Distribution and mineralogy of carbonate sediments on Antarctic shelves

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Abstract

We analyzed 214 new core-top samples for their CaCO₃ content from shelves all around Antarctica in order to understand their distribution and contribution to the marine carbon cycle. The distribution of sedimentary CaCO₃ 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 CaCO₃ contents of surface sediments are usually low, high (>15%) CaCO₃ contents occur at shallow water depths (150-200 m) on 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 CaCO₃ contents in the surface sediments.

The predominant mineral phase of CaCO₃ on the Antarctic shelves is

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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 CaCO₃ standing stocks do not increase the CaCO₃ 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.

Key words: Southern Ocean, carbonate sediments, ocean acidification, macrozoobenthos, carbon cycle

1 1. Introduction

- Human emissions of CO₂ lead to ocean acidification (OA): as the oceans
- 3 take up CO₂ from the atmosphere, carbonate equilibria in the oceans shift
- 4 towards lower pH and lower carbonate ion concentration. As a result, un-
- 5 dersaturation with respect to carbonate minerals can occur, leading to disso-

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lution 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 solubility. Within the polar regions, OA is intensified on the shallow shelves (Hauck et al., 2010; Arrigo et al., 2008b). 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 landwardsloping 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 4.4 10⁶ km² (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 30 only in shallow low-latitude sediments (e.g. Milliman (1994); Archer et al. 31 (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 underrepresented, and it is unknown, how abundant carbonates really are in Antarctic shelf sediments, and which main factors control their 37 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 CaCO₃ contents. Calcium carbonate is produced by marine organisms in the form of two 42 main polymorphs, calcite and aragonite. Its solubility increases with pressure and with decreasing temperature. The depth levels below which aragonite or

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

$$\Omega_C = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{snC}^*} \tag{1}$$

$$\Omega_A = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp\,A}^*} \tag{2}$$

where K_{sp}^* is the stoichiometric solubility product (Zeebe and Wolf-Gladrow, 2001; Mucci, 1983). By definition, Ω is > 1 above and < 1 below the saturation horizon. Aragonite is the more soluble phase, hence its saturation 50 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). 54 A variety of planktonic and benthic organisms produce CaCO₃ in the 55 Southern Ocean (SO), for example pteropods (aragonite), for aminifera (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) (Milliman, 1994; Blackmon and Todd, 1959; Kuklinski and Taylor, 2009; Weber et al., 1969). 60 One calcitic foraminifera species, Neogloboquadrina pachyderma (sin.), is 61 omnipresent and the dominant planktonic foraminfera species in the South-62

One calcitic foraminifera species, Neogloboquadrina pachyderma (sin.), is omnipresent and the dominant planktonic foraminfera species in the Southern Ocean (e.g. Bergami et al., 2009; Swadling et al., 2010; Donner and Wefer, 1994). Extremely high amounts of Neogloboquadrina pachyderma appear in sea ice (Lipps and Krebs, 1974; Spindler and Dieckmann, 1986; Dieckmann et al., 1991). Neogloboquadrina pachyderma in sea ice can be 70 times more abundant per volume than in the underlying sea water. The second largest planktonic carbonate producer are pteropods and the dominant species south of the Polar Front is the aragonitic species Limacina helicina (Hunt et al., 2008). The distribution of Limacina helicina based on meso- and macrozooplankton analyses is not well understood and appears to be very patchy (Swadling et al., 2010; Hunt et al., 2008; Boysen-Ennen and Piatkowski, 1988). Accornero et al. (2003) and Collier et al. (2000) found Limacina helicina to be the main contributor to carbonate fluxes from sediment trap studies in the Ross Sea, with minor contributions of Neogloboquadrina pachyderma. Other sediment trap studies on the eastern Weddell Sea shelf (Isla et al., 2009) and in Bransfield Strait (Donner and Wefer, 1994) observed Neogloboquadrina 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; Smith, 2007; Hayward, 1995). Together
with sponges, bryozoans are the most significant occupiers of the seafloor
and their remains may comprise the majority of the coarse bottom sediment
(Bullivant, 1961; Hayward, 1995; Barnes and Clarke, 1998). 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 CaCO₃ 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 CaCO₃ standing stocks. The knowledge about CaCO₃ 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.

os 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.

