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Glacial – interglacial atmospheric CO₂ change: a possible "standing volume" effect on deep-ocean carbon sequestration

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Standing volume role in CO₂ change

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Discussions

L. C. Skinner





Abstract

So far, the exploration of possible mechanisms for glacial atmospheric CO_2 draw-down and marine carbon sequestration has focussed almost exclusively on dynamic or kinetic processes (i.e. variable mixing-, equilibration- or export rates). Here an attempt

- ⁵ is made to underline instead the possible importance of changes in the standing volumes of intra-oceanic carbon reservoirs (i.e. different water-masses) in setting the total marine carbon inventory. By way of illustration, a simple mechanism is proposed for enhancing the carbon storage capacity of the deep sea, which operates via an increase in the volume of relatively carbon-enriched AABW-like deep-water filling the ocean
- ¹⁰ basins. Given the hypsometry of the ocean floor and an active biological pump, the water-mass that fills more than the bottom 3 km of the ocean will essentially determine the carbon content of the marine reservoir. A set of simple box-model experiments confirm the expectation that a deep sea dominated by AABW-like deep-water holds more CO₂, prior to any additional changes in ocean overturning rate, biological export
- or ocean-atmosphere exchange. The magnitude of this "standing volume effect" might be as large as the contributions that have been attributed to carbonate compensation, the thermodynamic solubility pump or the biological pump for example. If incorporated into the list of factors that have contributed to marine carbon sequestration during past glaciations, this standing volume mechanism may help to reduce the amount of glacial
- interglacial CO₂ change that remains to be explained by other mechanisms that are difficult to assess in the geological archive, such as reduced mass transport or mixing rates in particular. This in turn could help narrow the search for forcing conditions capable of pushing the global carbon cycle between glacial and interglacial modes.

1 Explaining glacial – interglacial CO₂ change

²⁵ Although it is clear that changes in atmospheric CO_2 have remained tightly coupled with global climate change throughout the past ~730 000 years at least (Siegenthaler et al.,



2005), the mechanisms responsible for pacing and moderating CO₂ change remain to be proven. The magnitude of the marine carbon reservoir, and its inevitable response to changes in atmospheric CO₂ (Broecker, 1982a), guarantees a significant role for the ocean in glacial – interglacial CO₂ change. Based on thermodynamic considerations,
⁵ glacial atmospheric CO₂ would be reduced by ~30 ppm simply due to the increased solubility of CO₂ in a colder glacial ocean (Sigman and Boyle, 2000); however this reduction would be counteracted by the reduced solubility of CO₂ in a more saline glacial ocean and by a large reduction in the terrestrial biosphere under glacial conditions (Broecker and Peng, 1989; Sigman and Boyle, 2000). The bulk of the glacial – inter¹⁰ glacial CO₂ change therefore remains to be explained by more complex inter-reservoir exchange mechanisms, and the most viable proposals involve either the biological-or the physical "carbon pumps" of the ocean. On this basis, any mechanism that is invoked to explain glacial – interglacial CO₂ change marine reservoir (Broecker, 1982a; Boyle, 1988b,

¹⁵ 1992; Broecker and Peng, 1989).

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To date, three main types of conceptual model have been advanced in order to explain glacial – interglacial atmospheric CO_2 change: 1) those involving an increase in the export of organic carbon to the deep sea, either via increased nutrient availability at low latitudes or via increased efficiency of nutrient usage at high latitudes (Broecker, 1982a; Broecker, 1982b; Knox and McElroy, 1984); 2) those involving a reduction in the "ventilation" of water exported to the deep Southern Ocean (Siegen-

- thaler and Wenk, 1984; Toggweiler and Sarmiento, 1985), either via sea-ice "capping" (Keeling and Stephens, 2001) or a change in the surface-to-deep mixing rate/efficiency (Toggweiler, 1999; Gildor and Tziperman, 2001; Watson and Naveira Garabato, 2006);
- and 3) those involving changes in whole ocean chemistry and "carbonate compensation", possibly promoted by changes in the ratio of organic carbon and carbonate fluxes to the deep sea (Archer and Maier-Reimer, 1994). Each of these conceptual models has its own set of difficulties in explaining the pattern and magnitude of past glacial – interglacial CO₂ change, and in fact none is likely to have operated in complete isola-



tion (Archer et al., 2000; Sigman and Boyle, 2000). Nevertheless, one aspect of all of the proposed models that emerges as being fundamental to any mechanism proposing to explain glacial – interglacial CO₂ change is the balance between biological carbon export from the surface-ocean and the return of carbon to the surface by the ocean's
 ⁵ overturning circulation. These two processes, one biological and one physical, essentially determine the balance of carbon input to and output from (and therefore the carbon content of) the deepest marine reservoirs (Toggweiler et al., 2003).

