Distribution and mineralogy of carbonate sediments on Antarctic shelves

Judith Hauck [a,*], Dieter Gerdes [a], Claus-Dieter Hillenbrand [b], Mario Hoppema [a], Gerhard Kuhn [a], Gernot Nehrke [a], Christoph Völker [a], Dieter A. Wolf-Gladrow [a]

[a] Alfred Wegener Institute for Polar and Marine Research, Postfach 12 01 61, 27515 Bremerhaven, Germany
[b] British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, United Kingdom

ARTICLE INFO

ABSTRACT

We analyzed 214 new core-top samples for their $CaCO_3$ content from shelves all around Antarctica in order to understand their distribution and contribution to the marine carbon cycle. The distribution of sedimentary $CaCO_3$ on the Antarctic shelves is connected to environmental parameters where we considered water depth, width of the shelf, sea-ice coverage and primary production. While $CaCO_3$ contents of surface sediments are usually low, high (>15%) $CaCO_3$ contents occur at shallow water depths (150–200 m) on the narrow shelves of the eastern Weddell Sea and at a depth range of 600–900 m on the broader and deeper shelves of the Amundsen, Bellingshausen and western Weddell Seas. Regions with high primary production, such as the Ross Sea and the western Antarctic Peninsula region, have generally low $CaCO_3$ contents in the surface sediments.

The predominant mineral phase of $CaCO_3$ on the Antarctic shelves is low-magnesium calcite. With respect to ocean acidification, our findings suggest that dissolution of carbonates in Antarctic shelf sediments may be an important negative feedback only after the onset of calcite undersaturation on the Antarctic shelves.

Macrozoobenthic $CaCO_3$ standing stocks do not increase the $CaCO_3$ budget significantly as they are two orders of magnitude lower than the budget of the sediments.

This first circumpolar compilation of Antarctic shelf carbonate data does not claim to be complete. Future studies are encouraged and needed to fill data gaps especially in the under-sampled southwest Pacific and Indian Ocean sectors of the Southern Ocean.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Human emissions of CO_2 lead to ocean acidification (OA): as the oceans take up CO_2 from the atmosphere, carbonate equilibria in the oceans shift toward lower pH and lower carbonate ion concentration. As a result, undersaturation with respect to carbonate minerals can occur, leading to dissolution of carbonates in marine sediments. The dissolution reaction releases carbonate ions and subsequently tends to increase pH. This mechanism is known as buffering, and it will occur on centennial time scales on the abyssal sea floor (Archer et al., 1997). Within this century, it will be significant and observable at those places where carbon chemistry will change significantly and seafloor sediments bear sufficient carbonate.

OA, which is measurable by change in pH, will be strongest in high latitudes (McNeil and Matear, 2008; Orr et al., 2005) due to the temperature dependence of carbonate equilibria and solubility. Within the polar regions, OA is intensified on the shallow shelves (Arrigo et al.,

2008b; Hauck et al., 2010). Antarctic shelves will undergo large changes in pH and calcite and aragonite saturation horizons in the near future. The GLODAP (Key et al., 2004) and CARINA (Key et al., 2010) projects have compiled extensive global biogeochemical data sets which give a broad picture of recent carbon inventories and ongoing acidification.

In contrast, it is not clear how abundant carbonate sediments are on the Antarctic shelves. The Antarctic shelf is unique compared to other continental shelves. It is deeper, has a rugged topography and often a landward-sloping profile, in particular in West Antarctica (Anderson, 1999). The overdeepening of the Antarctic shelf is mainly attributed to long-term glacial erosion, and to a minor degree to the isostatic depression of the bed by the Antarctic ice sheet. The area of the entire Antarctic shelf (depth<1000 m) is 4.4×10^6 km^2 (based on Timmermann et al. (2010)) and it has a mean water depth of approximately 500 m (Anderson, 1999).

It has been common knowledge that extensive carbonate oozes appear only in shallow low-latitude sediments (e.g. Archer and Maier-Reimer, 1994; Milliman, 1994; Seiter et al., 2004). However, a first data compilation including the Southern Ocean (Seiter et al., 2004) showed that also sediments from the Southern Ocean may have moderate to high carbonate contents. In the global data set of Seiter et al. (2004), though, samples from polar areas are still under-represented, and it is unknown, how abundant carbonates really are

* Corresponding author.
E-mail addresses: judith.hauck@awi.de (J. Hauck), dieter.gerdes@awi.de (D. Gerdes), hilc@bas.ac.uk (C.-D. Hillenbrand), mario.hoppema@awi.de (M. Hoppema), gerhard.kuhn@awi.de (G. Kuhn), gernot.nehrke@awi.de (G. Nehrke), christoph.voelker@awi.de (C. Völker), dieter.wolf-gladrow@awi.de (D.A. Wolf-Gladrow).

in Antarctic shelf sediments, and which main factors control their distribution. In the past, circum-Antarctic and regional carbonate distributions were mainly inferred from distributions of calcareous and agglutinated foraminifera in surface sediments (e.g. Anderson, 1975; Kellogg and Kellogg, 1987; McCoy, 1991) rather than from bulk $CaCO_3$ contents.

Calcium carbonate is produced by marine organisms in the form of two main polymorphs, calcite and aragonite. Its solubility increases with pressure and with decreasing temperature. The depth levels below which aragonite or calcite are undersaturated are denominated aragonite and calcite saturation horizons. The saturation states for calcite (Ω_C) and aragonite (Ω_A) are defined as

$$\Omega_C = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{K_{spC}^*} \qquad (1)$$

$$\Omega_A = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{K_{spA}^*} \qquad (2)$$

where K_{sp}^* is the stoichiometric solubility product (Mucci, 1983; Zeebe and Wolf-Gladrow, 2001). By definition, Ω is >1 above and <1 below the saturation horizon. Aragonite is the more soluble phase, hence its saturation horizon is shallower than that of calcite. An additional factor that controls the solubility of calcite is the amount of magnesium incorporated into calcite, with high-Mg calcite being more soluble than pure calcite (Mucci and Morse, 1984).

A variety of planktonic and benthic organisms produce $CaCO_3$ in the Southern Ocean (SO), for example pteropods (aragonite), foraminifera (calcite and high- and low-Mg calcite), bryozoans (calcite in Antarctica), echinoderms (high-Mg calcite), bivalves (calcitic and aragonitic species) and brachiopods (low-Mg calcite) (Blackmon and Todd, 1959; Kuklinski and Taylor, 2009; Milliman, 1994; Weber et al., 1969).

One calcitic foraminifera species, *Neogloboquadrina pachyderma (sin.)*, is omnipresent and the dominant planktonic foraminifera species in the Southern Ocean (e.g. Bergami et al., 2009; Donner and Wefer, 1994; Swadling et al., 2010). Extremely high amounts of *N. pachyderma* appear in sea ice (Dieckmann et al., 1991; Lipps and Krebs, 1974; Spindler and Dieckmann, 1986). *N. pachyderma* in sea ice can be 70 times more abundant per volume than in the underlying sea water. The second largest planktonic carbonate producers are pteropods and the dominant species south of the Polar Front is the aragonitic species *Limacina helicina* (Hunt et al., 2008). The distribution of *L. helicina* based on meso- and macrozooplankton analyses is not well understood and appears to be very patchy (Boysen-Ennen and Piatkowski, 1988; Hunt et al., 2008; Swadling et al., 2010). Accornero et al. (2003) and Collier et al. (2000) found *L. helicina* to be the main contributor to carbonate fluxes from sediment trap studies in the Ross Sea, with minor contributions of *N. pachyderma*. Other sediment trap studies on the eastern Weddell Sea shelf (Isla et al., 2009) and in the Bransfield Strait (Donner and Wefer, 1994) observed *N. pachyderma* to be the dominant foraminifera in their sediment traps, but do not report on whether pteropods occurred.

Benthic foraminifera are much more diverse than planktonic foraminifera. Mikhalevich (2004) found Antarctic shelf species to be circum-Antarctic, but highly patchy. Representative species include agglutinated, high-Mg calcitic and low-Mg calcitic species in equal shares (Blackmon and Todd, 1959). Bryozoans and echinoderms are crucial parts of the Antarctic macrobenthos (Brey and Gerdes, 1998; Gutt, 2007; Hayward, 1995; Smith, 2007). Together with sponges, bryozoans are the most significant occupiers of the seafloor and their remains may comprise the majority of the coarse bottom sediment (Barnes and Clarke, 1998; Bullivant, 1961; Hayward, 1995). Echinoderms can dominate the community standing stocks, especially at water depths >500 m (Brey and Gerdes, 1998; Brey et al., 1999). The

aragonitic bivalve *Laternula elliptica* is widespread in the Antarctic nearshore waters (Ahn and Shim, 1998) and is generally preserved in the sediments as it is one of the most common macrofossils of Antarctic Quaternary and Tertiary sediments (Tada et al., 2006). Other common calcareous macroorganisms in the Southern Ocean are the aragonitic bivalve *Yoldia eightsi* and calcitic gastropods and brachiopods (McClintock et al., 2009).

In this study we investigate the distribution of $CaCO_3$ in surface sediments from Antarctic shelves as well as its mineralogy in order to contribute to the understanding of the fate of biologically produced carbonate. In addition to the analysis of core-top sediments, we estimate the macrozoobenthic $CaCO_3$ standing stocks. The knowledge about $CaCO_3$ distribution and mineralogy leads to a qualitative statement about the buffering capacity of carbonates in surface sediments from Antarctic shelves and forms a basis for future quantification of carbonate dissolution effects.

2. Methods

2.1. Sample material

214 core-top samples from the core repositories at the British Antarctic Survey (BAS), the British Ocean Sediment Core Research Facility (BOSCORF), the Antarctic Marine Geology Research Facility (AMGRF, Florida State University, USA), from recent Polarstern cruises (ANT-XXVI/3 and ANT-XXIII/9) and from Jubany station (Potter Cove) were analyzed. The samples cover the eastern and western Antarctic Peninsula, the Bellingshausen and Amundsen Seas, the Ross Sea and small parts of the southwest Pacific and Indian shelf sectors of the Southern Ocean. All samples were taken from the surface sediments, mostly from 0–1 cm core depth, but a few samples were taken from 1–2, 2–3 or 3–4 cm depth. Wherever possible, we took the samples from box and multiple cores, because surface sediments in gravity and vibrocores are sometimes disturbed or partially lost.

