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Rapid invasion of anthropogenic CO₂ into the deep circulation of the Weddell Gyre

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Summary

Data are presented for Total carbon dioxide (TCO₂), oxygen and nutrients from 14 cruises covering two repeat sections across the Weddell Gyre, from 1973 to 2010. Assessments of the rate of increase of anthropogenic CO₂ (C_{ant}) are made at three locations. Along the Prime Meridian, TCO₂ is observed to steadily increase in the bottom water. Accompanying changes in silicate, nitrate and oxygen confirm the non-steady state of the Weddell circulation. The rate of increase of TCO₂ of $+0.12 \pm 0.05 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ therefore poses an upper limit to the rate of increase of C_{ant}. In contrast, the bottom water located in the central Weddell Sea exhibits no significant increase in TCO₂, suggesting that this water is less well ventilated at the southern margins of the Weddell Sea. At the tip of the Antarctic Peninsula (i.e., the formation region of the bottom water found at the Prime Meridian) the high rate of increase of TCO₂ over time observed at the lowest temperatures suggests that nearly full equilibration occurs with the anthropogenic CO₂ of the atmosphere. This observation constitutes rare evidence for the possibility that ice cover is not a major impediment for uptake of C_{ant} in this prominent deep water formation region.

Key words

Anthropogenic carbon; macronutrients; dissolved oxygen; Weddell Sea, Antarctic; Weddell Sea Bottom Water

Introduction

The perturbation of the global carbon cycle by human activity has been extensively documented. Measurements of atmospheric carbon dioxide (CO_2) at Mauna Loa Observatory have accurately revealed the continuous buildup of the CO_2 in the atmosphere since the 1950s [1] and have been instrumental in raising awareness of the global-scale climate experiment. Because of the intense exchange of gases between the atmosphere and the oceans, the carbon inventory of the oceans has also been increasing. However, it has proven difficult to quantify the carbon uptake and storage by the oceans. Mixing time scales of the oceans are several orders of magnitude larger than those of the atmosphere [2], implying that a time series approach such as that so successfully implemented at Mauna Loa (and subsequently at other sites) will not allow for a globally representative picture of the changing oceanic carbon reservoir at high temporal resolution.

Based on worldwide measurements of the partial pressure of CO_2 in the surface ocean and the atmosphere, Takahashi et al. [3] computed an oceanic CO_2 sink of $2 \pm 1 \text{ Pg C yr}^{-1}$ for the nominal year 2000. Results from other methods give similar estimates [4]. The uptake of anthropogenic CO_2 (C_{ant}) is not homogeneously distributed over the world oceans, but varies strongly depending on local characteristics (e.g., biological CO_2 fixation or respiration, seasonal cooling or warming, upwelling, deep water formation). The Southern Ocean is thought to be a region of disproportionately high CO_2 absorption [5,6] with the most recent estimate, based on different methods, amounting to $0.42 \text{ Pg C yr}^{-1}$ south of 44°S [6].

Uptake of C_{ant} occurs at the ocean surface, but long-term storage involves the deep and abyssal oceans. The surface and deep ocean are separated by the thermocline which impedes intense contact. However, at high latitudes the connectivity between the surface and deep oceans is high due to the small density differences between these layers; one may envision the polar oceans to provide a direct contact between the atmosphere and the deep ocean waters. Indeed, almost all of the abyssal water masses in the world oceans are generated in only a few restricted regions of the polar oceans. Within the Southern Ocean, one of those regions is the Weddell Sea and its eastward extensions, known collectively as the Weddell Gyre. The Weddell Gyre is located in the Atlantic sector of the Southern Ocean with the Antarctic Peninsula as its western boundary. The gyre is mainly wind-driven with westward flow in the south and eastward in the north. Upwelling of sub-surface waters occurs towards its interior due to its divergent nature, but also along the shelves [7]. From the Antarctic Circumpolar Current to the north, sub-surface water known as Circumpolar Deep Water (CDW) is imported mainly in the east [8]. This CDW is the main source water of the gyre from which almost all other water masses are derived. Locally known as Warm Deep Water (WDW), it is characterized by a temperature and salinity maximum just below the pycnocline. Along the shelves in the south and southwest of the Weddell Sea, surface waters cool and become saltier to form a dense water mass that will flow downslope into the abyssal Weddell Sea, entraining a (variable) fraction of WDW during its descent. At depth, the cold water mass is referred to as Weddell Sea Bottom Water (WSBW). This WSBW is one of the densest waters in the oceans and contributes to the Antarctic Bottom Water (AABW) which is found in the abyssal oceans.