Additional CaCO₃ Data. In addition to the 214 samples that were measured 119 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 12: 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 123 Antarctic Peninsula, the Bellingshausen and Amundsen Seas were included (Hillenbrand et al., 2003, 2010). Data from the George V shelf in East 125 Antarctica were supplied by Post et al. (2011). Furthermore, Antarctic shelf 126 data were extracted and quality controlled from the global data compilation 127 by Seiter et al. (2004). Only data where the water depth is at most 1000 m 128 were used. The location of the samples is depicted in Figure 1. 129

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.

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

48 2.2. Chemical analyses

All geochemical analyses were carried out on samples that were freezedried 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. Distribution of carbonate forming macrozoobenthos and their contribution to carbonate budgets is discussed in sections 2.4 and 3.3.

Phase identification. The bulk sediment was analyzed using a Philips PW diffraction analyzer with a cobalt anode ($CoK\alpha$ radiation, 40 kV, 40 mA). A range of 3-100° 2θ was scanned with a step scan speed of 0.02° 2θ per sec-165 ond. The diffractograms were evaluated with the program "X'Pert HighScore 166 Plus" (Version 2.2c, PANalytical B.V., Almelo, The Netherlands) without in-167 ternal standard. The position of the calcite peak was corrected for the offset of the quartz peak position from its theoretical value (Tucker, 1996). The 169 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 17 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 173 than 2% CaCO₃ (see Table in Pangaea) were used for the analysis of the 174 carbonate mineralogy. 175

176 CaCO₃ quantification. The percentage of calcium carbonate in the bulk sam-177 ple was determined on the basis of total inorganic carbon (TIC) which is 178 obtained from TC and TOC measurements. TC was measured on subsam-179 ples 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 183 TOC measurements (30 to 50 mg) were treated with three drops of ethanol 182 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 184 are reported per mass of salt-free dry sediment. Relative analytical precision expressed as the standard deviation obtained under repeatability conditions 186 are 2% for TC and 0.5% for TOC. The CaCO₃ percentage was converted to g $CaCO_3 m^{-2}$ following the procedure described in detail in Archer (1996). 188 This protocol calculates an average porosity (ϕ) for the top 10 cm of the sediment based on the percentage of CaCO₃. Calculated porosities range 190 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 192 which we assume the CaCO₃ content to be constant. The top 10 cm of the 193 sediment reflect the bioturbated layer in which dissolution can take place. 194 The $CaCO_3$ content in the 10 cm surface layer is then given as:

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

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

197 2.3. GLODAP and CARINA data

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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 20 (Key et al., 2004, 2010). The data were filtered to find stations adjacent 202 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 204 et al. (2010) was accepted. This procedure assured that only bottom data 205 were considered, but also that data were not discarded due to uncertainties 206 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 208 filtering procedure, 67 data points remained. These data cover the western 209 Antarctic Peninsula, Ross Sea, western Weddell Sea and southwest Pacific 210 and Indian shelf sectors of the Southern Ocean, include data from 1989 to 21: 2003 and allow a valid estimate for Ω_C and Ω_A during the period when most 212 of the sediment cores were taken. Dissolved inorganic carbon (DIC) and total 213 alkalinity (A_T) as well as potential temperature, salinity, pressure, phosphate 214 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 216 acid dissociation constants from Mehrbach et al. (1973) refit by Dickson and Millero (1987) and the KSO₄ dissociation constant by Dickson (1990) were used. 219

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 contri-231 bution of macrozoobenthic carbonate producers to the carbonate budget in surface sediments from the Antarctic shelves. The dataset consists of 243 sta-233 tions on the western Antarctic Peninsula and the southeastern Weddell Sea 234 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 236 and Van Veen grabs between 1985 and 2007. These samples were sieved over $500 \mu \text{m}$ meshsize screens and abundance and wet mass were determined for 238 35 major taxonomic groups. For the present study, only taxonomic groups which are known to produce CaCO₃ were considered: hydrozoa, bryozoa, 240 brachiopoda, polyplacophora, bivalvia, gastropoda, scaphopoda, echinoidea, holothuroidea, asteroidea, ophiuroidea and crinoidea. 242

