Rapid invasion of anthropogenic CO$_2$ into the deep circulation of the Weddell Gyre

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Data are presented for total carbon dioxide (TCO$_2$), oxygen and nutrients from 14 cruises covering two repeat sections across the Weddell Gyre, from 1973 to 2010. Assessments of the rate of increase in anthropogenic CO$_2$ ($C_{\text{ant}}$) are made at three locations. Along the Prime Meridian, TCO$_2$ 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 in TCO$_2$ of $+0.12 \pm 0.05 \, \mu$mol kg$^{-1}$ yr$^{-1}$ therefore poses an upper limit to the rate of increase in $C_{\text{ant}}$. By contrast, the bottom water located in the central Weddell Sea exhibits no significant increase in TCO$_2$, 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 in TCO$_2$ over time observed at the lowest temperatures suggests that nearly full equilibration occurs with the anthropogenic CO$_2$ of the atmosphere. This observation constitutes rare evidence for the possibility that ice cover is not a major impediment for uptake of $C_{\text{ant}}$ in this prominent deep water formation region.
1. Introduction

The perturbation of the global carbon cycle by human activity has been extensively documented. Measurements of atmospheric carbon dioxide (CO₂) at Mauna Loa Observatory, Hawaii, have accurately revealed the continuous build-up of the CO₂ 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 proved 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 CO₂ in the surface ocean and the atmosphere, Takahashi et al. [3] computed an oceanic CO₂ 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 CO₂ (C_{ant}) is not homogeneously distributed over the world oceans, but varies strongly depending on local characteristics (e.g. biological CO₂ fixation or respiration, seasonal cooling or warming, upwelling, deep water formation). The Southern Ocean is thought to be a region of disproportionately high CO₂ absorption [5,6] with the most recent estimate, based on different methods, amounting to 0.42 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 owing 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 owing 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 such as 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 [10–15]. 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.

2. Data and methods

Data are presented from two sections across the Weddell Gyre (figure 1), which have been occupied repeatedly during the past decades (see the electronic supplementary material, 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 (figure 1). 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 six cruises with data also at the Prime Meridian, supplemented by cruise ANT-X/7 (1993) [16].

The newest, previously unpublished data (EM Jones, M Hoppema 2011) 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 this 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 (San Diego, CA, USA). The precision during this cruise for TCO₂ and TA.
was 1.0 and 1.5 \(\mu\text{mol kg}^{-1}\), 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-analyser 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 seawater standards with known nutrient concentrations were measured for initial consistency control. A new Reference Material Nutrient Sample (RMNS; JRM Kanso, Japan) containing known concentrations of silicate, phosphate, nitrate and nitrite in seawater was also analysed 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 \(\mu\text{mol l}^{-1}\), 0.01 \(\mu\text{mol l}^{-1}\) and 0.3 \(\mu\text{mol l}^{-1}\), respectively. For more details, refer to [19].

Only data for dissolved oxygen (O\(_2\)) were 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 [17,20]. For all measurements, accuracy is better than \(\pm 0.003^\circ\text{C}\), \(\pm 0.003\) and \(\pm 2\) 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).

(a) 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 WDW to upper Weddell Sea Deep Water (WSDW). In this depth range (about 800–2200 m), the water column is least ventilated [21] and thus we also expect the lowest level of \(C_{\text{ant}}\). Data of TCO\(_2\) from between \(-0.4^\circ\text{C}\) and 0.2\(^\circ\text{C}\) from individual cruises were regressed against potential temperature, and the intercept at 0\(^\circ\text{C}\) 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\(^\circ\text{W}\), 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 the electronic supplementary material, table S2.

3. Results

(a) Prime Meridian

Shown in figure 2 are time trends of four relevant seawater properties (TCO\(_2\), oxygen, silicate and 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
Figure 2. Time trends (µmol kg⁻¹ yr⁻¹) in four seawater properties determined in the cores of four water masses at the Prime Meridian—from top to bottom: surface water, WDW, WSDW and 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 (shorter) lines. (Online version in colour.)
A significant trend in TCO$_2$ 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 a large impact on TCO$_2$. 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.

(b) Abyssal central Weddell Sea

In figure 3, we display the normalized TCO$_2$ in the WSBW in the Weddell Sea interior at 25–43° W ($\theta < -0.75^\circ$C). This location was chosen for its modest lateral CFC-12 maximum at the sea floor [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 TCO$_2$ was found between 1993 and 2011, in apparent contrast to the TCO$_2$ increase observed in the WSBW at the Prime Meridian.

(c) 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 are 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$_{\text{ant}}$ [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 ($\theta$; figure 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 $\theta$ (figure 4a); the mean depth of samples within each $\theta$-bin is shown in figure 4b.
Figure 4. Time rate of change of normalized TCO$_2$ ($d$TCO$_2$/d$t$) binned in 0.3°C ranges of $\theta$ 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, whereas horizontal lines represent the standard error of the determined time trend. The red dot on the right indicates the expected mean rate of increase, assuming pCO$_2$ equilibrium with the atmosphere during the decade 1995–2005. (b,d) The mean and standard deviation of the depths of the samples in each of the $\theta$ bins for the Antarctic Peninsula and Prime Meridian data, respectively. (Online version in colour.)