The regions of deep-water formation in the North Atlantic and especially in the Southern Ocean play a key role in setting the "physical side" of this balance, with which this study is primarily concerned. In the North Atlantic, carbon uptake via the "solubility pump" is enhanced by the large temperature change that surface water must undergo before being exported into the ocean interior. The formation of North Atlantic deepwater therefore represents an efficient mechanism for mixing CO₂ deep into the ocean interior (Sabine et al., 2004); though only to the extent that it is not completely com-

- pensated for (or indeed over-compensated for) by the eventual return flow of more carbon-enriched deep-water back to the surface (Toggweiler et al., 2003). Arguably, it is in controlling the extent to which the return flow of deep-water to the surface (which occurs primarily in the Southern Ocean) represents an effective "reflux" of carbon to the atmosphere, acting against biological export, that the formation of deep-water in
- ²⁰ the Southern Ocean plays a pivotal role in controlling the partitioning of CO_2 between the surface- and the deep ocean. We might say that if the southern overturning loop "leaks" too much, it will be an efficient carbon source to the atmosphere (Toggweiler et al., 2003); and if it does not leak much, it will simply become a large standing carbon reservoir. The degree to which the southern overturning loop "leaks" depends on
- the efficiency of equilibration of up-welled Southern Ocean deep-water with the atmosphere, relative to the efficiency of carbon export (dissolved and particulate) from the surface Southern Ocean (Toggweiler, 1999; Gildor and Tziperman, 2001).

Today, a significant portion of the deep ocean (although not the deep Atlantic – "deep" meaning greater than \sim 1 km in this context) is filled from the Southern Ocean



by Circumpolar Deep Water (CDW) that is exported northwards into the various ocean basins from the eastward circulating Antarctic Circumpolar Current (ACC) (Orsi et al., 1999). This deep-water remains relatively poorly equilibrated with the atmosphere and is inefficiently stripped of its nutrients, thus maintaining an elevated "pre-formed" carbon

- ⁵ content. In part this is because the rate of ocean atmosphere CO₂ exchange cannot keep up with the rate of overturning in the uppermost Southern Ocean (Bard, 1988); however it is primarily because the bulk of southern sourced deep- and bottom-water is either produced via a combination of brine rejection below sea-ice and entrainment from the sub-surface, or converted from "aged" northern-sourced deep-waters that are
- ¹⁰ up-welled in the Southern Ocean (Orsi et al., 1999; Speer et al., 2000; Webb and Suginohara, 2001). Intense turbulent mixing around topographic features in the deep Southern Ocean helps to enhance the amount of "carbon rich" sub-surface water that is incorporated into the CDW (from above and from below), and subsequently exported northwards to the Atlantic and Indo-Pacific (Orsi et al., 1999; Naviera Garabato et al.,
- ¹⁵ 2004). The process of Circumpolar Deep Water export in the deep Southern Ocean (as distinct from that in the North Atlantic, and the vertical mixing in the uppermost Southern Ocean) might therefore be viewed as a mechanism that helps to "recycle" carbonrich water within the ocean interior, circumventing ocean atmosphere exchange, and eventual CO₂ leakage to the atmosphere.
- It is notable that nearly all of the "physical pump" mechanisms that have been proposed as significant controls on glacial interglacial CO₂ change have referred to dynamical (water flow- or mixing *rate*) or kinetic (ocean atmosphere exchange *rate*) effects (Toggweiler, 1999; Tziperman and Gildor, 2003; Kohler et al., 2005). Consideration of the effect on atmospheric CO₂ of changes in the geometry, and there-
- fore the volumes, of different intra-oceanic carbon reservoirs (i.e. different deep-water "masses") has largely escaped explicit treatment. This is surprising, given that the residence time of a reservoir will scale inversely to its renewal rate or positively to its volume. It is also surprising from an "experimental" perspective, given that most of the palaeoceanographic evidence available to us can tell us something about changes in

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water-mass distribution (hence volume), but usually cannot tell us much about changes in circulation or mixing rates. Furthermore, if we consider what controls the energy and buoyancy budgets of the ocean (and hence the capacity to maintain an overturning circulation), it is not obvious that the net overturning *rate* of the ocean must have been significantly different from modern over long time periods in the past (Gordon, 1996; Wunsch, 2003) – even if it is true that the reconstructed hydrography of the glacial

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Wunsch, 2003) – even if it is true that the reconstructed hydrography of the glacial ocean is inconsistent with the modern circulation (especially in terms of vertical property distributions) (Marchal and Curry, 2008). The circulation rate (mass transport) of the glacial ocean therefore remains poorly constrained, despite well-defined property distribution (hence budgetary) changes.