The wet mass was converted to CaCO₃ by conversion factors from Brey et al. (2010). For bivalvia and gastropoda, CaCO₃ was calculated by con-

verting from wet mass with shell to wet mass without shell. The shell mass 245 was considered equivalent to CaCO₃ mass and was taken as CaCO₃ standing stock for bivalvia and gastropoda. For all other groups, wet mass was 24 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 CaCO₃. 249 This is a valid estimate as only groups with calcareous endo- and exoskeletons were considered. No conversion factor was available for polyplacophora, 25 therefore this group was discarded. The wet mass contribution of polyplacophora to the total wet mass at all stations is 0.2%. The CaCO₃ content per 253 dry mass for echinoderms as calculated with conversion factors by Brey et al. (2010) are comparable to the CaCO₃ contents of echinoderms as determined 25! by Lebrato et al. (2010) except for holothuroidea. Lebrato et al. (2010) mea-256 sured only one holothuroidean species with a CaCO₃ content of 3.46% per 25 drymass. In contrast, Brey et al. (2010) considered data of 51 species where 258 the ash content ranged from <10 to >80% of the dry weight (mean: 44.5%). 259 In Antarctica, holothuroidea are very diverse and many are heavily calcified 260 (Gutt, 1988). The CaCO₃ standing stocks are given in g CaCO₃ m⁻², where 26 the volume considered depends on the penetration depth of the sampling 262 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 264 (doi:10.1594/PANGAEA.757933).

3. Results and Discussion

3.1. Geographical and bathymetric CaCO $_3$ 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 sedi-

ments (Figure 2a and b). In the western and eastern Antarctic Peninsula re-276 gions, CaCO₃ is hardly preserved in the sediments with mean values of 1.3% 27 $CaCO_3$ (444 g $CaCO_3$ m⁻², n=45) and 1.0% (340 g $CaCO_3$ m⁻², n=72), 278 respectively, and CaCO₃ contents consistently lower than 10%. A similar 279 situation is found in the Ross Sea with a mean CaCO₃ content of 2.0% 280 $(714 \text{ g CaCO}_3 \text{ m}^{-2}, \text{ n}=52)$ and all CaCO₃ contents < 10%. Higher CaCO₃ 28 contents were found in the Amundsen Sea (mean: 5.1%, 2053 g CaCO₃ m⁻², 282 n=44), eastern Weddell Sea (mean: 6.8%, 3138 g CaCO₃ m⁻², n=24), west-283 ern Weddell Sea (mean: 4.3\%, 2153 g CaCO₃ m⁻², n=42), and especially in 284 the Bellingshausen Sea (mean 8.0%, 3546 g CaCO₃ m⁻², n=40). The swP/IO 285 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. 28 The mean $CaCO_3$ content of these samples is 2.0% (719 g $CaCO_3$ m⁻²).

The CaCO₃ content varies with depth (Figure 2b), and shows maxima 289 with $CaCO_3$ contents > 15% around 150 - 200 m and between 600 and 900 m. 290 However, variances at single depths are quite large. These two depth inter-29 vals reflect two different mechanisms of carbonate preservation. On the parts of the shelf shallower than 200 m, carbonates are preserved, where they were 293 produced and possibly concentrated by currents (winnowing). These carbonates include the entire range of carbonates produced by planktonic and 295 benthic organisms. In the depth interval between 600 and 900 m, carbonates are exclusively accumulated at the outer shelf or near the shelf break. 29 These are locations where carbonates are accumulated by currents and also terrigeneous sand contents are high. On the outer shelf in the BS, for exam-290 ple, sand and calcitic foraminifera are enriched by winnowing of silt and clay 300 (Hillenbrand et al., 2003, 2010). 30:

The different shelf regions can be grouped according to which CaCO₃ 302 preservation mechanism applies to them. In the regions with broad and 303 deep shelves, i.e, in the Bellingshausen and Amundsen Seas and in the wWS 304 (Figures 2b and 3), carbonates are found to be deposited on the outer shelf 305 (note that no data are available from depths shallower than 200 m in the 306 wWS and in the AS and only one data point in the BS). This corresponds to 30 calcareous for aminifer a distributions which were found in high concentrations 308 only on the outer shelf of the Amundsen and western Weddell Seas (Kellogg 309 and Kellogg, 1987; Anderson, 1975; Hillenbrand et al., 2003, 2010). 310

In the eWS, which is characterized by narrow, shallower shelves, CaCO₃

accumulates only at the shallow depth interval. High carbonate concen-312 trations in the eWS are mainly produced by benthic communities, such as 313 bryozoan colonies and molluscs (Gingele et al., 1997). While in our dataset 314 hardly any sample from the George V shelf contains > 10\% CaCO₃, Domack (1988) reported carbonate contents of 10 - 30% with barnacles, bryozoans, 316 and ostracods dominating the sand and gravel fractions of surface sediments. Post et al. (2010) observed bryozoans and foraminifera, with rare abundances 318 of bivalves, gastropods, ostracods, as well as aragonitic hydrocorals on the continental slope. The 13 samples from Prydz Bay are consistently below 320 2% CaCO₃.