By the process of deep water formation, the deep and bottom layers of the oceans are supplied with oxygen and other atmospheric gases like the anthropogenic chlorofluorocarbons (CFCs) and CO₂. Notably, dense water formation is potentially one of the main routes for C_{ant} to enter the abyss and be sequestered on time scales of centuries. The high latitudes of the Southern Ocean have the largest uncertainty regarding the invasion of anthropogenic CO₂, with different data-based methods giving different results [9].

The Weddell Gyre has, for this reason, been a major region of investigation of the carbon cycle and the anthropogenic perturbation thereof [10,11,12,13,14,15]. It is evident that the total storage of C_{ant} is relatively small [13], but a significant increase in CO₂ has been found in the deep and bottom layers of the gyre [14,15], although the latter studies differ in the vertical distribution of C_{ant}. We expand on these earlier studies of the accumulation of C_{ant} in the Weddell Gyre by investigating, in an extended measurement database, the trends in total CO₂ in the WSBW at (i) the Prime Meridian, (ii) the deep central Weddell Sea and (iii) the continental slope of the Antarctic Peninsula. This comprehensive use of the available data now allows an improved assessment of the invasion of anthropogenic CO₂ into the Weddell Gyre.

Data and Methods

Data are presented from two sections across the Weddell Gyre, which have been occupied repeatedly during the last decades (see table S1 for a detailed listing of cruises and where the data can be obtained). Both sections were in most years sampled consecutively during a single cruise with the German icebreaker FS Polarstern. The section along the Prime Meridian (or Greenwich Meridian) runs from about 55°S to the Antarctic continent. Van Heuven et al. [15] have extensively described the data at this section between 1973 and 2008 and here we add data from Polarstern cruise ANT-XXVII/2 in 2010/11 (see below). For nutrients and oxygen, data of two older cruises (ANT-VIII/2, 1989 and ANT-IX/2, 1990) are additionally included. The second section runs between Kapp Norvegia and Joinville Island near the tip of the Antarctic Peninsula; we present data between 1993 and 2011, consisting of 6 cruises with data also at the Prime Meridian, supplemented by cruise ANT-X/7 (1993) [16].

The newest, previously unpublished data were collected during cruise ANT-XXVII/2 from 28 November 2010, Cape Town, South Africa to 5 February 2011, Punta Arenas, Chile [17]. Measurements of Total CO₂ (TCO₂) and Total Alkalinity (TA; not used in the present study) were conducted with the same two instruments (VINDTA 3C, Marianda, Kiel, Germany) as used during the previous cruises ANT-XXIV/3 and ANT-XXIV/2 in 2008. TCO₂ was measured with the coulometric method [18]. Accuracy was set by measuring Certified Reference Material (CRM) from batches 100 and 105 obtained from Prof. Andrew Dickson of Scripps Institution of Oceanography (U.S.A.). The precision during this cruise for TCO₂ and TA was 1.0 and 1.5 μmol kg⁻¹, respectively, as determined from the average difference of in-bottle CRM replicates (n=87). A number of samples (unknowns and CRMs) were measured on both instruments to assess consistency between the two instruments.

The dissolved nutrients nitrate, phosphate and silicate were measured during ANT-XXVII/2 on the TRAACS 800 auto-analyzer system of the Royal Netherlands Institute for Sea Research (NIOZ, Texel, the Netherlands), which was also used on the cruises in 1996, 1998, 2005 and 2008. In all these cases, the same sea water standards with known nutrient concentrations were measured for initial consistency control. New Reference Material Nutrient Sample (RMNS; JRM Kanso, Japan) containing known concentrations of silicate, phosphate, nitrate and nitrite in seawater was also analyzed in triplicate during every run and used to standardize the results. Overall accuracy (with respect to RMNS) for nitrate, phosphate and silicate is better than 0.11 $\mu\text{mol/l}$, 0.01 $\mu\text{mol/l}$ and 0.3 $\mu\text{mol/l}$, respectively. For more details, refer to [19].

Only data for dissolved oxygen (O_2) was used that was measured with a standard (generally automated) Winkler technique; the precision is $\pm 0.2\%$ for the Polarstern cruises. Details of the measurements of temperature, salinity and pressure are given in [17] and [20]. For all measurements, accuracy is better than $\pm 0.003^\circ\text{C}$, ± 0.003 and ± 2 dbar, respectively. Salinity is given on the Practical Salinity Scale (PSS78).

Some clearly deviating cruise datasets were discarded for this study (TCO_2 for AJAX, 74JC10_1 and part of ANT-X/4; oxygen for ANT-XXIII/3, ANT-XXII/3 and parts of ANT-V/2&3 and GEOSECS; see [15] for the procedure).

