



## The role of Southern Ocean processes in orbital and millennial CO<sub>2</sub> variations – A synthesis

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### ARTICLE INFO

#### Article history:

Received 19 January 2009

Received in revised form

2 June 2009

Accepted 4 June 2009

### ABSTRACT

Recent progress in the reconstruction of atmospheric CO<sub>2</sub> records from Antarctic ice cores has allowed for the documentation of natural CO<sub>2</sub> variations on orbital time scales over the last up to 800,000 years and for the resolution of millennial CO<sub>2</sub> variations during the last glacial cycle in unprecedented detail. This has shown that atmospheric CO<sub>2</sub> varied within natural bounds of approximately 170–300 ppmv but never reached recent CO<sub>2</sub> concentrations caused by anthropogenic CO<sub>2</sub> emissions. In addition, the natural atmospheric CO<sub>2</sub> concentrations show an extraordinary correlation with Southern Ocean climate changes, pointing to a significant (direct or indirect) influence of climatic and environmental changes in the Southern Ocean region on atmospheric CO<sub>2</sub> concentrations.

Here, we compile recent ice core and marine sediment records of atmospheric CO<sub>2</sub>, temperature and environmental changes in the Southern Ocean region, as well as carbon cycle model experiments, in order to quantify the effect of potential Southern Ocean processes on atmospheric CO<sub>2</sub> related to these orbital and millennial changes. This shows that physical and biological changes in the SO are able to explain substantial parts of the glacial/interglacial CO<sub>2</sub> change, but that none of the single processes is able to explain this change by itself. In particular, changes in the Southern Ocean related to changes in the surface buoyancy flux, which in return is controlled by the waxing and waning of sea ice may favorably explain the high correlation of CO<sub>2</sub> and Antarctic temperature on orbital and millennial time scales. In contrast, the changes of the position and strength of the westerly wind field were most likely too small to explain the observed changes in atmospheric CO<sub>2</sub> or may even have increased atmospheric CO<sub>2</sub> in the glacial. Also iron fertilization of the marine biota in the Southern Ocean contributes to a glacial drawdown of CO<sub>2</sub> but turns out to be limited by other factors than the total dust input such as bioavailability of iron or macronutrient supply.

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### 1. Introduction

Carbon dioxide represents one of the most important greenhouse gases in the Earth's atmosphere, second only to the atmospheric content of water vapor (IPCC, 2007). Accordingly, significant variations in its atmospheric concentration lead to a respective change in radiative forcing. Due to anthropogenic

emissions of CO<sub>2</sub> by fossil fuel burning and land use changes, CO<sub>2</sub> has increased over the last 150 years from a preindustrial level of approximately 280 ppmv to 385 ppmv in recent years, as documented in both atmospheric (<http://www.cmdl.noaa.gov>) and ice core records (Etheridge et al., 1996; Indermühle et al., 1999; MacFarling Meure et al., 2006). From these data one can confidently state that the recent rate of increase (up to 2 ppmv/year) has not been seen at decadal or longer timescales for at least the last 20,000 years (Joos and Spahni, 2008) and past CO<sub>2</sub> concentrations in ice cores over the last 800,000 years have never come close to current CO<sub>2</sub> levels (Petit et al., 1999; Siegenthaler et al.,

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2005; MacFarling Meure et al., 2006; Lüthi et al., 2008). Resulting from this anthropogenic CO<sub>2</sub> increase is a change in radiative forcing of about 1.7 W/m<sup>2</sup> which is in large parts responsible for the 0.7 °C warming observed over the last century (IPCC, 2007).

Today, the global carbon cycle is being driven out of equilibrium primarily by the burning of fossil fuels and deforestation leading to a continuing increase in atmospheric CO<sub>2</sub> since the start of the industrialization. However, apart from the increasing anthropogenic emissions it is the carbon turnover and uptake capacity of the ocean and terrestrial biosphere that determines the long-term fate of this anthropogenic perturbation and its radiative forcing. In the pre-anthropocene, the natural shift from glacial to warm climate conditions initiated a significant increase in atmospheric CO<sub>2</sub> and in terrestrial biospheric carbon stocks while reducing the carbon storage in the deep ocean. In return, higher natural CO<sub>2</sub> levels lead an additional warming of the atmosphere via their feedback on the radiative balance (Fischer et al., 1999; Caillon et al., 2003). These natural CO<sub>2</sub> changes are well archived in Antarctic ice cores (Neftel et al., 1982; Stauffer et al., 1998; Fischer et al., 1999; Indermühle et al., 1999; Petit et al., 1999; Monnin et al., 2001; Siegenthaler et al., 2005; Ahn and Brook, 2008; Lüthi et al., 2008) and show about 100 ppmv lower CO<sub>2</sub> concentrations during glacial than interglacial times as well as significant millennial CO<sub>2</sub> variations during glacial periods. Accordingly, the global carbon cycle is intimately coupled to long-term climate changes. Besides the necessity of an increased radiative forcing by CO<sub>2</sub> and other greenhouse gases in the atmosphere to explain the glacial/interglacial temperature rise (Köhler et al., 2010) the climate induced changes in the carbon cycle and their consequence for atmospheric CO<sub>2</sub> also represent an important testbed for hypotheses invoking changes in ocean circulation or marine and terrestrial biogenic productivity in the past. For instance any theory invoking changes in ocean circulation would affect the carbon storage in the ocean and, thus, would also have to consider its effect on atmospheric CO<sub>2</sub>.

Despite the importance for climate changes today and in the past, the glacial/interglacial CO<sub>2</sub> changes could not be accounted for in carbon cycle models until recently. In recent model experiments, however, it has become possible to quantitatively explain the 100 ppmv glacial/interglacial shift in atmospheric CO<sub>2</sub> concentrations by combining the effects of different processes acting on the global carbon cycle, such as sea surface temperature (SST) and salinity changes, gas exchange, ocean circulation, marine biological export production, terrestrial carbon storage, and carbonate compensation in the deep ocean (Archer et al., 2000a; Sigman and Boyle, 2000; LeGrand and Alverson, 2001; Paillard and Parrenin, 2004; Köhler et al., 2005; Köhler and Fischer, 2006; Brovkin et al., 2007). Although the total 100 ppmv change can now in principle be accounted for, the contributions of each individual process to the overall change still carry substantial uncertainties that do not allow for a unique solution to the problem. However, all the models agree that changes in the biological or physical carbon fluxes in the Southern Ocean (SO) connected to export production of organic material at the surface and SO circulation changes, together with their carbonate compensation feedback (Broecker and Peng, 1987) in the deep ocean, represent the most important factors influencing atmospheric CO<sub>2</sub> on orbital time scales. Former comparisons of simulated atmospheric CO<sub>2</sub> to changes in high latitude processes suggested that more complex models are in some aspects less sensitive on SO processes than simpler carbon cycle box models (Archer et al., 2000b; Broecker et al., 1999). However, the comparison of completely different types of models is not straightforward (Lane et al., 2006) and a given model maybe high latitude sensitive to certain parameters but not to others. The challenge remains to explain the low glacial CO<sub>2</sub> in a self-consistent 3-dimensional dynamical model setting.

An important role of the SO in terms of the carbon cycle is also suggested by a very high correlation of atmospheric CO<sub>2</sub> and Antarctic temperatures over the last 800,000 years (Wolff et al., 2005; Lüthi et al., 2008), the latter being reliably archived in the stable water isotope record in Antarctic ice cores (Jouzel et al., 2007). Despite this agreement on the role of the SO for atmospheric CO<sub>2</sub> levels, disagreement exists on the importance of ocean circulation vs. export production changes, and about the physical processes that cause ocean circulation changes and affect carbon fluxes in the SO (Sigman and Boyle, 2000; Matsumoto et al., 2002; Köhler et al., 2005; Toggweiler et al., 2006; Watson and Garabato, 2006; Menviel et al., 2008; Parekh et al., 2008; Tschumi et al., 2008; Martínez-García et al., 2009).

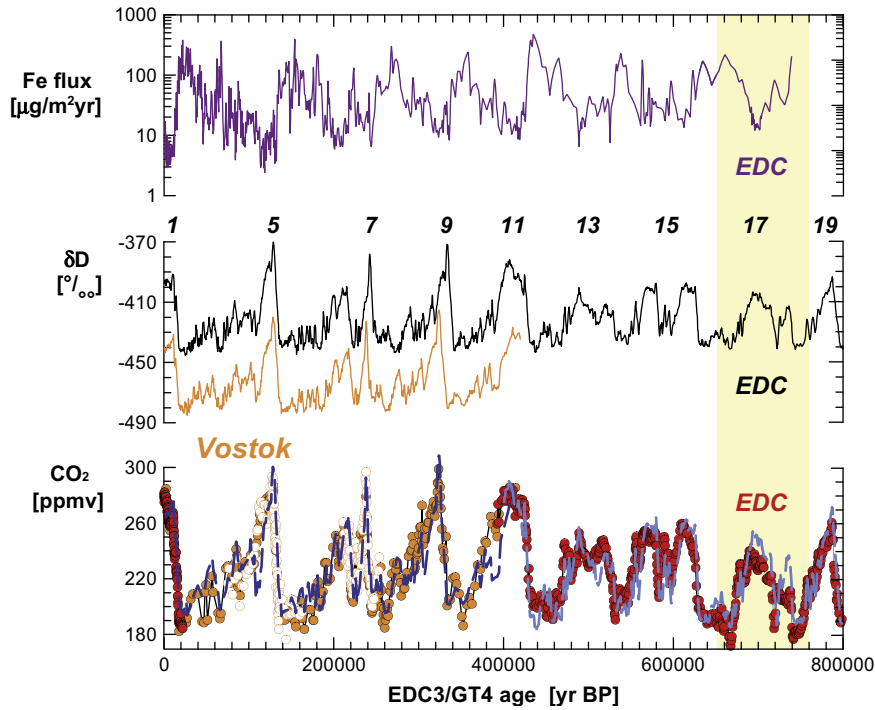
The goal of this paper is to discuss the potential SO processes that can lead to a glacial drawdown of atmospheric CO<sub>2</sub> and to confront these hypotheses with the various marine sediment, ice core and modeling evidence. To this end, we will review the latest ice core observations on glacial/interglacial and millennial CO<sub>2</sub> changes, the theoretical background of SO circulation changes and their role for carbon storage in the deeper ocean, as well as modeling exercises to constrain those changes and their effect on atmospheric CO<sub>2</sub>. We intentionally do not discuss carbon cycle processes outside the SO region, which are either rather well constrained (such as global SST and salinity) or beyond the scope of this paper (such as the terrestrial biosphere or carbonate compensation). However, it has to be kept in mind, that although SO processes dominate the atmospheric CO<sub>2</sub> changes in the past, the full CO<sub>2</sub> story can only be told when processes outside the SO are also taken into account.

## 2. Ice core data of atmospheric CO<sub>2</sub> changes

Bubble enclosures in polar ice cores represent the only direct atmospheric archive that allows for reconstruction of the atmospheric composition over hundred thousands of years. In the case of CO<sub>2</sub>, Antarctic ice cores represent the only unaltered archive of past atmospheric CO<sub>2</sub> concentrations, while in Greenland ice cores high carbonate and low pH in combination with higher concentrations of organic impurities in the ice leads to *in situ* production of CO<sub>2</sub> (Anklin et al., 1995; Smith et al., 1997). In Antarctic ice cores, no such artifacts have been observed so far as illustrated by the low scatter of high-resolution samples in bubble ice (Indermühle et al., 1999; Stauffer and Tschumi, 2000; Monnin et al., 2001; Lüthi et al., 2008) that is below the analytical uncertainty, by the consistency of Antarctic ice core records from different locations, and by the very good agreement of ice core data with atmospheric measurements in the overlapping interval between 1958 and 1975 (Etheridge et al., 1996; MacFarling Meure et al., 2006).

However, due to the slow bubble enclosure process, the age of the gas enclosed in air bubbles at a particular depth has a certain distribution, leading to an inherent low-pass filtering of the dynamics in atmospheric CO<sub>2</sub> in the ice core archive (Schwander and Stauffer, 1984). Because of this process, ice cores covering the last glacial cycle and beyond (which are necessarily located in low accumulation regions) only provide CO<sub>2</sub> records with an effective resolution of a few centuries (Spahni et al., 2003). The lowest resolution is achieved during cold climate conditions, when snow accumulation is reduced by about 50% compared to present conditions (EPICA community members, 2004; EPICA community members, 2006).