2.1.1. Additional CaCO₃ data

In addition to the 214 samples that were measured for the first time in this study, we compiled literature data to cover a representative area in terms of geographical coverage and water depth, resulting in a total of 390 data points. Data from the shelves in the Weddell Sea were taken from Melles et al. (1991) and additional published data from the Antarctic Peninsula, the Bellingshausen and Amundsen Seas were included (Hillenbrand et al., 2003, 2010). Data from the George V shelf in East Antarctica were supplied by Post et al. (2011). Furthermore, Antarctic shelf data were extracted and quality controlled from the global data compilation by Seiter et al. (2004). Only data where the water depth is at most 1000 m were used. The location of the samples is depicted in Fig. 1.

This study makes use of previously sampled sediment cores and literature data. The regional and bathymetric distribution of our data is therefore not random, but induced by the availability of data and samples. Data from easily accessible areas as the Antarctic Peninsula are frequent, whereas other more remote areas and very shallow depth regions are underrepresented. Data from shallower than 200 m are available from the Bellingshausen Sea ($n = 1$), Ross Sea ($n = 1$), eastern Weddell Sea ($n = 3$), western Antarctic Peninsula ($n = 9$), southwestern Pacific and Indian shelf sectors of the Southern Ocean ($n = 5$), but not from the Amundsen Sea, eastern Antarctic Peninsula and western Weddell Sea. Hence, only 5% of the total 390 data points are from water depths shallower than 200 m. The shallow depth regions contribute only a small percentage to the total area of the Antarctic shelves. Furthermore, these shallows are not easily accessible, because the bathymetry is poorly known and therefore research vessels rarely sample sediments in these areas.
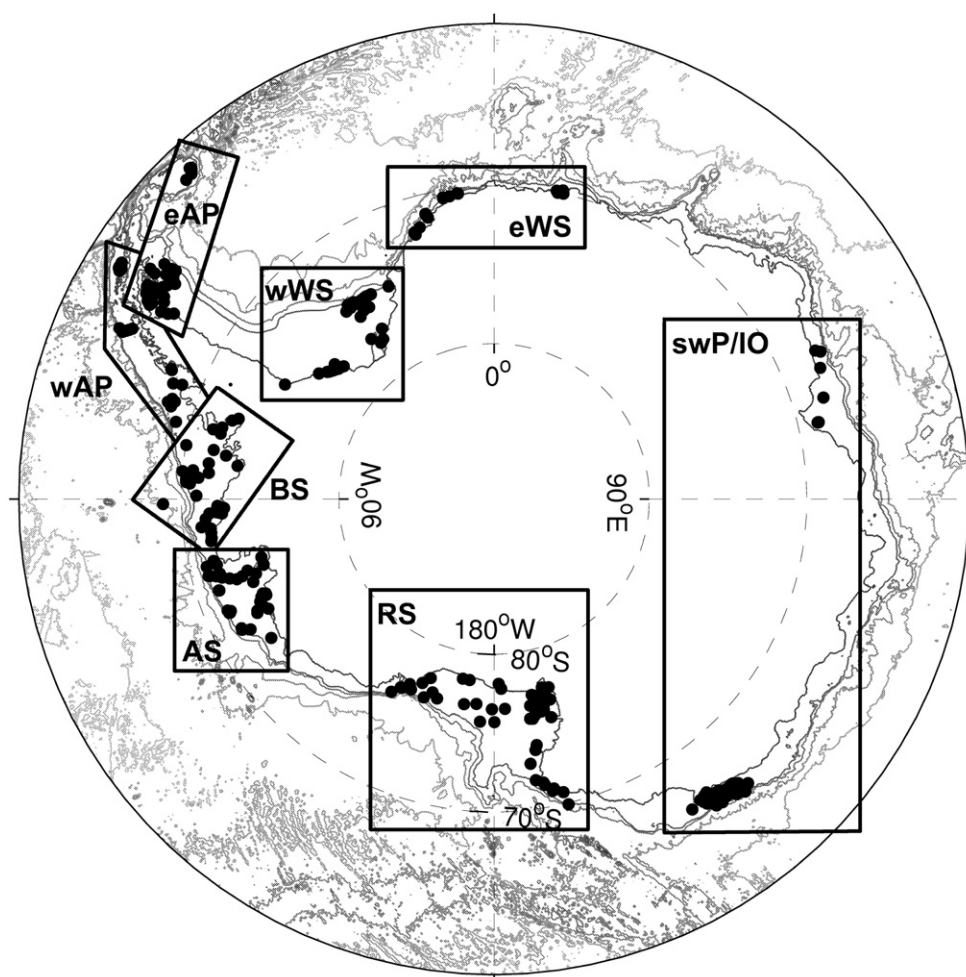
Fig. 1. Position of all core-top data (new and literature data). Isolines are from the topography of Timmermann et al. (2010) and lines are drawn every 1000 m. Different shelf regions are indicated by boxes. AS: Amundsen Sea; BS: Bellingshausen Sea; eAP: eastern Antarctic Peninsula; eWS: eastern Weddell Sea; RS: Ross Sea; swP/IO: southwest Pacific/Indian Ocean; wAP: western Antarctic Peninsula; wWS: western Weddell Sea.

The CaCO₃ data and all metadata such as position, sample depth, core type and data origin of all individual samples are listed in a data table in Pangaea (doi:10.1594/PANGAEA.757933).

2.2. Chemical analyses

All geochemical analyses were carried out on samples that were freeze-dried and ground to homogeneous powders. The mineralogical phase identification was done by means of X-ray diffraction (XRD) on all samples. In a second step, total carbon (TC) and total organic carbon (TOC) were determined.

Large calcareous particles, such as fragments of bryozoans or entire bivalves were excluded, i.e., taken out of the sample before grinding and measurement of TC and TOC. These particles do contribute to the sedimentary CaCO₃ inventory, but from a small core-top sample it is difficult to decide, whether these particles are representative for the region and how abundant they are over a larger area. Therefore, our CaCO₃ data give a lower boundary of CaCO₃ contents. The distribution of carbonate forming macrozoobenthos and their contribution to carbonate budgets is discussed in Sections 2.4 and 3.3.

2.2.1. Phase identification

The bulk sediment was analyzed using a Philips PW diffraction analyzer with a cobalt anode (CoKα radiation, 40 kV, 40 mA). A range of 3–100° 2θ was scanned with a step scan speed of 0.02° 2θ per second. The diffractograms were evaluated with the program "X'Pert HighScore

Plus" (Version 2.2c, PANalytical B.V., Almelo, The Netherlands) without internal standard. The position of the calcite peak was corrected for the offset of the quartz peak position from its theoretical value (Tucker, 1996). The Bragg equation was used to convert the 2θ angle into lattice spacing (d). The relationship of Goldsmith et al. (1961) was employed to relate the peak shift of the d_{104} peak with the Mg content in the calcite of the specific sample as recommended by Milliman (1994) and Tucker (1996). Samples with more than 2% CaCO₃ (doi:10.1594/PANGAEA.757933) were used for the analysis of the carbonate mineralogy.

2.2.2. CaCO₃ quantification

The percentage of calcium carbonate (in wt. %) in the bulk sample was determined on the basis of total inorganic carbon (TIC) which is obtained from TC and TOC measurements. TC was measured on subsamples of 10 to 20 mg using a combustion analyzer (Vario EL III, Elementar Analysensysteme GmbH, Germany) and TOC by a carbon–sulfur determinator (LECO CS-125, LECO Instrumente GmbH, Germany). Samples for TOC measurements (30 to 50 mg) were treated with three drops of ethanol and 0.5 ml HCL (37%) and heated for two hours at 250 °C to remove TIC. A salt correction was applied to TC and TOC raw data, hence CaCO₃ contents are reported per mass of salt-free dry sediment. Relative analytical precision expressed as the standard deviation obtained under repeatability conditions is 2% for TC and 0.5% for TOC. The CaCO₃ percentage was converted to g CaCO₃ m⁻² following the procedure described in detail in Archer (1996). This protocol calculates

an average porosity (ϕ) for the top 10 cm of the sediment based on the percentage of $CaCO_3$. Calculated porosities range between 0.751 and 0.863 with a mean of 0.857. We use an average grain density (ρ) of 2.5 g cm^{-3} and consider the top 10 cm (d) of the sediment in which we assume the $CaCO_3$ content to be constant. The top 10 cm of the sediment reflect the bioturbated layer in which dissolution can take place. The $CaCO_3$ content in the 10 cm surface layer is then given as:

$$CaCO_3 \left(g\ m^{-2} \right) = \frac{CaCO_3 (\%)}{100} \cdot \rho \cdot (1-\phi) \cdot d \cdot f \tag{3}$$

where f is the conversion factor from g cm^{-2} to g m^{-2}.

2.3. GLODAP and CARINA data

The GLODAP and CARINA data bases were used to estimate bottom water saturation states of calcite and aragonite on the Antarctic shelves. These data bases provide global, extensive quality controlled and internally consistent full water column data of carbon and carbon-relevant variables (Key et al., 2004, 2010). The data were filtered to find stations adjacent to the Antarctic continent with water depths shallower than 1500 m. An offset in water depth of 300 m compared to the bathymetry by Timmermann et al. (2010) was accepted. This procedure assured that only bottom data were considered, but also that data were not discarded due to uncertainties in water depth. As discussed for the sediment samples (Section 2.1), also the GLODAP and CARINA data sets consist mainly of non-shelf data. After the filtering procedure, 67 data points remained. These data cover the western Antarctic Peninsula, Ross Sea, western Weddell Sea and the southwest Pacific and Indian shelf sectors of the Southern Ocean, include data from 1989 to 2003 and allow a valid estimate for Ω_C and Ω_A during the period when most of the sediment cores were taken. Dissolved inorganic carbon (DIC) and total alkalinity (A_T) as well as potential temperature, salinity, pressure, phosphate and silicate data were used from GLODAP/CARINA to calculate Ω_C and Ω_A with the program CO2SYS (Lewis and Wallace, 1998). The carbonic acid dissociation constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987) and the KSO$_4$ dissociation constant by Dickson (1990) were used.

