Carbon dioxide effects of Antarctic stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and synthesis in a geochemical box model

Mathis P. Hain,1,2 Daniel M. Sigman,1 and Gerald H. Haug2,3

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In a box model synthesis of Southern Ocean and North Atlantic mechanisms for lowering CO2 during ice ages, the CO2 changes are parsed into their component geochemical causes, including the soft-tissue pump, the carbonate pump, and whole ocean alkalinity. When the mechanisms are applied together, their interactions greatly modify the net CO2 change. Combining the Antarctic mechanisms (stratification, nutrient drawdown, and sea ice cover) within bounds set by observations decreases CO2 by no more than 36 ppm, a drawdown that could be caused by any one of these mechanisms in isolation. However, these Antarctic changes reverse the CO2 effect of the observed ice age shoaling of North Atlantic overturning: in isolation, the shoaling raises CO2 by 16 ppm, but alongside the Antarctic changes, it lowers CO2 by an additional 13 ppm, a 29 ppm synergy. The total CO2 decrease does not reach 80 ppm, partly because Antarctic stratification, Antarctic sea ice cover, and the shoaling of North Atlantic overturning all strengthen the sequestration of alkalinity in the deepest ocean, which increases CO2 both by itself and by decreasing whole ocean alkalinity. Increased nutrient consumption in the sub-Antarctic causes as much as an additional 35 ppm CO2 decrease, interacting minimally with the other changes. With its inclusion, the lowest ice age CO2 levels are within reach. These findings may bear on the two-stepped CO2 decrease of the last ice age.

1. Introduction

Temporal variations of the atmospheric CO2 mixing ratio have been reconstructed from air trapped in polar ice that accumulated over the late Pleistocene, providing a record that is astonishingly reminiscent of the glacial-interglacial climate cycles themselves [Petit et al., 1999]. Only the ocean carbon reservoir is adequately large and dynamic to drive the observed 80–100 ppm variations in atmospheric CO2 on glacial-interglacial timescales. It is broadly suspected that the Southern Ocean is the key region of the ocean modulating these variations [e.g., Sigman and Boyle, 2000; Sigman et al., 2010].

The high sensitivity to Southern Ocean changes is fundamentally related to the tight grip it has on the efficiency of the “biological (or soft-tissue) pump”, which sequesters carbon at depth by sinking organic matter, lowering atmospheric CO2. Today, the Southern Ocean is the principal “leak” in the soft-tissue pump because its organic matter rain is inadequate to prevent the evasion of deeply sequestered carbon when deep water comes to its surface [Sigman and Haug, 2003; Ito and Follows, 2005; Marinov et al., 2006; Sigman et al., 2010]. Moreover, sequestration of carbon at depth lowers the pH of deep waters, making them more corrosive to sinking carbonate shells. This rain of CaCO3, the “carbonate pump”, delivers alkalinity to the deep ocean, which raises pH and makes deep waters less corrosive. Changing CaCO3 saturation state, in turn, affects the depth of the lysocline; the depth level above which CaCO3 is buried on the seafloor and alkalinity is lost from the ocean lowering “whole ocean alkalinity” [e.g., Broecker and Peng, 1987; Boyle, 1988b; Sigman et al., 1998; Toggweiler, 1999; Archer et al., 2000; Sigman and Haug, 2003; Sigman et al., 2010]. These processes set atmospheric CO2 on the timescales relevant to ice ages: more respired carbon (a stronger soft-tissue pump), less regenerated alkalinity (a weaker carbonate pump) and a
Figure 1. Atmospheric CO₂ over the last glacial cycle reconstructed from ice cores [Petit et al., 1999; Ahn and Brook, 2008] and key proxy data related to the mechanisms driving its variability. A global stack of benthic foraminiferal δ¹⁸O [Lisiecki and Raymo, 2005] reflecting both global ice volume and deep ocean temperatures illustrates the close relationship between atmospheric CO₂ and the glacial cycle. The temporal correlation between the first major decrease of CO₂ during Marine Isotope Stage (MIS) 5 and rapid Antarctic cooling (EPICA δD) [Petit et al., 1999] may indicate an important role for the onset of Antarctic stratification and/or sea ice expansion. During MIS 4, 3, and 2, aeolian iron supply, productivity (Alkenones) [Martinez-Garcia et al., 2009], and nutrient consumption (as reconstructed from diatom-bound δ¹⁵N, δ¹⁵Ndb [R. S. Robinson et al., 2005]) increased in the sub-Antarctic. During MIS 4, 3, and 2, the benthic foraminiferal δ¹³C at two sites currently bathed by NADW decreased (purple and red) [Shackleton et al., 2000; Hodell et al., 2003], while δ¹³C increased at a Caribbean site that monitors intermediate-depth Atlantic waters (blue) [Oppo et al., 1995]. These collective observations fit into the widespread evidence for a shoaling of North Atlantic overturning (from NADW to GNAIW) [Lynch-Stieglitz et al., 2007]. The fertilization of the sub-Antarctic and/or the formation of GNAIW may have been important contributors to the second major decrease in atmospheric CO₂ at the MIS 4/5 transition.
higher whole ocean alkalinity all act to partition $\text{CO}_2$ from the atmosphere into the ocean.

[4] Using a geochemical ocean/atmosphere box model, we systematically probe and analyze the most promising oceanographic hypothesis for the low levels of $\text{CO}_2$ during ice ages: (1) polar Antarctic stratification and sea ice expansion restricting air-sea gas exchange, (2) polar Antarctic nutrient drawdown, (3) shoaling of North Atlantic overturning, and (4) subantarctic nutrient drawdown. A new diagnostic tool quantitatively parses simulated $\text{CO}_2$ change into its component geochemical causes (see above), providing mechanistic insight into how these ocean changes operate to influence atmosphere chemistry. This exercise reveals a new dynamic involving the carbonate pump, which reduces the leverage of the polar Antarctic “barrier mechanisms”, stratification and sea ice expansion, and thus renders the other ocean changes relatively more important. The central outcome of this study, however, is the surprising magnitude of interactions among the oceanographic hypotheses for glacial $\text{CO}_2$ drawdown. These interactions, which to this point have not been characterized, greatly affect the $\text{CO}_2$ drawdown that can be achieved.

[5] Below, before discussing our model simulations, we provide more information and constraints on the hypotheses we set out to investigate.