Fig. 1 shows a compilation of the CO<sub>2</sub> concentrations from the EPICA (European Project for Ice Coring in Antarctica) Dome C (EDC) and Vostok ice cores, which as a whole cover the last 800,000 years (Fischer et al., 1999; Petit et al., 1999; Monnin et al., 2001; Siegenthaler et al., 2005; Lüthi et al., 2008). Also shown are



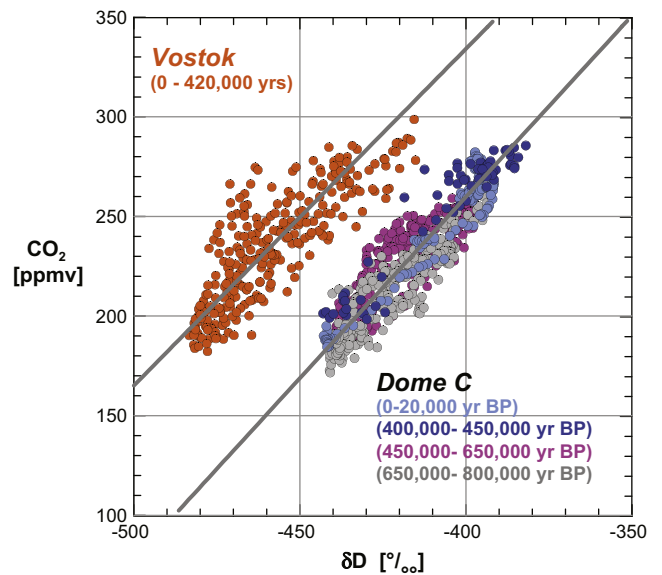
**Fig. 1.** CO<sub>2</sub> concentrations measured on the EDC (red dots (Monnin et al., 2001; Siegenthaler et al., 2005; Lüthi et al., 2008)) and Vostok ice cores (filled orange dots (Petit et al., 1999), open orange circles (Fischer et al., 1999)). Bold dashed blue lines represent a CO<sub>2</sub> estimate derived from the linear regressions in Fig. 2. Also plotted are continuous stable water isotope records (δD, black and orange lines) derived on the same cores (Petit et al., 1999; EPICA community members, 2004; Jouzel et al., 2007) in 500 yr resolution together with spotwise iron fluxes (purple line) for EDC interpolated to 500 yr resolution (Martínez-García et al., 2009). Ages are given on the EDC3 and GT4 age scale for the EDC and the Vostok ice cores, respectively. Bold numbers indicate interglacial MIS, the yellow bar the time interval from MIS 16 to 18, when CO<sub>2</sub> is lower than expected from a linear regression.

temperature proxy records (δD of water) in 500 yr resolution (i.e. approximately the temporal resolution that can be achieved in glacial CO<sub>2</sub> records at these low accumulation sites) measured on the same ice cores (Petit et al., 1999; EPICA community members, 2004; Jouzel et al., 2007). Note that the Vostok and EDC ice core records are plotted on individual time scales, explaining the significant differences in the timing of Marine Isotope Stages (MIS) 7 and 9 in Fig. 1.

The CO<sub>2</sub> concentrations vary between 170–190 ppmv during glacials and 250–300 ppmv during interglacials, with generally lower interglacial concentrations prior to 450,000 years before present (BP, where present is defined as 1950). In this time period, interglacial temperatures were also significantly lower in Antarctica than during the last four glacial cycles. Although the amplitude of glacial/interglacial temperature changes in East Antarctic is higher than for the SO sea surface temperatures (Gersonde et al., 2005), the temporal changes in Antarctic and SO temperature (Martínez-García et al., 2009) and sea ice coverage (Wolff et al., 2006) are strongly linked. Accordingly, we assume that the temporal evolution of the precise and high-resolution temperature changes reconstructed from the EPICA ice cores are at first order representative for the whole circum-Antarctic region (Watanabe et al., 2003; EPICA community members, 2006; Martínez-García et al., 2009).

A linear regression (Fig. 2) of CO<sub>2</sub> and δD over the entire data sets explains 71% and 84% of the variance in the CO<sub>2</sub> data for the Vostok and EDC ice cores, respectively. Note that this correlation is only representative for the time scales of CO<sub>2</sub> variations that can be resolved in ice cores from the central East Antarctic ice sheet, i.e. on the order of a few centuries. The somewhat larger scatter of the Vostok data may be in part due to the fact that some of the measured depth intervals come from the clathrate formation zone between approximately 700 and 1300 m depth. In that depth

interval, the analytical uncertainty is higher because of different extraction efficiencies of air from bubbles vs. clathrates, in combination with a fractionation of the CO<sub>2</sub> concentration in clathrates relative to that in air bubbles (Stauffer and Tschumi, 2000). A high



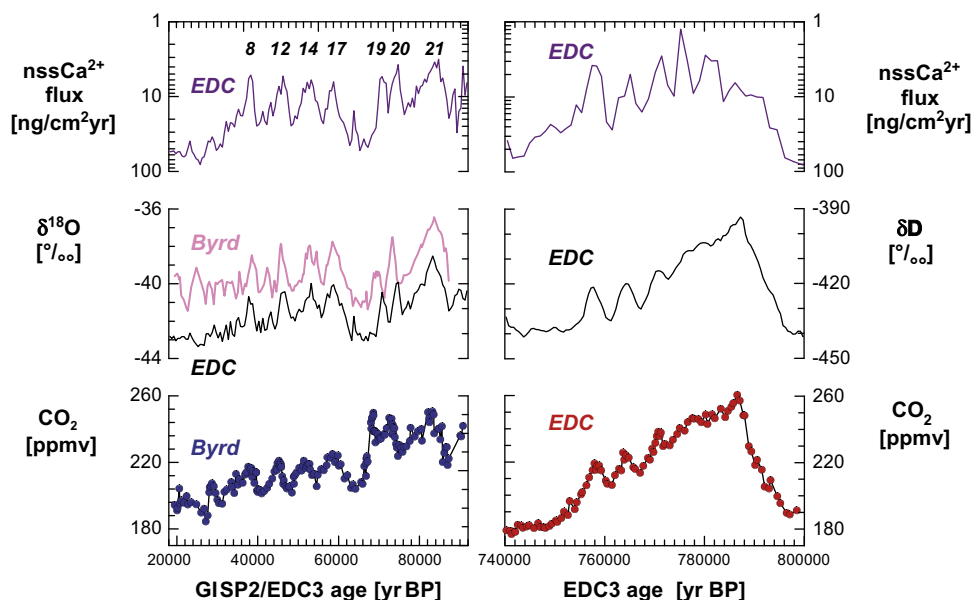
**Fig. 2.** CO<sub>2</sub> concentrations vs. δD as shown in Fig. 1. Respective δD values for each CO<sub>2</sub> value were calculated by linear age interpolation of the δD values in 500 yr resolution to ensure a temporal resolution comparable to the one for glacial CO<sub>2</sub> data. Straight lines represent two-sided linear regressions over the entire data sets. Note, that EDC CO<sub>2</sub> concentrations prior to 450,000 yr BP do not span the whole CO<sub>2</sub> range but show a similar linear relationship with temperature. Only CO<sub>2</sub> data during MIS 16–18 are systematically reduced by about 10 ppmv.

correlation between CO<sub>2</sub> and δD ( $r^2 = 0.64$ ) has previously been observed in the Vostok ice core over the last glacial cycle (Cuffey and Vimeux, 2001). Correcting the δD record for changes in the isotopic composition and temperature of the water vapor source using the deuterium excess, Cuffey and Vimeux (2001) were able to show that this correction improves the correlation even further and that such corrected Antarctic temperatures can account for more than 84% of the CO<sub>2</sub> variance. Note, that these very high correlation values are representative for unlagged correlation, ignoring a potential phase shift between CO<sub>2</sub> and temperature, which may increase the correlation even further. Thus, taking the Antarctic isotope temperature records as a surrogate for the temporal evolution of the entire SO ocean region more than 80% of the multimillennial variability in CO<sub>2</sub> concentrations could be attributed to circum-Antarctic temperature changes, in case some physical link between the two can be established. Fig. 1 also shows time intervals, where the deviations from this linear relationship with Antarctic temperature are the largest, i.e. during interglacials and the glacial inceptions, where processes outside the SO (such as changes in the terrestrial carbon storage) may offset the balance between the atmosphere and the SO. In addition, CO<sub>2</sub> concentrations between MIS 16 and 18 are approximately 10 ppmv lower than expected from the linear regression.

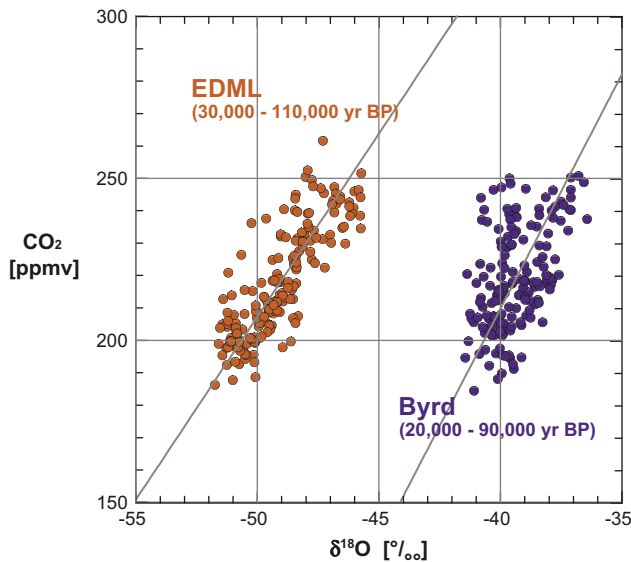
A strong connection between CO<sub>2</sub> data and Antarctic temperature in centennial resolution also holds for millennial CO<sub>2</sub> variations during the last ice age. Recently, Ahn and Brook (2008) published a high-resolution CO<sub>2</sub> record from the Byrd ice core over the last glacial period as shown in Fig. 3, which is also in very good agreement with CO<sub>2</sub> data from Taylor Dome over the time interval 25,000–65,000 yr BP (Indermühle et al., 2000) as well as unpublished data from the EPICA ice core from Dronning Maud Land (EDML) (Lüthi, unpublished). Since the accumulation rate at Byrd is about 3–4 times higher than at EDC, this ice core allows for an effective resolution of better than 200 years, even for glacial conditions. The main feature of this CO<sub>2</sub> record covering the last glacial are concentrations elevated by about 20 ppmv in parallel to

the strongest Antarctic Isotope Maxima (AIM) (EPICA community members, 2006). These AIM events are related to Dansgaard Oeschger events 8, 12, 14, 17, 19, 20 and 21 in the northern hemisphere (North Greenland Ice Core Project members, 2004; Jouzel et al., 2007) via the bipolar seesaw (Stocker and Johnsen, 2003; EPICA community members, 2006). Despite the obvious covariance in Fig. 3, the correlation between CO<sub>2</sub> and δ<sup>18</sup>O measured on the Byrd ice core is not very strong ( $r^2 = 0.25$  for the entire data set from 20 to 90,000 yr BP and  $r^2 = 0.2$  for the time interval 30–90,000 yr BP) although significantly different from zero (Fig. 4). A comparable CO<sub>2</sub> record from the EDML ice core (Lüthi, unpublished data) exhibits essentially the same CO<sub>2</sub> variations as in the Byrd record but yields a much higher correlation (Fig. 4) with EDML δ<sup>18</sup>O values in 300 yr resolution ( $r^2 = 0.69$  for the entire data set from 30 to 110,000 yr BP and  $r^2 = 0.63$  for the time interval shared with the Byrd record from 30 to 90,000 yr BP). This difference in the correlation coefficients could be explained in two ways: i) the glacial Byrd δ<sup>18</sup>O data show a higher variability compared to the EPICA records, which may be in part related to local temperature changes potentially connected to altitude changes at Byrd, which is located on the West Antarctic Ice Sheet, while the EPICA ice cores and Vostok are located on the more stable East Antarctic Ice Sheet; ii) an insufficient age synchronization between the gas and ice record at Byrd may deteriorate the correlation. Interestingly, a very high correlation ( $r^2 = 0.93$ ) on a millennial time scale is also clearly documented for the oldest glaciation (750,000–778,000 yr BP) in the EDC record as shown in Fig. 3.