Potential temperature and salinity were utilized to group the data into different water masses (see Table 2). The following water masses were considered: Circumpolar Deep Water (CDW) which is transported around the continent with the Antarctic Circumpolar Current (ACC). This water mass is mixed with Antarctic Surface Water (AASW) south of the ACC to form modified Circumpolar Deep Water (mCDW). In certain regions (mainly Weddell and Ross Sea), the release of heat and salt during sea-ice formation on the shelf produces High-Salinity Shelf Water (HSSW) and Ice Shelf Water (ISW). These water masses can sink to depth and mix with surrounding mCDW producing Antarctic Bottom Water (AABW).

2.4. Macrozoobenthos data

Macrozoobenthic wet mass data were analyzed to estimate the contribution of macrozoobenthic carbonate producers to the carbonate budget in surface sediments from the Antarctic shelves. The data-set consists of 243 stations on the eastern and western Antarctic Peninsula and the eastern and western Weddell Sea shelf and slope. Only data where the water depth is <1000 m were used (218 stations). Samples were collected with giant box corers, multiple box corers and Van Veen grabs between 1985 and 2007. These samples were sieved over 500 μm meshsize screens and abundance and wet mass were determined for 35 major taxonomic groups. For the present study, only taxonomic groups which are known to produce $CaCO_3$ were considered: hydrozoa, bryozoa, brachiopoda, polyplacophora, bivalvia, gastropoda, scaphopoda, echinoidea, holothuroidea, asteroidea, ophiuroidea and crinoidea.

The wet mass was converted to $CaCO_3$ by conversion factors from Brey et al. (2010). For bivalvia and gastropoda, $CaCO_3$ was calculated by converting from wet mass with shell to wet mass without shell. The shell mass was considered equivalent to $CaCO_3$ mass and was taken as $CaCO_3$ standing stock for bivalvia and gastropoda. For all other groups, wet mass was converted to dry mass and ash-free dry mass. We use the ash mass, i.e., the difference between dry mass and ash-free dry mass, as a proxy for $CaCO_3$. This is a valid estimate as only groups with calcareous endo- and exoskeletons were considered. No conversion factor was available for polyplacophora, therefore this group was discarded. The wet mass contribution of polyplacophora to the total wet mass at all stations is 0.2%. The $CaCO_3$ content per dry mass for echinoderms as calculated with conversion factors by Brey et al. (2010) is comparable to the $CaCO_3$ contents of echinoderms as determined by Lebrato et al. (2010) except for holothuroidea. Lebrato et al. (2010) measured only one holothuroidean species with a $CaCO_3$ content of 3.46% per dry mass. In contrast, Brey et al. (2010) considered data of 51 species where the ash content ranged from <10 to >80% of the dry weight (mean: 44.5%). In Antarctica, holothuroidea are very diverse and many are heavily calcified (Gutt, 1988). The $CaCO_3$ standing stocks are given in g $CaCO_3$ m^{-2}, where the volume considered depends on the penetration depth of the sampling device into the sediment. The penetration depth varied with the sediment type and was between 10 and 40 cm. These data are available in Pangaea (doi:10.1594/PANGAEA.757933).

Table 1
List of acronyms.

Acronym	Full name
AABW	Antarctic Bottom Water
AASW	Antarctic Surface Water
ACC	Antarctic Circumpolar Current
AS	Amundsen Sea
A_T	Total alkalinity
BS	Bellingshausen Sea
CDW	Circumpolar Deep Water
DIC	Dissolved inorganic carbon
eAP	Eastern Antarctic Peninsula
eWS	Eastern Weddell Sea
HSSW	High-Salinity Shelf Water
ISW	Ice-Shelf Water
mCDW	Modified Circumpolar Deep Water
RS	Ross Sea
SO	Southern Ocean
swP/IO	Southwestern Pacific and Indian Ocean
TC	Total carbon
TIC	Total inorganic carbon
TOC	Total organic carbon
XRD	X-ray diffraction
wAP	Western Antarctic Peninsula
wWS	Western Weddell Sea

Table 2
Main water masses occurring in the Antarctic shelf and slope region.

Water mass [a]	θ [b] (°C)	Salinity	Reference
AABW	−1.7 to 0	34.64 to 34.73	Gordon (1974); Carmack (1977)
AASW	−1.7 to 0.5	<34.4	Grosfeld et al. (2001); Orsi et al., (1995)
CDW [c]	>0		Orsi et al. (1993, 1995)
HSSW	−1.9 to −1.7	>34.65	Grosfeld et al. (2001)
ISW	<−1.9		Grosfeld et al. (2001)

[a] AABW: Antarctic Bottom Water, AASW: Antarctic Surface Water, HSSW: High-Salinity Shelf Water, ISW: Ice-Shelf Water, CDW: Circumpolar Deep Water.
[b] Potential temperature.
[c] Modified Circumpolar Deep Water (mCDW) is defined as being colder and less saline than CDW (Whitworth et al., 1998).

3. Results and discussion

3.1. Geographical and bathymetric CaCO₃ distribution

The sediment samples can be grouped into different regions: the western Antarctic Peninsula (wAP) including Marguerite Bay; the eastern Antarctic Peninsula (eAP) including the South Orkney Islands; the Bellingshausen Sea (BS); the Amundsen Sea (AS); the eastern Weddell Sea (eWS), the western Weddell Sea (wWS) and the Ross Sea (RS). Samples from the southwestern Pacific and Indian shelf sectors of the Southern Ocean (swP/IO) are rare and thus were not further split into different regions.

The regions show distinct patterns of carbonate preservation in the sediments (Fig. 2). In the western and eastern Antarctic Peninsula regions, $CaCO_3$ is hardly preserved in the sediments with mean values of 1.3% $CaCO_3$ (444 g $CaCO_3$ m^{-2}, n = 45) and 1.0% (340 g $CaCO_3$ m^{-2}, n = 72), respectively, and $CaCO_3$ contents consistently lower than 10%. A similar situation is found in the Ross Sea with a mean $CaCO_3$ content of 2.0% (714 g $CaCO_3$ m^{-2}, n = 52) and all $CaCO_3$ contents <10%. Higher $CaCO_3$ contents were found in the Amundsen Sea (mean: 5.1%, 2053 g $CaCO_3$ m^{-2}, n = 44), eastern Weddell Sea (mean: 6.8%, 3138 g $CaCO_3$ m^{-2}, n = 24), western Weddell Sea (mean: 4.3%, 2153 g $CaCO_3$ m^{-2}, n = 42), and especially in the Bellingshausen Sea (mean 8.0%, 3546 g $CaCO_3$ m^{-2}, n = 40). The swP/IO region is not well captured by our data set because of low sample coverage; 58 of the 71 samples are from the George V shelf and 13 from Prydz Bay. The mean $CaCO_3$ content of these samples is 2.0% (719 g $CaCO_3$ m^{-2}).

The $CaCO_3$ content varies with depth (Fig. 2b), and shows maxima with $CaCO_3$ contents >15% around 150–200 m and between 600 and 900 m. However, variances at single depths are quite large. These two depth intervals reflect two different mechanisms of carbonate preservation. On the parts of the shelf shallower than 200 m, carbonates are preserved, where they were produced and possibly concentrated by currents (winnowing). These carbonates include the entire range of carbonates produced by planktonic and benthic organisms. In the depth interval between 600 and 900 m, carbonates are exclusively accumulated at the outer shelf or near the shelf break. These are locations where carbonates are accumulated by currents and also terrigeneous sand contents are high. On the outer shelf in the BS, for example, sand and calcitic foraminifera are enriched by winnowing of silt and clay (Hillenbrand et al., 2003, 2010).

The different shelf regions can be grouped according to which $CaCO_3$ preservation mechanism applies to them. In the regions with broad and deep shelves, i.e., in the Bellingshausen and Amundsen Seas and in the wWS (Figs. 2b and 3), carbonates are found to be deposited on the outer shelf (note that no data are available from depths shallower than 200 m in the wWS and in the AS and only one data point in the BS). This corresponds to calcareous foraminifera distributions which were found in high concentrations only on the outer shelf of the Amundsen and western Weddell Seas (Anderson, 1975; Hillenbrand et al., 2003, 2010; Kellogg and Kellogg, 1987).
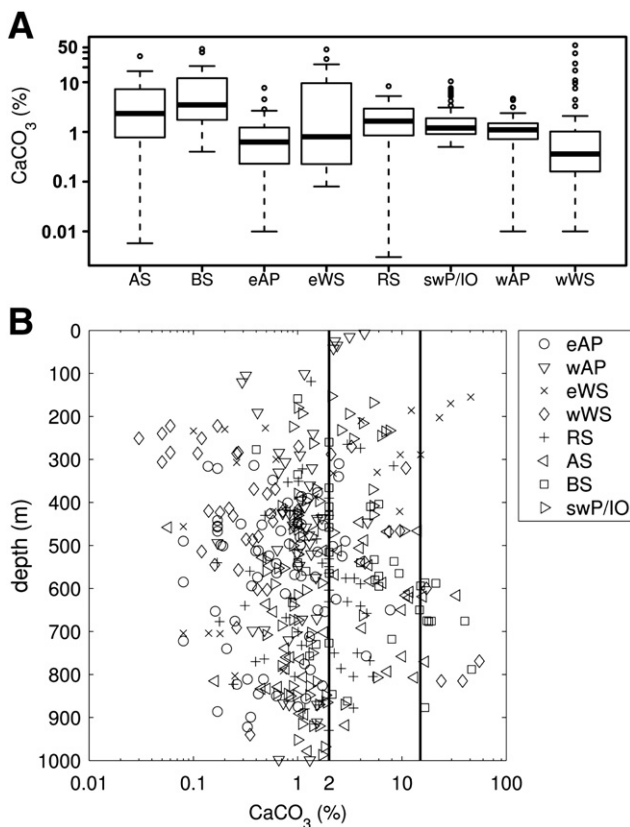
In the eWS, which is characterized by narrow, shallower shelves, $CaCO_3$ accumulates only at the shallow depth interval. High carbonate concentrations in the eWS are mainly produced by benthic communities, such as bryozoan colonies and molluscs (Gingele et al., 1997). While in our dataset hardly any sample from the George V shelf contains >10% $CaCO_3$, Domack (1988) reported carbonate contents of 10–30% with barnacles, bryozoans, and ostracods dominating the sand and gravel fractions of surface sediments. Post et al. (2010) observed bryozoans and foraminifera, with rare abundances of bivalves, gastropods, ostracods, as well as aragonitic hydrocorals on the continental slope. The 13 samples from Prydz Bay are consistently below 2% $CaCO_3$.