1.1. Antarctic

[6] The Antarctic is arguably a more important contributor to the Southern Ocean leak in the soft-tissue pump than the subantarctic zone because (1) it ventilates the voluminous deep rather than the smaller-volume mid-depth ocean (e.g., that ventilated by subantarctic mode water) and (2) its concentration of “preformed” nutrients carried into the ocean interior together with the water instead of sinking organic matter is much greater [Marinov et al., 2006]. Accordingly, hypotheses have focused on closing the Antarctic component of the Southern Ocean leak in the soft-tissue pump. First, nutrient consumption in the Antarctic surface may have increased [Sarmiento and Toggweiler, 1984; Martin, 1990; François et al., 1997]. Second, reduced exchange between the Antarctic surface and the underlying ocean may have decreased the rate of exposure of $\text{CO}_2$ charged deep water (often summarized as “stratification”) [François et al., 1997; Toggweiler, 1999]. Third, extensive sea ice cover may have prevented evasion of $\text{CO}_2$ during the glacial [Stephens and Keeling, 2000]. In the polar Antarctic, which ventilates the deep ocean, stratification and gas-exchange reduction, when taken to completion, have equivalent capacities to lower $\text{CO}_2$ and may collectively be called “barrier mechanisms” [Archer et al., 2003].

[7] Antarctic export production appears to have been reduced during ice ages [François et al., 1997; Frank et al., 2000; Kumar et al., 1993; Mortlock et al., 1991; Kohfeld et al., 2005], arguing against a simple productivity-driven increase in nutrient consumption. If, however, gross nutrient supply to the Antarctic surface decreased as export production decreased (and especially if the nutrient supply decreased more), atmospheric $\text{CO}_2$ might have been lowered without violating the apparent productivity constraint. Unfortunately, the parameter of singular importance, the surface nutrient status of the ice age Antarctic, is debated [e.g., Keigwin and Boyle, 1989; De La Rocha et al., 1998; De La Rocha, 2006; Sigman et al., 1999; Elderfield and Rickaby, 2000; Crosta and Shemesh, 2002; Robinson et al., 2004; Robinson and Sigman, 2008].

[8] Previous studies have been taken to indicate that substantial fractions of the ice age $\text{CO}_2$ drawdown can be driven by either of the two Antarctic barrier mechanisms (reducing Antarctic overturning [Toggweiler, 1999]; reduced Antarctic $\text{CO}_2$ efflux by sea ice cover [Stephens and Keeling, 2000]). This raises the question of whether the barrier mechanisms could be combined to explain the entire $\text{CO}_2$ drawdown. If so, nutrient status and non-Antarctic mechanisms would be relegated to a role of secondary importance. Below, we will show that the carbonate pump reduces the sensitivity of $\text{CO}_2$ to the barrier mechanisms, and we will argue that the studies above underestimate its importance. We also show that the three proposed Antarctic mechanisms, when combined, can achieve little more $\text{CO}_2$ drawdown than any one of them in isolation. This motivates inclusion of other oceanographic changes and their interaction with the Antarctic mechanisms.

1.2. Shoaling of North Atlantic Overturning

[9] During parts of the last glacial cycle, the conversion from deep (NADW) to intermediate (GNAIW) water formation in the North Atlantic left the abyssal Atlantic dominated by southern sourced water (possibly akin to modern Antarctic Bottom Water; AABW) [Boyle and Keigwin, 1982; Duplessy et al., 1984, 1988; Boyle, 1988a; Yu et al., 1996; Marchitto et al., 2002; McManus et al., 2004; Curry and Oppo, 2005; L. F. Robinson et al., 2005; Gherardi et al., 2009]. This may have contributed to the development of an apparent “chemical divide” at ~2–2.5 km depth in the ice age ocean, best documented for the Atlantic [e.g., Lynch-Stieglitz et al., 2007] but also evident from some data in the Indo-Pacific [Kallel et al., 1988; Herguera, 1992; Boyle et al., 1995; Keigwin, 1998; Matsumoto and Lynch Stieglitz, 1999; Matsumoto et al., 2002; Galbraith et al., 2007]. The “NADW-to-GNAIW switch” has been proposed to isolate the ocean’s deepest waters, making them prone to the accumulation of nutrients and excess carbon, as is supported by paleoceanographic data [Boyle and Keigwin, 1987; Boyle et al., 1995; Duplessy et al., 1988; Kallel et al., 1988].

[10] The NADW-to-GNAIW switch may help Antarctic hypotheses for $\text{CO}_2$ change in two ways. First, it supports the Antarctic stratification hypothesis (see above) in the sense that, even with reduced Antarctic overturning during ice ages, southern sourced waters might have filled a larger volume of the abyssal ocean than observed during interglacials; in this way, it helps to match observations. Second, the focusing of respired carbon in the abyssal ocean, as opposed to mid-depths, would have made the waters overlying the lysocline more corrosive, raising whole ocean alkalinity and further lowering $\text{CO}_2$ levels [Boyle, 1988a, 1988b].
However, an opposing CO2 effect of the NADW-to-GNAIW switch, operating through the soft-tissue pump, would work to raise CO2 during ice ages: Relative to NADW and its downstream forms, modern AABW has a large burden of preformed nutrients. If abyssal depths of all the glacial ocean basins were occupied by AABW with near its present-day burden of preformed nutrients (as opposed to regenerated nutrients from sinking organic matter), the increase in volumetric importance of AABW would have driven higher, not lower, atmospheric CO2 [e.g., Marinov et al., 2008]. Understanding how these different carbon cycle aspects interact to yield a net CO2 effect from the NADW-to-GNAIW switch, under various Southern Ocean conditions, is the second goal of this study.

1.3. Subantarctic Nutrient Drawdown

The subantarctic zone (SAZ) of the Southern Ocean, unlike the Antarctic, was more productive during the last ice age, and nutrient consumption may also have been greater than is observed today [Kumar et al., 1995; Mashioita et al., 1997; Rosenthal et al., 1997, 2000; R. S. Robinson et al., 2005; Kohfeld et al., 2005; Robinson and Sigman, 2008; Martinez-Garcia et al., 2009], perhaps explained by natural iron fertilization of the region by dust during parts of the last and previous ice ages [Watson et al., 2000; Martinez-Garcia et al., 2009]. As a result, a number of workers have pointed to its potential role in explaining the low CO2 of ice ages [e.g., Watson et al., 2000; R. S. Robinson et al., 2005; Matsumoto and Sarmiento, 2008].

The subantarctic zone ventilates a smaller volume of the ocean interior than does the Antarctic. Thus, its control on the biological pump should be limited. However, the subantarctic zone is the gate keeper for nutrients attempting to pass from the Southern Ocean into the mid-deep ocean of the low latitudes where they fuel biogenic fluxes out of the low-latitude surface ocean [Toggweiler et al., 1991; Sarmiento et al., 2004]. As a result, it may affect the carbon cycle through a number of processes involving ocean alkalinity [Keir, 1988]. First, more complete nutrient consumption in the SAZ should work to keep regenerated nutrients and respired CO2 in the deep (rather than mid-depth) ocean, where it can transiently shoal the lysocline and force a rise in whole ocean alkalinity. Second, by reducing the nutrient supply to the lower latitudes, SAZ nutrient depletion may work to lower the rain of CaCO3 out of low-latitude ocean [e.g., Matsumoto et al., 2002; Loubere et al., 2004; Matsumoto and Sarmiento, 2008], which would drive the ocean to deepen its steady state lysocline to balance the river input of alkalinity, further raising whole ocean alkalinity [Sigman et al., 1998]. Third, muted CaCO3 rain would reduce the amount of regenerated alkalinity found in the ocean interior at any given time; a weakened carbonate pump.