In the Ross Sea, carbonate concentrations are generally low, independent 322 of water depth (Figure 2a and b). This is surprising in the light of reports of high densities of aragonitic pteropods in the water column (Hunt et al., 2008) 324 and sediment traps (Accornero et al., 2003). A total number of 52 sediment 325 samples from the Ross Sea were analysed, however, the shallow banks in 326 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 328 shallow banks. Despite the high number of data points in the RS, the mean 329 carbonate deposition might be underestimated due to the fact that these 330 banks are undersampled and often contain winnowed bioclastic carbonates 33 (Anderson, 1999). Likewise, the eastern and western Antarctic Peninsula are 332 very poor in $CaCO_3$ independent of water depth. 333

Different factors control the deposition and preservation of carbonates in

the surface sediments. Important are the flux of organic matter to the ocean floor (related to primary production) and the 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 CaCO₃ data.

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 343 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 345 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 the phytoplankton 34 growing season and total production, which likely leads to a reduction of the 348 export production. Respiration in the sediments of the RS and wAP with 340 their high primary production rates is expected to be orders of magnitude 350 higher than in the other shelf regions and alters carbonate chemistry. High 35: export production feeds a benthic community which includes carbonate pro-352 ducers (Dayton et al., 1982; Cattaneo-Vietti et al., 1999, 2000; Smith, 2007), 353 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 *Neogloboquadrina 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).

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 favours an enrichment of calcitic particles in the sand fraction. Carbonates are mainly represented by Neogloboquadrina pachyderma (Hillenbrand
et al., 2003). Winnowing by strong currents on the outer shelf and continental slope was suggested to facilitate carbon accumulation by other studies
(Gingele et al., 1997; Melles and Kuhn, 1993).

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 Figures 4, 5a and b. A regression through the data points provides an estimate of the aragonite saturation horizon of about 1100 m (Figure 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, 390 and they also interact. Primary production appears to be the dominant factor, determining whether significant proportions of $CaCO_3$ (> 2%) can 392 be preserved in the sediments. In addition, carbonate production, width of 393 shelf, sea-ice coverage and calcite saturation state of the overlying seawater 394 impact CaCO₃ distribution. The calcite saturation state of the overlying 395 water mass will only play a role when it falls below a threshold. This critical 396 value is dependent on the region and all contributing factors. While a defined 39 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. 400

Further physical and biological processes play a role in the disintegration of CaCO₃ within the sediment (e.g., Smith and Nelson, 2003; Nelson, 1988).

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 (Figure 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.

417 3.2. Mineralogy

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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 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 % MgCO₃.

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 427 be a reason at certain locations, but cannot explain the general absence of aragonite. In Figure 4, locations with $\Omega_A < 1$ are highlighted. These occur 429 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 431 explained by the relation between Ω_A and depth (Figure 5b). Here, aragonite undersaturation is found at water depths between 963 and 1233 m which fall 433 in the range of the saturation horizon. The data points below 1000 m water depth show the characteristics of Antarctic Bottom Water (Figure 5c). Solely 435 the one point at 963 m water depth is less saline. 436

Aragonite undersaturation appears at water depths of 413 and 734 m on 437 the wAP shelf, at 317 m water depth in Prydz Bay and at 398 m water depth 438 at 48°E. The link between these locations is their exposure to Circumpolar 439 Deep Water (CDW, see Figure 5c). The southern boundary of the ACC 440 comes close to the shelf break in these areas (Orsi et al., 1995). CDW can 44 penetrate onto the shelf either directly or further altered as modified Cir-442 cumpolar Deep Water (mCDW). Salinity and potential temperature reveal that the seawater at locations with $\Omega_A < 1$ belong to CDW (wAP and Prydz 444 Bay locations) or modified Circumpolar Deep Water (at 48°E). The ACC transports these warm and CO₂-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 (Figure 4). The large gyres impede the exposure of the shelf to naturally 450 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, 452 which indicates aragonite undersaturation, we hypothesize that in the small gyre CDW is less modified and therefore more acidic than in the large gyres. 454 Ice Shelf Water, High-Salinity Shelf Water and Antarctic Surface Water are not undersaturated with respect to aragonite (Figure 5c). This is in 456 contrast to the conclusion of Anderson (1975) that relates the absence of 45 calcareous for a minifera in the southwestern Weddell Sea to the predominance 458 of Ice Shelf Water. We hypothesize that the low numbers of calcareous, but 459 also arenaceous for aminifera are caused by the low primary productivity in 460 this area which cannot feed a benthic community. 46