In the Ross Sea, carbonate concentrations are generally low, independent of water depth (Fig. 2). This is surprising in the light of reports of high densities of aragonitic pteropods in the water column (Hunt et al., 2008) and sediment traps (Accornero et al., 2003). A total number of 52 sediment samples from the Ross Sea were analyzed, however, the shallow banks in the western Ross Sea are represented by only two samples. Domack et al. (1999) reported $CaCO_3$ contents of >10% for two cores from one of these shallow banks. Despite the high number of data points in the RS, the mean carbonate deposition might be underestimated due to the fact that these banks are undersampled and often contain winnowed bioclastic carbonates (Anderson, 1999). Likewise, the eastern and western Antarctic Peninsula regions are very poor in $CaCO_3$ independent of water depth.
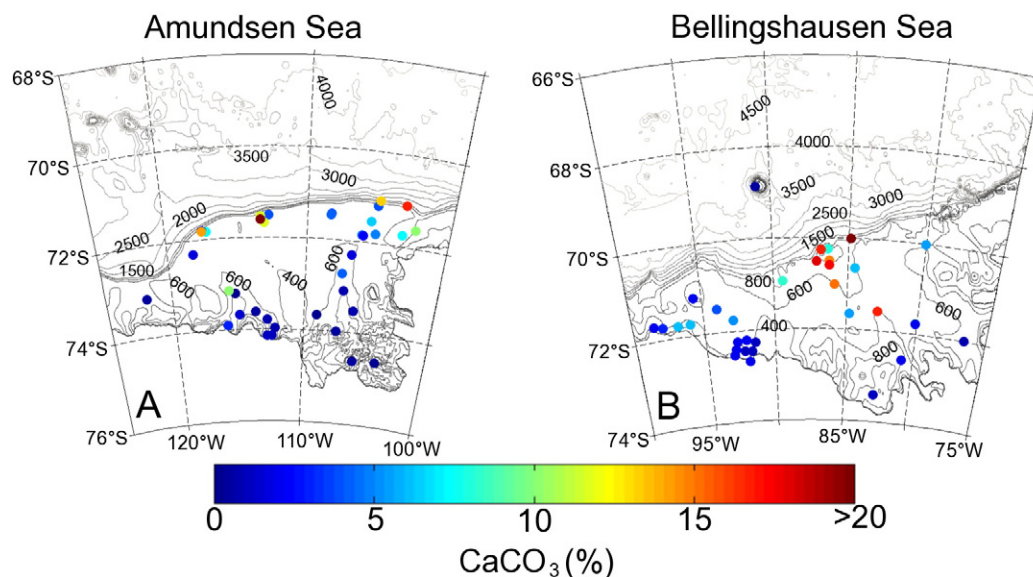
Different factors control the deposition and preservation of carbonates in the surface sediments. Important is the flux of organic matter to the ocean floor (related to primary production) and its respiration/remineralization in the sediments, transport of carbonate material by currents and calcium carbonate saturation states of the water mass above the sediment. These factors are discussed below with respect to the distribution of our $CaCO_3$ data.

Fig. 2. (A) Boxplots of sedimentary $CaCO_3$ content (%) in the different Antarctic shelf regions. The box shows the upper and lower quartiles of the data, i.e., 50% of the data are within the box and the line through the box indicates the median. The whiskers extend to the most extreme data points if they are not more than 1.5 times the interquartile range from the box. The dots show data points outside this range. AS: Amundsen Sea (n = 44); BS: Bellingshausen Sea (n = 40); eAP: eastern Antarctic Peninsula (n = 72); eWS: eastern Weddell Sea (n = 24); RS: Ross Sea (n = 52); swP/IO: southwest Pacific/Indian Ocean (n = 71); wAP: western Antarctic Peninsula (n = 45); wWS: western Weddell Sea (n = 42), (B) Sedimentary $CaCO_3$ content (%) versus water depth on the Antarctic shelves. Different shelf regions are indicated by different symbols. Bold lines indicate 2 and 15% $CaCO_3$, respectively.

3.1.1. Primary production

The Ross Sea and the western Antarctic Peninsula are regions known for very high primary production within the Southern Ocean (Arrigo et al., 2008a; Smith and Gordon, 1997). The mean chlorophyll a concentrations from in situ data are four and five times higher in the western Antarctic Peninsula region and Ross Sea, respectively, than in the remaining SO (Arrigo et al., 2008b). The BS, AS, wWS and large parts of the George V shelf are covered by sea ice for most of the year, limiting

Fig. 3. Sedimentary CaCO₃ content (%) (A) on the Amundsen Sea shelf and (B) on the Bellingshausen Sea shelf. Isolines are from the topography of Timmermann et al. (2010), lines are drawn every 200 m between 0 and 1000 m and every 500 m at water depths >1000 m.

the phytoplankton growing season and total production, which likely leads to a reduction of the export production. Respiration in the sediments of the RS and wAP with their high primary production rates is expected to be orders of magnitude higher than in the other shelf regions and alters carbonate chemistry. High export production feeds a benthic community which includes carbonate producers (Cattaneo-Vietti et al., 1999, 2000; Dayton et al., 1982; Smith, 2007), but this carbonate is dissolved after the death of the organisms and thus not preserved in the sediments. Accordingly, in regions with low primary productivity and export production, there is a small benthic community with few calcareous organisms. Carbonate contents thus reflect the concentration of planktonic foraminifera. These are especially abundant in sea ice. Spindler and Dieckmann (1986), Dieckmann et al. (1991) and Thomas et al. (1998) report large abundances of *N. pachyderma* in sea ice of the Weddell and Amundsen Seas. This disparity in primary productivity may be the dominant factor in CaCO₃ distribution (Hillenbrand et al., 2003).

3.1.2. Currents

Current velocities are not available for the entire study region. There are indications for a strong current in the BS close to the shelf edge, associated with the southern boundary of the ACC with velocities of up to 28 cm s^{-1} (Read et al., 1995). This current probably winnows silt and clay and favors an enrichment of calcitic particles in the sand fraction. Carbonates are mainly represented by *N. pachyderma* (Hillenbrand et al., 2003, 2010). Winnowing by strong currents on the outer shelf and continental slope was suggested to facilitate carbonate accumulation by other studies (Gingele et al., 1997; Melles and Kuhn, 1993).

3.1.3. Calcium carbonate saturation state of water masses

The overlying water mass is another factor controlling carbonate chemistry besides respiration. If the water is undersaturated with respect to one of the carbonate minerals, this mineral will dissolve. The Antarctic shelves with water depths down to 1000 m are today still supersaturated with respect to calcite. This is demonstrated using joint data products from GLODAP and CARINA (see Section 2.3). Bottom water calcite and aragonite saturation states for all stations with water depths down to 1500 m adjacent to the Antarctic continent are shown in Figs. 4, 5a and b. A regression through the data points provides an estimate of the aragonite saturation horizon of about 1100 m (Fig. 5b). However, single data points indicate that the water is undersaturated with respect to aragonite at even shallower depths at

particular locations, even though the data do not take into account sedimentary respiration. Thus, dissolution of aragonite by CO₂-rich water masses might play a role on certain locations of the Antarctic shelves already, especially where ACC water masses protrude onto the shelf (see Section 3.2). In contrast, dissolution of calcite due to undersaturated water masses can be ruled out for the recent past.

All these factors affect the distribution of CaCO₃ in core-top sediments, and they also interact. Primary production appears to be the dominant factor, determining whether significant proportions of CaCO₃ (>2%) can be preserved in the sediments. In addition, carbonate production, width of shelf, sea-ice coverage and calcite saturation state of the overlying seawater impact CaCO₃ distribution. The calcite saturation state of the overlying water mass will only play a role when it falls below a threshold. This critical value is dependent on the region and all contributing factors. While a defined calcite saturation state of the bottom water might lead to undersaturation in pore waters in the high-productivity regions, wAP and RS, it might not have any effect in the BS or any other low-productivity region.

Further physical and biological processes play a role in the disintegration of CaCO₃ within the sediment (e.g., Nelson, 1988; Smith and Nelson, 2003). Early sea-floor processes include abrasion, bioturbation and bioerosion. The latter involves microbial organisms, that burrow, bore and excavate the carbonate substrate (Smith and Nelson, 2003). Further petrographic work could shed light on the impact of microbially mediated dissolution. This is beyond the scope of our study, which is trying to disentangle environmental impacts on CaCO₃ distribution and mineralogy.

Although we observe general patterns of carbonate distribution, these patterns do not imply that the entire shallow shelf of the eastern Weddell Sea, for example, is covered by biogenic carbonates. The distribution of CaCO₃ is highly patchy, as subsets of samples taken very close to each other in the Lazarev Sea (eWS) demonstrate (Fig. 6, data from Gingele et al. (1997)). The patchiness is not well understood, but we assume it is triggered by small-scale topographic features, e.g., differences in substratum for benthic communities or variations of currents.