Our model can differentiate subantarctic and Antarctic processes (see below) allowing us to probe subantarctic fertilization for its isolated CO2 drawdown capacity as well as its interactions with the Antarctic and North Atlantic mechanisms discussed above. In particular, Watson et al. [2000] have simulated that iron fertilization applied to the entire Southern Ocean in the context of an interglacial background state may explain the component of atmospheric CO2 decline that correlates to enhanced dust supply to the region (Figure 1). The third goal of our study is to answer if subantarctic (rather than Southern Ocean) nutrient status, in the context of the Antarctic mechanisms and the NADW-to-GNAIW switch, maintains the same effect on CO2.

2. Model Description

We employ the CYCLOPS biogeochemical box model [Keir, 1988] with the addition of (1) a dynamical lysocline [Sigman et al., 1998], (2) a subantarctic zone (SAZ) surface box [R. S. Robinson et al., 2005], and (3) a polar Antarctic zone (PAZ) box representing the surface between the Antarctic polar front and the continental margin [Sigman et al., 2009]. This model geometry allows for consideration of the different productivity changes observed in these component regions of the Southern Ocean [e.g., Mortlock et al., 1991; Frank et al., 2000; Kohfeld et al., 2005; Martinez-Garcia et al., 2009] and spatially separates upper and lower cell biogeochemical dynamics [Toggweiler, 1999; Marinov et al., 2006].

As noted above, we carry out “stratification” experiments by varying two aspects of the polar Antarctic. First, the rate of mixing between the polar Antarctic zone surface (PAZ box) and the circumpolar deep water (CDW box) below is varied between 0 and 0.1 Sv. Second, we vary the surface nutrient concentration in the PAZ from the standard value of 2 down to 0 pM of [PO4]. From the standard interglacial case, this effectively increases PAZ nutrient consumption, that is, the fraction of gross nutrient supply being utilized for export production.

To address apparent changes between interglacial and glacial hydrography, we construct a “glacial” circulation pattern characterized by (1) the formation of intermediate depth water in the North Atlantic (GNAIW circulation) (similar to the circulation schemes explored by Sigman et al. [2003]) and (2) upwelling of intermediate depth water rather then CDW into the open Antarctic surface (Figure 2).
More efficient nutrient consumption in the subantarctic zone of the Southern Ocean is simulated by a reduction of surface $[\text{PO}_4^{3-}]$ concentrations in our SAZ box from 1.2 $\mu$M in the reference to 0.7 $\mu$M, as adopted from R. S. Robinson et al. [2005]. This change is conducted in the context of both NADW- and GNAIW-circulation.

In CYCLOPS, the high-latitude surface boxes (all Southern Ocean boxes as well as the North Atlantic) are
assumed not to produce a CaCO3 rain [Keir, 1988]. For the export out of the low-latitude surface boxes, at a depth of 200 m, we follow the original CYCLOPS CaCO3/Corg rain ratio of 0.4 [Keir, 1988]. This value is higher than estimated from vertical ocean gradients [Sarmiento et al., 2002], data-driven model optimization [Kwon and Primeau, 2008] and than used in other box models [e.g., Toggweiler, 1999; Stephens and Keeling, 2000; Köhler et al., 2005; Peacock et al., 2006]. However, the high rain ratio of 0.4 in conjunction with our mid-depth CaCO3/Corg regeneration ratio of ~0.1 [Anderson and Sarmiento, 1994] (Figure 2) results in particulate rain to the deep boxes with a CaCO3/Corg ratio of 2, which broadly agrees with sediment trap data of the deep ocean [Klaas and Archer, 2002]. If one were to use the proposed export rain ratio of < 0.1 [Sarmiento et al., 2002; Kwon and Primeau, 2008] along with a mid-depth CaCO3/Corg regeneration ratio of ~0.1 [Anderson and Sarmiento, 1994] and a typical organic carbon regeneration profile [e.g., Berelson, 2001], then none of the CaCO3 sinking out of the surface ocean would reach the deep seabed, and the model’s ocean CaCO3 budget could not simulate observed conditions. Further, our choice of export rain ratio gives rise to 69 μM ocean average alkalinity regenerated from CaCO3 and thus a carbonate pump of terrestrial biosphere, the effect of higher ocean salinity ($\Delta pCO_2$=+15 ppm; $\Delta pCO_2$=+6.5 ppm) [Sigman and Boyle, 2000], and the reduction in ocean volume (+8 ppm) [Brovkin et al., 2007].

Finally, we conduct an experiment in which, rather than decreasing PAZ/deep water exchange, we reduce the CO2 air/sea gas-exchange rate of the PAZ box, as a simple way to assess the geochemical potential to reduce ice age atmospheric CO2 by increased sea ice cover [Stephens and Keeling, 2000]. This gas-exchange experiment, which is reported only in the context of the NADW circulation, allows for comparison with the CO2 effects of PAZ “stratification”. All of our experiments are summarized in Table 1.

The reference for our experiments below is the model’s representation of the present interglacial state of the ocean. This state is characterized by an atmospheric CO2 mixing ratio of 270.4 ppm (Figures 3a, 4a, 5a, and 6a show the deviation from this reference value). If gas exchange were infinite in this reference case, some deeply sequestered CO2 could evade, in particular from the PAZ, and atmospheric CO2 would be ~2 ppm higher (upper right corner in Figure 3b). Moreover, in all of our experiments, we isolate the CO2 effects of the soft-tissue pump, the carbonate pump (internal carbonate cycle) and whole ocean alkalinity (open system carbonate cycle) as well as their interaction. A brief description of the separation technique is in the online supporting information (Text S1).

3. Model Results

Before assessing plausible glacial parameter combinations, we describe the dominant dynamics that arise throughout our experiments (Figures 3, 4, 5, and 6), an exercise that also clarifies the separation of geochemical components used herein.