High respiration rates in the sediment-water interface can further reduce Ω_A . CO₂ is produced in Southern Ocean shelf sediments due to respiration and can be assessed assuming that 1 mol CO₂ is produced for 1 mol O₂ 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 μ mol kg⁻¹, this would bring the actual aragonite saturation horizon to about 400 m depth (Figure 5b). An increase of 20 μ mol kg⁻¹ DIC is a conservative estimate, a

 $_{471}$ 100 - 200 μ mol 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 shal-473 lower 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 47! limited primary productivity where CO₂-rich water masses do not impinge onto the shelf. The review of Hunt et al. (2008) identified the Antarctic 477 Peninsula, Weddell Sea, Lazarev Sea and a coastal region between 30 and 90°E as regions with low Limacina helicina densities. South Georgia and 479 the Ross Sea are regions of high *Limacina helicina* densities. Additionally a continuous plankton recorder transect between 60 and 160°E longitude 48 and between 50°S and the Antarctic continent exhibited high abundances of 482 Limacina spp.. This is in accordance with the finding of large numbers of 483 pteropods by E. Domack (pers. communication) at very shallow depths on 484 the George V shelf. A. Post (pers. communication) found traces of pteropods 485 at two stations at water depths of 233 and 520 m on the George V shelf. 486

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 CaCO₃ 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 Laternula 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 CaCO₃ and XRD analysis. Therefore, the contribution of macrozoobenthos to carbonate distribution is assessed in the following section.

505 3.3. Macrozoobenthic carbonate abundance

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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 Figure 7. The largest CaCO₃ standing stock from macrozoobenthic communities is found in the eastern Weddell Sea with 24.5 g CaCO₃ per m². 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 community

CaCO₃ contribution (mean: 10.4 g CaCO₃ per m²) is very patchily distributed. The macrozoobenthic CaCO₃ 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 CaCO₃ standing stock of 1.6 g CaCO₃ per m². At the tip of the Antarctic Peninsula, benthic communities thrive under the high primary productivity and export flux. Most CaCO₃ is produced by ophiuroidea (43%), echinoidea (19%), and bivalvia (13%) in the wAP region.

The eastern Antarctic Peninsula region, which is represented in this data set mainly by data from the Larsen shelf and the South Orkney Islands, and the western Weddell Sea show lower CaCO₃ contributions (7.4 and 5.4 g CaCO₃ m⁻², respectively). This is at least partly related to trophic limitations caused by extensive sea-ice cover. CaCO₃ 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 CaCO₃ standing stocks on the Antarctic shelves are bi-valvia (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 CaCO₃ by macrozoobenthic organisms (15.6 \pm 45.4 g CaCO₃ m⁻²) and its range (0.001 - 585 g CaCO₃ 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 54 the Antarctic shelves, although numbers are generally two orders of magnitude lower for macrozoobenthos. This high degree of variability is caused by 543 several factors. Mühlenhardt-Siegel (1989) named sediment structure as the most important parameter determining Antarctic zoobenthos assemblages. 545 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 547 Depression area. Additional factors are productivity of the water column and disturbance by ice action (Mühlenhardt-Siegel, 1988). The influence of 540 iceberg scouring was investigated in Gerdes et al. (2003, 2008). Iceberg scour-550 ing wipes out benthic communities, thereby reducing the total abundance of 55 macrozoobenthos and CaCO₃ standing stocks. During recolonization, motile 552 fauna such as echinoderms dominate the earliest succession stage, followed 553 by sessile pioneers such as bryozoans. The disturbance by icebergs may also 554 partly explain the low CaCO₃ standing stocks in the eAP and wWS region. 555 Within the phylum of echinodermata, ophiuroidea (39%) provide most 556 CaCO₃, followed by asteroidea (22%). We observe that echinoidea make up 22% which is significantly more than the 9% found by Lebrato et al. 558 (2010) and more than holothuroidea (13%). Crinoidea account for 4% of the 559 echinodermata CaCO₃ standing stock. 560

