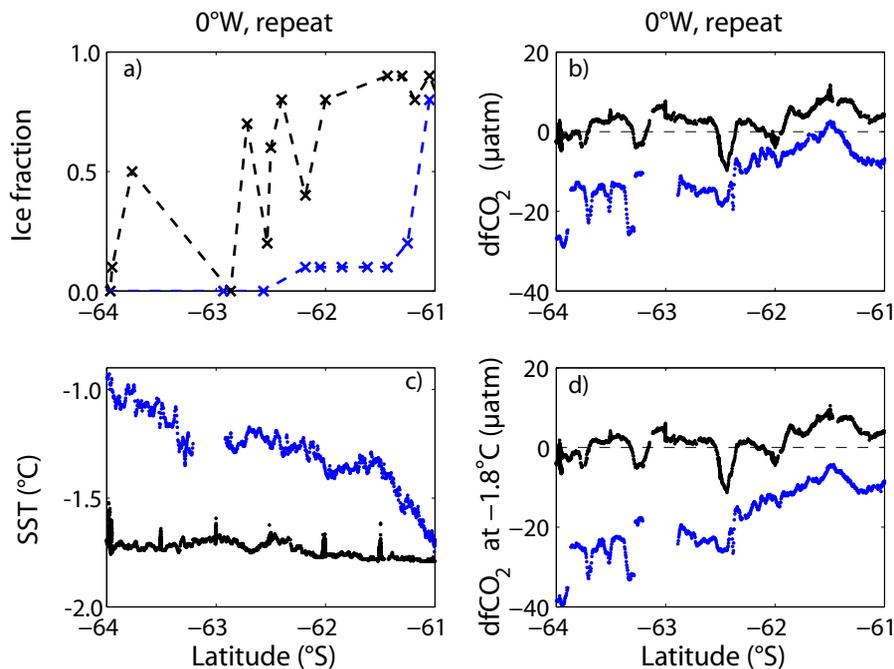


Fig. 4. (a) Sea ice cover (fraction), (b) the difference of $f\text{CO}_2$ across the sea surface, $\Delta f\text{CO}_2(w-a)$, (c) sea surface temperature, and (d) $\Delta f\text{CO}_2(w-a)$ for $f\text{CO}_2w$ corrected to -1.8°C , on 8 to 10 December 2002 (black) and 20 December 2002 (blue) for 61°S to 64°S along 0°W .

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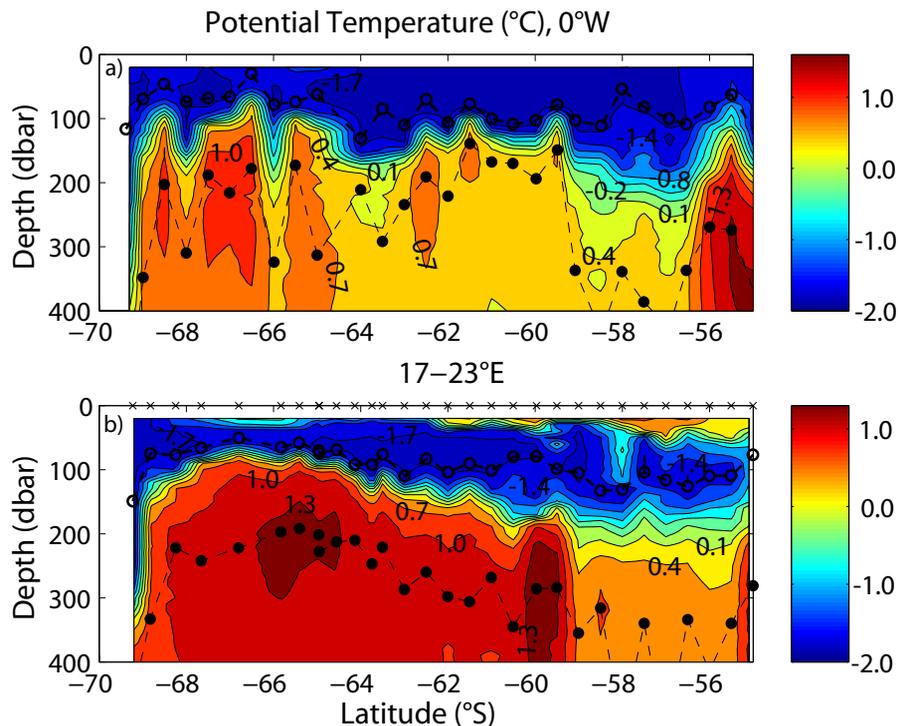


Fig. 5. Potential temperature in the upper 400 m (a) along 0° W, and (b) 17° E to 23° E with indication of the temperature minimum plus 0.02°C (open circles) and the temperature maximum (filled circles). Contours are at 0.3°C intervals.