First, $P^*$, the fraction of ocean $[PO_4^{3-}]$ that is regenerated, describes the efficiency of the soft-tissue pump, either with respect to a given deep ocean ventilation pathway or the global ocean [Ito and Follows, 2005]. When the fraction of unutilized $[PO_4^{3-}]$ in the PAZ surface (i.e., $[PO_4^{3-}]_{PAZ}/[PO_4^{3-}]_{CDW}$) equals the 1-$P^*$ of CDW, the global ocean $P^*$ (and thus the global soft-tissue pump) becomes insensitive to the simulated changes in PAZ/CDW mixing (dashed line “P” in Figures 3 to 6).

Second, as PAZ/CDW mixing approaches zero, the PAZ is effectively not participating in ocean dynamics (i.e., it is not ventilating the ocean interior, Figure 7). Thus, the

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<th>Table 1. Summary of Model Experiments Conducted</th>
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1Auxiliary materials are available with the HTML. doi:10.1029/2010GB003790.
ocean carbon cycle and atmospheric CO₂ become insensitive to PAZ nutrient status (along the left edge of the panels in Figures 3, 4, 5, and 6). This is also true for complete sea ice cover of the PAZ (Figure S1).

[26] Third, in contrast to the soft-tissue pump (panels d and g in Figures 3, 4, 5, and 6), the carbonate pump (panel f) as represented by regenerated alkalinity from carbonate dissolution at depth (panel i) is primarily influenced by PAZ/CDW mixing, not PAZ nutrient status, because (1) export production in the PAZ is not associated with a CaCO₃ rain in our model, consistent with observations [Honjo, 2004], and (2) the ventilation of abyssal water in the PAZ is the most direct conduit through which regenerated alkalinity surfaces and takes up CO₂ from the atmosphere (i.e., transforms into preformed alkalinity). Thus, the ventilation of deep waters in the Southern Ocean represents an important leak in the global carbonate pump that, in contrast to the leak in the soft-tissue pump, lowers atmospheric CO₂ [cf. Broecker and Peng, 1989].

[27] Fourth, having isolated these two geochemical components, the soft-tissue and carbonate pumps, it becomes clear that whole ocean alkalinity amplifies their combined

Figure 3
CO₂ effect in a surprisingly simple way. To demonstrate this, we plot the whole ocean alkalinity component of simulated CO₂ change versus the sum of all other components (i.e., “closed system”) (Figure 8). All model runs within a given experiment fall onto a common trend, while each experiment occupies a unique region in the plot. The trends within each experiment are roughly linear, and their slope varies as a function of the background global ocean circulation (1/6 and 1/3 with the NADW- and GNAIW-associated circulation, respectively; Figure 8). Hence, the open system CaCO₃ cycle amplifies polar Antarctic-driven CO₂ changes by a factor 1.16 (NADW) or 1.32 (GNAIW). In detail, whole ocean alkalinity change amplifies each of the other major geochemical components: a more efficient soft-tissue pump, a sea ice–driven reduction in PAZ CO₂ evasion (i.e., the sea-air disequilibrium component; Figure 8, gray markers), and a stratification-strengthened carbonate pump (amplifying the effect of this component to raise CO₂). The stronger amplification of the PAZ-driven changes under the GNAIW circulation (i.e., the greater slope in Figure 8) results from the greater fraction of the deep ocean ventilated by the PAZ in the GNAIW case, so that the polar Antarctic exerts a stronger control on the GNAIW experiments in Figure 8 also results from the expanded volume of PAZ ventilation in the GNAIW case, which lends more CO₂ leverage to PAZ surface nutrient concentration.

[28] Fifth, the consistent offset toward greater whole ocean alkalinity–driven CO₂ drawdown in the experiments with GNAIW formation and/or subantarctic (SAZ) fertilization (Figure 8; vertical offset among experiments) is largely caused by “nutrient deepening” [Boyle, 1988a, 1988b], through two mechanisms: (1) respired carbon is focused at the depth of the lysocline, causing a dissolution event (i.e., transient lysocline shoaling), and (2) there is a decline in low-latitude productivity and thus CaCO₃ rain (Table 2), causing the steady state lysocline to deepen [Sigman et al., 1998]. In addition, specific to the NADW–to-GNAIW switch, the incursion of corrosive Indo-Pacific deep water into the Atlantic basin causes a dissolution event there [Emerson and Archer, 1992].

[29] Sixth, at the particular degree of PAZ nutrient consumption at which the opposing sensitivities of the soft-tissue pump and the carbonate pump exactly cancel one another, there is no change in the partitioning of CO₂ between the atmosphere and ocean as PAZ/CDW mixing and sea ice cover change (dashed line labeled “E/I” in Figures 3, 4, 5, and 6). At this degree of nutrient consumption, PAZ pCO₂(aq) must equal atmospheric CO₂, with CO₂ evasion (E) above and invasion (I) below. Along the E/I line, deep ocean [CO₃²⁻] can also not change, so lysocline depth and whole ocean alkalinity remain constant in the face of the changing strength of a PAZ barrier to air-sea CO₂ exchange (Figures 3e, 4e, 5e, and 6e). Below the E/I line, PAZ stratification and sea ice cover act to raise atmospheric CO₂.

### 3.1. PAZ Changes Under Interglacial Circulation

#### 3.1.1. PAZ Nutrient Drawdown

[30] In the context of the interglacial (NADW-based) circulation, a maximal drawdown of atmospheric CO₂ is achieved by an enhancement of nutrient consumption in the PAZ while keeping mixing at the interglacial control value of 20 Sv (following the right edge of the panels in Figure 3). This transforms the PAZ box from the least efficient end-member in terms of soft-tissue pump to being as efficient as the low-latitude surface ocean, leading to a strong increase in the fraction of regenerated nutrients in the ocean (Figure 3d) [Sigman and Haug, 2003; Ito and Follows, 2005; Marinov et al., 2008]. Moreover, the additional carbon released by respiration in the ocean interior decreases the carbonate ion concentration ([CO₃²⁻]), causing a dissolution event that increases whole ocean alkalinity (Figure 3e) until [CO₃²⁻] is restored and the alkalinity budget of the ocean comes back into balance [Sigman et al. 1998]. The net atmospheric CO₂ decline is 58 ppm (Figure 3a), dominated by the soft-tissue pump (ΔpCO₂ = −62 ppm; Figure 3d) and whole ocean alkalinity (ΔpCO₂ = −8 ppm; Figure 3e). The carbonate pump (Figures 3f and 3i) is not a factor in this scenario. At a
surface $[\text{PO}_4^{3-}]$ of $\sim 0.9 \ \mu\text{M}$, the PAZ switches from a region of $\text{CO}_2$ evasion to one of invasion (below “E/I” in Figure 3), which reverses the net $\text{CO}_2$ effect of air-sea gas-exchange limitation from $-2$ ppm $\text{CO}_2$ in the standard interglacial case to $+6$ ppm such that infinite gas exchange would have yielded an 8 ppm greater $\text{CO}_2$ drawdown (Figure 3b). Since the ocean becomes more alkaline, the sensitivity of atmospheric $\text{CO}_2$ to the stronger soft-tissue pump is lowered, leading to slightly higher $p\text{CO}_2$ (by $\sim +2$ ppm) than calculated from the isolated geochemical components: the “nonlinear $\text{CO}_2$ effect” (Figure 3c).