Bivalves produce 32% of macrozoobenthic CaCO₃ standing stocks, but,

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although aragonitic species occur, it is unknown to us which percentage of bivalves are aragonitic. However, as macrozoobenthic CaCO₃ inventories appear to be two orders of magnitude lower than sedimentary carbonates, aragonite is definitely only an insignificant part of the total CaCO₃. Echinoderms are responsible for half of macrozoobenthic CaCO₃ 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 skeltons as well as calcitic foraminifera will be affected.

570 4. Conclusions

We presented the first circum-Antarctic data set of carbonate content and mineralogy. Up to today, there was no systematic sampling effort to study CaCO₃ production and preservation on Antarctic shelves. Large areas, especially in the southwest Pacific and Indian Ocean sectors of the Antarctic shelves are still largely under-sampled. Future research in these regions is essential to achieve a process-based understanding of the fate of CaCO₃ in the sediments and the Southern Ocean CaCO₃ 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 CO₂ from the atmosphere; the CO₂ increase in the deeper layers is much smaller due to mixing with waters poor in anthropogenic CO₂. Once the saturation horizon for calcite will become as shallow to reach the Antarctic shelves, locally present carbonate-rich sedi-

ments will dissolve. The capacity to buffer future acidification is small in high-productivity regions as the western Antarctic Peninsula and the Ross Sea and higher in the Bellingshausen, Amundsen and Weddell Seas. The 586 buffering effect cannot be quantified yet, but this will be attempted in a modelling approach.

The water masses most corrosive to CaCO₃ are Antarctic Bottom Water and Circumpolar Deep Water. Today, the cyclonic gyres, the Weddell, Ross 590 and Kerguelen Gyres, keep the corrosive Circumpolar Deep Water away from the shelf in the respective regions. Undersaturation with respect to aragonite 592 at depths shallower than 1100 m is found only outside these gyres. The corrosiveness of pore water depends on the combination of carbonate saturation 594 state of the bottom water and the amount of CO_2 released by respiration. 595

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. 598

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Comparison of the contributions of sedimentary carbonate and macro-599 zoobenthic carbonate (> 500 μ m) in the regions, from which data from 600 both analyses is available (compare Figure 7), emphasized the sedimentary 601 carbonate to be quantitatively more important in the marine carbon cy-602 cle. Sedimentary carbonate contents are two orders of magnitude higher 603 than macrozoobenthic carbonate contents. Hence, neglecting large debris in 604 the determination of sedimentary CaCO₃ content does not lead to a significant underestimation of the total CaCO₃ 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 600 sedimentary CaCO₃ is uniformly distributed, but low compared to the other regions. In the eastern Weddell Sea (eWS), both the CaCO₃ percentages 61: in sediments and calcareous macrozoobenthos abundance are very high on their respective scales. Here, strong production and preservation favour high 613 CaCO₃ contents. Considering only the eAP, wAP and eWS regions, there appears to be a relation between macrozoobenthic stocks and sedimentary 615 carbonate contents. The western Weddell Sea is different. The macrozooben-616 thic carbonate abundance is the smallest within the study area, but the 617 sedimentary part is comparable to the one in the eastern Weddell Sea. This 618 underlines that in the regions with broad shelves, major sea-ice cover and lim-619 ited primary production, benthic CaCO₃ production has a minor influence 620 on sedimentary CaCO₃ contents (compare section 3.1). Calcium carbonate 621 is mainly produced by planktonic organisms, presumably to a large extent by Neogloboquadrina pachyderma living in the water column and in the sea 623 ice. 624

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 CaCO₃ 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.

5. Acknowledgements

This paper is a contribution to the German project Biological Impacts of
Ocean ACIDication (BIOACID), funded by Federal Ministry of Education
and Research (BMBF, FKZ 03F0608B). This research used samples provided
by the Antarctic Marine Geology Research Facility (AMGRF) at Florida
State University. The AMGRF is sponsored by the U.S. National Science
Foundation. The British Ocean Sediment Core Repository (BOSCOR) is
thanked for supplying sediment samples. We are grateful to Patrick Monien
for bringing sediment samples from Jubany station.