The purpose of the present study is to focus attention on the importance of distinguishing between past changes in the distribution of water-masses (which we can know something about) and past changes in their renewal rates (which we tend to know very little about), in particular when considering the role of the ocean circulation ¹⁵ in setting the marine carbon inventory. By way of illustration, the simple hypothesis is advanced that changes in the *volumes* of different glacial deep-water masses, prior to their overturning or mixing *rates* (and prior to any major changes in the biological pump

can be "bottled up" in the deep ocean. Of course, the suggestion is not that changes in circulation rate are unimportant; but rather that they are not exclusively important.

or pre-formed water-mass chemistry) may significantly affect the amount of carbon that

- The distinction between these two aspects of the ocean circulation (i.e. water-mass distribution *versus* overturning rate), and the evaluation of their individual impacts on atmospheric CO_2 , could prove to be important in assessing the mechanisms of glacial interglacial CO_2 change, in particular if it is possible for these two aspects of the
- ²⁵ ocean circulation to become decoupled, for example on long time-scales or for specific forcing. Put another way: if the mechanisms or time-scales required to alter the marine carbon inventory via changes in overturning rates and water-mass volumes differ, then they cannot be usefully conflated in the single term "ocean circulation" when considering the causes of glacial – interglacial CO₂ change.



In this paper additional emphasis is placed on how the hypsometry of the ocean basins (the area distribution at different water depths) may affect the efficiency of volumetric water-mass changes that are caused by the vertical shoaling/deepening of water-mass mixing boundaries. A notable fact in this regard is that ~56% of the seafloor lies between 6000 and 3000 m (Menard and Smith, 1966), thus accounting for a majority increment in the ocean's volume. If a water mass that once occupied the >5 km interval in the Atlantic comes to occupy the >2 km interval, it will have increased its volume in this basin almost four-fold.

2 A thought experiment: a "southern flavour ocean"

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- ¹⁰ Arguably, one of the least ambiguous aspects of the palaeoclimate archive is the record of glacial – interglacial change in δ^{13} C recorded by benthic foraminifera from the Atlantic Ocean (Duplessy et al., 1988; Curry and Oppo, 2005). The data suggest a very positive δ^{13} C of DIC in the upper ~2 km of the Atlantic, and a very negative δ^{13} C of DIC below this in the deepest Atlantic. These data do not appear to be consistent ¹⁵ with the modern circulation (Marchal and Curry, 2008). The most widespread and wellsupported interpretation of these data is that they represent a redistribution of glacial northern – and southern sourced deep- and intermediate water-masses, including in particular an incursion of glacial southern-sourced deep-water (rich in pre-formed and re-mineralised nutrients, and hence low δ^{13} C) into the deep North Atlantic, up to a wa-²⁰ ter depth of ~2–3 km (Curry et al., 1988; Duplessy et al., 1988; Oppo and Fairbanks,
- 1990; Oppo et al., 1990; Boyle, 1992; Hodell et al., 2003; Curry and Oppo, 2005). This interpretation is now strongly supported by glacial Atlantic benthic foraminiferal Cd/Ca, Zn/Ca and B/Ca ratios (Boyle, 1992; Keigwin and Lehmann, 1994; Marchitto et al., 2002; Marchitto and Broecker, 2005; Yu and Elderfield, 2007). Auxiliary support has
- ²⁵ been provided by benthic radiocarbon measurements from the North Atlantic (Keigwin, 2004; Skinner and Shackleton, 2004; Robinson et al., 2005), and neodymium isotope measurements (ε_{Nd}) from the Southern Ocean (Rutberg et al., 2000; Piotrowski et



al., 2004; Piotrowski et al., 2005). An elegant box-model investigation of the possible causes of glacial deep-ocean chemistry (Michel et al., 1995) and coupled atmosphere – ocean general circulation model (AOGCM) simulations of the "last glacial maximum" circulation (e.g. Kim et al., 2003; Shin et al., 2003) have also added weight to this interpretation of glacial deep-water mass geometry. If we assume that the relationships between deep-water radiocarbon activity, carbonate ion concentration, δ^{13} C of DIC and TCO_2 remained similar between glacial and interglacial (pre-industrial) times, at least for deep-water formed in the Southern Ocean, then we may also infer that the water that apparently replaced NADW in the Atlantic and dominated CDW export to the Indo-Pacific basins was also of relatively high TCO_2 .