3.2. Mineralogy

The X-ray diffractograms of the samples with more than 2% CaCO₃ (52 out of 189 samples available for X-ray diffraction) showed only one carbonate component to be present and this was calcite throughout all samples. Only in one sample, a calcite and a weak aragonite
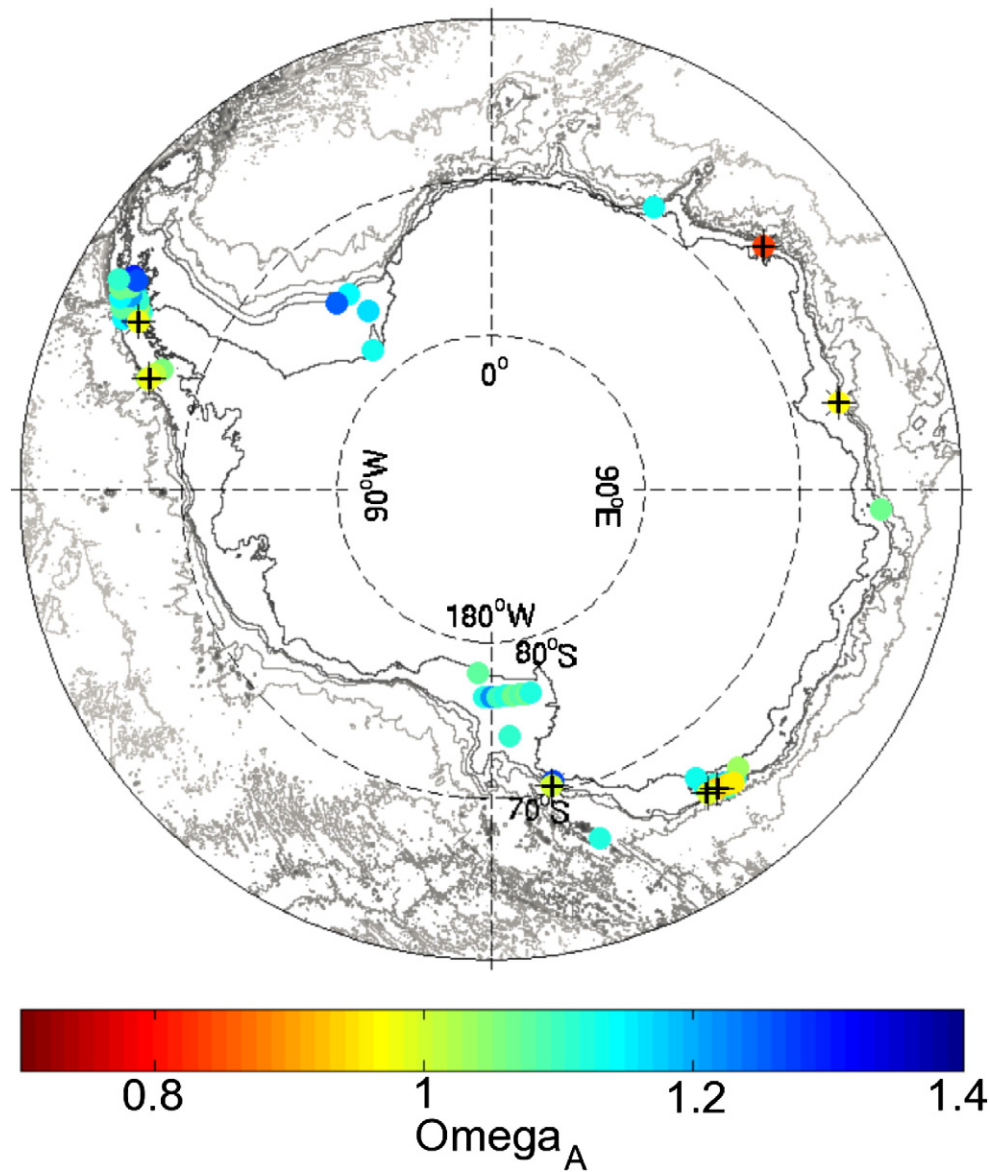
Fig. 4. Bottom water Ω_A on the Antarctic shelves from GLODAP and CARINA data. Occurrence of undersaturation at depths shallower than 1100 m is marked with a black cross. Iso-lines are from the topography of Timmermann et al. (2010) and lines are drawn every 1000 m.
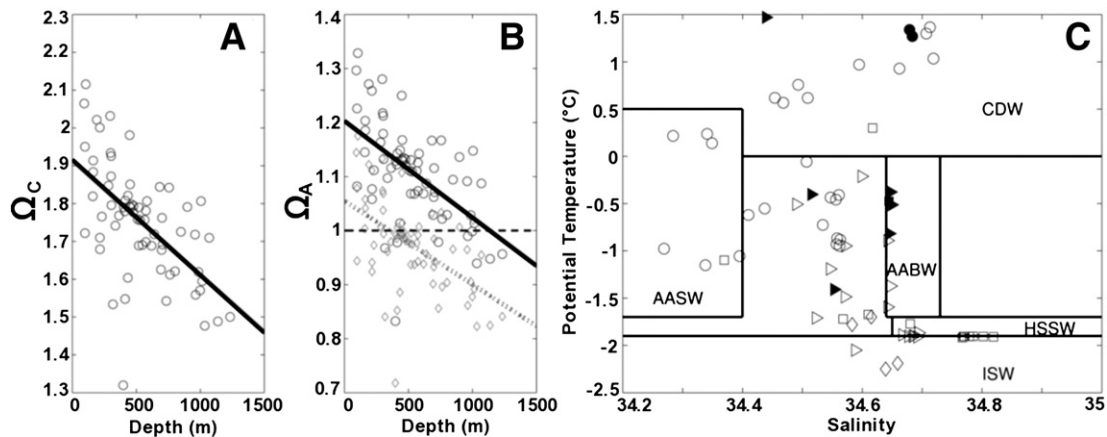

Fig. 5. Bottom water saturation states (a) Ω_C and (b) Ω_A on the Antarctic shelves and slope from GLODAP and CARINA data. Calcite is supersaturated at all depths. A linear regression through Ω_A reveals a mean saturation horizon of about 1100 m with certain areas being undersaturated at even shallower depths. The gray diamonds and dotted regression line were calculated assuming a DIC increase of 20 μmol kg^{-1} within the first cm of the sediment related to oxic remineralization of organic matter. (c) T/S-diagram of Antarctic shelf data from the GLODAP and CARINA data sets. Filled markers indicate $\Omega_A < 1$. Different markers indicate different regions: Ross Sea (squares), western Antarctic Peninsula (circles), western Weddell Sea (diamonds), southwest Pacific and Indian shelf sectors of the Southern Ocean (triangles). The properties of the main water masses are indicated by boxes. Modified Circumpolar Deep Water is not indicated, but is defined as being colder and less saline than Circumpolar Deep Water. See text, Tables 1 and 2 for further explanation and abbreviations.
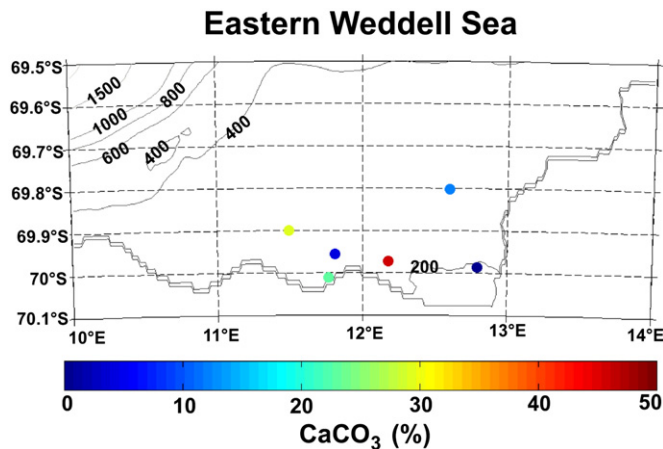
Eastern Weddell Sea

Fig. 6. Sedimentary CaCO$_3$ content (%) on the eastern Weddell Sea shelf with data from Gingele et al. (1997).

peak were detected. Low-Mg calcite is dominating throughout the samples, whereas high-Mg calcite was detected in 8% of the samples with a range of 9.9 to 13.9 mol% MgCO$_3$.

Given that aragonitic pteropods and bivalves (see also Section 3.3) are common in their respective habitats in the SO, it is astonishing that no aragonite was found.

As discussed above, aragonite undersaturation in the overlying water may be a reason at certain locations, but cannot explain the general absence of aragonite. In Fig. 4, locations with $\Omega_A<1$ are highlighted. These occur on the wAP shelf and in the swP/IO region. The occurrences of aragonite undersaturation on the George V shelf and close to the Ross Sea can be explained by the relation between Ω_A and depth (Fig. 5b). Here, aragonite undersaturation is found at water depths between 963 and 1233 m which fall in the range of the saturation horizon. The data points below 1000 m water depth show the characteristics of Antarctic Bottom Water (Fig. 5c). Solely the one point at 963 m water depth is less saline.

Aragonite undersaturation appears at water depths of 413 and 734 m on the wAP shelf, at 317 m water depth in Prydz Bay and at 398 m water depth at 48°E. The link between these locations is their exposure to Circumpolar Deep Water (CDW, see Fig. 5c). The southern boundary of the ACC comes close to the shelf break in these areas (Orsi et al., 1995). CDW can penetrate onto the shelf either directly or further altered as modified Circumpolar Deep Water (mCDW). Salinity and potential temperature reveal that the seawater at locations with $\Omega_A<1$ is CDW (wAP and Prydz Bay locations) or modified Circumpolar Deep Water (at 48°E). The ACC transports these warm and CO$_2$-rich water masses around the Antarctic continent. In the large cyclonical gyres, i.e. the Weddell, Ross and Kerguelen Gyres, the ACC cannot penetrate near to the shelf. This is consistent with the finding of $\Omega_A>1$ in the Ross and Weddell Seas and the Kerguelen Gyre (Fig. 4). The large gyres impede the exposure of the shelf to naturally more acidic water masses (CDW). There is also a cyclonic gyre in the Prydz Bay region. Although there is only one data point available in Prydz Bay, which indicates aragonite undersaturation, we hypothesize that in the small gyre CDW is less modified and therefore more acidic than in the large gyres.

Ice Shelf Water, High-Salinity Shelf Water and Antarctic Surface Water are not undersaturated with respect to aragonite (Fig. 5c). This is in contrast to the conclusion of Anderson (1975) that relates the absence of calcareous foraminifera in the southwestern Weddell Sea to the predominance of Ice Shelf Water. We hypothesize that the low numbers of calcareous, but also arenaceous foraminifera are caused by the low primary productivity in this area which cannot sustain a rich benthic community.

High respiration rates in the sediment-water interface can further reduce Ω_A. CO$_2$ is produced in Southern Ocean shelf sediments due to respiration and can be assessed assuming that 1 mol CO$_2$ is produced for 1 mol O$_2$ respired at constant alkalinity as a first approximation. Oxygen consumption is highly variable in the Antarctic shelf and slope sediments with oxygen penetration depths reaching from 1.2 cm up to several meters (Sachs et al., 2009). If we assume an increase in DIC in the sediment by 20 μmol kg^{-1}, this would bring the actual aragonite saturation horizon to about 400 m depth (Fig. 5b). An increase of 20 μmol kg^{-1} DIC is a conservative estimate, a 100–200 μmol kg^{-1} DIC increase is conceivable in high productivity areas based on the oxygen profiles by Sachs et al. (2009).