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Figure 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

Figure 2: (a) Boxplots of sedimentary $CaCO_3$ content (%) in the different Antarctic shelf regions. 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 symbols. Bold lines indicate 2 and 15 % $CaCO_3$

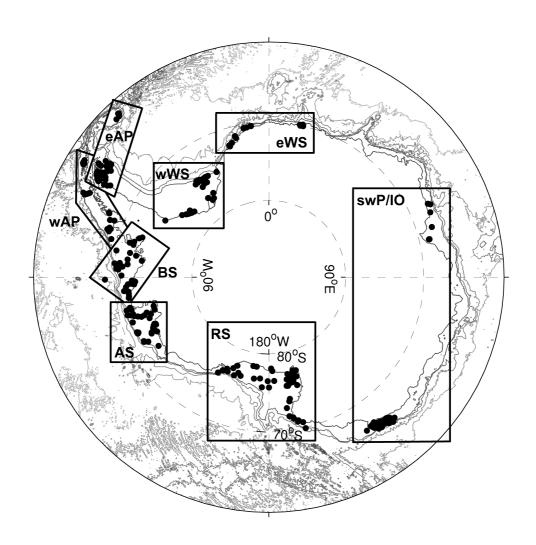
Figure 3: Sedimentary $CaCO_3$ content (%) (a) on the Amundsen Sea shelf and (b) on the Bellingshausen Sea shelf. Isolines are from the topography of Timmermann et al. (2010), lines are drawn every 200 m between 0 and 1000 m and every 500 m at water depths > 1000 m.

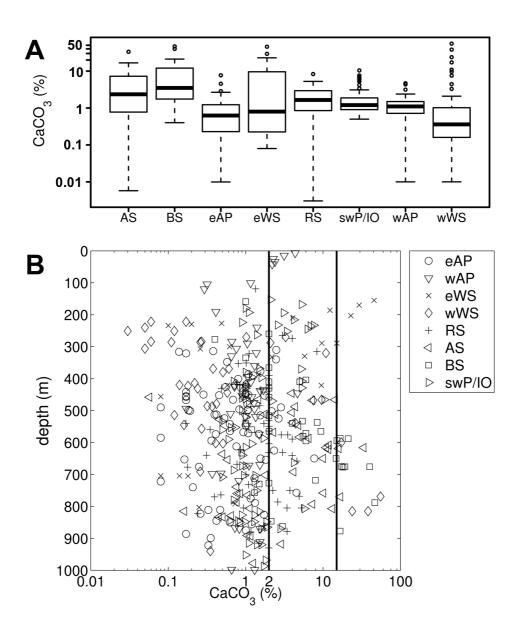
Figure 4: Bottom water Ω_A on the Antarctic shelves from GLODAP and CA-RINA data. Occurrence of undersaturation at depths shallower than 1100 m is marked with a black cross. Isolines are from the topography of Timmermann et al. (2010) and lines are drawn every 1000 m.

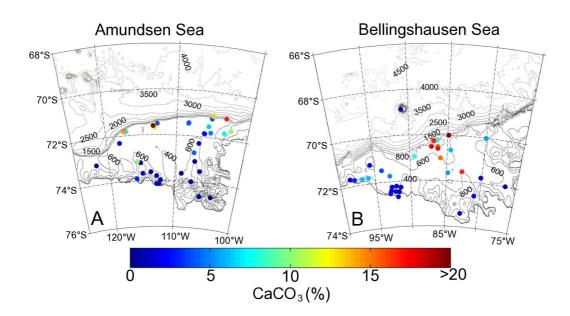
Figure 5: Bottom water saturation states (a) Ω_C and (b) Ω_A on the Antarctic shelves and slope from GLODAP and CARINA data. Calcite is supersaturated at all depths. A linear regression through Ω_A reveals a mean saturation horizon of about 1100 m with certain areas being undersaturated at even shallower depths. The grey diamonds and dotted regression line were calculated assuming a DIC increase of 20 μ mol 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 watermasses 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, Table 1 and Table 2 for further explanation and abbreviations.