Given this one apparently robust constraint on the deep-water hydrography near the height of the last glaciation (Lynch-Steiglitz et al., 2007), one question immediately arises: how much must the *volume* of southern-sourced deep-water have increased, regardless of its export *rate*, in order to accomplish the observed change (i.e. filling

- the deep Atlantic, and dominating the deep-water export to the Indian and Pacific basins)? Further, and more importantly, what would have been the immediate effect on deep-water CO₂ sequestration, if any? Answering the first question is straightforward enough: as noted above, based on the hypsometry of the Atlantic basin (Menard and Smith, 1966), raising the upper boundary of southern-sourced deep-water (assumed basin).
- ²⁰ for the sake of argument to be approximately flat) from 5 km to 2.5 km in the Atlantic requires this water-mass to increase its Atlantic volume from under 20 million km³ to nearly 70 million km³ (just under a 4-fold increase). In order to determine the eventual impact of this volumetric change on the carbon-storage capacity of the ocean we would obviously require knowledge of the chemistry of the various deep-water masses in the
- ocean as well as their turnover and "ventilation" (atmosphere equilibration) rates, and the flux of dissolved carbon that they eventually incorporate via biological export. However, if we assume simplistically that nothing in the ocean changes except the volume occupied by southern-sourced deep-water (i.e. the chemistry of all water-masses stays the same, but not their volumetric contribution to the ocean's total budget), then we can



infer that for a 4-fold increase in the volume of AABW at the expense of NADW (having average total dissolved CO_2 concentrations of ~2280 μ mol kg⁻¹ and ~2180 μ mol kg⁻¹, respectively, Broecker and Peng, 1989) the ocean would need to gain ~63 Gt of carbon. If we assume that all this carbon must come from the atmosphere, then atmospheric pCO_2 would have to drop by ~30 ppm, given 1 ppm change per 2.12 Gt carbon removed from the atmosphere (Denman et al., 2007). This is equivalent to ~38% of the

total observed glacial – interglacial CO₂ change (Siegenthaler et al., 2005), and is comparable to the magnitude of atmospheric CO₂ changes that are likely to have arisen from other viable mechanisms such as biological export, or carbonate compensation (Peacock et al., 2006).

Clearly many of the assumptions made in the above thought experiment might not be valid: the chemistry and dynamics, not to mention the character and rate of biological export, of the glacial ocean will probably not have remained constant. Nevertheless, palaeoceanographic proxy evidence holds that the basic premise of the thought experiment is valid: the values of doop water clearly recombling medars equitation accurately and the part of the second seco

¹⁵ iment is valid: the volume of deep water closely resembling modern southern-sourced deep-water apparently increased significantly during the last glaciation. It seems warranted therefore to evaluate the impacts of this premise in a slightly more sophisticated way. The question to be answered is: does a deep ocean dominated by AABW-like deep-water hold more carbon at steady state (on time-scales longer than the mixing
 ²⁰ time of the ocean)? Below, a very simple box model is used as a first step toward answering this question.

3 Box-model description

Figure 1 illustrates a simple box-model that has been constructed in order to explore in more detail the implications of deep-water mass geometry (*versus* overturning rate) changes for glacial – interglacial CO₂ variability. This model comprises an atmosphere