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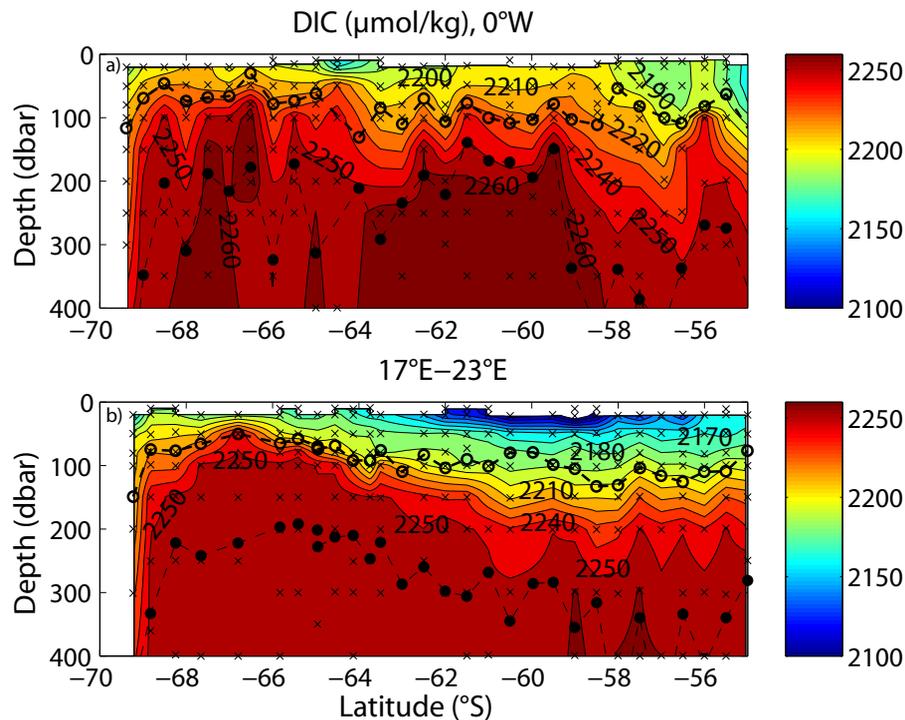


Fig. 6. The distribution of dissolved inorganic carbon (DIC) in upper 400 m **(a)** along 0° W and **(b)** 17° E to 23° E with indication of the temperature minimum plus 0.02°C (open circles) and the temperature maximum (closed circles). Contours are at 10 $\mu\text{mol kg}^{-1}$ intervals. Crosses indicate sampling depths.

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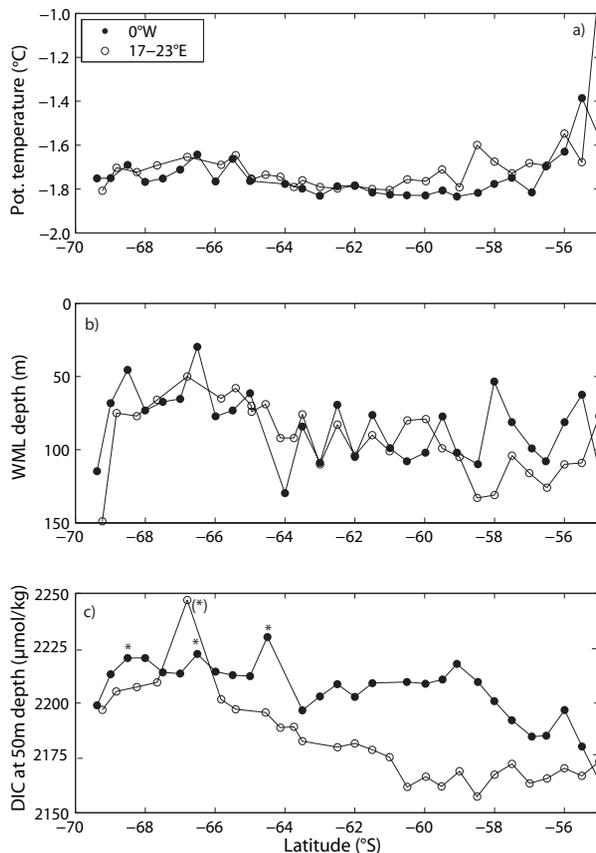