In summary, we find that a large part of the variance is shared between CO<sub>2</sub> concentrations and Antarctic temperatures. This fact calls for processes that connect atmospheric CO<sub>2</sub> to climate changes occurring in the SO region. In case such a link can be convincingly established, the high correlation between CO<sub>2</sub> and δD implies that more than 80% of the glacial/interglacial and more than 60% of the millennial CO<sub>2</sub> variations during the last glacial could be ascribed to such SO processes.



**Fig. 3.** Millennial CO<sub>2</sub> variations over the last glacial (left) and the glaciation from MIS19 to MIS 18 (right) measured on the Byrd (blue dots) and the EDC (red dots) ice cores. Also given are the isotope temperature records of both ice cores (Byrd δ<sup>18</sup>O (left axis, pink line in 200 yr resolution (Ahn and Brook, 2008); EDC δD (right axis, black line in 500 yr resolution (EPICA community members, 2004; Jouzel et al., 2007)) and the EDC non-sea-salt (nss) Ca<sup>2+</sup> (purple line) as a mineral dust indicator. Ages are given on the Greenland Ice Sheet Project (GISP) 2 age scale and the EDC3 age scale for Byrd and EDC, respectively. Bold numbers indicate Antarctic Isotope Maxima and the respective Dansgaard Oeschger events in Greenland (North Greenland Ice Core Project members, 2004; EPICA community members, 2006; Jouzel et al., 2007).



**Fig. 4.** CO<sub>2</sub> concentrations vs.  $\delta^{18}\text{O}$  isotope temperatures for the Byrd ice core (purple dots) as shown in Fig. 3 as well as EDML CO<sub>2</sub> concentrations (Lüthi, unpublished data) vs. EDML  $\delta^{18}\text{O}$  after correction for sea level and upstream altitude effects (EPICA community members, 2006) (orange dots). Respective isotope values for each CO<sub>2</sub> value were calculated by linear age interpolation based on the  $\delta^{18}\text{O}$  values in 200 yr resolution for Byrd and  $\delta^{18}\text{O}$  values in 300 yr resolution for EDML to ensure a temporal resolution comparable to the CO<sub>2</sub> records. The straight lines represent two-sided linear regressions over the entire data sets.

### 3. Southern Ocean carbon cycle processes

Current understanding essentially suggests that in addition to the effect of the higher solubility of CO<sub>2</sub> in SO surface waters during colder climate periods, which accounts for about 15 ppmv lower glacial atmospheric CO<sub>2</sub> (Köhler and Fischer, 2006), two classes of SO processes could account for such a correlation: (i) changes in marine biological productivity in the SO, and (ii) changes in SO circulation (advection or mixing), that vary the exchange between carbon-enriched deep waters and the surface and change the degree of nutrient utilization at the surface. In general, photosynthetic production of organic material in the surface water and the subsequent export of that organic matter to the deep ocean depletes atmospheric CO<sub>2</sub> and at the same time enriches the dissolved inorganic carbon content of the deep ocean by respiration. The ocean circulation has the opposite effect on atmospheric CO<sub>2</sub>, bringing this phytoplankton-mediated carbon back to the surface. In the following, we will briefly review the background of those two classes of processes and discuss their influence on atmospheric CO<sub>2</sub> based on observations and modeling evidence.

#### 3.1. Marine biological productivity changes

In contrast to most other ocean basins, the SO is characterized by high macronutrient (nitrate and phosphate) concentrations in surface waters and, yet, a limited biological productivity, as reflected by a relatively low chlorophyll content. This implies that the phytoplankton in the SO is not able to quantitatively use the available nutrients, probably related to a limitation of micronutrients such as iron. This leads to a large fraction of the available nutrients being unutilized before they are exported again as so-called “preformed” nutrients to deeper ocean layers (Marinov et al., 2008). Accordingly, it has been recognized that a relaxation or complete removal of the iron limitation by enhanced iron

deposition connected to an increase in aeolian dust could lead to increased carbon fixation in the SO biosphere (if ocean circulation remained unchanged). Connected to an increased export of this organic matter to the deep ocean, this could lead to a draw down of atmospheric CO<sub>2</sub> (Martin, 1990). This iron fertilization hypothesis was directly tested for recent conditions by ship-based iron fertilization experiments in the SO (Boyd et al., 2000; de Baar et al., 2005). These experiments, showed a clear increase in primary productivity but very little evidence of increased carbon export after artificial iron input into the surface waters, questioning the effectiveness of the iron fertilization in drawing down atmospheric CO<sub>2</sub>.

Elevated dust fluxes are unambiguously recorded in the EDC ice core over the last eight glacials (Fig. 1) and the flux of soluble iron in the ice cores increased by a factor of 20 during glacial times (Gaspari et al., 2006; Wolff et al., 2006; Lambert et al., 2008; Martínez-García et al., 2009). From this it can be deduced that the aeolian iron deposition into the SO surface waters was significantly higher during glacial times as well. In fact, recently derived Th-normalized iron fluxes in a marine sediment record from the Atlantic sector of the SO show dust fluxes higher by a factor of 4–5 in the glacial compared to the Holocene (Martínez-García et al., 2009).

Besides these orbital variations in iron deposition, what observational evidence for a possibly enhanced CO<sub>2</sub> uptake in the SO by iron fertilization exists for the last glacial? In absence of a continuous Fe record over MIS 3, we use the ice core dust derived Ca<sup>2+</sup> records as a proxy for iron deposition. The ice core dust records show clear dust variations in the last glacial (Röthlisberger et al., 2004; Fischer et al., 2007) in parallel to the millennial CO<sub>2</sub> variations (Fig. 3). Note, however, that the long-term trend in CO<sub>2</sub> concentrations from AIM 17 to AIM 8 is not seen in the dust flux, while it is clearly present in Antarctic temperatures. Again, the steep decrease in CO<sub>2</sub> around 70,000 yr BP has no equivalent in the dust or the  $\delta^{18}\text{O}$  record, suggesting that additional processes must be responsible for this atmospheric CO<sub>2</sub> change. During the last glacial/interglacial transition the majority of the CO<sub>2</sub> increase occurred only after iron fluxes had already reached interglacial levels (Wolff et al., 2006) and – based on the timing of the dust decline – a maximum of 20–30 ppmv of the CO<sub>2</sub> rise during the last transition can be attributed to the increasing iron limitation. Similarly, dust fluxes decreased to nearly interglacial levels during the warm events in MIS3, however, this decrease was accompanied by an increase in atmospheric CO<sub>2</sub> of only 20 ppmv (Röthlisberger et al., 2004). Thus, additional factors are required to explain the full glacial/interglacial increase of atmospheric CO<sub>2</sub> of 100 ppmv (note that the glacial/interglacial CO<sub>2</sub> flux from the ocean was even higher than required to explain a measured 100 ppmv increase in the atmospheric carbon pool only. For instance the concurrent carbon uptake by the terrestrial biosphere carbon storage during the last glacial termination required an additional flux out of the ocean equivalent to a 30 ppmv change in atmospheric CO<sub>2</sub>). The EPICA ice core records also provide more direct evidence of changes both in biological nitrogen and sulfur production, based on the NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> fluxes derived from continuous chemical ice core analyses. These records show glacial/interglacial variations of only 20–30%, i.e. within the uncertainty of the accumulation rate estimate used to calculate the deposition fluxes (Kaufmann et al., 2010; Wolff et al., 2006). In any case, they do not support a strong increase in biological productivity in the SO during glacial times.

Marine geological evidence for an increased export production during the glacial is controversial. Observations based on the joint interpretation of various productivity indicators in the SO point to a reduced biological export production south of the recent Polar Front (PF), while they indicate somewhat elevated export rates north of it (Kohfeld et al., 2005; Martínez-García et al., 2009).

In contrast, the latest inferences on the productivity in the Atlantic sector of the SO based on small diatom resting spores, which contribute little to the total sedimentation rate but are less affected by dissolution, also point to increased diatom productivity south of the PF (Abelmann et al., 2006). Finally, an increase in  $\delta^{15}\text{N}$  values in SO sediments during the glacial points to an increased utilization of nitrate in the surface waters at that time (Francois et al., 1997). This could be due to enhanced export production caused by iron fertilization (if ocean circulation remained unchanged) or to reduced upwelling of nutrients to the surface and, thus, a higher utilization of a reduced macronutrient concentration in the surface waters as suggested by Francois et al. (1997). In fact, clear indications of changes in upwelling of deep waters have been recently found in SO opal records (Anderson et al., 2009). Those show a twofold increase in opal flux to the ocean floor during MIS 3 and 4 in parallel to the  $\text{CO}_2$  increases in the Byrd ice core (Ahn and Brook, 2008) and a most pronounced sixfold increase during the last glacial termination, which has been attributed to increased upwelling of Si enriched deep water to the SO surface stimulating opal production (Anderson et al., 2009). Despite these intervals being times of increased opal production at the surface they are times of increasing atmospheric  $\text{CO}_2$ . Obviously, the degassing of  $\text{CO}_2$  from the old carbon-enriched upwelling water was able to increase atmospheric  $\text{CO}_2$  concentrations, putting a strong limit on the effectivity of increased biological (opal) production in the SO on reducing atmospheric  $\text{CO}_2$ .

Models of the marine carbon cycle may further elucidate how strong an iron fertilization effect might be. The applicability of observations from iron fertilization experiments in models for glacial conditions, however, is hampered because of unsolved issues regarding the percentage of mineral dust derived iron that is in a form available for biological uptake. Carbon cycle models assuming that available iron is proportional to the soluble iron concentration (which again is proportional to the aeolian iron deposition) predict a drawdown of glacial atmospheric  $\text{CO}_2$  of 10–40 ppmv relative to preindustrial levels, depending on model configuration (Archer et al., 2000a; Watson et al., 2000; Bopp et al., 2003; Ridgwell, 2003; Köhler et al., 2005; Brovkin et al., 2007). However, the bioavailability of soluble iron is not only dependent

on the iron input but also on the concentration of iron-binding organic ligands that ensure that the iron remains in its bioavailable form (Parekh et al., 2008). When taking reasonable ligand concentrations in the SO into account in an ocean carbon cycle model, the iron fertilization effect of glacial dust is strongly reduced and accounts for only a 10 ppmv change in atmospheric  $\text{CO}_2$  concentrations when the dust flux is increased by a factor of 100 and only by 5–8 ppmv, when realistic dust flux changes are prescribed for AIM 8, 12, 14 and 17 (Parekh et al., 2008).

In summary, the occurrence of a dust-induced iron fertilization of SO primary production seems very likely, however, its effect on export production and, following, on atmospheric  $\text{CO}_2$  changes is limited. Based on state-of-the-art model exercises, this effect can likely explain about 10 ppmv (and maximum 40 ppmv) of the glacial/interglacial change in atmospheric  $\text{CO}_2$ . For the millennial  $\text{CO}_2$  variations during the glacial, a higher relative portion of the 20 ppmv changes may be explained by iron fertilization but again the effect is most likely limited to less than 10 ppmv. Accordingly, other processes connecting atmospheric  $\text{CO}_2$  and SO temperature changes are required to explain the strong correlation described above.