Data adjustment

For data collected prior to 1993, no internationally recognized CRMs for TCO_2 were available and systematic offsets due to calibration issues may have gone unnoticed. To minimize such inaccuracies, data from all cruises have been adjusted to be unbiased (with respect to each other) in the lower Warm Deep Water to upper Weddell Sea Deep Water. In this depth range (about 800 to 2200 m) the water column is least ventilated [21] and thus we also expect the lowest level of C_{ant} . Data of TCO_2 from between -0.4°C and 0.2°C from individual cruises were regressed against potential temperature and the intercept at 0°C was determined (note that the definition of WDW proper and WSDW proper are different from this). Each cruise was then adjusted to the average intercept of the cruises from the CRM era (a more comprehensive description of the data standardization methodology is given in [15]). This procedure was followed for both data from the Prime Meridian and for those in the central and western Weddell Sea (in the latter case using only data from east of 43°W , to avoid re-using ‘standardization samples’ in subsequent analyses). The results are considered to improve local data consistency, and should not be taken to represent overall biases of individual cruises. For the cruises during the CRM era the (additive) adjustments of TCO_2 were smaller than the commonly reported upper limit for accuracy of $2 \mu\text{mol kg}^{-1}$, and also below the threshold of $4 \mu\text{mol kg}^{-1}$ used in the major data quality control efforts GLODAP and CARINA [22]. In fact, only cruise ANT-V/2&3 (1986) required a significant (upward) correction of TCO_2 . In the remainder of this work, we use TCO_2 normalized to a salinity of 34.65, to partially account for TCO_2 changes due to mixing.

For the other variables presented here, no CRM was available and thus adjustments were implemented similarly. Modest multiplicative adjustments of 0.5-2% were generally applied to nutrients. Adjustment details are available in Table S2.

Results

Prime Meridian

Shown in Fig. 2 are time trends of four relevant sea water properties (TCO₂, oxygen, silicate, nitrate) in four different water masses at the Prime Meridian. These were obtained by means of linearly regressing the mean values of each cruise, in each water mass, against the year of measurement. A significant trend in TCO₂ of $+0.12 \pm 0.05 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ is found in the WSBW between 1973 and 2011. This rate is very similar to the rate observed during the era of CRM use (i.e., 1996-2010; $+0.16 \pm 0.14 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$). In the surface layer the trend is larger ($+0.53 \pm 0.21 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$), as is the variability, which is not surprising because several processes, such as biological activity and air-sea exchange (and also the variation in sampling season), tend to have large impact on TCO₂. Interestingly, there are also trends in the steady state tracers oxygen (decreasing in the deeper water masses) and silicate (increasing in the deeper water masses). The small trend observed in nitrate is only barely significant. The new data from 2010/2011 fall nearly exactly on the existing deep water trends of all four properties.

Abyssal central Weddell Sea

In Figure 3 we display the normalized TCO₂ in the WSBW in the Weddell Sea interior at 25-43°W ($\theta < -0.75^\circ\text{C}$). This location was chosen for its modest lateral CFC-12 maximum at the sea floor (see [23]), suggesting modest recent ventilation – note that the magnitude of the CFC maximum is similar to that in the core of WSBW on the Prime Meridian [23]. The mean age of WSBW both on the Prime Meridian and in the Weddell Sea interior is 120-160 years [23]. However, within the (relatively small) inter-annual variability, no significant trend in TCO₂ was found between 1993 and 2011, in apparent contrast to the TCO₂ increase observed in the WSBW at the Prime Meridian.

Tip of the Antarctic Peninsula

The WSBW is generated along the margins of the western and southwestern Weddell Sea, where nascent plumes of WSBW descend the continental slope [23,24]. Such a plume can be observed near the western end of all our sections across the Weddell Sea. The annual and inter-annual variability of WSBW formation is rather large [25,26], and the narrow vertical extent of the plume complicates its sampling. Because of that, there exists, on the shelf as well as on the slope, an (apparent) variability of water types, ranging from near-freezing former surface water to nearly unmodified WDW from the Weddell Sea interior. It is, therefore,

nearly impossible to compute a simple trend of TCO_2 from our repeat sections, although changes between two occupations may give indications for the uptake of C_{ant} [27]. To nonetheless extract temporal trends from our dataset, we assess the time rate of change of normalized TCO_2 for discreet selections of potential temperature (θ ; Fig. 4). To that end, TCO_2 data from all cruises were binned in 0.3°C intervals. For each interval, the TCO_2 averages (one per cruise) were then regressed against time, yielding the rate of increase at a certain θ (Fig. 4A); the mean depth of samples within each θ -bin is shown in Figure 4B.