Given the observation that carbonate accumulations occur either shallower than 200 m or deeper than 600 m, aragonite could only be preserved at very shallow depths, i.e., at narrow shelves with limited sea-ice cover and limited primary productivity where CO$_2$-rich water masses do not impinge onto the shelf. The review of Hunt et al. (2008) identified the Antarctic Peninsula, Weddell Sea, Lazarev Sea and a coastal region between 30 and 90°E as regions with low *L. helicina* densities. South Georgia and the Ross Sea are regions of high *L. helicina* densities. Additionally a continuous plankton recorder transect between 60 and 160°E longitude and between 50°S and the Antarctic continent exhibited high abundances of *Limacina spp.*. This is in accordance with the finding of large numbers of pteropods by E. Domack (pers. communication) at very shallow depths on the George V shelf. A. Post (pers. communication) found traces of pteropods at two stations at water depths of 233 and 520 m on the George V shelf.

As discussed in Section 2, shallow depth intervals are undersampled for several reasons. From the samples available for X-ray diffraction analysis only 10 samples were available from this important depth interval. Nine of those were from the wAP and one from the RS, which all fall into the domain of very high primary productivity and poor CaCO$_3$ preservation. We would expect to find pteropods to be preserved in regions with high pteropod densities, average primary productivity and seasonal sea-ice cover on rather narrow, shallow shelves where the ACC does not penetrate onto the shelf. This reduces possible accumulation sites for pteropods to few locations on the shallow swP/IO shelf, especially the Kerguelen Gyre. More samples along the coast would be needed to prove or disprove this hypothesis.

The aragonitic bivalve *L. elliptica* is reported to be preserved in sediments as a macrofossil (Tada et al., 2006). As stated in Section 2, large calcareous particles were disregarded for the bulk sediment analysis. If this bivalve is preserved as a whole and not ground into a smaller size fraction by natural processes, it will be completely missed by the bulk CaCO$_3$ and XRD analysis. Therefore, the contribution of macrozoobenthos to carbonate distribution is assessed in the following section.

3.3. Macrozoobenthic carbonate abundance

Since the contribution of the macrozoobenthic community is not included in the core-top analyses, we present an estimate of the carbonate abundance due to this group of organisms from our analysis of box corers and grab samples. Mean macrozoobenthic carbonate standing stocks are presented in Fig. 7. The largest CaCO$_3$ standing stock from macrozoobenthic communities is found in the eastern Weddell Sea with 24.5 g CaCO$_3$ m^{-2}. This is in line with the report of coarse calcareous debris in the Lazarev Sea (eWS) by, e.g., Gingele et al. (1997). The main contributors are: bivalvia (38%), asteroidea (15%), bryozoa (14%), and ophiuroidea (12%).

In the western Antarctic Peninsula region macrozoobenthic CaCO$_3$ contribution (mean: 10.4 g CaCO$_3$ m^{-2}) is very patchy. The macrozoobenthic CaCO$_3$ contribution in the wAP region is concentrated around the tip of the wAP, especially in the Bransfield Strait. The wAP south of 64°S alone has a mean CaCO$_3$ standing stock of 1.6 g CaCO$_3$ m^{-2}. At the tip of the Antarctic Peninsula, benthic communities thrive under the high primary productivity and export
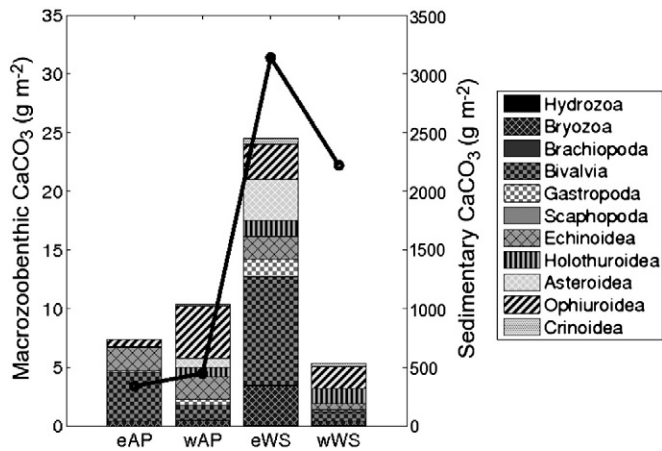
Fig. 7. Mean carbonate contribution in g m^{-2} for the west and east Antarctic Peninsulas (wAP and eAP) and western and eastern Weddell Sea (wWS and eWS) regions. Bars show the contribution by macrozoobenthos (left scale) and circles depict sedimentary CaCO$_3$ (right scale).

flux. Most CaCO$_3$ is produced by ophiuroidea (43%), echinoidea (19%), and bivalvia (13%) in the wAP region.

The eastern Antarctic Peninsula, which is represented in this data set mainly by data from the Larsen shelf and the South Orkney Islands, and the western Weddell Sea regions show lower CaCO$_3$ contributions (7.4 and 5.4 g CaCO$_3$ m^{-2}, respectively). This is at least partly related to trophic limitations caused by extensive sea-ice cover. CaCO$_3$ is mainly produced by bivalvia (56%) and echinoidea (27%) in the eAP region and by ophiuroidea (35%), holothuroidea (24%) and bivalvia (15%) in the wWS region.

In general, the most important taxonomic groups that contribute to macrozoobenthic CaCO$_3$ standing stocks on the Antarctic shelves are bivalvia (32%), ophiuroidea (20%), asteroidea (12%), echinoidea (11%) and bryozoa (11%). Holothuroidea and gastropoda play a minor role and brachiopoda, scaphopoda, crinoidea and aragonitic hydrozoans contribute less than 2% each. The mean standing stock of CaCO$_3$ by macrozoobenthic organisms (15.6 $\pm$ 45.4 g CaCO$_3$ m^{-2}) and its range (0.001–585 g CaCO$_3$ m^{-2}) on the Southern Ocean shelves is comparable to the numbers found by Lebrato et al. (2010), who only considered echinodermata. The high degree of variability that was found for the carbonate contents of the sediments (Section 3.1) characterizes also the distribution of calcareous macrozoobenthos on the Antarctic shelves, although numbers are generally two orders of magnitude lower for macrozoobenthos. This high degree of variability is caused by several factors. Mühlenhardt-Siegel (1989) named sediment structure as the most important parameter determining Antarctic zoobenthos assemblages. Gerdes et al. (1992) reported that a high portion of soft-bottom sediment and strong water currents caused the absence of bryozoans in the Filchner Depression area. Additional factors are productivity of the water column and disturbance by iceberg grounding (Mühlenhardt-Siegel, 1988). The influence of iceberg scouring was investigated in Gerdes et al. (2003, 2008). Iceberg scouring wipes out benthic communities, thereby reducing the total abundance of macrozoobenthos and CaCO$_3$ standing stocks. During recolonization, motile fauna such as echinoderms dominate the earliest succession stage, followed by sessile pioneers such as bryozoans. The disturbance by icebergs may also partly explain the low CaCO$_3$ standing stocks in the eAP and wWS region.

Within the phylum of echinodermata, ophiuroidea (39%) provide most CaCO$_3$, followed by asteroidea (22%). We observe that echinoidea make up 22% which is significantly more than the 9% found by Lebrato et al. (2010) and more than holothuroidea (13%). Crinoidea account for 4% of the echinodermata CaCO$_3$ standing stock.

Bivalves produce 32% of macrozoobenthic CaCO$_3$ standing stocks, but, although aragonitic species occur, it is unknown to us which

percentage of bivalves is aragonitic. However, as macrozoobenthic CaCO$_3$ inventories appear to be two orders of magnitude lower than sedimentary carbonates, aragonite is definitely only an insignificant part of the total CaCO$_3$. Echinoderms are responsible for half of macrozoobenthic CaCO$_3$ standing stocks and produce high-Mg calcite (Weber et al., 1969). Thus their skeletons will probably be the first to dissolve, before calcitic bryozoan and bivalve skeletons as well as calcitic foraminifera will be affected.

4. Summary

We presented the first circum-Antarctic data set of carbonate content and mineralogy. Up to today, there was no systematic sampling effort to study CaCO$_3$ production and preservation on Antarctic shelves. Large areas, especially in the southwest Pacific and Indian Ocean sectors of the Antarctic shelves are still largely undersampled. Future research in these regions is essential to achieve a process-based understanding of the fate of CaCO$_3$ in the sediments and the Southern Ocean CaCO$_3$ cycle in general.

Over the next decades, Antarctic Surface Water might become the most acidic water mass in the Southern Ocean (Hauck et al., 2010) as the surface ocean accumulates most CO$_2$ from the atmosphere; the CO$_2$ increase in the deeper layers is much smaller due to mixing with waters poor in anthropogenic CO$_2$. Once the saturation horizon for calcite will become as shallow to reach the Antarctic shelves, locally present carbonate-rich sediments will dissolve. The capacity to buffer future acidification is small in high-productivity regions, such as the western Antarctic Peninsula and the Ross Sea but higher in the Bellingshausen, Amundsen and Weddell Seas. The buffering effect cannot be quantified yet, but this will be attempted in a modeling approach.

The water masses most corrosive to CaCO$_3$ are Antarctic Bottom Water and Circumpolar Deep Water. Today, the cyclonic gyres, the Weddell, Ross and Kerguelen Gyres, keep the corrosive Circumpolar Deep Water away from the shelf in the respective regions. Undersaturation with respect to aragonite at depths shallower than 1100 m is found only outside these gyres. The corrosiveness of pore water depends on the combination of carbonate saturation state of the bottom water and the amount of CO$_2$ released by respiration.

Dissolution of aragonite is not a mechanism which can buffer ocean acidification in the Southern Ocean, as aragonite is not a prominent constituent of surface sediments on the Antarctic shelves.