### 3.2. Southern Ocean circulation changes

#### Theoretical background

The carbon fluxes in the SO reflect a fine balance between carbon-enriched deep waters and surface waters subject to air/sea exchange of  $\text{CO}_2$ . Part of the deep water in the SO has initially been subducted in the North Atlantic and transported to the SO as North Atlantic Deep Water (NADW) spreading southward. The other part is derived from localized Antarctic Bottom Water (AABW) formation close to the Antarctic continent (Fig. 5), which represents globally the second most important deep water source. In addition, Antarctic Intermediate Water (AAIW) formation subducts water to intermediate depths north of the Antarctic PF after air/sea exchange of  $\text{CO}_2$ . Finally, the upwelling of Circumpolar Deep Water (CDW) and modified NADW at the Antarctic divergence (Rintoul et al., 2001) closes the cycle, and brings carbon-enriched deep waters back to the surface. In addition to these advective transport

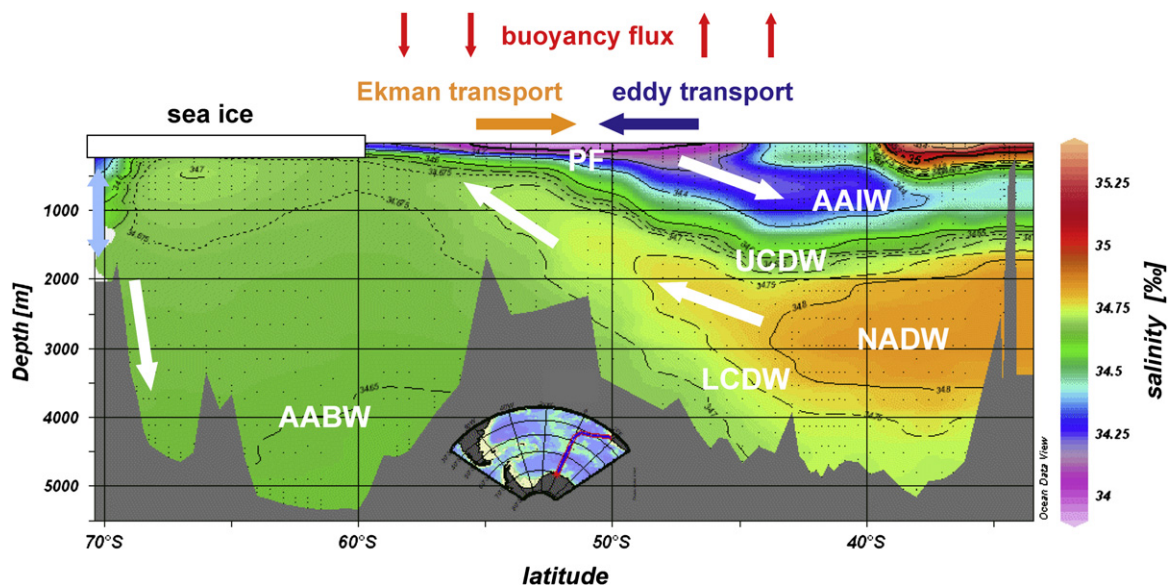


Fig. 5. Salinity cross section through the Atlantic sector of the Southern Ocean together with a schematic view of the Southern Ocean water masses and the SOMOC. Abbreviations indicate the location of the PF (Polar Front), AABW (Antarctic Bottom Water), LCDW (Lower Circumpolar Deep Water), NADW (North Atlantic Deep Water), UCDW (Upper Circumpolar Deep Water), AAIW (Antarctic Intermediate Water). Figure adapted from Ocean Data View.

processes, convective mixing of deeper and surface water also contributes to the ventilation of the deep SO. For instance, AABW formation today mainly occurs in cold shallow shelf waters (most importantly the Weddell and Ross Seas) where heat loss and brine rejection during sea ice formation are strong enough to destabilize the water column overlying the continental shelf and to cause convection. Subsequently, AABW export at the shelf edge provides deep water spreading into other ocean basins below NADW or recirculating back to the SO surface.

Very important for the net upwelling of deep waters along the Antarctic Circumpolar Current (ACC) is the Southern Ocean Meridional Overturning Circulation (furtheron referred to as SOMOC), established by the northward transport of water at the SO surface that requires upward movement of water from below. These deep waters are enriched in carbon due to the remineralization of organic carbon and provide CO<sub>2</sub> to the atmosphere when they come back to the surface (Watson and Garabato, 2006). The net northward transport of water at the surface is partly a consequence of the meridional Ekman transport induced by the strong westerly winds prevailing in the SO (Fig. 6a). Accordingly, a change in zonal wind speed is expected to also change the SOMOC and, thus, the carbon flux to the surface with higher zonal wind speeds increasing atmospheric CO<sub>2</sub> (Toggweiler et al., 2006). In addition, Toggweiler et al. (2006) suggested that a glacial northward shift of the westerly wind belt could reduce the SOMOC and, thus, CO<sub>2</sub> in the atmosphere.

However, Ekman transport is only part of the story. As demonstrated by Karsten and Marshall (2002) and later taken up with respect to atmospheric CO<sub>2</sub> by Watson and Garabato (2006), the net meridional transport of water (referred to as “residual circulation” by Karsten and Marshall (2002)) is the sum of the mean Ekman transport  $\Psi_{\text{Ekman}}$  and opposing mean eddy transport  $\Psi_{\text{eddy}}$  over the ACC (see also Fig. 5). Using oceanographic data, Karsten and Marshall (2002) were able to quantify these two components (Fig. 7), showing that the southward eddy transport partly offsets the northward Ekman transport south of the PF and even overcompensates the Ekman component north of it. Karsten and Marshall (2002) conclude that the residual northward and upward flow averaged over the ACC south of the PF is about 13 Sv, while the

Ekman transport alone amounts to 21 Sv. On the northern side of the polar front, Karsten and Marshall (2002) derive a southward residual flux of about 10 Sv. In fact, it is this convergence of cold waters from the south and warmer waters from the north that forms the PF and leads to subduction of AAIW. Accordingly, a change in the eddy transport over time could also lead to a change in the SOMOC and, thus, atmospheric CO<sub>2</sub> (Watson and Garabato, 2006).

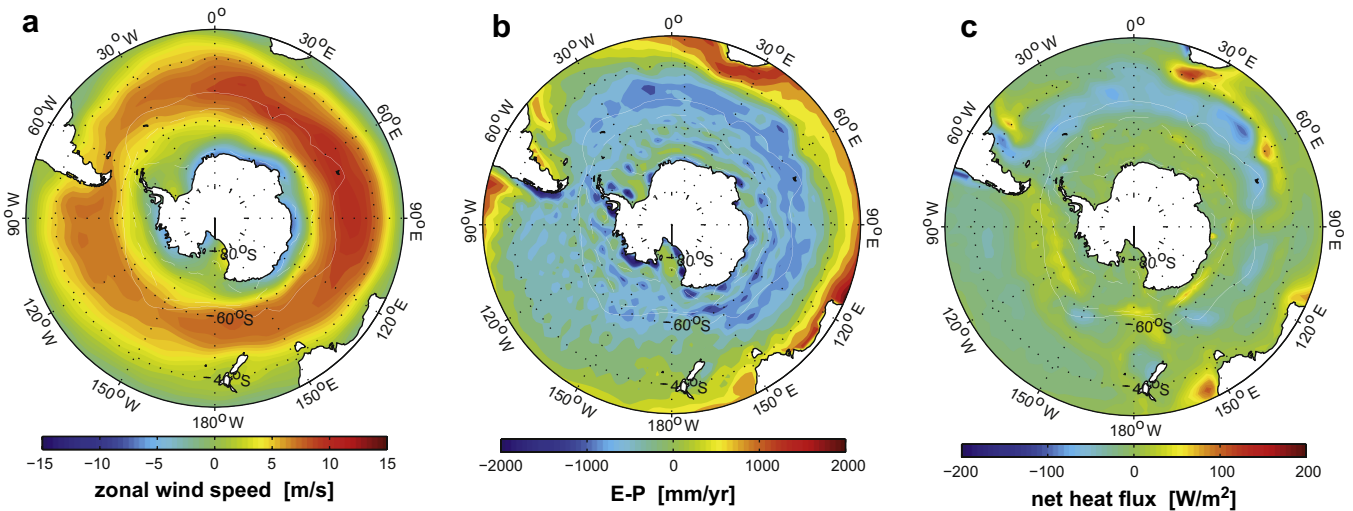
Using the buoyancy balance at the surface, Karsten and Marshall (2002) showed that the residual circulation  $\Psi_{\text{res}}$  at the base of the mixed layer is given by:

$$\Psi_{\text{res}}(z = -h_m) \frac{\partial b_m}{\partial y} = B_s - \kappa \frac{\partial b_m}{\partial z}(z = -h_m) \quad (1)$$

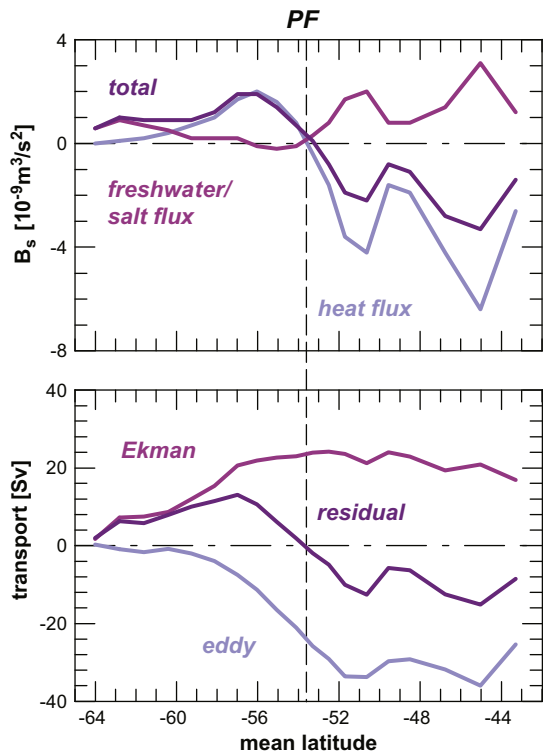
where  $h_m$  is the mixed layer depth,  $b_m$  the mixed layer buoyancy, and  $\kappa$  the vertical eddy diffusivity that removes buoyancy from the mixed layer downwards.  $B_s$  is the surface buoyancy flux

$$B_s = \frac{g}{\rho_0} \left( \frac{\alpha}{c_w} Q_{\text{net}} + \rho_0 \beta S(E - P) \right) \quad (2)$$

where  $\alpha$  and  $\beta$  are the thermal and haline expansion/contraction coefficients of sea water,  $\rho_0$  the reference density,  $c_w$  the specific heat capacity of sea water, and  $S$  the salinity. As becomes clear from equation (2), the buoyancy flux at the surface is determined by the net heat flux  $Q_{\text{net}}$  (Fig. 6b) and the freshwater flux  $E - P$  (Fig. 6c) at the surface (where the latter may also be influenced by the lateral sea ice transport in the SO). The vertical downward diffusion of buoyancy is generally small compared to the surface buoyancy flux in the SO (Karsten and Marshall, 2002; Watson and Garabato, 2006). Thus, taking into account that for modern conditions the net heat flux averaged over the ACC dominates the buoyancy flux at the surface, equation (1) shows that for a given mixed layer meridional buoyancy gradient  $\partial b_m / \partial y$ , the residual circulation is controlled primarily by the heat gain of the waters when travelling northward. Accordingly, a decrease in the surface buoyancy flux in the past may have led to a reduction in the SOMOC and atmospheric CO<sub>2</sub>, independent of zonal wind speed changes (Watson and Garabato, 2006) if  $\partial b_m / \partial y$  remained constant. Vice versa, an increase in the



**Fig. 6.** a) Zonal wind speed, b) evaporation minus precipitation (E-P) with evaporation estimated from the latent heat flux, c) surface net heat flux calculated from the sum of net shortwave and net longwave radiation, sensible heat flux and latent heat flux (net downward heat fluxes taken as negative) in the Southern Ocean region, derived from NCEP/NCAR reanalysis data (Kalnay et al., 1996). Note that the reanalysis data are model dependent. Furthermore, b) represents only the vertical freshwater exchange with the atmosphere and no salt/freshwater fluxes due to sea ice formation and melting are included. Accordingly, b) and c) are given only to provide an overall picture of the zonal and meridional structure but cannot be directly compared to the buoyancy fluxes in Fig. 7. Dashed white lines represent the current summer and winter sea ice edge, while the solid white line indicates the average position of the modern PF. In the glacial, the position of the winter sea ice edge is close to the position of the modern PF.