²⁵ changes for glacial – interglacial CO₂ variability. This model comprises an atmosphere and six ocean boxes (Southern Ocean, low-latitude, North Atlantic, northern deepwater, intermediate-water and southern deep-water), and involves two coupled circula-



tion cells driven by down welling in the southern- and northern high latitudes. Particle fluxes are treated as directly exported dissolved matter, with carbon, phosphate, and nitrogen being exported in fixed proportions, as defined by modified Redfield Ratios (C:N:P:O₂=130:16:1:-169)(Toggweiler and Sarmiento, 1985), and carbonate being exported in fixed proportion to the total dissolved CO₂ of the water. Particle fluxes are diagnosed for a baseline "pre-industrial" box-model scenario according to observed phosphate concentrations in the modern ocean (Najjar et al., 1992):

$$P = \frac{C^*}{P^*} \left(\frac{([PO_4] - [PO_4]_{mod})V}{\tau} \right)$$

Where *P* is the instantaneous organic carbon flux, C^*/P^* is the ratio of organic carbon to phosphate in the particulate matter, *V* is the box volume, τ is the restoring timescale (set to 0.1 year), and [PO₄] and [PO₄]_{mod} are the instantaneous and restoring phosphate concentrations respectively. In subsequent "altered" box-model scenarios, particle fluxes vary according to "Michaelis-Menton" type dynamics (Dugdale, 1967), with less export being supported by lower nutrient concentrations. This removes the possibility of unrealistically high/low export productivity for very low/high nutrient levels respectively:

$$P = \frac{C^*}{P^*} \left(\frac{\omega[PO_4]}{k_m + [PO_4]} \right)$$

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In the above equation, k_m is set to $2.5 e^{-4} \text{ mol m}^{-3}$ (Schulz et al., 2001), and ω (the biological uptake rate) is diagnosed from the equilibrium conditions for the "modern box-model scenario" (preceding equation).

The calculated components of the model include phosphate, alkalinity, total dissolved CO_2 (TCO_2), carbonate ion (CO_3^{2-}), pCO_2 , apparent oxygen utilisation (AOU) and normalised radiocarbon concentration ($\Delta^{14}C$). Because the modelled radiocarbon concentrations are not normalised with respect to $\delta^{13}C$, $\Delta^{14}C$ reported here is actually equivalent to $d^{14}C$ by definition (Stuiver and Polach, 1977). Idealised mass-balance

equations for the evolution of box concentrations are of the form:

$$V_n \frac{dC_n}{dt} = F_n(C_l - C_n) + f_{ni}(C_i - C_n) - P_n \frac{C^*}{P^*} + F_{AO} \text{ (e.g. northern surface box)}$$
$$V_{sd} \frac{dC_{sd}}{dt} = F_s(C_s - C_{sd}) + f_{ns}(C_{nd} - C_{sd}) + P_l \frac{1}{R_{ns}} \frac{C^*}{P^*} \text{ (e.g. southern deep box)}$$

Where *C* indicates the box concentration, *F* and *f* indicate water fluxes, *P* indicates ⁵ particulate carbon fluxes (multiplied by chemical export/consumption ratios for different constituents, C^*/P^*) and F_{AO} indicates an air-sea exchange term (applicable to carbon dioxide and radiocarbon). Surface boxes have AOU set to zero.

For the calculation of the TCO_2 of the surface boxes, and extra exchange term with the atmosphere must be included:

¹⁰
$$V_n \frac{dC_n}{dt} = F_n(C_l - C_n) + f_{ni}(C_i - C_n) - P_n\left(\frac{C}{C_{\text{org}}}\right) \dots$$

 \dots + (CO₂)_{SOL-n} (e.g. southern surface box)

The air-sea gas exchange ((CO_2)_{SOL}) is defined according to the thermodynamics of Millero (1995) (equations 26, 41 and 42 therein), and follows a similar scheme to that of Toggweiler and Sarmiento (1985), such that:

¹⁵ (CO₂)_{SOL-s} =
$$[(\rho CO_2)_s - (\rho CO_2)_{atm}] A_s g_s \alpha_s$$

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where A_s and g_s are southern surface box area (m²) and gas piston velocity (kg m⁻² yr⁻¹) respectively; (ρ CO₂)_s and (ρ CO₂)_{atm} are the partial pressures for CO₂ in the southern surface box and the atmosphere respectively, and where α_s is the southern surface box solubility coefficient for CO₂. The solubility coefficient, α_s , is given by:

$$\ln \alpha_s = -60.2409 + \frac{9345.17}{T_s} + 23.3585 \ln(T_s/100) + \dots$$
$$\dots + S_s \left[0.023517 \right) - 0.023656 (T_s/100) + 0.0047036 (T_s/100)^2 \right]$$
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The carbonate system is treated using the C-SYS calculation scheme of (Zeebe and Wolf-Gladrow, 2001) given alkalinity, TCO_2 , pressure, temperature and salinity. The atmospheric pCO_2 is updated at each time step by integrating the air-sea CO_2 fluxes from each surface box:

$$V_{\text{atm}} \frac{d(pCO_2)_{\text{atm}}}{dt} = [(pCO_2)_s - (pCO_2)_{\text{atm}}] A_s g_s \alpha_s + \dots \\ \dots + [(pCO_2)_l - (pCO_2)_{\text{atm}}] A_l g_l \alpha_l + [(pCO_2)_n - (pCO_2)_{\text{atm}}] A_n g_n \alpha_n$$