Most conspicuously, in the very coldest waters below -1°C (i.e., in the most recently ventilated waters), we observe the TCO_2 trend to become steeper with decreasing temperature, approaching $0.8\text{--}1.0 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ at freezing temperature (not enough such freezing point samples are available for trend determination). For θ between -1 and -0.5°C , the rate of increase in TCO_2 is at its minimum. At higher θ , i.e., in the upper WSDW ($-0.2^\circ\text{C} < \theta < 0^\circ\text{C}$), an intermediate rate of increase of about $0.2 \mu\text{mol kg}^{-1} \text{ a}^{-1}$ is observed, which is somewhat surprising as this water mass is considered not well ventilated – note that based on the ‘lower WDW/upper WSDW’ adjustment of the data, one might inherently expect no changes at θ of -0.2°C ; however, the adjustments were performed on data east of 43°W , i.e., towards the central Weddell Sea, and therefore an absence of trends at the slope is not necessarily expected. For comparison, we performed a similar analysis for the data along the Prime Meridian (Fig. 4C and 4D). Because the bottom water is nowhere colder than -1°C here (implying significant admixture of warmer, less ventilated waters), changes are not so pronounced, but agree with the earlier estimate of TCO_2 increase in the WSBW. The WSDW/WDW at the Prime Meridian does not exhibit an appreciable TCO_2 increase.

Discussion

All methods for determining C_{ant} contain the assumption of steady state conditions in hydrography and biogeochemistry of the region under investigation. This also holds for our straightforward way of detecting trends in measured TCO_2 data; the rise of TCO_2 could also be (partly) caused by non-anthropogenic processes. At the Prime Meridian, the main increase in TCO_2 is observed to occur in the WSBW, largely provoked by a core of recently ventilated water centered at 58°S which originates from the bottom water formation regions in the western Weddell Sea [15,21,23]. However, significant decadal variability (and trends) in the potential temperature and salinity of the WSBW, and a decadal decrease of its volume, have been documented [20,28], suggesting a non-steady state. Moreover, Huhn et al. [23] using CFC data, suggest that the ventilation rate of the WSBW has significantly decreased. The downward trend of oxygen and upward trends of silicate and nitrate (Fig. 2) are in line with such non-steady state conditions and less ventilation. Circulation changes that would lead to increased admixture of WDW would cause a decrease of oxygen in the WSBW. A reduction of the ventilation of WSBW would result in longer residence times of the water near the bottom, which in turn would tend to increase the silicate concentration, as high silicate concentration in the Weddell basin are eventually caused by transfer from the sediments [29]. The small, barely significant trend observed for nitrate (Fig. 2) is explained by the very small gradients of nitrate in the water column of the Weddell Gyre (only about $2 \mu\text{mol kg}^{-1}$ over

more than 4000 m; see typical concentrations in Fig. 2); in such conditions, variations in admixture of water masses do not yield significant changes beyond measurement uncertainty. These observations strengthen an earlier suspicion [15] that changes in hydrographic conditions to some extent underlie the observed increase in TCO₂. Nonetheless, the expected effect of hydrographic trends on TCO₂ (ca. 0.025 $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$) is not enough to explain the full size of the observed trend on TCO₂ (as stated, $+0.12 \pm 0.05 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$). We cannot rule out changes in deep ocean remineralization.

Along the section across the Weddell Sea, WSBW is found overlying most of the sea floor, though its eastward extent has been shrinking during the last decades (G. Rohardt, 2013, AWI, unpublished data). This bottom water is thought to be originating from the Filcher-Ronne Shelf in the south [24,26]. In the most ventilated deep part of the section, we do not find a significant TCO₂ increase (Fig. 3), this in apparent contrast to the increase in the WSBW on the Prime Meridian and on the continental shelf to the west (note that this also holds when at the Prime Meridian only the data from the CRM era are considered (see Fig. 2), i.e., the same period of time as for the central Weddell Sea). Using the CFC-based Transit Time Distribution (TTD) technique, Huhn et al. [23] found a non-zero level of C_{ant} in this ventilated water mass, but estimated the increase herein over the last two decades to be only about 1 $\mu\text{mol kg}^{-1}$. Assuming the TTD generates the correct magnitude of anthropogenic TCO₂ increases, it is manifest that such a small increase is not significantly discernible in TCO₂ data which spread about 5-10 $\mu\text{mol kg}^{-1}$ in this water mass (see Fig. 3). The anthropogenic signal is small because of relatively limited ventilation [23]. It is encouraging that the results from CFCs and direct measurements are in such fine agreement.