Comparison of the contributions of sedimentary carbonate and macrozoobenthic carbonate (>500 μm) in the regions, from which data from both analyses is available (compare Fig. 7), emphasized the sedimentary carbonate to be quantitatively more important in the marine carbon cycle. Sedimentary carbonate contents are two orders of magnitude higher than macrozoobenthic carbonate contents. Hence, neglecting large debris in the determination of sedimentary CaCO$_3$ content does not lead to a significant underestimation of the total CaCO$_3$ content. In the eastern Antarctic Peninsula (eAP) region, macrozoobenthic contribution and sedimentary carbonate contents are low. In the western Antarctic Peninsula (wAP) region the macrozoobenthic carbonate standing stock is very patchy, whereas the sedimentary CaCO$_3$ is uniformly distributed, but low compared to the other regions. In the eastern Weddell Sea (eWS), both the CaCO$_3$ percentages in sediments and calcareous macrozoobenthos abundance are very high on their respective scales. Here, strong production and preservation favor high CaCO$_3$ contents. Considering only the eAP, wAP and eWS regions, there appears to be a relation between macrozoobenthic stocks and sedimentary carbonate contents. The western Weddell Sea is different. The macrozoobenthic carbonate abundance is the smallest within the study area, but the sedimentary part is comparable to the one in the eastern Weddell Sea. This underlines that in the regions with broad shelves, major sea-ice cover and limited primary production, benthic CaCO$_3$ production has a minor influence

on sedimentary $CaCO_3$ contents (compare Section 3.1). Calcium carbonate is mainly produced by planktonic organisms, presumably to a large extent by *N. pachyderma* living in the water column and in the sea ice.

Although we have no macrozoobenthos data from the Ross Sea, Bellingshausen Sea, Amundsen Sea, southwest Pacific and Indian Ocean, the classification we found in Section 3.1 indicates that a situation similar to that in the wWS applies to the Bellingshausen and Amundsen Seas. We expect macrozoobenthic $CaCO_3$ stocks similar to the wAP in the Ross Sea and similar to the eWS in the Kerguelen Gyre. This classification is based on environmental conditions such as sea-ice cover, primary production, width of the shelf and water mass distribution. There was not enough data available to make statements about the entire southwest Pacific and Indian Ocean region.

Acknowledgments

References

Accornero, A., Manno, C., Esposito, F., Gambi, M.C., 2003. The vertical flux of particulate matter in the polynya of Terra Nova Bay. Part II. Biological components. Antarctic Science 15, 175–188.

Ahn, I.Y., Shim, J.H., 1998. Summer metabolism of the Antarctic clam, *Laternula elliptica* (King and Broderip) in Maxwell Bay, King George Island and its implications. Journal of Experimental Marine Biology and Ecology 224, 253–264.

Anderson, J.B., 1975. Factors controlling $CaCO_3$ dissolution in Weddell Sea from foraminiferal distribution patterns. Marine Geology 19, 315–332.

Anderson, J.B., 1999. Antarctic Marine Geology. Cambridge University Press.

Archer, D., 1996. An atlas of the distribution of calcium carbonate in sediments of the deep-sea. Global Biogeochemical Cycles 10, 159–174.

Archer, D., Maier-Reimer, E., 1994. Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration. Nature 367, 260–263.

Archer, D., Kheshgi, H., Maier-Reimer, E., 1997. Multiple timescales for neutralization of fossil fuel CO_2. Geophysical Research Letters 24, 405–408.

Arrigo, K.R., van Dijken, G., Long, M., 2008a. Coastal Southern Ocean: a strong anthropogenic CO_2 sink. Geophysical Research Letters 35, L21602. doi:10.1029/2008GL035624.

Arrigo, K.R., van Dijken, G.L., Bushinsky, S., 2008b. Primary production in the Southern Ocean, 1997–2006. Journal of Geophysical Research-Oceans 113, C08004. doi:10.1029/2007JC004551.

Barnes, D.K.A., Clarke, A., 1998. The ecology of an assemblage dominant: the encrusting bryozoan *Fenestrulina rugula*. Invertebrate Biology 117, 331–340.

Bergami, C., Capotondi, L., Langone, L., Giglio, F., Ravaioli, M., 2009. Distribution of living planktonic foraminifera in the Ross Sea and the Pacific sector of the Southern Ocean (Antarctica). Marine Micropaleontology 73, 37–48.

Blackmon, P., Todd, R., 1959. Mineralogy of some foraminifera as related to their classification and ecology. Journal of Paleontology 33, 1–15.

Boysen-Ennen, E., Piatkowski, U., 1988. Mesozooplankton and macrozooplankton communities in the Weddell Sea, Antarctica. Polar Biology 9, 17–35.

Brey, T., Gerdes, D., 1998. High Antarctic macrobenthic community production. Journal of Experimental Marine Biology and Ecology 231, 191–200.

Brey, T., Gerdes, D., Gutt, J., Mackensen, A., Starmans, A., 1999. Growth and age of the Antarctic bryozoan *Cellaria incula* on the Weddell Sea shelf. Antarctic Science 11, 408–414.

Brey, T., Müller-Wiegmann, C., Zittier, Z.M.C., Hagen, W., 2010. Body composition in aquatic organisms—a global data bank of relationships between mass, elemental composition and energy content. Journal of Sea Research 64, 334–340.

Bullivant, J., 1961. Photographs of the Antarctic bottom fauna. Polar Record 10, 505–508.

Carmack, E., 1977. Water characteristics of the Southern Ocean south of the polar front. In: Angel, M. (Ed.), A Voyage of Discovery. Pergamon, Tarrytown, N.Y., pp. 15–41.

Cattaneo-Vietti, R., Chiantore, M., Misic, C., Povero, P., Fabiano, M., 1999. The role of pelagic–benthic coupling in structuring littoral benthic communities at Terra Nova Bay (Ross Sea) and in the Straits of Magellan. Scientia Marina 63, 113–121.

Cattaneo-Vietti, R., Chiantore, M., Schiaparelli, S., Albertelli, G., 2000. Shallow- and deep-water mollusc distribution at Terra Nova Bay (Ross Sea, Antarctica). Polar Biology 23, 173–182.

Collier, R., Dymond, J., Honjo, S., Manganini, S., Francois, R., Dunbar, R., 2000. The vertical flux of biogenic and lithogenic material in the Ross Sea: moored sediment trap observations 1996–1998. Deep-Sea Research Part II–Topical Studies in Oceanography 47, 3491–3520.

Dayton, P., Newmann, W., Oliver, J., 1982. The vertical zonation of the deep-sea Antarctic acorn barnacle, *Bathylasma corolliforme* (Hoek): experimental transplants form the shelf into shallow water. Journal of Biogeography 9, 95–109.

Dickson, A.G., 1990. Standard potential of the reaction $AgCl(s) + 1/2H_2(g) = Ag(s) + HCl(aq)$ and the standard acidity constant of the ion HSO_4^- in synthetic seawater from 273.15 K to 318.15 K. The Journal of Chemical Thermodynamics 22, 113–127.

Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep-Sea Research Part A–Oceanographic Research Papers 34, 1733–1743.

Dieckmann, G.S., Spindler, M., Lange, M.A., Ackley, S.F., Eicken, H., 1991. Antarctic sea ice—a habitat for the foraminifera *Neogloboquadrina pachyderma*. Journal of Foraminiferal Research 21, 182–189.

Domack, E., 1988. Biogenic facies in the Antarctic glacimarine environment: basis for a polar glacimarine summary. Palaeogeography, Palaeoclimatology, Palaeoecology 63, 357–372.

Domack, E., Taviani, M., Rodriguez, A., 1999. Recent sediment remolding on a deep shelf, Ross Sea: implications for radiocarbon dating of Antarctic marine sediments. Quaternary Science Reviews 18, 1445–1451.

Donner, B., Wefer, G., 1994. Flux and stable-isotope composition of *Neogloboquadrina pachyderma* and other planktonic foraminifers in the Southern Ocean (Atlantic sector). Deep-Sea Research Part I–Oceanographic Research Papers 41, 1733–1743.

Gerdes, D., Klages, M., Arntz, W., Herman, R., Galéron, J., Hain, S., 1992. Quantitative investigations on macrobenthos communities of the southeastern Weddell Sea shelf based on multibox corer samples. Polar Biology 12, 291–301.

Gerdes, D., Hilbig, B., Montiel, A., 2003. Impact of iceberg scouring on macrobenthic communities in the high-Antarctic Weddell Sea. Polar Biology 26, 295–301.

Gerdes, D., Isla, E., Knust, R., Mintenbeck, K., Rossi, S., 2008. Response of Antarctic benthic communities to disturbance: first results from the artificial Benthic Disturbance Experiment on the eastern Weddell Sea Shelf, Antarctica. Polar Biology 31, 1469–1480.

Gingele, F.X., Kuhn, G., Maus, B., Melles, M., Schone, T., 1997. Holocene ice retreat from the Lazarev Sea Shelf, East Antarctica. Continental Shelf Research 17, 137–163.

Goldsmith, J., Graf, D., Heard, H., 1961. Lattice constants of the calcium–magnesium carbonates. American Mineralogist 46, 453–457.

Gordon, A., 1974. Varieties and variability of Antarctic Bottom Water. Processus de Formation des Eaux Océanique Profondes en Particulier en Méditerrannée Occidentale. Centre Nationale de la Recherche Scientifique, Paris, pp. 33–47.

Grosfeld, K., Schröder, M., Fahrbach, E., Gerdes, R., Mackensen, A., 2001. How iceberg calving and grounding change the circulation and hydrography in the Filchner Ice Shelf-Ocean System. Journal of Geophysical Research-Oceans 106, 9039–9055.

Gutt, J., 1988. Zur Verbreitung und Ökologie der Seegurken (Holothuroidea, Echinodermata) im Weddellmeer (Antarktis). Berichte zur Polarforschung 41, 92.

Gutt, J., 2007. Antarctic macro-zoobenthic communities: a review and an ecological classification. Antarctic Science 19, 165–182.

Hauck, J., Hoppema, M., Bellerby, R.G.J., Völker, C., Wolf-Gladrow, D., 2010. Data-based estimation of anthropogenic carbon and acidification in the Weddell Sea on a decadal timescale. Journal of Geophysical Research-Oceans 115, C03004. doi:10.1029/2009JC005479.

Hayward, P., 1995. Antarctic cheilostomatous bryozoa. Oxford University Press.

Hillenbrand, C.D., Grobe, H., Diekmann, B., Kuhn, G., Fütterer, D.K., 2003. Distribution of clay minerals and proxies for productivity in surface sediments of the Bellingshausen and Amundsen seas (West Antarctica)—relation to modern environmental conditions. Marine Geology 193, 253–271.