**Fig. 7.** Bottom: Oceanographic reconstruction (Karsten and Marshall, 2002) of the residual circulation (northward circulation positive) in the Southern Ocean (purple line) together with its components derived from Ekman (pink line) and eddy (blue line) transport. Top: Total surface buoyancy flux  $B_s$  (buoyancy fluxes increasing the mixed layer buoyancy (directed downward into the ocean) are plotted positive) derived from the residual circulation (purple line) and its components derived from the net heat flux (blue line) and the salt/freshwater flux (pink line). Fluxes were derived along lines of equal stream function of the ACC, which vary in latitude from one ocean basin to the other. Accordingly the two graphs represent a zonally averaged cross section through the ACC. Figures adapted from Karsten and Marshall (2002).

mixed layer meridional buoyancy gradient in equation (1) could also decrease the SOMOC if  $B_s$  was fixed.

#### Changes in the Southern Ocean westerlies

We first discuss the possibility that only the Ekman transport has changed in the glacial due to wind speed changes or the location of the westerly wind belt in the SO. Direct observational evidence of wind speed (or wind stress on the ACC) changes is sparse. Using the differential change in the flux of glacial dust derived from Patagonian dust sources (Delmonte et al., 2004) at the two EPICA ice core sites, Fischer et al. (2007) were able to show that there was little change in the transport time of dust from Patagonia to the East Antarctic Ice Sheet. This also suggests that there was little change in zonal wind speed. If at all, zonal wind speed was slightly enhanced during colder periods. This implies that the Ekman transport and, thus, upwelling and  $\text{CO}_2$  fluxes out of the surface ocean remained largely unchanged or slightly increased during cold periods. Recent comparisons of coupled general circulation models (GCM) for glacial conditions (Menviel et al., 2008; Rojas et al., 2008) also show very little change in the strength of the zonal wind stress on the SO (with minor changes in opposite directions in different models) in line with the ice core evidence. In addition, coupled ocean carbon cycle model experiments (Menviel et al., 2008; Tschumi et al., 2008) fail to explain significant  $\text{CO}_2$  changes by reasonable variations in zonal wind speed. For example, in the model experiment by Tschumi et al. (2008), zonal wind speeds had to be reduced by 75% to explain a 50 ppmv drawdown

in atmospheric  $\text{CO}_2$ ; such a reduction in wind speed is clearly not supported by any observational or modeling evidence. Similarly, in the model used by Toggweiler et al. (2006) an increase in wind speed by 50% is required to increase  $\text{CO}_2$  by 35 ppmv. Accordingly, any significant change in the SOMOC due to a change in the strength of the westerlies appears unlikely.

Furthermore, a northward shift of the westerly wind belt as hypothesized by Toggweiler et al. (2006) is also unlikely to be responsible for a significant  $\text{CO}_2$  drawdown. Again, the intercomparison of GCM runs for glacial conditions showed no clear shift in the location of the westerly wind belt (Menviel et al., 2008; Rojas et al., 2008) and only very small latitudinal movements of the wind belt in opposite directions for different models. Artificially moving the westerly wind belt in an ocean carbon cycle model northward by up to  $10^\circ$  latitude changed the atmospheric  $\text{CO}_2$  concentration by only about 10 ppmv. Moreover, it increased the atmospheric  $\text{CO}_2$  concentration (Tschumi et al., 2008) in contrast to the hypothesis by Toggweiler et al. (2006) which stipulated a decrease. The reason for this is primarily an enlargement of the upwelling region in the model when the wind belt is moved further to the north.

#### Changes in buoyancy forcing

Thus, the SOMOC was unlikely to have been substantially changed in the past due to changes in the northward Ekman transport, however, the combined effect of Ekman and eddy transport, which is controlled by buoyancy forcing, could have potentially changed the SOMOC. Northward expansion of the sea ice extent represents an efficient way to change the surface buoyancy flux. For modern conditions, summer sea ice is very limited and winter sea ice is still far away from the PF, where significant heat uptake occurs. During the glacial winter, sea ice encroached as far as the modern PF in all regions around Antarctica, as reflected in diatom records from the SO (Gersonde et al., 2005). Summer sea ice was also largely expanded in the Weddell Sea region as far as the modern winter sea ice edge but little summer sea ice change occurred between  $90$  and  $120^\circ$  W (Gersonde et al., 2005). For all other regions, the current marine geological data base does not allow a reliable reconstruction of the summer sea ice coverage. However latest ice core (Wolff et al., 2006; Fischer et al., 2007; Röthlisberger et al., 2008) and atmospheric aerosol studies from central and coastal Antarctica (Wagenbach et al., 1998; Rankin et al., 2000; Rankin and Wolff, 2003; Hara et al., 2004; Yang et al., 2008) indicate that sea salt aerosol in Antarctica is at least partly derived from the sea ice surface and that sea salt records in ice cores can provide a continuous proxy for regional sea ice coverage in the SO. The ice core studies show that for the major part of the climate records the sea salt aerosol flux, hence sea ice coverage, is linearly related to Antarctic temperatures (Wolff et al., 2006; Fischer et al., 2007; Röthlisberger et al., 2008). Only for very cold glacial conditions the sea ice proxy becomes increasingly insensitive due to the long transport time of sea salt aerosol from the northernmost sea ice regions and its strong depletion during transport. Here we assume that Antarctic temperatures are to first order also representative for the northward expansion of sea ice in the SO, showing that Antarctic temperature and, hence, sea ice changed largely in parallel to atmospheric  $\text{CO}_2$  (Figs. 1–4). Based on this evidence, the waxing and waning of sea ice coverage could have directly modulated the annual net heat gain of the SO surface waters. In return, the reduced buoyancy gain would have changed the strength of the SOMOC controlling the upwelling of carbon-enriched deep water.

This physical link between SO temperature, sea ice extent and the SOMOC may explain the high correlation between  $\text{CO}_2$  and Antarctic temperature both on orbital as well as millennial time scales. The natural northern border of the northward expansion of sea ice is the PF, where SST increases sharply northward and does



not allow for the presence of sea ice. When this northern sea ice border was reached during the Last Glacial Maximum (LGM), the SOMOC is expected to have ceased completely and the maximum drawdown effect on atmospheric CO<sub>2</sub> levels would have been reached. Using a multibox model approach to quantify the effect of a reduction in the SOMOC during the LGM, a drawdown of CO<sub>2</sub> by about 35 ppmv could be explained without iron fertilization (Watson and Garabato, 2006). This effect is subsequently amplified by carbonate compensation (Broecker and Peng, 1987).

A fly in the ointment of this buoyancy forcing hypothesis is the unknown location of the PF during glacial times. Marine geological evidence based on diatom species (Gersonde et al., 2003) points to a general northward movement of SST isotherms across the SO but is so far not able to resolve the frontal structure in the SO for glacial conditions. Thus, the marine sediment data allow for a northward movement of the PF. However, the PF, as defined by a strong temperature gradient, could also have remained at a similar location as today while the overall temperature north and south of it was generally lower, allowing for a latitudinal shift in diatom assemblages. Circumstantial evidence for an unchanged location may be derived from the fact that the modern location of the PF has remained the region of upwelling of Si enriched deep waters during the last deglaciation and for intervals during MIS 3 as evidenced by an increased opal production (Anderson et al., 2009). Physical oceanographic reasoning requires that the location of the PF is geographically pinned by the bottom form stress in regions with strong bottom topography and the PF cannot migrate northward during glacial times in these regions (Moore et al., 2000; Olbers et al., 2004). This is the case in the Weddell Sea region as well as in the region where the mid ocean ridges cross the ACC. In other regions of the SO, however, a change in the PF may be possible, which would reduce the sea ice effect on the SOMOC by an additional heat gain in regions where the PF had moved northward.

Another open question concerns the unknown change of the meridional gradient of the mixed layer buoyancy  $\partial b_m/\partial y$  for glacial conditions. Hypothetically, even with a strongly reduced surface buoyancy flux, residual circulation could be maintained if the meridional mixed layer buoyancy gradient across the ACC ( $\partial b_m/\partial y$  in equation (1)) decreased in parallel to the surface buoyancy flux. Watson and Garabato (2006) regard such a change in  $\partial b_m/\partial y$  as rather unlikely. In fact, the glacial SSTs point to a significant positive temperature and, thus, density gradient over the ACC north of the sea ice edge (Gersonde et al., 2005). In addition, the increase in sea ice formation during glacial times is expected to have increased salinity in the mixed layer in the sea ice formation zone, due to brine rejection and to have reduced salinity further north due to melting of exported, salt-depleted sea ice. Accordingly, this process would tend to strengthen the meridional buoyancy gradient, which would enforce the effect of the reduction in surface buoyancy flux on the residual circulation in equation (1). Experiments using eddy-resolving models (Hallberg and Gnanadesikan, 2006) for changed surface buoyancy fluxes in the past could elucidate the response of the meridional mixed layer buoyancy gradient and, hence, the SOMOC.

#### *Southern Ocean stratification changes*

An alternative way to decrease the ventilation of the deep SO and, thus, to decrease atmospheric CO<sub>2</sub> is to decrease the deep vertical convective mixing. This requires no net change in the SOMOC. Köhler et al. (2005) were able to reduce atmospheric CO<sub>2</sub> by about 35 ppmv by shutting off vertical mixing in the SO during the glacial in a multibox model. Again, this effect is subsequently amplified by carbonate compensation (Broecker and Peng, 1987).

Such a reduction of vertical mixing has to be linked to a change in a physical process in the SO. By simulating climate and biogeochemical changes during MIS3 in response to changes in NADW

formation, a clear bipolar seesaw response in Antarctic temperatures on the freshwater forcing in the North Atlantic and an accompanying change in CO<sub>2</sub> could be found in an ocean GCM coupled to an atmospheric energy balance model (Schmittner and Galbraith, 2008). A similar CO<sub>2</sub> response on a NADW reduction during the Younger Dryas was previously discussed by Marchal et al. (1999). Both the time scale and the amplitude (25 ppmv) of the CO<sub>2</sub> changes during MIS 3 are in line with the ice core observations (Schmittner and Galbraith, 2008). They ascribe the CO<sub>2</sub> change to a reduced stratification of the SO, as a consequence of the decrease in the NADW salt export into the SO, and an accompanying expansion of AABW in the deep ocean. Both effects favor the increased export of preformed nutrients to the deep ocean, thus diminishing the biological pump and increasing atmospheric CO<sub>2</sub>. Note that no iron fertilization was prescribed in their model experiment and that the circulation changes in the SO could entirely account for the millennial CO<sub>2</sub> changes during MIS3 observed in the ice cores. This could provide an alternative explanation for CO<sub>2</sub> variations following Heinrich events and their strong connection with SO temperature in MIS 3 by changes in the Atlantic Meridional Overturning Circulation via the bipolar seesaw. However it cannot explain the overall reduced CO<sub>2</sub> level during the glacial, where the strength of the Atlantic Meridional Overturning Circulation was probably only slightly reduced (McManus et al., 2004; Lynch-Stieglitz et al., 2007). Note also, that in the study by Schmittner and Galbraith (2008), the CO<sub>2</sub> background level was about 255 ppmv, which is significantly higher than the CO<sub>2</sub> concentrations found in the ice core record during MIS 3 and indicates that their model setup did not reflect full glacial boundary conditions.

Alternatively, the enhanced export of sea ice during cold climate periods provides freshwater to the surface north of the perennial sea ice, which stabilizes the water column and prevents communication of surface and deeper layers in the SO. This process is mainly restricted to the upper ocean layers and does not directly influence deep convection. Enhanced brine rejection in the perennial sea ice zone may increase the mixing there, partly compensating for the higher stratification further north. Surface stratification in the sea ice export region, however, would also decrease the nutrient supply to the surface water in that region and, thus, increase the nutrient utilization and decrease the export of preformed nutrients to the deeper ocean, reducing atmospheric CO<sub>2</sub> (Francois et al., 1997; Marinov et al., 2008).

A decrease in atmospheric CO<sub>2</sub> due to SO processes may be additionally strengthened by a reduction of the air/sea gas exchange in sea ice covered areas. Such a hypothesis, linking atmospheric CO<sub>2</sub> to the Antarctic sea ice extent via variation in the air/sea gas exchange, was put forward by Stephens and Keeling (2000). This process alone cannot account for the majority of the glacial/interglacial CO<sub>2</sub> change since it requires an unrealistically impermeable lid over the SO all the way to the PF to draw down CO<sub>2</sub> by 70 ppmv (Stephens and Keeling, 2000). In view of the strong seasonality of sea ice coverage over the SO during the glacial (Gersonde et al., 2005), when summer sea ice did not reach the upwelling regions south of the PF, and in view of the divergent wind field in the SO that continuously opens leads within the sea ice, such a lid seems impossible to maintain. However, a reduction in air-sea gas exchange during winter may have strengthened other processes, leading to a further reduction of CO<sub>2</sub> in the atmosphere.