On the shelf and continental slope of the Antarctic Peninsula, the rate of increase of TCO₂ as a function of θ (Fig 4A) convincingly reveals significant uptake of (anthropogenic) CO₂ by the cold waters that, upon densification during winter, may contribute significantly to the ventilation of the deep Weddell Gyre. The coldest waters (below -1.5°C) are then the nascent bottom waters on the shelf and upper slope. The rate of increase of TCO₂ in these water equals the theoretical rate (red circle in Fig 4A) that is expected for freezing shelf water in pCO₂ equilibrium with the atmospheric pCO₂ of the early 2000s (calculated using CO2SYS [30], assuming $\theta = -1.88^\circ\text{C}$, $S=34.4$ and the mean yearly increase in $p\text{CO}_2^{\text{atm}}$ from 1995 to 2005 of 1.8 $\mu\text{atm yr}^{-1}$). This leads us to believe that almost complete equilibration of the surface water with the increasingly CO₂-rich atmosphere occurs on a regular basis. Near the Antarctic Peninsula and at the Prime Meridian (Fig 4C), water between about -1°C and -0.3°C is observed to have a low rate of increase of TCO₂. Probably this is water that circulates within the gyre without much contact with the atmosphere. Water of intermediate temperature between -1.5°C and -1°C likely are mixtures of descending shelf water and entrained, warmer, C_{ant} -poor WDW and WSDW from the Weddell Sea interior. Towards higher θ , i.e., in the upper WSDW and WDW, the rate of increase gets higher as well (Fig. 4A). This hints at mixing of those deep water masses with C_{ant} -enriched shelf waters, a process occurring along the shelf break [31,32]. On the Prime Meridian, such an increase of the rate of increase of TCO₂ in the WDW is not observed (Fig. 4C), likely owing to the local absence of admixture of shelf waters. Also, at the Prime Meridian the TCO₂ trend in the surface water is, unlike at the Peninsula not following the atmospheric increase of CO₂; the two reasons are the

definition of surface water (<200 m), which thus includes some C_{ant} -poor WDW at some locations, and the dilution of the surface waters by upwelled deep water poor in C_{ant} . Much of the C_{ant} -charged upper WSDW/WDW that is formed at the Peninsula may exit the Weddell Gyre to the north before reaching the Prime Meridian. Such a mechanism of dense water masses dynamically moving along the slope through the passages in the South Scotia Ridge has been reported before [33].

The hydrographic conditions of the northern Weddell Sea margin may be conducive to full equilibration of $p\text{CO}_2$. The typical time scale of full CO_2 equilibration between ocean and atmosphere is in the order of 6-12 months, implying that with full equilibration, the residence time of the surface water should also be in that order of magnitude. This may be accomplished by the shelf water moving around the Weddell Gyre as part of the Antarctic Coastal Current [34]. Due to the divergent nature of the gyre, the exchange of the shelf water with interior water masses is restricted [31] thus enhancing the residence time. However, sea ice covers the shelf waters during a considerable part of the year. In winter the TCO_2 of the shelf waters is probably high due to some upwelling of high- TCO_2 Warm Deep Water and some remineralization of organic matter, while outgassing is impeded due to the contiguous ice cover. In spring and summer, major biological activity in and around the sea ice and the water causes strong $p\text{CO}_2$ undersaturation [35,36] which results in an influx of CO_2 from the atmosphere. High wind speeds towards the end of summer and in autumn strongly enhance the air-sea fluxes. This causes the shelves to be sinks both for natural and anthropogenic CO_2 and a high level of equilibration may thus be reached.

Although the coastal region of the Southern Ocean has been considered to be a strong sink for anthropogenic CO_2 (e.g., [35]), several other oceanographic studies have (explicitly or otherwise) suggested the CO_2 saturation to be significantly lower than 100% (e.g., [11,12]). In the current work however, the well-defined, long term positive trend, increasing in slope with decreasing temperature, is relatively unambiguous in its suggestion of a saturated source water mass. Our observation that these important deep water formation regions appear to track the increasing atmospheric $p\text{CO}_2$ is likely to be of great value to studies in which a surface saturation of C_{ant} has to be prescribed (notably, transit time distribution studies; e.g., [23]).

Conclusions

We present new evidence for the notion of significant invasion of anthropogenic CO_2 into the deep Weddell Gyre. Along the Prime Meridian, the longest and most frequently sampled series of repeat sections exists. Newly added data, collected in 2010-2011, strengthens our confidence in an earlier observation of increasing TCO_2 in the Weddell Sea Bottom Water at the Prime Meridian [15], improving the estimate to $+0.12 \pm 0.05 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ over the period 1973-2010. For the more recent era of CRM use, the rate is determined to be $+0.16 \pm 0.14 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. The accompanying trends that are observed in the concentrations of oxygen, silicate and nitrate suggest the presence of changes in biogeochemistry and/or circulation, congruent with prior observations of the changes in hydrography and ventilation of the

abyssal waters [20,23]. Such processes may account for part of the observed time trend of TCO_2 . Observations since 1993 of the bottom water of the central Weddell Sea do not reveal a significantly increasing TCO_2 . This is in line with earlier TTD-based results [23], which show only a very small increase in C_{ant} ; such a small increase would not be discernible in the TCO_2 data due to natural variability in the region. Ventilation and replenishment of these waters must be very slow to be compatible with these observations. Sluggish air-sea gas exchange at the source region of these waters, the Filcher-Ronne Shelf, is speculated to underlie the observed low rate of increase in the bottom water.