This scenario is nearly identical to the one explored by Marinov et al. [2006], and the $\text{CO}_2$ sensitivity to the soft-tissue pump that they derive with a GCM is startlingly similar to our box model derived estimate (compare our Figures 3d and 3g with their Figure 2a). A linear approximation of the $\text{CO}_2$ sensitivity to the soft-tissue pump at today’s ocean chemistry gives 13.3 ppm $\text{CO}_2$ drawdown per 0.1 $\mu\text{M}$ regenerated $[\text{PO}_4^{3-}]$ increase in good agreement with a GCM-based estimate [Marinov et al., 2008] when corrected for their different soft-tissue stoichiometry. However, underlying the above changes is a $\sim 6.4$ fold increase in PAZ productivity, which violates evidence for lower Antarctic export production during the glacial [Mortlock et al., 1991; Kumar et al., 1993; François et al., 1997; Frank et al., 2000; Kohfeld et al., 2005].

3.1.2. Reduced PAZ Deep Water Formation

Now we consider reduced exchange between the PAZ and CDW, which represents the “stratification” hypothesis, broadly framed [François et al., 1997]. We first assume that PAZ productivity decreases in step with gross nutrient input from CDW (i.e., a constant degree of nutrient consumption). Because CDW $[\text{PO}_4^{3-}]$ does not change as a result of decreasing CDW/PAZ exchange under these conditions, PAZ $[\text{PO}_4^{3-}]$ is also constant in this case (following the upper edge of the panels in Figure 3 from right to left). Atmospheric $p\text{CO}_2$ decreases by 36 ppm as surface-deep exchange approaches zero, the principle reason again being an increase in the global fraction of regenerated nutrients ($P^*$, $HAIN ET AL.: ATMOSPHERIC CO2 DURING THE LAST ICE AGE  GB4023

Figure 4. Model results for the polar Antarctic zone stratification experiment, conducted with glacial-like “GNAIW circulation” (see section 3.2; for description, see Figure 3). The fraction of regenerated nutrients, whole ocean and regenerated alkalinity concentration can be found in Figure S3. Note that the $\text{CO}_2$ change associated with (d) the soft-tissue pump, (e) whole ocean alkalinity, (f) carbonate pump, (c) nonlinear effect, and the productivity constraints (curves labeled 50% and 100%) are all relative to the interglacial reference (upper right corner in Figure 3).
Figure 3g), that is, a strengthening of the soft-tissue pump ($\Delta p_{CO_2} = -43$ ppm, Figure 3d). In contrast to the previous scenario, this CO2 drawdown is achieved by reducing the fraction of ocean volume that is ventilated by the PAZ, which is highly inefficient in terms of the soft-tissue pump, and it occurs despite declining PAZ productivity.

This decrease in deep ocean ventilation has a second, less broadly appreciated consequence: continued low-latitude rain and dissolution of calcium carbonate leads to a deep ocean buildup of regenerated alkalinity (Figure 3f). This corresponds to a strengthening of the carbonate pump, raising atmospheric CO2 ($\Delta p_{CO_2} = +10$ ppm; Figures 3i and 3f). The sequestration of alkalinity in the deep ocean, moreover, makes these waters less corrosive to CaCO3 rain, working against the influence of the strengthened soft-tissue pump, and thus curbs the dissolution-driven increase in whole ocean alkalinity ($\Delta p_{CO_2} = -5$ ppm) (Figures 3e and 3h).

3.1.3. Combined Reductions in PAZ Nutrients and Deep Water Formation

So far we have explored two scenarios, both achieving significant CO2 drawdown but conflicting with ice age observations. We now explore a third scenario: decreased PAZ productivity coupled with an even greater decrease in gross nutrient supply by PAZ/CDW exchange, leading to a drop in PAZ $[PO_4^{3-}]$ (i.e., higher nutrient consumption). Given an 85% decrease in PAZ/CDW exchange (to 3 Sv) and a simultaneous 50% decrease in PAZ productivity (curved line labeled “50%” in Figure 3a), corresponding to a ~50% decrease in PAZ $[PO_4^{3-}]$ concentration (to 1 $\mu$M), CO2 decreases by 36 ppm. Again, the soft-tissue pump dominates this CO2 change (~41 ppm), but in this case because of a combination of the PAZ becoming more efficient and less volumetrically important. As in the previous “stratification-only” scenario, the reduction of PAZ/CDW exchange prevents deep ocean regenerated alkalinity to come into contact with the atmosphere, a strengthening of the carbonate pump (+7 ppm). Again, the CO2 effect of both...
soft-tissue and carbonate pump are being amplified (factor 7/6; Figure 8) by transient lysocline adjustments causing whole ocean alkalinity change (~5 ppm). Even for complete [PO₄³⁻] consumption at constant PAZ productivity, the atmospheric CO₂ decrease reaches only 44 ppm (Figure 3a).

3.1.4. PAZ CO₂ Gas-Exchange Reduction by Sea Ice Cover

[36] If the effective gas-exchange rate in the PAZ is reduced as a simple way to simulate the reduction in CO₂ due to sea ice expansion, the resulting decrease in atmospheric pCO₂ is essentially identical to a reduction in PAZ overturning (Figure S2a), reaching the maximal CO₂ effect of a complete cessation of deep ocean ventilation through the PAZ surface (i.e., no exchange between PAZ and CDW; [Archer et al., 2003]). It follows that no combination of sea ice and stratification can exceed this maximal CO₂ drawdown of 36 ppm associated with PAZ barrier mechanisms [Stephens and Keeling, 2000] (Text S2); their CO₂ effects are not additive but rather compete for this finite CO₂ drawdown potential. In subsequent experiments, sea ice is not explicitly simulated, but the potential of complete sea ice cover to further lower CO₂ can be assessed from the pCO₂ difference between a given scenario and complete stratification (0 Sv PAZ/CDW exchange).

[37] The most important difference between PAZ stratification and sea ice–driven gas-exchange reduction involves the supply of nutrients to the surface ocean: only stratification decreases gross nutrient supply. As a result, a further decrease in CO₂ in the sea ice cover simulation due to greater surface nutrient drawdown would require an increase of PAZ productivity (gray shading in Figure S2a), which appears inconsistent with observations.