#### **4. Other evidence for SO hydrography changes**

Both the iron fertilization as well as the westerly wind belt hypothesis have now been tested using climate and carbon cycle models, showing limited effect of a dust-induced increase in marine biological productivity and no change in zonal wind and the

connected SOMOC. The surface buoyancy forcing hypothesis and the SO stratification hypothesis still lack a stringent model test, at least partly because of the limitation of global ocean circulation models in resolving eddy processes in the ocean. In the absence of such a test, the role of the buoyancy forcing on SOMOC changes or changes in deep mixing remains an open question. However, based on other marine evidence, we can at least substantiate the consequence of such a forcing, i.e. changes in the strength of the deep and surface water exchange and a connected higher carbon storage in the deep ocean.

Probably the most direct evidence of reduced ventilation of the deep SO is based on the very depleted carbon isotopes in benthic foraminifera in the Atlantic sector of the SO (Hodell et al., 2003) and the extremely high glacial salinities in this ocean basin, derived from pore water reconstruction (Adkins et al., 2002). The former is a consequence of continuing mineralization of organic material in a poorly ventilated deep water mass in the SO. The  $\delta^{13}\text{C}$  decline observed in benthic foraminifera reflects the isotopic depletion in dissolved inorganic carbon in the deep SO during the LGM (Hodell et al., 2003). The size of this  $\delta^{13}\text{C}$  depletion ( $-1.5\%$ ) is quantitatively in line with carbon cycle modeling results for a shutdown of deep mixing in the SO (Köhler et al., 2005). The salinity increase is a consequence of the increased brine rejection in the SO, due to sea ice formation in the glacial, in combination with a reduced recirculation of AABW to the surface. Interestingly, higher salinities of bottom water formed by brine rejection in the absence of melting caverns below ice shelves are also predicted by an ice shelf model (Hellmer, 2004); a situation encountered during the LGM when the ice sheet progressed all the way to the continental shelf break.

The continued production of AABW together with a reduced recirculation in the SO and a shallower glacial NADW mass necessarily requires that AABW spread further into other ocean basins during the glacial. This is clearly observed in synchronous  $\delta^{18}\text{O}$  records from planktonic and benthic foraminifera in the North Atlantic all the way to the latitude of the Iberian peninsula during the LGM (Shackleton et al., 2000). These show fast Dansgaard/Oeschger changes at the surface but a slower Antarctic bipolar seesaw temperature signal at the bottom. It is also reflected by the distribution of paleonutrient proxies in the North Atlantic such as benthic foraminiferal  $\delta^{13}\text{C}$  (Duplessy et al., 1988) or benthic foraminiferal Cd/Ca (Marchitto and Broecker, 2006), which clearly illustrate the northward expansion of AABW during the glacial, filling the North Atlantic below a depth of about 3000 m. A similar horizontal hydrographic front with poorly ventilated water below 2000 m could also be evidenced in the Indian Ocean (Kallel et al., 1988). Note that another direct consequence of a reduced SOMOC during the glacial (but not of a reduced deep mixing in the SO) is a lower AAIW formation, which could be observed in marine sediment records. In fact, an increase of AAIW formation has been traced in the Southwest Pacific in parallel to the large AIM events during glacial times (Pahnke and Zahn, 2005) and could be attributed to intermittent increases in the SOMOC.

Finally, the slow build up of a poorly ventilated deep ocean water mass during the glaciation would lead to an accumulation of carbon in that water mass. During the transition from a glacial maximum to an interglacial, when the deep water mass is returning to the surface, this carbon must be released to the atmosphere. Several lines of evidence support this. Both marine radiocarbon as well as marine  $\delta^{13}\text{C}$  records indicate the transport of an old water mass (depleted in  $^{13}\text{C}$  and  $^{14}\text{C}$ ) to upper water bodies (Spero and Lea, 2002; Marchitto et al., 2007). The decrease in  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  in marine records over the last termination started at around 18,000 yr BP in line with the increase in atmospheric  $\text{CO}_2$  recorded in the EDC ice core (Monnin et al., 2001). However, the maximum 190‰ decline in atmospheric  $\Delta^{14}\text{C}$  in the middle of the last glacial/

interglacial transition would have required a very large  $^{14}\text{C}$  depleted deep ocean reservoir, which so far could not be quantitatively accounted for (Broecker and Barker, 2007). The opal production in the SO (Abelmann et al., 2006; Anderson et al., 2009) also shows a pronounced maximum during the transition (not in the glacial when dust-derived iron input was the largest), pointing to the transport of deep water with high nutrient concentrations back to the surface enhancing biological export production. The latter indicates that the vertical transport of macro- and micronutrients to the SO surface at that time had a much stronger influence on biological productivity in the SO than the input of iron from aeolian dust, as is also suggested for modern conditions (Wagener et al., 2008).

## 5. Summary & conclusions

Already more than 20 years ago, the important role of high latitude oceans in controlling atmospheric  $\text{CO}_2$  was recognized (Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1985). However, only recent ice core data from the EPICA and other ice cores, as well as improved model approaches, have allowed us to appreciate the dominant role of the SO to its full extent. Although none of the processes is able to explain the 100 ppmv glacial/interglacial  $\text{CO}_2$  change by itself, models and paleoclimatic data point to a reduction in SO ventilation (either by a reduced SOMOC or by decreased mixing) being a prime factor in the control of carbon storage in the abyss and, therefore, atmospheric  $\text{CO}_2$ . Model experiments show that it is most likely not a change in the westerly wind belt and the accompanying northward Ekman transport that alter the SOMOC. Theoretical considerations point to a strong increase in the southward eddy return flow forced by changes in the surface buoyancy flux being responsible for a potential change in SOMOC. Such a buoyancy forcing of the SOMOC would be in line with the idea that waxing and waning of sea ice (due to temperature changes) controls the heat exchange at the SO surface. Alternatively, reduced convective mixing during the glacial may also lead to reduced transport of dissolved inorganic carbon and macronutrients to the surface. However, a physical link with temperature or sea ice extent to explain the high correlation of  $\text{CO}_2$  and Antarctic temperature seems not to be as straightforward as in the case of SOMOC changes.

In addition, a change in biological productivity as a result of dust-induced iron fertilization appears to be very likely, however, its effect is probably not as large as initial estimates predicted. In fact, some of the indications of increased productivity in the SO may reflect the higher utilization of a reduced supply of nutrients to the SO surface from below (Francois et al., 1997) and not a higher productivity. We estimate the increase in export production to explain 10–20 ppmv of the total glacial/interglacial  $\text{CO}_2$  increase and 5–10 ppmv of the millennial  $\text{CO}_2$  changes during MIS 3. The question of how much and where export production and nutrient utilization changed in the SO has not been settled and requires further marine geological evidence to resolve apparent contradictions of various productivity proxies as well as lab experiments on the bioavailability of iron supplied by glacial dust.

A limited influence of iron fertilization on SO carbon storage also has far reaching implications for potential geoengineering plans to draw down anthropogenic  $\text{CO}_2$  by artificial iron fertilization of the SO. In addition to the unknown ecological consequences of such plans, a similar experiment was already performed by nature in the last glacial with very limited effect, despite a 5–20 fold increase in iron supply. Moreover, the much stronger ventilation of the modern SO compared to the glacial (as suggested by ample marine evidence) would be able to bring any additional carbon that was exported by an enhanced biological pump quickly back to the surface, damping any potential iron fertilization effect in the longer run.

Clearly, other factors – such as changes in the terrestrial biosphere, global ocean temperature changes and, especially, carbonate compensation – are responsible for part of the change in atmospheric CO<sub>2</sub> between glacial and interglacials but these processes cannot explain the extraordinary correlation between atmospheric CO<sub>2</sub> and Antarctic temperatures, hence, climate conditions in the SO. The hypothesis of a reduced SOMOC joins together the available puzzle pieces of marine geological as well as ice core evidence on changes in the carbon cycle both on an orbital as well as a millennial time scale. Alternatively, changes in SO mixing could also have taken place. A best guess estimate of these SO ventilation changes on glacial CO<sub>2</sub> is a reduction by about 40 ppmv (with a range between 20 and 50 ppmv). Together with the solubility effect for colder surface waters, the iron fertilization effect and the carbonate compensation feedback, this can explain a glacial/interglacial CO<sub>2</sub> change of about 80 ppmv. However, a crucial piece of this puzzle is still missing, i.e. a stringent model representation of the surface buoyancy forcing and the eddy-induced circulation in the SO for past climate conditions. On the observational side, the position of the glacial PF represents a very important open question with a strong impact on any hypothesis that invoke changes in the SO hydrography as cause of a glacial drawdown of CO<sub>2</sub>. Moreover, a changed hydrography of the SO has also an impact on the strength in the zonal circulation of the SO. Hence, detailed reconstruction of the SO temperature distribution in the glacial SO, of the strength and structure of the ACC, together with respective ACC model experiments for past climate conditions will further advance our understanding on paleoceanographic and carbon storage changes in the SO.

## Acknowledgments

This work is a contribution to the European Project for Ice Coring in Antarctica (EPICA), a joint European Science Foundation/European Commission scientific programme, funded by the EU (EPICA-MIS) and by national contributions from Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland and the United Kingdom. The main logistic support was provided by IPEV and PNRA (at Dome C) and AWI (at Dronning Maud Land). TFS acknowledges support by the Swiss National Science Foundation and the Prince Albert II of Monaco Foundation. This is EPICA publication no. 225.