For radiocarbon, an extra term is included in the equations to account for radioactive decay. Thus for the northern surface box, the mass balance equation for radiocarbon is:

¹⁰
$$V_n \frac{dC_n}{dt} = F_n(C_l - C_n) + f_{ni}(C_i - C_n) - P_n \frac{C^*}{P^*} + F_{AO} - \lambda C_n$$

Here λ is the radiocarbon decay constant (1.2097 e⁻⁴ yr⁻¹). Radiocarbon is transported as a concentration (μ mol kg⁻¹), such that the ratio of radiocarbon to total carbon (R^{14} C) is determined by dividing the radiocarbon concentration by the total carbon concentration of the relevant box at each time-step. The normalised radiocarbon concentration is then determined as:

$$\Delta^{14} \mathrm{C}_{\mathrm{box}} = \left(\frac{R^{14} \mathrm{C}_{\mathrm{box}}}{R^{14} \mathrm{C}_{\mathrm{std}}} - 1\right) \times 1000$$

The radiocarbon concentrations of the various boxes are expressed relative to the preindustrial standard ¹⁴C/C ratio of 1.176 e⁻¹². Biological uptake/release of radiocarbon and cosmogenic radiocarbon production are not treated explicitly in this model. Instead these terms are diagnosed for an equilibrium atmospheric radiocarbon concentration equal to the pre-industrial standard (¹⁴C/C=1.176 e⁻¹²). Once diagnosed, both terms are kept constant for experiments that involve modifications in box-model geometry.

The global radiocarbon budget is also fixed at its pre-industrial value, and can be maintained at this constant level once a pre-industrial equilibrium has been attained. Atmosphere – ocean exchange of radiocarbon is calculated as formulated for example by Müller et al. (2006), such that:

$$F_{AO} = gA_oK_h \frac{\rho CO_{2-atm}}{TCO_{2-o}} \left(R^{14}C_{atm} - R^{14}C_o \right)$$

Where F_{AO} is the atmosphere to ocean radiocarbon flux, g is the gas piston velocity (fixed at 3 ms^{-1}), A_o is the exposed ocean box area, K_h is the CO₂ solubility constant for the ocean surface and subscripts _atm and _o refer to atmospheric- and oceanic carbon concentrations or radiocarbon ratios.

- A numerical integration method (ODE-45 in Matlab's Simulink) is used to update the box concentration at the end of each time step, until all boxes reach a steady equilibrium. In order for radiocarbon to reach equilibrium the model must be integrated for ~20 000 model years. In the model, a correction scheme is used to check that the global budgets of phosphate, alkalinity and (radio-) carbon do not drift, and are all maintained at prescribed constant values. This correction scheme in fact only needs to be invoked for radiocarbon, since it is the only modelled species that includes diagnosed net input/output terms (production, decay and terrestrial biosphere uptake). Radiocarbon budget correction factors thus differ from 1 during the "wind-up" to equilibrium, while the atmospheric input and output terms (cosmogenic production minus)
- ²⁰ biosphere uptake) are being diagnosed. Note that box-volumes in the model do not change during simulations (dV/dt=0). It should also be noted that although the flow scheme of the box model essentially represents an Atlantic Ocean (i.e. it has two deep overturning "limbs"), it is scaled to global proportions so that the volumes and concentrations of the atmosphere and the ocean balance with global budgets (all of which
- are fixed input parameters). Nevertheless, the volumes of the two deep-water boxes are scaled relative to each other according to the hypothesised representation of North Atlantic and Antarctic deep-water end-members throughout the global ocean.

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The model is initiated with the concentrations of all boxes set to the global average, except for the pCO_2 of the surface boxes and the atmosphere, which are set arbitrarily close to zero (this avoids singularities in the calculation of initial radiocarbon concentrations). Equilibrium outcomes were not found to be sensitive to changes in these initial concentration conditions, since global budgets are maintained. In all model runs temperatures and salinities are also kept constant, in order to investigate exclusively the effect of water-mass geometry changes "ceteris paribus".