3.2. PAZ Changes Under Glacial Circulation

[38] The glacial circulation characterized by the formation of intermediate depth waters in the North Atlantic (GNAIW) leaves the deep ocean less well ventilated and thus prone to accumulation of both respired CO₂ and regenerated alkalinity. Also, interbasin (i.e., Atlantic-to-Indo-Pacific) gradients in the deep ocean set up by the ocean conveyor are relaxed. To assess the role of GNAIW formation and its relationship with the Antarctic stratification hypothesis, we focus our attention on (1) the NADW-to-GNAIW switch in isolation and (2) NADW-to-GNAIW switch...
coupled to PAZ stratification and enhanced nutrient drawdown (3 Sv, 1 μM).

Two opposing dynamics affect the soft-tissue pump in our GNAIW simulation. First, the abdication of the deep ocean by the North Atlantic leaves this voluminous body of water dominated by PAZ ventilation (Figure 7b) with the associated 2 μM burden of preformed [PO₄³⁻], lowering the efficiency of the soft-tissue pump. Second, sequestration of nutrients in the isolated deep ocean depletes the mid-depth ocean (“nutrient deepening”, [Boyle, 1988a, 1988b]), decreasing the burden of preformed [PO₄³⁻] content of GNAIW by 50%, to 0.26 μM. In the absence of PAZ stratification, the first effect dominates, so that the soft-tissue pump works to raise CO₂ by 35 ppm (Figure 4d).

The switch from NADW to GNAIW drives a transient dissolution event, primarily by allowing the higher-respired CO₂, more corrosive deep Indo-Pacific water to flood the deep North Atlantic [Emerson and Archer, 1992] but also by allowing respired CO₂ more time to accumulate in the deep ocean before being brought up to the surface [Boyle, 1988a, 1988b]. Moreover, nutrient deepening starves low-latitude productivity, which decreases the CaCO₃ rain, raising whole ocean alkalinity through a deepening of the steady state lysoclone [Sigman et al., 1998]. As a result, whole ocean alkalinity rises so as to lower CO₂ (−14 ppm, Figure 4e), countering the weaker soft-tissue pump. The carbonate pump strength is roughly unchanged upon the switch from NADW to GNAIW (−1 ppm; Figure 4f), because of opposition between (1) reduced CaCO₃ rain onto the deep seafloor and (2) more time for regenerated alkalinity to accumulate in the deep ocean before being brought up to the surface. In net, the GNAIW switch by itself raises CO₂ by 16 ppm (Figures 4a and 9).

The above result suggests that GNAIW raises CO₂. But this is not the case in the context of the proposed Antarctic changes. If PAZ/CDW exchange is reduced to 3 Sv (−85%) and PAZ nutrient levels are decreased by 50% (to 1 μM [PO₄³⁻]), both the volumetric importance and the preformed nutrient content of PAZ ventilated water decrease (Figure 7b), making the soft-tissue pump more efficient (−43 ppm instead of +35 ppm without PAZ stratification and nutrient drawdown; Figure 4d). However, this closing of the Southern Ocean leak of the biological pump also strengthens the carbonate pump by accumulating regenerated alkalinity in the deep ocean, raising CO₂ (+22 ppm, Figures 4f and 9b). The effect of the strengthened soft-tissue pump on deep ocean carbonate saturation, although partially offset by the stronger carbonate pump, makes the abyssal water more corrosive, and

Figure 7. Simulated water masses and ventilation of the deep Atlantic box (>1500 m) for the (a) NADW–associated and (b) GNAIW–associated circulation. Ventilation is determined by two tracers set to 100% in the PAZ and North Atlantic (boreal) surface boxes, respectively, which are restored to zero in all other surface boxes. Water masses are determined by two tracers set to 100% in the northern component water box (NCW) and the circumpolar deep water (CDW) boxes, respectively, which are restored to zero in all surface boxes and the CDW/NCW box accordingly. Since there is no advective path in Figure 7b by which North Atlantic–sourced or North Atlantic–ventilated water reaches the deep Atlantic, it has been entirely mixed down from intermediate depth. In Figure 7b, the volume of North Atlantic–ventilated water in the deep Atlantic is greater than that of GNAIW–tagged water. This indicates that GNAIW–derived water enters the deep Southern Ocean without being ventilated in the Antarctic surface, after which it flows into the deep Atlantic box from the south. In the real ocean, GNAIW may have been entrained into the newly formed Antarctic–ventilated deep water as it sinks to the abyss along the Antarctic margin. This poorly studied process is a potentially important mechanism by which deep waters with low preformed nutrients might fill the deep ocean during glacial times, lowering CO₂ in the process [Sigman et al., 2010].
carbonate compensation raises ocean alkalinity, further lowering CO$_2$ ($\sim$28 ppm, 15 ppm more drawdown than with GNAIW alone). Hence, GNAIW in conjunction with the Antarctic mechanisms lowers CO$_2$ by 48 ppm relative to the interglacial reference. This is greater than the 36 ppm CO$_2$ drawdown achieved by Antarctic stratification and greater nutrient consumption in the context of the NADW circulation (Figure 9a).

[42] Thus, the CO$_2$ impact of GNAIW depends critically on the status of the Antarctic. In isolation, it raises CO$_2$ by 16 ppm. However, when combined with the Antarctic stratification, it enhances the CO$_2$ drawdown by 12.9 ppm, a 28.7 ppm difference in net effect (Figure 9a). In this combined North Atlantic and Antarctic scenario, PAZ productivity is 40% lower than in the interglacial reference and thus satisfies the paleoproductivity evidence (Table 2).

[43] One conceptually important symptom of the CO$_2$ interaction between PAZ conditions and the NADW-to-GNAIW switch is that it has a profound effect on the CO$_2$ leverage of PAZ surface [PO$_4$] change in the context of PAZ stratification. With NADW, the cases of 2 and 0 $\mu$M [PO$_4$] in a PAZ surface with 3 Sv of overturning yield CO$_2$ levels that are 28 and 44 ppm lower than the interglacial case, respectively, a 16 ppm difference (Figure 3a). With GNAIW, the CO$_2$ reductions are 23 and 67 ppm, a 44 ppm difference (Figure 4a). This suggests that evidence for high degrees of LGM nutrient consumption in the PAZ surface are important for explaining the full amplitude of LGM CO$_2$ drawdown [Robinson and Sigman, 2008], a conclusion that might not have been reached if simulations were conducted with an NADW background circulation.