Hillenbrand, C.D., Larter, R.D., Dowdeswell, J.A., Ehrmann, W., Cofaigh, C.O., Benetti, S., Graham, A.G.C., Grobe, H., 2010. The sedimentary legacy of a palaeo-ice stream on the shelf of the southern Bellingshausen Sea: clues to West Antarctic glacial history during the Late Quaternary. Quaternary Science Reviews 29, 2741–2763.

Hunt, B.P.V., Pakhomov, E.A., Hosie, G.W., Siegel, V., Ward, P., Bernard, K., 2008. Pteropods in Southern Ocean ecosystems. Progress in Oceanography 78, 193–221.

Isla, E., Gerdes, D., Palanques, A., Gili, J.M., Arntz, W.E., König-Langlo, G., 2009. Downward particle fluxes, wind and a phytoplankton bloom over a polar continental shelf: a stormy impulse for the biological pump. Marine Geology 259, 59–72.

Kellogg, D.E., Kellogg, T.B., 1987. Microfossil distributions in modern Amundsen Sea sediments. Marine Micropaleontology 12, 203–222.

Key, R.M., Kozyr, A., Sabine, C.L., Lee, K., Wanninkhof, R., Bullister, J.L., Feely, R.A., Millero, F.J., Mordy, C., Peng, T.H., 2004. A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP). Global Biogeochemical Cycles 18, GB4031. doi:10.1029/2004GB002247.

Key, R.M., Tanhua, T., Olsen, A., Hoppema, M., Jutterstroem, S., Schirnick, C., van Heuven, S., Kozyr, A., Lin, X., Velo, A., Wallace, D., Mintrop, L., 2010. The CARINA data synthesis project: introduction and overview. Earth System Science Data 2, 105–121.

Kuklinski, P., Taylor, P., 2009. Mineralogy of Arctic bryozoan skeletons in a global context. Facies 55, 489–500.

Lebrato, M., Iglesias-Rodriguez, D., Feely, R.A., Greeley, D., Jones, D.O.B., Suarez-Bosche, N., Lampitt, R.S., Cartes, J.E., Green, D.R.H., Alker, B., 2010. Global contribution of echinoderms to the marine carbon cycle: $CaCO_3$ budget and benthic compartments. Ecological Monographs 80, 441–467.

Lewis, E., Wallace, D., 1998. CO2SYS-program developed for the CO_2 system calculations. Carbon Dioxide Information Analysis Center. Report ORNL/CDIAC-105.

Lipps, J., Krebs, W., 1974. Planktonic foraminifera associated with Antarctic sea ice. Journal of Foraminiferal Research 4, 80–85.

McClintock, J.B., Angus, R.A., McDonald, M.R., Amsler, C.D., Catledge, S.A., Vohra, Y.K., 2009. Rapid dissolution of shells of weakly calcified Antarctic benthic macroorganisms indicates high vulnerability to ocean acidification. Antarctic Science 21, 449–456.

McCoy, F., 1991. Southern Ocean sediments: circum-Antarctic to 30°S. In: Hayes, D. (Ed.), Marine Geological and Geophysical Atlas of the Circum-Antarctic to 30°S. American Geophysical Union, Washington D.C., pp. 37–46.

McNeil, B.I., Matear, R.J., 2008. Southern Ocean acidification: a tipping point at 450-ppm atmospheric CO_2. Proceedings of the National Academy of Sciences of the United States of America 105, 18860–18864.

Mehrbach, C., Cuberson, C., Hawley, J., Pytkowicz, R., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnology and Oceanography 18, 897–907.

Melles, M., Kuhn, G., 1993. Subbottom profiling and sedimentological studies in the southern Weddell Sea, Antarctica—evidence for large-scale erosional depositional processes. Deep-Sea Research Part I—Oceanographic Research Papers 40, 739–760.

Melles, M., Kuhn, G., Fütterer, D., Meischner, D., 1991. Paläoglaziologie und Paläozeanographie im Spätquartär am Kontinentalrand des südlichen Weddellmeeres, Antarktis (Late quaternary paleoglaciology and paleoceanography at the continental margin of the southern Weddell Sea, Antarctica). Berichte zur Polar- und Meeresforschung 81, 190.

Mikhalevich, V.I., 2004. The general aspects of the distribution of Antarctic foraminifera. Micropaleontology 50, 179–194.

Milliman, J., 1994. Recent Sedimentary Carbonates 1: Marine Carbonates. Springer-Verlag.

Mucci, A., 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. American Journal of Science 283, 780–799.

Mucci, A., Morse, J.W., 1984. The solubility of calcite in seawater solutions of various magnesium concentration, $I_t = 0.697$ m at 25 °C and one atmosphere total pressure. Geochimica et Cosmochimica Acta 48, 815–822.

Mühlenhardt-Siegel, U., 1988. Some results on quantitative investigations of macrozoobenthos in the Scotia Arc (Antarctica). Polar Biology 8, 241–248.

Mühlenhardt-Siegel, U., 1989. Quantitative investigations of Antarctic zoobenthos communities in winter (May/June) 1986 with special reference to the sediment structure. Archiv für Fischereiwissenschaft 39, 123–141.

Nelson, C. (Ed.), 1988. Non-tropical shelf sediments—modern and ancient: Sedimentary Geology, Vol. 60, pp. 1–367.

Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner, G.K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig, M.F., Yamanaka, Y., Yool, A., 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437, 681–686.

Orsi, A.H., Nowlin, W.D., Whitworth, T., 1993. On the circulation and stratification of the Weddell Gyre. Deep-Sea Research Part I—Oceanographic Research Papers 40, 169–203.

Orsi, A.H., Whitworth, T., Nowlin, W.D., 1995. On the meridional extent and fronts of the Antarctic Circumpolar Current. Deep-Sea Research Part I—Oceanographic Research Papers 42, 641–673.

Post, A.L., O'Brien, P.E., Beaman, R.J., Riddle, M.J., De Santis, L., 2010. Physical controls on deep water coral communities on the George V Land slope, East Antarctica. Antarctic Science 22, 371–378.

Post, A.L., Beaman, R.J., O'Brien, P.E., Eléaume, M., Riddle, M.J., 2011. Community structure and benthic habitats across the George V Shelf, East Antarctica: trends through space and time. Deep Sea Research II 58, 105–118. doi:10.1016/j.dsr2.2010.05.020.

Read, J.F., Pollard, R.T., Morrison, A.I., Symon, C., 1995. On the southerly extent of the Antarctic Circumpolar Current in the southeast Pacific. Deep-Sea Research Part II—Topical Studies in Oceanography 42, 933–954.

Sachs, O., Sauter, E.J., Schlüter, M., van der Loeff, M.M.R., Jerosch, K., Holby, O., 2009. Benthic organic carbon flux and oxygen penetration reflect different plankton provinces in the Southern Ocean. Deep-Sea Research Part I—Oceanographic Research Papers 56, 1319–1335.

Seiter, K., Hensen, C., Schroter, E., Zabel, M., 2004. Organic carbon content in surface sediments—defining regional provinces. Deep-Sea Research Part I—Oceanographic Research Papers 51, 2001–2026.

Smith, A.M., 2007. Age, growth and carbonate production by erect rigid bryozoans in Antarctica. Palaeogeography, Palaeoclimatology, Palaeoecology 256, 86–98.

Smith, W.O., Gordon, L.I., 1997. Hyperproductivity of the Ross Sea (Antarctica) polynya during austral spring. Geophysical Research Letters 24, 233–236.

Smith, A.M., Nelson, C.S., 2003. Effects of early sea-floor processes on the taphonomy of temperate shelf skeletal carbonate deposits. Earth-Science Reviews 63, 1–31.

Spindler, M., Dieckmann, G.S., 1986. Distribution and abundance of the planktic foraminifer *Neogloboquadrina pachyderma* in sea ice of the Weddell Sea (Antarctica). Polar Biology 5, 185–191.

Swadling, K.M., Kawaguchi, S., Hosie, G.W., 2010. Antarctic mesozooplankton community structure during BROKE-West (30°E–80°E), January–February 2006. Deep-Sea Research Part II—Topical Studies in Oceanography 57, 887–904.

Tada, Y., Wada, H., Miura, H., 2006. Seasonal stable oxygen isotope cycles in an Antarctic bivalve shell (*Laternula elliptica*): a quantitative archive of ice melt runoff. Antarctic Science 18, 111–115.

Thomas, D., Lara, R., Haas, C., Schnack-Schiel, S., Dieckmann, G., Kattner, G., Nöthig, E., Mizdalski, E., 1998. Biological soup within decaying summer sea ice in the Amundsen Sea, Antarctica. In: Lizotte, M., Arrigo, K. (Eds.), Antarctic Sea Ice Biological Processes, Interactions and Variability. American Geophysical Union, Washington D.C., pp. 161–171.

Timmermann, R., Le Brocq, A., Deen, T., Domack, E., Dutrieux, P., Galton-Fenzi, B., Hellmer, H., Humbert, A., Jansen, D., Jenkins, A., Lambrecht, A., Makinson, K., Niederjasper, F., Nitsche, F., Nøst, O.A., Smedsrud, L.H., Smith, W.H.F., 2010. A consistent data set of Antarctic ice sheet topography, cavity geometry, and global bathymetry. Earth System Science Data 2, 261–273.

Tucker, M., 1996. Methoden der Sedimentologie. Ferdinand Enke Verlag.

Weber, J., Greer, R., Voight, B., White, E., Roy, R., 1969. Unusual strength properties of echinoderm calcite related to structure. Journal of Ultrastructure Research 26, 355–366.

Whitworth III, T., Orsi, A., Kim, S., Nowlin Jr., W., Locarnini, R., 1998. Water masses and mixing near the Antarctic slope front. In: Jacobs, S., Weiss, R. (Eds.), Ocean, Ice and Atmosphere: Interactions at the Antarctic Continental Margin. American Geophysical Union, Washington D.C., pp. 1–27.

Zeebe, R., Wolf-Gladrow, D., 2001. CO_2 in seawater: equilibrium, kinetics, isotopes. Number 65 in Elsevier Oceanography Series. Elsevier, p. 346.