Fig. 7. (a) The potential temperature and (b) the depth of the temperature minimum plus 0.02°C, as well as (c) the DIC concentration at 50 m depth along 0° W and 17° E to 23° E. (b) The winter mixed layer (WML) depth is taken as the depth of the temperature minimum plus 0.02°C. (c) Star symbols indicate stations with a temperature minimum at or above 50 m depth.

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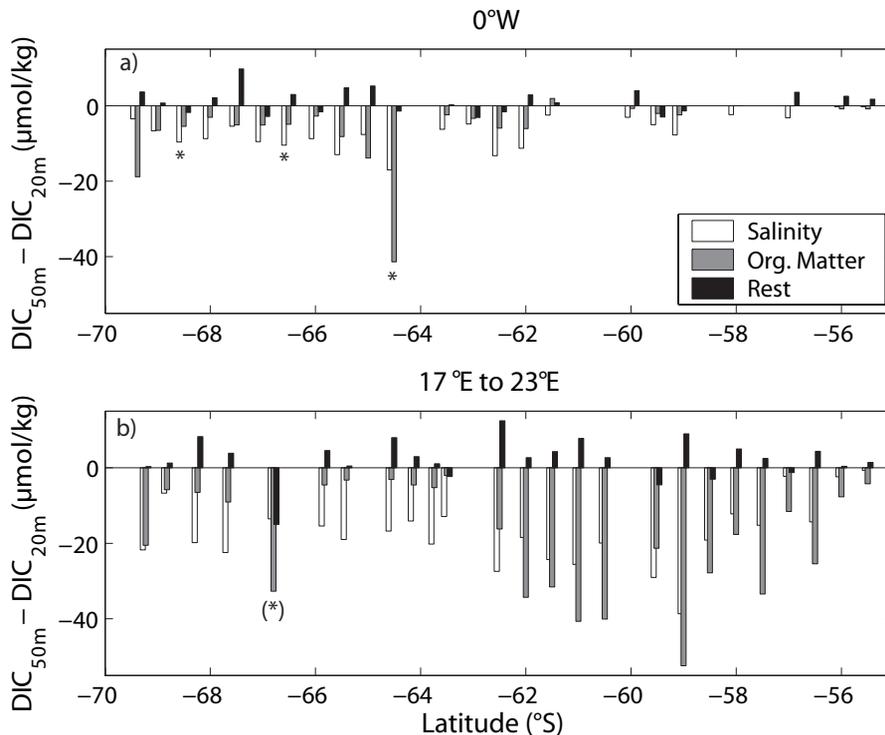


Fig. 8. The difference in the DIC concentration from 50 m to 20 m depth **(a)** for 0°W and **(b)** 17°E to 23°E . The changes are ascribed to freshwater input, biological carbon uptake for organic matter production and further processes, including CO_2 air-sea exchange and CaCO_3 precipitation or dissolution. Star symbols indicate stations with a temperature minimum at or above 50 m depth. The effect of biological carbon uptake has been calculated for a ratio of 117 moles of carbon to 16 moles of nitrate (Anderson and Sarmiento, 1994).