3.3. Glacial Subantarctic Nutrient Consumption

[44] Data and concepts support the hypothesis of higher degrees of nutrient consumption in the ice age sub-Antarctic as a result of natural iron fertilization [e.g., Watson et al. 2000; R. S. Robinson et al., 2005; Kohfeld et al., 2005; Martinez-Garcia et al., 2009]. In our model, there are three mechanisms by which this would lower CO$_2$: (1) less pre-formed nutrients are fed from the sub-Antarctic into the mid-depth global ocean, increasing the efficiency of the soft-tissue pump; (2) lower nutrient concentration at mid-depth reduces low-latitude productivity and thus the CaCO$_3$ rain into the ocean interior, weakening the carbonate pump; and (3) the weaker carbonate pump and the stronger soft-tissue pump, as well as the reduced calcium carbonate rain in itself [Keir, 1988; Sigman et al., 1998; Matsumoto and Sarmiento, 2008; Loubere et al., 2004], would cause lysocline adjustments that render the whole ocean more alkaline (Figures 8 and 9b).

[45] Applying the subantarctic forcing in the absence of PAZ stratification (i.e., PAZ: 20 Sv, 2 $\mu$M), CO$_2$ is drawn down by 39 ppm (SAZ only in Figure 8a). The soft-tissue pump ($\sim$27 ppm, Figure 6d) and the whole ocean alkalinity effect ($\sim$17 ppm, Figure 6e) dominate, and the magnitude of CO$_2$ change is similar to previous estimates [Watson et al., 2000; R. S. Robinson et al., 2005; Brovkin et al., 2007].

[46] In the context of NADW, the subantarctic nutrient drawdown acting alongside a stratified and lower-nutrient PAZ decreases atmospheric CO$_2$ by 35 ppm (Figure 5a) in addition to the 36 ppm drawdown achieved by the Antarctic mechanisms alone (Figure 3a). Net CO$_2$ interactions with PAZ changes and the NADW-to-GNAIW switch are minor although partitioned differently between the geochemical components (Table 2): in the context of GNAIW, the drawdown is 38 ppm (in addition to 48 ppm; Figure 4a). Thus, the subantarctic mechanism robustly lowers CO$_2$ by 35 to 40 ppm, irrespective of both GNAIW and Antarctic changes. However, this CO$_2$ decrease is reduced and a CO$_2$-reducing SAZ/GNAIW interaction arises when subantarctic CaCO$_3$ rain is included (Table S1 and Figure S1). Despite this caveat, the combination of the Antarctic mechanisms, GNAIW and the fertilized sub-Antarctic, in both rain ratio schemes, lowers CO$_2$ by the full amplitude of glacial/interglacial CO$_2$ variability (Figures 9 and S1). PAZ productivity in this scenario is 30% reduced, still in apparent agreement with the paleoproductivity proxies (Table 2).

4. Discussion

4.1. Mechanisms and Their Interactions

[47] Multiple Antarctic changes (nutrient status [e.g., Sarmiento and Toggweiler, 1984], stratification [Toggweiler, 1999] and sea ice cover [Stephens and Keeling, 2000]) have been studied with box models to understand their potential to explain low ice age CO$_2$. But how would these hypothesized changes interact with each
### Table 2. Key Model Output for Selected Model Runs\(^a\)

<table>
<thead>
<tr>
<th>PAZ Forcing: Mixing/Phosphate (Sv/μM)</th>
<th>CO(_2) Change</th>
<th></th>
<th>O(_2) Utilization(^b)</th>
<th>Deep [CO(_3)(^2)](^{−}) Lysocline</th>
<th>Ventilation Region</th>
<th>Productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta pCO_2) (ppm)</td>
<td>(\Delta ST) (ppm)</td>
<td>(\Delta CP) (ppm)</td>
<td>(\Delta WOA) (ppm)</td>
<td>(\Delta AS^{d}) (ppm)</td>
<td>(\Delta NLE^{e}) (ppm)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
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<td>35.4</td>
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<td>-17</td>
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<td>-6.4</td>
<td>-31.8</td>
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<td>-1.1</td>
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<td>-21.5</td>
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<td>4.6</td>
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</table>

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\(^a\)The first (20/2; NADW) and the last experiment (3/1; GNAIW+SAZ) represent the interglacial reference and our best guess LGM scenario, respectively. A square marker in Figures 3 to 6 highlights the model runs shown here.

\(^b\)Volumetrically averaged.

\(^c\)Arithmetic mean for boxes with lysocline.

\(^d\)Absolute export relative to reference.

\(^e\)ΔAS, contribution from finite air-sea exchange, deviation from reference value (−2.7 ppm).

\(^f\)ΔNLE, contribution of nonlinear effect to simulated CO\(_2\) change.
other and with other (e.g., North Atlantic) changes? Can we simply add up their CO2 effects?

As already pointed out by Archer et al. [2003], Antarctic sea ice and stratification are equivalent in their CO2 effect, which stems from their role as a barrier to CO2 evasion to the atmosphere, and thus they compete for a limited potential CO2 reduction. In comparison, a change in Antarctic nutrient status in isolation has a greater maximum capacity to lower atmospheric CO2 than either of the barrier mechanisms, partly because it can cause a greater decrease in the preformed nutrient concentration of the ocean interior and partly because its strengthening of the soft-tissue pump is not countered by strengthening of the carbonate pump. Greater Antarctic nutrient consumption can work with the barrier mechanisms to lower atmospheric CO2. However, because Antarctic nutrient status affects Antarctic surface water pCO2, the CO2 drawdown capacity of the barrier mechanisms is usurped by an increase in Antarctic nutrient consumption, and vice versa. This highly nonlinear interaction limits the combined CO2 drawdown in our simulations to ≤ 36 ppm, if ice age Antarctic productivity is not allowed to be higher than today. For illustration and to excuse our implicit treatment of the sea ice mechanism, if we add complete polar Antarctic sea ice cover to our full LGM scenario, only 3 ppm of additional CO2 decline ensues (to a total of 89 ppm; compare to Figure 6). This does not discount the sea ice mechanism, which is very potent in isolation [e.g., Stephens and Keeling, 2000] and able to drive the entire Antarctic contribution to CO2 reduction (i.e., ~ 36 ppm) when areal coverage is near complete. Rather, this example highlights the importance of interactions among the Antarctic mechanisms.

One reason that the Antarctic “barrier” mechanisms lower atmospheric CO2 much less in our simulations than in previous studies [Toggweiler, 1999; Stephens and Keeling, 2000] is that both mechanisms sequester in the deep ocean not only respired CO2 but also alkalinity from the dissolution of the CaCO3 rain (see Text S2). In this way, the
barrier mechanisms strengthen the carbonate pump along with the soft-tissue pump, and the former counters the atmospheric CO₂ decline driven by the latter (Figure 9b). The concentration of regenerated alkalinity in our interglacial reference case (69 µM) matches the estimated global average of ∼70 µM [Sabine et al. 2002; Feely et al., 2002; Chung et al., 2003], suggesting that our experiments are capturing an appropriate response strength for the carbonate pump. In contrast, Toggweiler [1999], by using the same regeneration profile for both CaCO₃ and organic carbon rain, and Stephens and Keeling [2000], having 35 µM regenerated alkalinity in their interglacial reference, do not adequately account for this effect and its amplification by whole ocean alkalinity (Figure 8 and Text S2). Hence, these studies circumvent the adverse effects of a carbonate pump strengthening and probably overestimate the potential for stratification or sea ice cover alone to draw down atmospheric CO₂.