## References

- Abelmann, A., Gersonde, R., Cortese, G., Kuhn, G., Smetacek, V., 2006. Extensive phytoplankton blooms in the Atlantic sector of the glacial Southern Ocean. *Paleoceanography* 21, PA1013. doi:10.1029/2005PA001199.
- Adkins, J.F., McIntyre, K., Schrag, D.P., 2002. The salinity, temperature, and  $\delta^{18}\text{O}$  of the glacial deep ocean. *Science* 298, 1769–1773.
- Ahn, J., Brook, E.J., 2008. Atmospheric CO<sub>2</sub> and climate on millennial time scales during the last glacial period. *Science* 322, 83–85.
- Anderson, R.F., Ali, S., Bradtmiller, L.L., Nielsen, S.H.H., Fleisher, M.Q., Anderson, B.E., Burckle, L.H., 2009. Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO<sub>2</sub>. *Science* 323, 1443–1448.
- Anklin, M., Barnola, J.-M., Schwander, J., Stauffer, B., Raynaud, D., 1995. Processes affecting the CO<sub>2</sub> concentrations measured in Greenland ice. *Tellus* 47 (4), 461–470.
- Archer, D., Winguth, A., Lea, D., Mahowald, N., 2000a. What caused the glacial/interglacial atmospheric pCO<sub>2</sub> cycles? *Reviews of Geophysics* 38 (2), 159–189.
- Archer, D.E., Eshel, G., Winguth, A., Broecker, W., Pierrehumbert, R., Tobis, M., Jacob, R., 2000b. Atmospheric pCO<sub>2</sub> sensitivity to the biological pump in the ocean. *Global Biogeochemical Cycles* 14 (4), 1219–1230.
- Bopp, L., Kohfeld, K.E., Le Quere, C., Aumont, O., 2003. Dust impact on marine biota and atmospheric CO<sub>2</sub> during glacial periods. *Paleoceanography* 18 (2), 1046.
- Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., Zeldis, J., 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* 407, 695–702.
- Broecker, W., Barker, S., 2007. A 190‰ drop in atmosphere's  $\Delta^{14}\text{C}$  during the “Mystery Interval” (17.5 to 14.5 ky). *Earth and Planetary Science Letters* 256, 90–99.
- Broecker, W., Lynch-Stieglitz, J., Archer, D., Hofmann, M., Maier-Reimer, E., Marchal, O., Stocker, T., Gruber, N., 1999. How strong is the Harvardton-Bear constraint. *Global Biogeochemical Cycles* 13 (4), 817–820.
- Broecker, W.S., Peng, T.-H., 1987. The role of CaCO<sub>3</sub> compensation in the glacial to interglacial atmospheric CO<sub>2</sub> change. *Global Biogeochemical Cycles* 1 (1), 15–29.
- Brovkin, V., Ganopolski, A., Archer, D., Rahmstorf, S., 2007. Lowering of glacial pCO<sub>2</sub> in response to changes in oceanic circulation and marine biogeochemistry. *Paleoceanography* 22, PA4202. doi:10.1029/2006PA001380.
- Caillon, N., Severinghaus, J.P., Jouzel, J., Barnola, J.-M., Kang, J., Lipenkov, V.Y., 2003. Timing of atmospheric CO<sub>2</sub> and Antarctic temperature changes across Termination III. *Science* 299, 1728–1731.
- Cuffey, K.M., Vimeux, F., 2001. Covariation of carbon dioxide and temperature from the Vostok ice core after deuterium-excess correction. *Nature* 412, 523–527.
- de Baar, H.J.W., Boyd, P.W., Coale, K.H., Landry, M.R., Tsuda, A., Assmy, P., Bakker, D.C.E., Bozec, Y., Barber, R.T., Brzezinski, M.A., Buesseler, K.O., Boyle, M., Croot, P.L., Gervais, F., Gorbunov, M.Y., Harrison, P.J., Hiscock, W.T., Laan, P., Lancelot, C., Law, C.S., Levasseur, M., Marchetti, A., Millero, F.J., Nishioka, J., Nojiri, Y., van Oijen, T., Riebesell, U., Rijkenberg, M.J.A., Saito, H., Takeda, S., Timmermans, K.R., Veldhuis, M.J.W., Waite, A.M., Wong, C.-S., 2005. Synthesis of iron fertilization experiments: from the iron age to the age of enlightenment. *Journal of Geophysical Research* 110, doi:10.1029/2004JC002601.
- Delmonte, B., Basile-Doelsch, I., Petit, J.R., Maggi, V., Revel-Rolland, M., Michard, A., E. J., Grousset, F., 2004. Comparing the EPICA and Vostok dust records during the last 220,000 years: stratigraphical correlation and provenance in glacial periods. *Earth-Science Reviews* 66, 63–87.
- Duplessy, J.C., Shackleton, N.J., Fairbanks, R.G., Labeyrie, L., Oppo, D., Kallel, N., 1988. Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation. *Paleoceanography* 3 (3), 343–360.
- EPICA Community Members, 2004. Eight glacial cycles from an Antarctic ice core. *Nature* 429, 623–628.
- EPICA community members, 2006. One-to-one coupling of glacial climate variability in Greenland and Antarctica. *Nature* 444, 195–198.
- Etheridge, D.M., Steele, L.P., Langenfelds, R.L., Francey, R.J., Barnola, J.-M., Morgan, V.I., 1996. Natural and anthropogenic changes in atmospheric CO<sub>2</sub> over the last 1000 years from air in Antarctic ice and firn. *Journal of Geophysical Research* 101 (2), 4115–4128.
- Fischer, H., Fundel, F., Huybrechts, P., Rybak, O., Oerter, H., Twarloh, B., Wegener, A., Ruth, U., Udisti, R., Becagli, S., Castellano, E., Fattori, I., Severi, M., Wolff, E., Littot, G., Röthlisberger, R., Mulvaney, R., Hutterli, M., Kaufmann, P., Federer, U., Lambert, F., Bigler, M., Stauffer, B., Hansson, M., Jonsell, U., de Angelis, M., Gabrielli, P., Boutron, C., Siggaard-Andersen, M.-L., Steffensen, J.P., Barbante, C., Gaspari, V., Wagenbach, D., 2007. Reconstruction of millennial changes in dust emission, transport and regional sea ice coverage using the deep EPICA ice cores from the Atlantic and Indian Ocean sector of Antarctica. *Earth and Planetary Science Letters* 260, 340–354.
- Fischer, H., Wahlen, M., Smith, J., Mastroianni, D., Deck, B., 1999. Ice core records of atmospheric CO<sub>2</sub> around the last three glacial terminations. *Science* 283, 1712–1714.
- Francois, R., Altabet, M.A., Yu, E.-F., Sigman, D.M., Bacon, M.P., Frank, M., Bohrmann, G., Bareille, G., Labeyrie, L.D., 1997. Contribution of southern ocean surface-water stratification to low atmospheric CO<sub>2</sub> concentrations during the last glacial period. *Nature* 389, 929–935.
- Gaspari, V., Barbante, C., Cozzi, G., Cescon, P., Boutron, C., Gabrielli, P., Capodaglio, G., Ferrari, C., Petit, J.R., Delmonte, B., 2006. Atmospheric iron fluxes over the last deglaciation: climatic implications. *Geophysical Research Letters* 33, L03704. doi:10.1029/2005GL024352.
- Gersonde, R., Abelmann, A., Brathauer, U., Bequey, S., Bianchi, C., Cortese, G., Grobe, H., Kuhn, G., Niebler, H.-S., Segl, M., Sieger, R., Zielinski, U., Fütterer, D.K., 2003. Last glacial sea surface temperatures and sea-ice extent in the Southern Ocean (Atlantic-Indian sector): a multiproxy approach. *Paleoceanography* 18 (3), doi:10.1029/2002PA000809.
- Gersonde, R., Crosta, X., Abelmann, A., Armand, L., 2005. Sea-surface temperature and sea ice distribution of the Southern Ocean at the EPILOG Last Glacial Maximum – a circum-Antarctic view based on siliceous microfossil records. *Quaternary Science Reviews* 24, 869–896.
- Hallberg, R., Gnanadesikan, A., 2006. The role of eddies in determining the structure and response of the wind-driven southern hemisphere overturning: results from the modeling eddies in the Southern Ocean (MESO) project. *Journal of Physical Oceanography* 36, 2232–2252.
- Hara, K., Osada, K., Kido, M., Hayashi, M., Matsunaga, K., Iwasaka, Y., Yamanouchi, T., Hashida, G., Fukatsu, T., 2004. Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: compositional differences between coastal and inland stations. *Journal of Geophysical Research* 109, D20208. doi:10.1029/2004JD004713.
- Hellmer, H.H., 2004. Impact of Antarctic ice shelf basal melting on sea ice and deep ocean properties. *Geophysical Research Letters* 31, L10307. doi:10.1029/2004GL019506.
- Hodell, D.A., Venz, K.A., Charles, C.D., Ninnemann, U.S., 2003. Pleistocene vertical carbon isotope and carbonate gradients in the South Atlantic sector of the Southern Ocean. *Geochemistry Geophysics Geosystems* 4 (1), doi:10.1029/2002GC000367.