Most conspicuously, in the very coldest waters below $-1^\circ$C (i.e. in the most recently ventilated waters), we observe the TCO$_2$ trend to become steeper with decreasing temperature, approaching 0.8–1.0 µmol kg$^{-1}$ yr$^{-1}$ at freezing temperature (not enough such freezing point samples are available for trend determination). For $\theta$ between $-1$ and $-0.5^\circ$C, the rate of increase in TCO$_2$ is at its minimum. At higher $\theta$, i.e. in the upper WSDW ($-0.2^\circ$C $< \theta < 0^\circ$C), an intermediate rate of increase of about 0.2 µmol kg$^{-1}$ yr$^{-1}$ 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 $\theta$ of $-0.2^\circ$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 (figure 4c,d). Because the bottom water is nowhere colder than $-1^\circ$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.
4. Discussion

All methods for determining $C_{\text{ant}}$ 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 centred at $58^\circ$ 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 (figure 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 concentrations in the Weddell basin are eventually caused by transfer from the sediments [29]. The small, barely significant trend observed for nitrate (figure 2) is explained by the very small gradients of nitrate in the water column of the Weddell Gyre (only about 2 $\mu$mol kg$^{-1}$ over more than 4000 m; see typical concentrations in figure 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 TCO$_2$. Nonetheless, the expected effect of hydrographic trends on TCO$_2$ (ca. 0.025 $\mu$mol kg$^{-1}$ yr$^{-1}$) is not enough to explain the full size of the observed trend on TCO$_2$ (as stated, $+0.12 \pm 0.05$ $\mu$mol kg$^{-1}$ 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 past decades (G Rohardt 2013, unpublished data). This bottom water is thought to be originating from the Filchner-Ronne Shelf in the south [24,26]. In the most ventilated deep part of the section, we do not find a significant TCO$_2$ increase (figure 3); this is 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 (figure 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 $C_{\text{ant}}$ in this ventilated water mass, but estimated the increase herein over the past two decades to be only about 1 $\mu$mol kg$^{-1}$. Assuming the TTD generates the correct magnitude of anthropogenic TCO$_2$ increases, it is manifest that such a small increase is not significantly discernible in TCO$_2$ data which spread about 5–10 $\mu$mol kg$^{-1}$ in this water mass (figure 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 in TCO$_2$ as a function of $\theta$ (figure 4a) convincingly reveals significant uptake of (anthropogenic) CO$_2$ by the cold waters that, upon densification during winter, may contribute significantly to the ventilation of the deep Weddell Gyre. The coldest waters (below $-1.5^\circ$C), are then the nascent bottom waters on the shelf and upper slope. The rate of increase in TCO$_2$ in these waters equals the theoretical rate (red circle in figure 4a) that is expected for freezing shelf water in pCO$_2$ equilibrium with the atmospheric pCO$_2$ of the early 2000s (calculated using CO2SYS [30], assuming $\theta = -1.88^\circ$C, $S = 34.4$ and the mean yearly increase in pCO$_2^{\text{atm}}$ from 1995 to 2005 of 1.8 $\mu$atm yr$^{-1}$). This leads us to believe that almost complete equilibration of the surface water with the increasingly CO$_2$-rich atmosphere occurs on a regular basis. Near the Antarctic Peninsula and at the Prime Meridian (figure 4c), water between about $-1^\circ$C and $-0.3^\circ$C is observed to have a low rate of increase in TCO$_2$. Probably this is water that circulates within the gyre without much contact with the
atmosphere. Waters of intermediate temperature between $-1.5\,^\circ\text{C}$ and $-1\,^\circ\text{C}$ are likely to be mixtures of descending shelf water and entrained, warmer, $\text{C}_{\text{ant}}$-poor WDW and WSDW from the Weddell Sea interior. Towards higher $\theta$, i.e. in the upper WSDW and WDW, the rate of increase gets higher as well (figure 4a). This hints at mixing of those deep water masses with $\text{C}_{\text{ant}}$-enriched shelf waters, a process occurring along the shelf break [31,32]. On the Prime Meridian, such an increase in the rate of increase in TCO$_2$ in the WDW is not observed (figure 4c), probably because of the local absence of admixture of shelf waters. Also, at the Prime Meridian the TCO$_2$ trend in the surface water is, unlike at the Peninsula, not following the atmospheric increase in CO$_2$; the two reasons are the definition of surface water (less than 200 m), which thus includes some $\text{C}_{\text{ant}}$-poor WDW at some locations, and the dilution of the surface waters by upwelled deep water poor in $\text{C}_{\text{ant}}$. Much of the $\text{C}_{\text{ant}}$-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 pCO$_2$. 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]. Owing 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$_2$ WDW 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 pCO$_2$ undersaturation [35,36] that 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 for both 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$_2$ [35], several other oceanographic studies have (explicitly or otherwise) suggested the CO$_2$ saturation to be significantly lower than 100% [11,12]. In this 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 pCO$_2$ is likely to be of great value to studies in which a surface saturation of $\text{C}_{\text{ant}}$ has to be prescribed (notably, transit time distribution studies; e.g. [23]).

5. Conclusion

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 WSBW 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 $\text{C}_{\text{ant}}$; such a small increase would not be discernible in the TCO$_2$ data owing 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 Filchner-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 pCO₂. This suggests that, at that location, ice cover, which is ubiquitously present in this region, does not constitute a major impediment for air–sea CO₂ 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 pCO₂. Frequent occurrences of coastal polynyas may also contribute. A considerable part of the C₅₆-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.

This study illustrates the paramount value of long-term time-series measurements for the elucidation of the C₅₆ 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 C₅₆ sequestration potential of the Southern Ocean.

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