We find strong indications that the shelf water and nascent bottom water in the western Weddell Sea (i.e., the source waters of the WSBW at the Prime Meridian) to large extent track the atmospheric $p\text{CO}_2$. This suggests that at that location, ice cover, which is ubiquitously present in this region, does not constitute a major impediment for air-sea CO_2 equilibration on annual time scales. Conceivably, the enhanced residence time of the shelf water in a gyre system combined with the yearly period of ice-free conditions suffice to complete air-sea equilibration of $p\text{CO}_2$. Frequent occurrences of coastal polynyas may also contribute. A considerable part of the C_{ant} -enriched shelf and nascent bottom water may exit the Weddell Sea under topographic constraints relatively straight to the north, where it may be mixed into the deeper layers.

The present study illustrates the paramount value of long-term time series measurements for the elucidation of the C_{ant} dynamics of regions of high variability such as the Weddell Gyre. Such measurement series should be sustained in order to further our understanding of the abyssal C_{ant} sequestration potential of the Southern Ocean.

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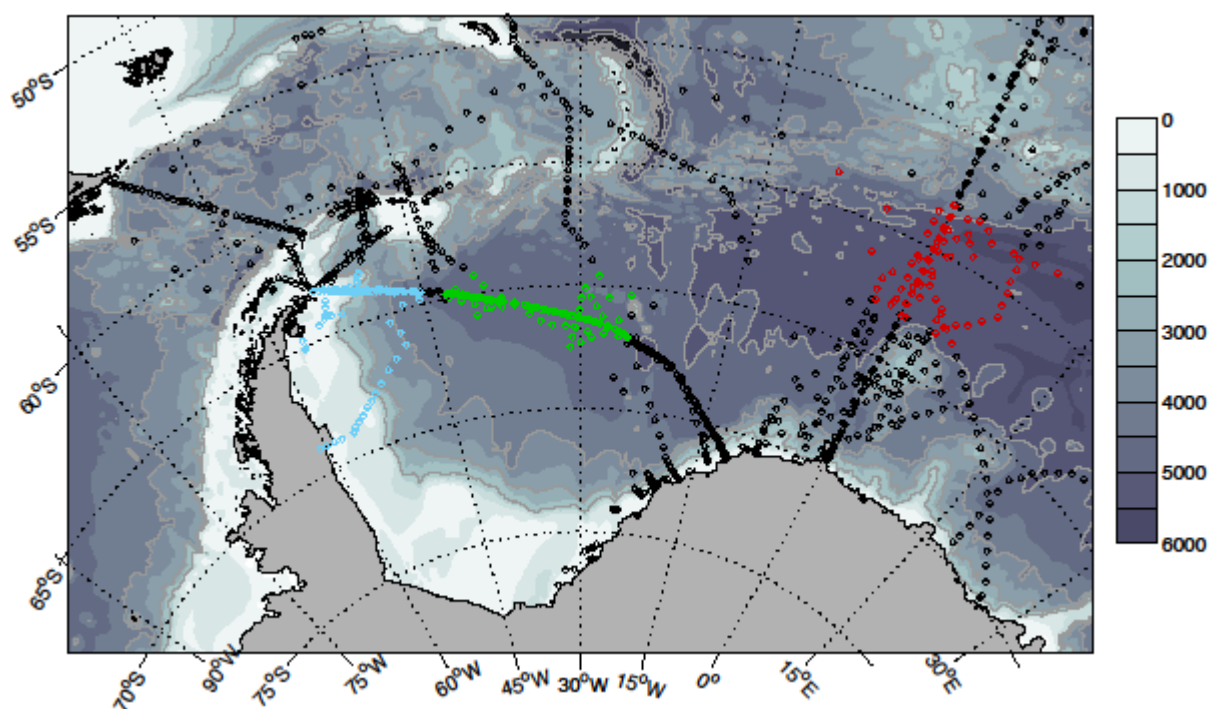


Figure 1. Bathymetric map of the Weddell Sea and surroundings. All oceanographic research stations of all cruises included in this study are drawn as black circles. Red circles indicate the stations from which data is used in the Prime Meridian analysis. Green circles: abyssal Weddell Sea analysis. Blue circles: Antarctic Peninsula analysis.