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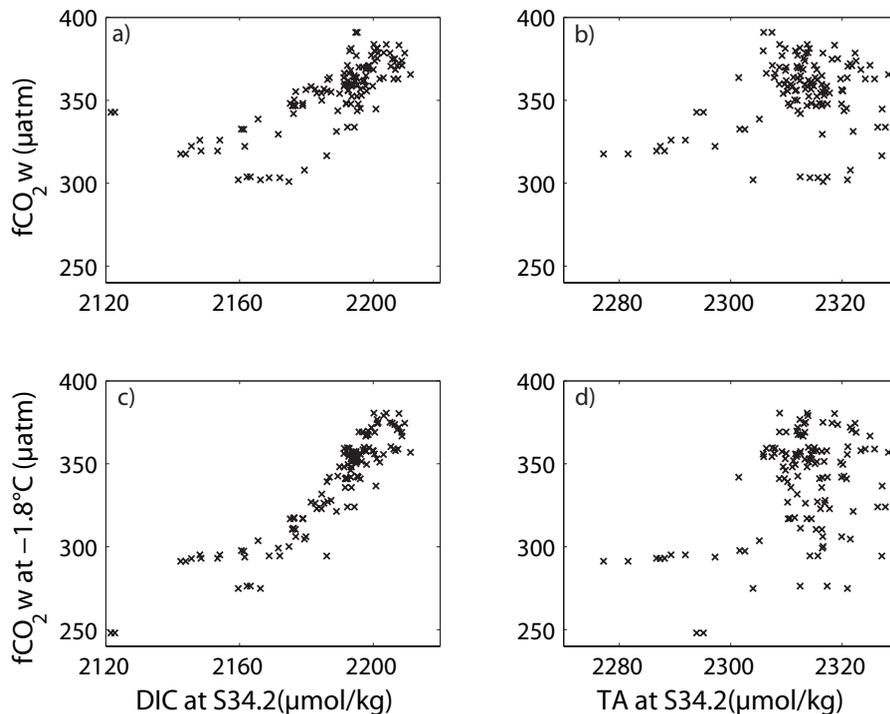


Fig. 9. Surface water $f\text{CO}_2$ and $f\text{CO}_2$ corrected to -1.8°C (**a**, **c**) for DIC from 20 m depth normalized to a salinity of 34.2, and (**b**, **d**) for alkalinity normalized to a salinity of 34.2. Total alkalinity has been calculated from surface water $f\text{CO}_2$ and DIC at 20 m depth.

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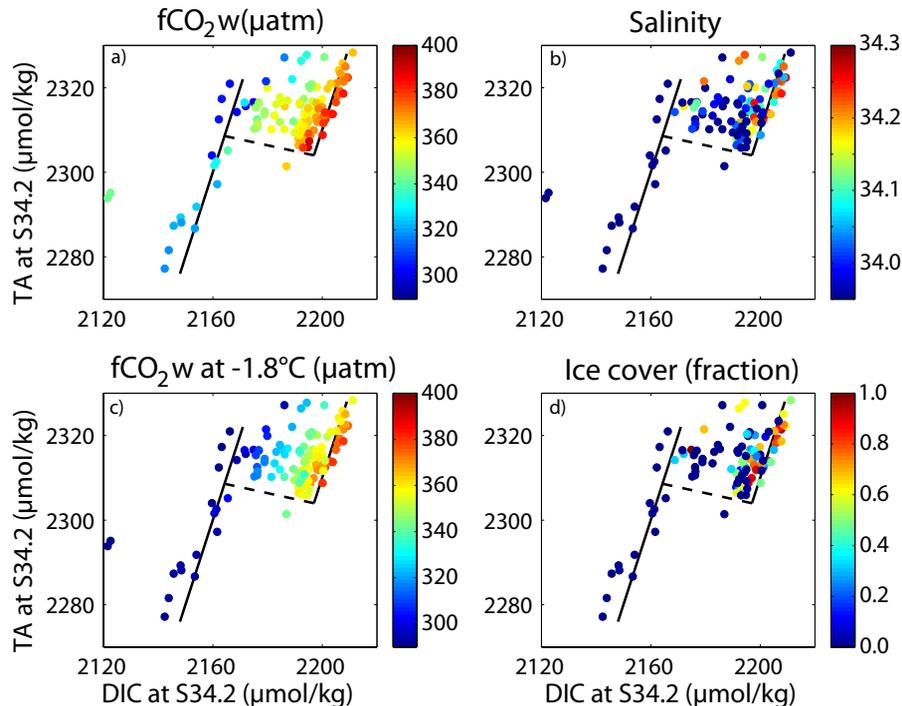


Fig. 10. Alkalinity and DIC normalized to a salinity of 34.2 **(a)** for surface water $f\text{CO}_2$, **(b)** salinity, **(c)** $f\text{CO}_2$ corrected to -1.8°C , and **(d)** the shipboard observations of the sea ice fraction interpolated to the timing of the CTD casts. The continuous lines correspond to theoretical changes in TA and DIC in a ratio of 2:1 by precipitation and dissolution of CaCO_3 , while the dashed line indicates the effect of organic matter production and remineralisation at a ratio for TA to DIC of $-0.14:1$ (Anderson and Sarmiento, 1994).

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