- Indermühle, A., Monnin, E., Stauffer, B., Stocker, T.F., Wahlen, M., 2000. Atmospheric CO<sub>2</sub> concentration from 60 to 20 kyr BP from the Taylor Dome ice core. *Antarctica Geophysical Research Letters* 27 (5), 735–738.
- Indermühle, A., Stocker, T.F., Joos, F., Fischer, H., Smith, H.J., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R., Stauffer, B., 1999. Holocene carbon-cycle dynamics based on CO<sub>2</sub> trapped in ice at Taylor Dome. *Antarctica Nature* 398, 121–126.
- IPCC, 2007. *Climate Change 2007–The Physical Science Basis*. Cambridge University Press, Cambridge.
- Joos, F., Spahni, R., 2008. Rates of change in natural and anthropogenic radiative forcing over the past 20,000 years. *Proceedings of the National Academy of Sciences* 105 (5), 1425–1430.
- Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J., Barnola, J.-M., Chappellaz, J., Fischer, H., Gallet, J.C., Johnsen, S., Leuenberger, M., Loulergue, L., Lüthi, D., Oerter, H., Parrenin, F., Raisbeck, G., Raynaud, D., Schwander, J., Spahni, R., Souchez, R., Selmo, E., Schilt, A., Steffensen, J.P., Stenni, B., Stauffer, B., Stocker, T.F., Tison, J.-L., Werner, M., Wolff, E.W., 2007. Orbital and millennial Antarctic climate variability over the last 800,000 years. *Science* 317, 793–796.
- Kallel, N., Labeyrie, L.D., Juillet-Leclerc, A., Duplessy, J.-C., 1988. A deep hydrological front between intermediate and deep-water masses in the glacial Indian Ocean. *Nature* 333, 651–655.
- Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Chelliah, M., Ebisuzaki, W., Higgins, R., Janowiak, J., Mo, K.C., Ropelewski, C., Wang, J., Leetmaa, A., Reynolds, R., Jenne, R., Joseph, D., 1996. The NCEP/NCAR 40-year reanalysis project. *Bulletin of the American Meteorological Society* 77 (3), 437–471.
- Karsten, R.H., Marshall, J., 2002. Constructing the residual circulation of the ACC from observations. *Journal of Physical Oceanography* 32, 3315–3327.
- Kaufmann, P., Fundel, F., Fischer, H., Bigler, M., Ruth, U., Udisti, R., Hansson, M., de Angelis, M., Barbante, C., Wolff, E.W., Hutterli, M., Wagenbach, D., 2010. Ammonium and non-sea-salt sulfate in the EPICA ice cores as indicator of biological activity in the Southern Ocean. *Quaternary Science Reviews* 29, 313–323.
- Knox, F., McElroy, M.B., 1985. Changes in atmospheric CO<sub>2</sub>: factors regulating the glacial to interglacial transition. In: Sundquist, E.T., Broecker, W.S. (Eds.), *The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations Archaean to Present*, 32. American Geophysical Union, Washington, pp. 154–162.
- Kohfeld, K.E.C.L.Q., Harrison, S.P., Anderson, R.F., 2005. Role of marine biology in glacial–interglacial CO<sub>2</sub> cycles. *Science* 308, 74–78.
- Köhler, P., Fischer, H., 2006. Simulating low frequency changes in atmospheric CO<sub>2</sub> during the last 740,000 years. *Climate of the Past* 2, 57–78.
- Köhler, P., Fischer, H., Munhoven, G., Zeebe, R.E., 2005. Quantitative interpretation of atmospheric carbon records over the last glacial termination. *Global Biogeochemical Cycles* 19, GB4020. doi:10.1029/2004GB002345.
- Köhler, P., Bintanja, R., Fischer, H., Joos, F., Knutti, R., Lohmann, G., Masson-Delmotte, V., 2010. What caused Earth's temperature variations during the last 800,000 years? Data-based evidences on radiative forcing and constraints on climate sensitivity. *Quaternary Science Reviews* 29, 129–145.
- Lambert, F., Delmonte, B., Petit, J.R., Bigler, M., Kaufmann, P.R., Hutterli, M.A., Stocker, T.F., Ruth, U., Steffensen, J.P., Maggi, V., 2008. Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core. *Nature* 452, 616–619.
- Lane, E., Peacock, S., Restrepo, J.M., 2006. A dynamic-flow carbon-cycle box model and high-latitude sensitivity. *Tellus* 58B, 257–278.
- LeGrand, P., Alverson, K., 2001. Variations in atmospheric CO<sub>2</sub> during glacial cycles from an inverse ocean modeling perspective. *Paleoceanography* 16 (6), 604–616.
- Lüthi, D., Le Floch, M., Bereiter, B., Blunier, T., Barnola, J.-M., Siegenthaler, U., Raynaud, D., Jouzel, J., Fischer, H., Kawamura, K., Stocker, T.F., 2008. High-resolution carbon dioxide concentration record 650,000–800,000 years before present. *Nature* 453, 379–382.
- Lynch-Stieglitz, J., Adkins, J.F., Curry, W., Dokken, T.M., Hall, I.R., Herguera, J.C., Hirschi, J.J.-M., Ivanova, E.V., Kissel, C., Marchal, O., Marchitto, T.M., McCave, I.N., McManus, J.F., Mulitza, S., Ninnemann, U., Peeters, F., Yu, E.-F., Zahn, R., 2007. Atlantic meridional overturning circulation during the Last Glacial maximum. *Science* 316, 66–69.
- MacFarling Meure, C., Etheridge, D., Trudinger, C.M., Steele, P., Langenfelds, R., Van Ommen, T., Smith, A., Elkins, J., 2006. Law Dome CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O ice core records extended to 2000 years BP. *Geophysical Research Letters* 33, L14810. doi:10.1029/2006GL026152.
- Marchal, O., Stocker, T.F., Joos, F., Indermühle, A., Blunier, T., Tschumi, J., 1999. Modelling the concentration of atmospheric CO<sub>2</sub> during the Younger Dryas climate event. *Climate Dynamics* 15, 341–354.
- Marchitto, T.M., Broecker, W.S., 2006. Deep water mass geometry in the glacial Atlantic Ocean: a review of constraints from the paleonutrient proxy Cd/Ca. *Geochemistry Geophysics Geosystems* 7 (12). doi:10.1029/2006GC001323.
- Marchitto, T.M., Lehman, S.J., Ortiz, J.D., Flückiger, J., van Geen, A., 2007. Marine radiocarbon evidence for the mechanism of deglacial CO<sub>2</sub> rise. *Science* 316, 1456–1459.
- Marinov, I., Gnanadesikan, A., Sarmiento, J.L., Toggweiler, J.R., Follows, M., Mignone, B.K., 2008. Impact of oceanic circulation on biological carbon storage in the ocean and atmospheric pCO<sub>2</sub>. *Global Biogeochemical Cycles* 22, GB3007. doi:10.1029/2007GB002958.
- Martin, J., 1990. Glacial–interglacial CO<sub>2</sub> change: the iron hypothesis. *Paleoceanography* 5, 1–13.
- Martínez-García, A., Rosell-Melé, A., Geibert, W., Gersonde, R., Masqué, P., Gaspari, V., Barbante, C., 2009. Links between iron supply, marine productivity, sea surface temperature and CO<sub>2</sub> over the last 1.1 Myr. *Paleoceanography* 24, doi:10.1029/2008PA001657.
- Matsumoto, K., Sarmiento, J.L., Brzezinski, M.A., 2002. Silicic acid leakage from the Southern Ocean: a possible explanation for glacial atmospheric pCO<sub>2</sub>. *Global Biogeochemical Cycles* 16 (3), 1031. doi:10.1029/2001GB001442.
- McManus, J.F., Francois, R., Gherardi, J.-M., Kegwin, L.D., Brown-Leger, S., 2004. Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. *Nature* 428, 834–837.
- Menviel, L., Timmermann, A., Mouchet, A., Timm, O., 2008. Climate and marine carbon cycle response to changes in the strength of the southern hemispheric westerlies. *Paleoceanography* 23, PA4201. doi:10.1029/2008PA001604.
- Monnin, E., Indermühle, A., Dällenbach, A., Flückiger, J., Stauffer, B., Stocker, T.F., Raynaud, D., Barnola, J.-M., 2001. Atmospheric CO<sub>2</sub> concentration over the last termination. *Science* 291, 112–114.
- Moore, J.K., Abbott, M.R., Richman, J.G., Nelson, D.M., 2000. The Southern Ocean at the last glacial maximum: a strong sink for atmospheric carbon dioxide. *Global Biogeochemical Cycles* 14 (1), 455–475.
- Neftel, A., Oeschger, H., Schwander, J., Stauffer, B., Zumbund, R., 1982. Ice core sample measurements give atmospheric CO<sub>2</sub> content during the past 40,000 yr. *Nature* 295, 220–223.
- North Greenland Ice Core Project Members, 2004. High resolution climate record of the northern hemisphere reaching into the last interglacial period. *Nature* 431, 147–151.
- Olbers, D., Borowski, D., Völker, C., Wolff, J.O., 2004. The dynamical balance, transport and circulation of the Antarctic Circumpolar Current. *Antarctic Science* 16 (4), 79–110.
- Pahnke, K., Zahn, R., 2005. Southern hemisphere water mass conversion linked with North Atlantic climate variability. *Science* 307, 1741–1746.
- Paillard, D., Parrenin, F., 2004. The Antarctic ice sheet and the triggering of deglaciations. *Earth and Planetary Science Letters* 227, 263–271.
- Parekh, P., Joos, F., Müller, S.A., 2008. A modeling assessment of the interplay between aeolian iron fluxes and iron-binding ligands in controlling carbon dioxide fluctuations during Antarctic warm events. *Paleoceanography* 23, PA4202. doi:10.1029/2007PA001531.
- Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., Stievenard, M., 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core. *Antarctica Nature* 399, 429–436.
- Rankin, A.M., Auld, V., Wolff, E.W., 2000. Frost flowers as a source of fractionated sea salt aerosol in the polar regions. *Geophysical Research Letters* 27 (21), 3469–3472.
- Rankin, A.M., Wolff, E.W., 2003. A year-long record of size-segregated aerosol composition at Halley, Antarctica. *Journal of Geophysical Research* 108, D24. doi:10.1029/2003JD003993.
- Ridgwell, A.J., 2003. Implications of the glacial CO<sub>2</sub> iron hypothesis for Quaternary climate change. *Geochemistry Geophysics Geosystems* 4, 1976. doi:10.1029/2003GC000563.
- Rintoul, S.R., Hughes, C.W., Olbers, D., 2001. The Antarctic Circumpolar Current system. In: Siedler, G., Church, J., Gould, J. (Eds.), *Ocean Circulation and Climate: Observing and Modelling the Global Ocean*. Academic Press, San Diego, pp. 271–302.
- Rojas, M., Moreno, P., Kageyama, M., Crucifix, M., Hewitt, C., Abe-Ouchi, A., Ohgaito, R., Brady, E.C., Hope, P., 2008. The Southern Westerlies during the last glacial maximum in PMIP2 simulations. *Climate Dynamics*. doi:10.1007/s00382-00008-00421-00387.
- Röthlisberger, R., Bigler, M., Wolff, E.W., Joos, F., Monnin, E., Hutterli, M.A., 2004. Ice core evidence for the extent of past atmospheric CO<sub>2</sub> change due to iron fertilisation. *Geophysical Research Letters* 31. doi:10.1029/2004GL020338.
- Röthlisberger, R., Mudelsee, M., Bigler, M., de Angelis, M., Fischer, H., Hansson, M., Lambert, F., Masson-Delmotte, V., Sime, L., Udisti, R., E.W. W., 2008. The southern hemisphere at glacial terminations: insights from the Dome C ice core. *Climate of the Past* 4, 345–356.
- Sarmiento, J.L., Toggweiler, J.R., 1984. A new model for the role of the oceans in determining atmospheric CO<sub>2</sub>. *Nature* 308, 621–624.
- Schmittner, A., Galbraith, E.D., 2008. Glacial greenhouse gas fluctuations controlled by ocean circulation changes. *Nature* 456, 373–376.
- Schwander, J., Stauffer, B., 1984. Age difference between polar ice and the air trapped in its bubbles. *Nature* 311, 45–47.
- Shackleton, N.J., Hall, M.A., Vincent, E., 2000. Phase relationships between millennial-scale events 64,000–24,000 years ago. *Paleoceanography* 15 (6), 565–569.
- Siegenthaler, U., Stocker, T.F., Monnin, E., Lüthi, D., Schwander, J., Stauffer, B., Raynaud, D., Barnola, J.-M., Fischer, H., Masson-Delmotte, V., Jouzel, J., 2005. Stable carbon cycle-climate relationship during the late Pleistocene. *Science* 310, 1313–1317.
- Siegenthaler, U., Wenk, T., 1984. Rapid atmospheric CO<sub>2</sub> variations and ocean circulation. *Nature* 308, 624–626.
- Sigman, D.M., Boyle, E.A., 2000. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* 407, 859–869.
- Smith, H.J., Wahlen, M., Mastroianni, D., Taylor, K.C., 1997. The CO<sub>2</sub> concentration of air trapped in GISP2 ice from the Last Glacial Maximum–Holocene transition. *Geophysical Research Letters* 24 (1), 1–4.

- Spahni, R., Schwander, J., Flückiger, J., Stauffer, B., Chappellaz, J., Raynaud, D., 2003. The attenuation of fast atmospheric CH<sub>4</sub> variations recorded in polar ice cores. *Geophysical Research Letters* 30 (11). doi:10.1029/2003GL017093.
- Spero, H.J., Lea, D.W., 2002. The cause of carbon isotope minimum events on glacial terminations. *Science* 296, 522–525.
- Stauffer, B., Blunier, T., Dällenbach, A., Indermühle, A., Schwander, J., Stocker, T.F., Tschumi, J., Chappellaz, J., Raynaud, D., Hammer, C.U., Clausen, H.B., 1998. Atmospheric CO<sub>2</sub> concentration and millennial-scale climate change during the last glacial period. *Nature* 392, 59–62.
- Stauffer, B., Tschumi, J., 2000. Reconstruction of past atmospheric CO<sub>2</sub> concentrations by ice core analyses. In: Hondoh, T. (Ed.), *Physics of Ice Core Records*. Hokkaido University Press, Sapporo, pp. 217–241.
- Stephens, B.B., Keeling, R.F., 2000. The influence of Antarctic sea ice on glacial–interglacial CO<sub>2</sub> variations. *Nature* 404, 171–174.
- Stocker, T., Johnsen, S., 2003. A minimum thermodynamic model of the bipolar seesaw. *Paleoceanography* 18 (4). doi:10.1029/2003PA000920.
- Toggweiler, J.R., Russell, J.L., Carson, S.R., 2006. Midlatitude westerlies, atmospheric CO<sub>2</sub>, and climate change during the ice ages. *Paleoceanography* 21, PA2005. doi:10.1029/2005PA001154.
- Tschumi, T., Joos, F., Parekh, P., 2008. How important are Southern Hemisphere wind changes for low glacial carbon dioxide? A model study. *Paleoceanography* 23, PA4208. doi:10.1029/2008PA001592.
- Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A., Legrand, M., Hall, J.S., Wolff, E.W., 1998. Sea-salt aerosol in coastal Antarctic regions. *Journal of Geophysical Research* 103 (D9), 10961–10974.
- Wagner, T., Guieu, C., Losno, R., Bonnet, S., Mahowald, N., 2008. Revisiting atmospheric dust export to the Southern Hemisphere ocean: biogeochemical implications. *Global Biogeochemical Cycles* 22, GB2006. doi:10.1029/2007GB002984.
- Watanabe, O., Jouzel, J., Johnsen, S., Parrenin, F., Shoji, H., Yoshida, N., 2003. Homogeneous climate variability across East Antarctica over the past three glacial cycles. *Nature* 422, 509–512.
- Watson, A.J., Bakker, D.C.E., Ridgwell, A.J., Boyd, P.W., Law, C.S., 2000. Effect of iron supply on Southern Ocean CO<sub>2</sub> uptake and implications for glacial atmospheric CO<sub>2</sub>. *Nature* 407, 730–733.
- Watson, A.J., Garabato, A.C.N., 2006. The role of Southern Ocean mixing and upwelling in glacial–interglacial atmospheric CO<sub>2</sub> change. *Tellus* 58B, 73–87.
- Wolff, E.W., Fischer, H., Fundel, F., Ruth, U., Twarloh, B., Littot, G.C., Mulvaney, R., de Angelis, M., Boutron, C.F., Hansson, M., Jonsell, U., Hutterli, M., Bigler, M., Lambert, F., Kaufmann, P., Röthlisberger, R., Steffensen, J.P., Siggaard-Andersen, M.-L., Udisti, R., Becagli, S., Castellano, E., Severi, M., Wagenbach, D., Barbante, C., Gabrielli, P., Gaspari, V., 2006. Southern Ocean sea ice, DMS production and iron flux over the last eight glacial cycles. *Nature* 440, 491–496.
- Wolff, E.W., Kull, C., Chappellaz, J., Fischer, H., Miller, H., Stocker, T.F., Watson, A.J., Flower, B., Joos, F., Köhler, P., Matsumoto, K., Monnin, E., Mudelsee, M., Paillard, D., Shackleton, N., 2005. Modelling atmospheric CO<sub>2</sub>: results of a challenge. *EOS* 86 (38) 341/345.
- Yang, X., Pyle, J.A., Cox, R.A., 2008. Sea salt aerosol production and bromine release: role of snow on sea ice. *Geophysical Research Letters* 35, L16815. doi:10.1029/2008GL034536.