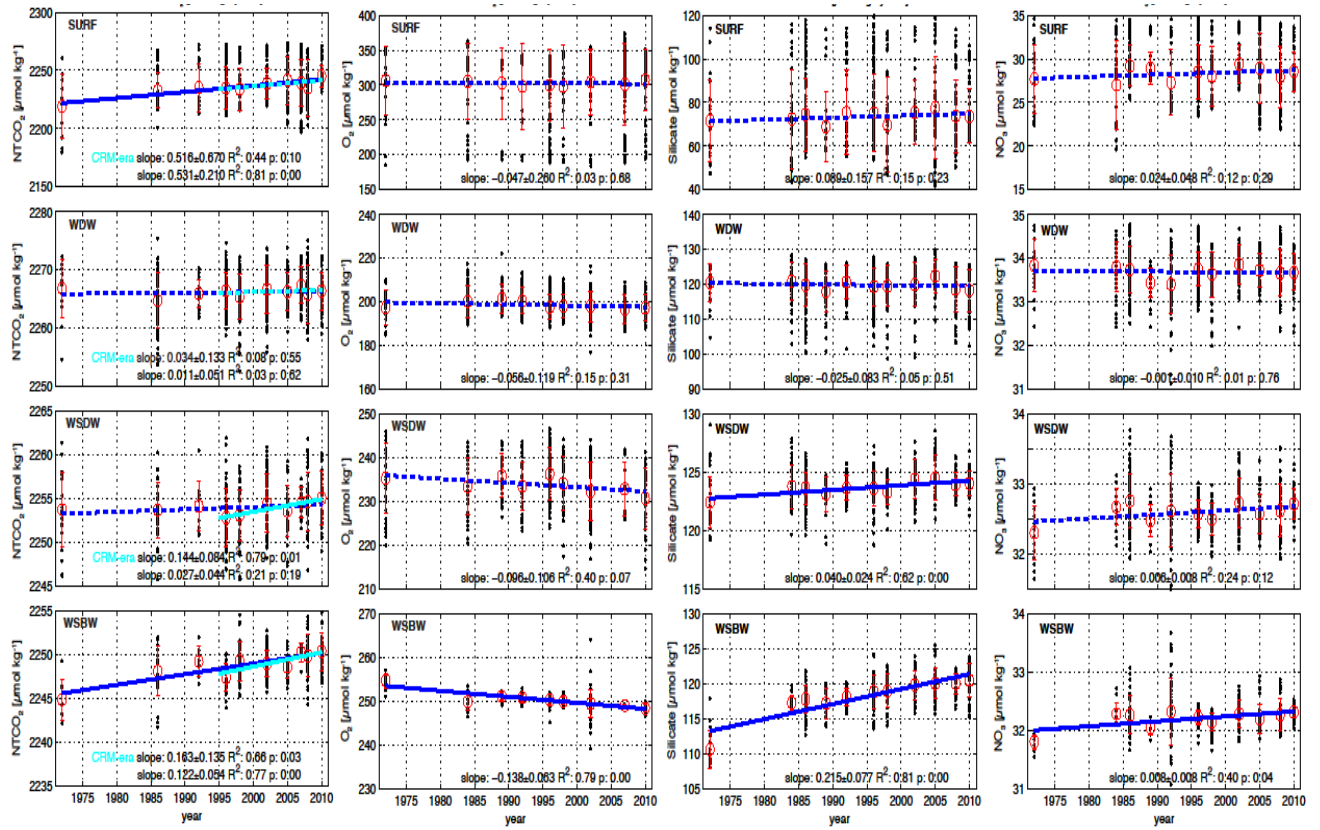


Figure 2. Time trends (μmol kg⁻¹ yr⁻¹) in four seawater properties determined in the cores of 4 water masses at the Prime Meridian - from top to bottom: Surface water, Warm Deep Water (WDW), Weddell Sea Deep Water (WSDW) and Weddell Sea Bottom Water (WSBW). Trends were computed using least squares regression of the means of each cruise against time. Significant trends are indicated by drawn lines, statistically insignificant trends by dotted lines. For TCO₂ the trends are additionally shown for the CRM era with light blue lines.

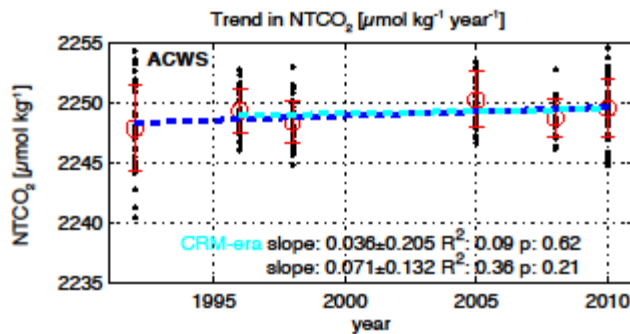


Figure 3. Trend of the mean TCO₂ concentration in the bottom water (within 250 m from the seafloor) of the Weddell Sea interior between 25°W and 43°W from 1992 to 2011. The slight increase is not significant (blue dotted line). From 1996 onwards, CRMs were used to ascertain TCO₂ data accuracy (light blue dotted line); the trend is not significant either.