[50] A weakness specific to Antarctic stratification is that it drastically reduces the fraction of the ocean ventilated through the Southern Ocean surface, at least in the context of box models (Figure 7 and Table 2). Although this makes the soft-tissue pump more effective and reduces Antarctic productivity as required by observations, it seems at odds with reconstructions of the main water masses of the glacial ocean, in particular in the Atlantic where southern sourced “AABW” dominated the basin below 2–2.5 km depth [e.g., Rutherg et al., 2000; Marchitto et al., 2002; Curry and Oppo, 2005; Galbraith et al., 2007; Lea and Boyle, 1990]. The shift in deep ocean ventilation from partially Antarctic sourced to almost entirely non-Antarctic sourced is arguably the “dark secret” of many present box model experiments lowering CO₂ by a reduction in Antarctic overturning [e.g., Toggweiler, 1999; Peacock et al., 2006].

[51] The ice age shoaling of North Atlantic overturning (i.e., the switch from NADW to GNAIW) has the potential to resolve this problem. The “GNAIW circulation” we employ to simulate peak glacial conditions increases the deep Atlantic volume ventilated by the PAZ ~4-fold relative to the “NADW circulation” stratification experiments. Under GNAIW conditions, even if the Antarctic is stratified (3 Sv), it still ventilates almost twice as much of the deep Atlantic as in the interglacial reference case (Figure 7). Moreover, if one traces northward and southward penetrating water rather than actual ventilation from specific polar surface boxes, the change from NADW to GNAIW mimics the observed dominance of “AABW” in the deep Atlantic (Figure 7). Nevertheless, we want to caution that entrainment of low preformed nutrient mid-depth water into the deep ocean does occur in our model, strengthening the soft-tissue pump. Along these lines, we want to stress that it is of great importance to develop approaches to distinguish between southern sourced and southern ventilated water, which become distinct with the onset of Antarctic stratification (Figure 7). An appropriate carbon isotope depth gradient arising in our full glacial simulation (Table 2) suggests that δ¹³C observations in the LGM Atlantic [e.g., Curry and Oppo, 2005] may be interpreted as the result of “aging” rather then a difference in ventilation region.

[52] The second important set of CO₂ interactions that we document arises between GNAIW and the Antarctic mechanisms. We find that GNAIW obstructs the model’s capacity to achieve the full glacial drawdown unless Antarctic changes, in particular enhanced nutrient drawdown, are considered as well. Previous studies that simulate stratification [e.g., Toggweiler, 1999; Peacock et al., 2006] do not encounter the need for lower preformed nutrient content of glacial deep water ventilated in the Antarctic because they lower global preformed nutrient concentration by unrealistically shifting the direct ventilation of the abyss to the North Atlantic (see above). On the other hand, studies that simulate an appropriate change in Atlantic hydrography have come to the variable conclusion that GNAIW lowers [Brovkin et al., 2007] or raises CO₂ [Marinov et al., 2008]. We believe that this disagreement is a symptom of the interaction between GNAIW and the Antarctic mechanisms described herein: While Marinov et al. [2008] consider GNAIW in isolation, the Brovkin et al. [2007] study is characterized by an efficient Antarctic barrier for CO₂ (in their case sea ice rather than stratification).

[53] In contrast to GNAIW and the Antarctic mechanisms, nutrient drawdown in the subantarctic zone (SAZ) yields no net interaction with the other oceanographic drivers, contributing a CO₂ drawdown of 35 to 40 ppm. If we assume that the sub-Antarctic does produce and export CaCO₃ (not the standard case assumption), the CO₂ effect of subantarctic nutrient drawdown decreases, while an offsetting interaction with the NADW-to-GNAIW switch emerges (Table S1 and Figure S1). Because we suspect that increased nutrient drawdown would have increased CaCO₃ rain there and because CYCLOPS may overestimate the ocean volume ventilated by the glacial sub-Antarctic, we choose to think of our subantarctic CO₂ effect estimate as a upper bound. Overall, our simulations suggest that all mechanisms, including their interactions, are required to explain the lowest ice age CO₂ levels in a manner consistent with available oceanographic constraints.

4.2. Timing and pCO₂ During the Glacial

[54] The decline in atmospheric CO₂ during the progression of the last glacial cycle was apparently punctuated rather than gradual (Figure 1) [e.g., Ahn and Brook, 2008; Petit et al., 1999; Peacock et al., 2006]. In the spirit of Peacock et al. [2006], we propose a sequence of oceanographic changes that explains the first-order temporal pattern of CO₂ over the last glacial cycle without violating proxy evidence. The sudden drop in atmospheric CO₂ at the MIS 5e/d transition that is coincident with Antarctic cooling as recorded by ice core δD (~−40 ppm; Figure 1) may have been related to the onset of polar Antarctic stratification without the necessity for unsupported major changes in North Atlantic deep water formation at that time (~−36 ppm; Figure 9), accompanied by some ocean cooling. The modeled CO₂ drawdown for stratification with an interglacial circulation is based almost entirely on a more efficient soft-tissue pump that may respond quickly to the onset of stratification.

[55] The second major shift in atmospheric CO₂ at the MIS 4/5 transition (~−35 ppm) [Petit et al., 1999; Ahn and
CO2 by two changes acting along a stratified Antarctic to draw down among the mechanisms. From which to assess the importance of the interactions, we establish a basis (Figure 1) 

NADW formation may also have occurred during MIS 3, our interpretation is that we might have expected the occurrence with the Antarctic mechanisms lowers CO2 by 36 ppm, and increased nutrient consumption – stratification and sea ice which may explain the slightly higher but also variable so did the proposed iron fertilization [61] Taking a step back, a general insight gained, central is, the volume of the ocean ventilated through a given surface region: In any model, atmospheric CO2 is essentially set by the pCO2 of surface waters weighted by their ventilation volume. Along these lines, our model is successful in reaching the lowest ice age CO2 levels only because it implicitly allows for the entrainment of mid-depth, subantarctic- and North Atlantic–ventilated water into the abyss; this is also the case in previous studies [e.g., Toggweiler, 1999; Köhler et al., 2005; Peacock et al., 2006]. Concerned about the physical oceanographic meaning of this solution, we suggest that resolving entrainment processes in the ocean interior, in particular along the Antarctic margin, is of central importance for the simulation of ice age CO2 cycles.

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