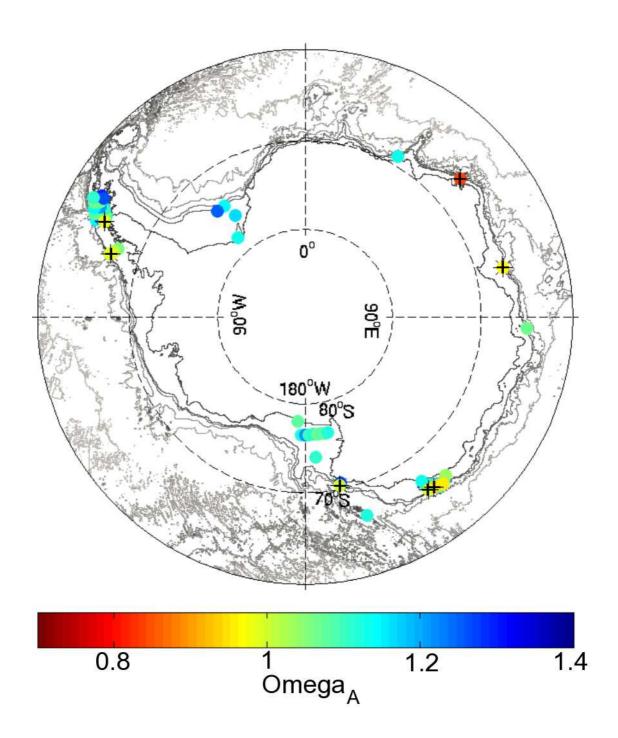
Figure 6: Sedimentary CaCO₃ content (%) on the eastern Weddell Sea shelf with data from Gingele et al. (1997).

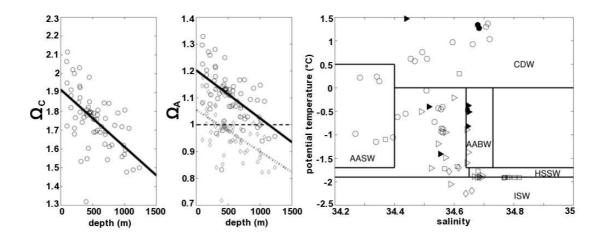
Figure 7: Mean carbonate contribution in g m $^{-2}$ for the west and east Antarctic Peninsula (wAP and eAP) and western and eastern Weddell Sea (wWS and eWS) regions. Bars show the contribution by macrozoobenthos (left scale) and circles depict sedimentary CaCO₃ (right scale)



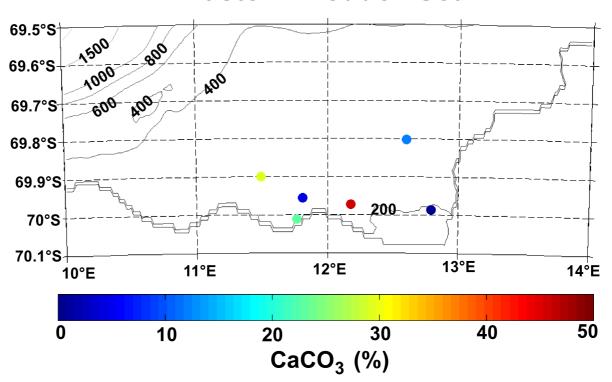








Eastern Weddell Sea



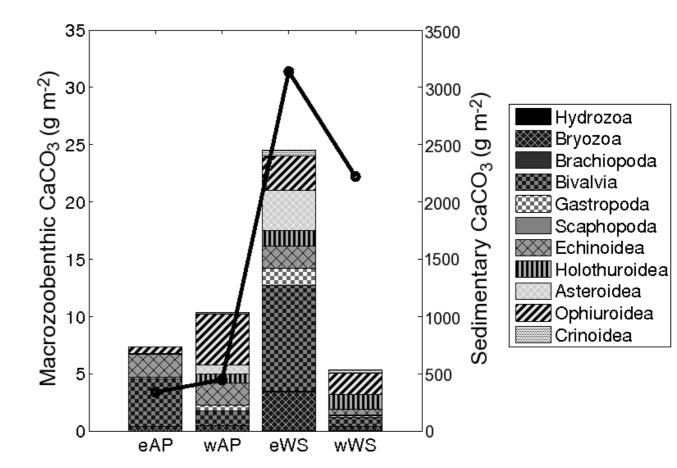


Table 1: List of acronyms

Table 1. Dist of actoryths				
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	Orsi et al. (1995); Grosfeld et al. (2001)
CDW^{-c}	> 0		Orsi et al. (1995, 1993)
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 III et al., 1998)