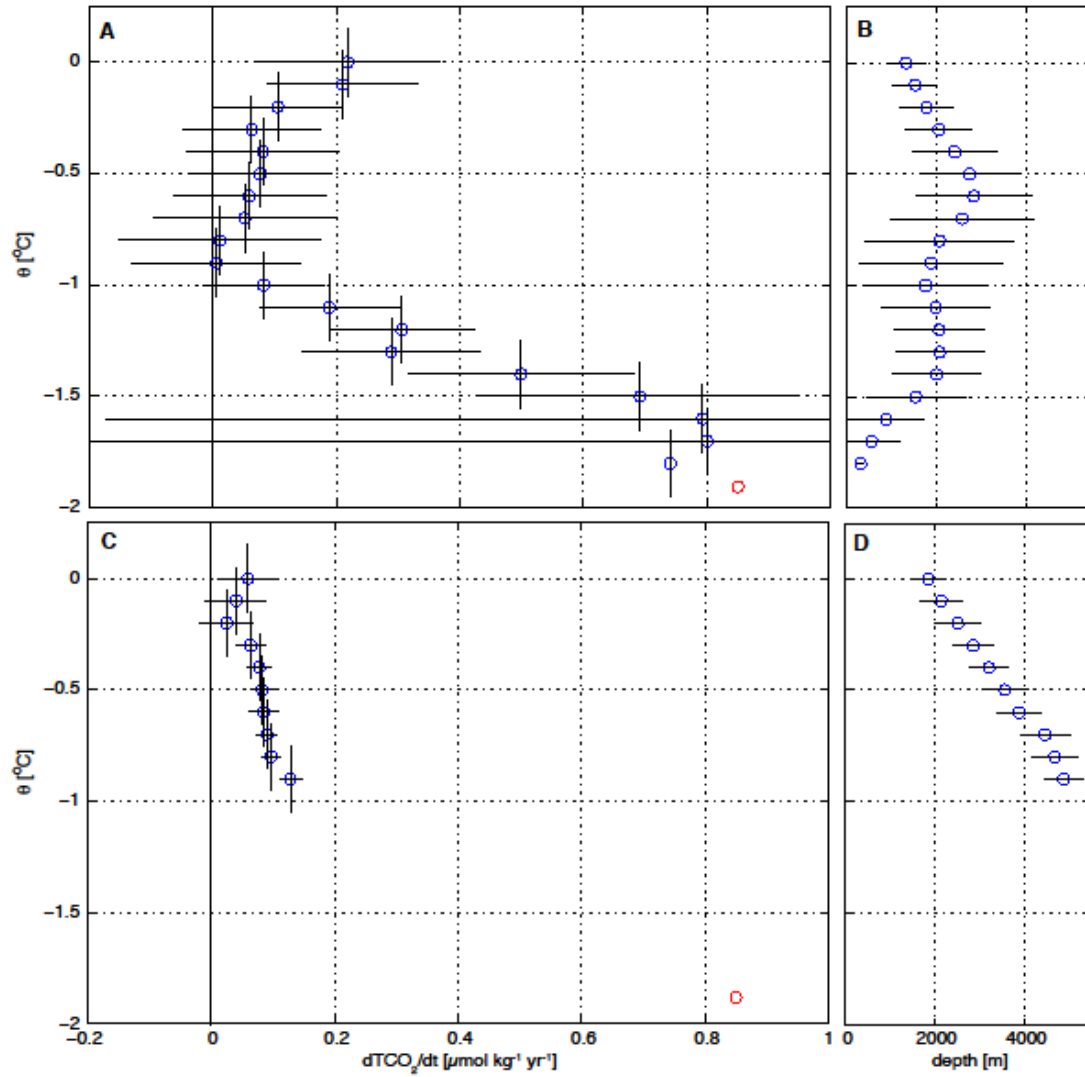


Figure 4. Time rate of change of normalized TCO₂ (dTTCO₂/dt) binned in 0.3°C ranges of θ for (A) data over the continental shelf and slope of the tip of the Antarctic Peninsula (west of 40°W; within 1750 m of seafloor but not shallower than 250 m depth), and (C) data along the Prime Meridian (below 500 m). Vertical lines indicate the bin ranges, horizontal lines represent the standard error of the determined time trend. The red dot indicates the expected mean rate of increase, assuming pCO₂ equilibrium with the atmosphere during the decade 1995-2005. (B) and (D) show the mean and standard deviation of the depths of the samples in each of the θ bins for the Antarctic Peninsula and Prime Meridian data, respectively.