3.1 Model parameterisation and sensitivity

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The parameterisation of the model's mass transport and mixing rate terms is outlined in Table 1. Circulation rates for the (modern) northern and southern overturning loops were initially set according to (Ganachaud and Wunsch, 2000). These export rates were then augmented in fixed proportion to each other (1:1.7) in order to achieve deep ocean radiocarbon concentrations that more closely matched the modern ocean (average deep-ocean age ~1400 years) and such that atmospheric carbon dioxide reached an appropriate pre-industrial value (~280 ppm) when restoring to modern surface phos-

- phate concentration estimates (see below). Mixing rates between boxes were set arbitrarily to 10 Sv in the high latitudes and 5 Sv for the deep-ocean and the low-latitude surface ocean, where it can be argued that up-welling should be small compared to high-latitude overturning (Gnanadesikan et al., 2007). The sensitivity of the variable
- ²⁰ biological export was diagnosed by restoring to prescribed surface phosphate concentrations, as described above, once appropriate mass transport rates were estimated (see Table 1). With the net biological export to the deep boxes estimated to be ~10% of export production at 100 m (Martin et al., 1987), the total biological export at 100 m in the baseline model run is ~20 PgCyr⁻¹. Although this value is rather high, there
- ²⁵ is ample scope for reducing it by prescribing a more sluggish net overturning rate in the model, while maintaining approximate pre-industrial atmospheric pCO_2 , and rediagnosing (necessarily lower) biological uptake rates. As illustrated below, this can be done without significantly affecting the carbon and radiocarbon distributions in the



model, and indeed without affecting the outcome of this study. Directly tuning the model to expected net biological export rates (closer to $\sim 10 \text{ PgCyr}^{-1}$, Kohler et al., 2005) can therefore be safely avoided.

Figure 2 illustrates the sensitivity of modelled atmospheric pCO_2 and deep-ocean 5 radiocarbon ventilation with respect to changes in the physical transport and mixing rate parameters. As expected, the parameter that most strongly constrains both the ocean – atmosphere radiocarbon- and CO₂ partitioning is the net overturning transport rate $(F_n + F_s)$, where $F_s = F_n/1.7$; see Fig. 1). In the majority of the sensitivity tests illustrated in Fig. 2 (solid lines), biological "uptake rates" (ω , the variable-export sensitivity) were maintained at the values diagnosed for the baseline "pre-industrial" scenario (i.e. 10 for $F_n = 28 \text{ Sv}$, $F_s = 16.5 \text{ Sv}$, and for modern surface-ocean phosphate concentrations; see Table 1). However, when surface-ocean nutrient (phosphate) concentrations are restored to modern values while at the same time changing the mixing rate parameters, the impact of large changes in overturning rates on atmospheric pCO₂ is greatly reduced (crossed circles in Fig. 2). This demonstrates how the balance between phys-15 ical overturning and biological export effectively sets the carbon sequestration capacity of the deep ocean for a given deep-water geometry (e.g. Sarmiento and Toggweiler, 1984). It also illustrates that a lower net biological export could be obtained with a

lower net overturning rate, while approximately maintaining pre-industrial pCO_2 and deep-ocean $\Delta^{14}C$.

Clearly, a box-model like the one presented here represents a highly conceptualised system, though in this case only radiocarbon (as a ventilation time-scale indicator), surface-ocean phosphate concentration (as a biological export rate indicator), and atmospheric *p*CO₂ (as a carbon climatology indicator) are used to "tune" the model. The rest of the box-model equilibrium chemistry is determined by these conditions, and can therefore be used for a first-order evaluation of the model behaviour. The "realism" of the baseline pre-industrial model scenario is illustrated in Fig. 3 relative to modern/pre-industrial observations (Broecker and Peng, 1982; Key et al., 2004). The modern/pre-industrial "observations" should be seen merely as indications of what plausible box



concentrations might be, for their counterparts in reality are difficult to assess. The concentrations, volumes and chemical inventories of the boxes for the baseline control scenario are listed in Table 2. As shown in Fig. 3, even this highly simplified model is capable of mimicking the chemical distribution of the modern ocean with adequate realism, without being explicitly tuned to do so.

The goal will be to explore differences in the equilibrium carbon-sequestration capacity of the box-model ocean for a series of different deep-water box geometries. In order to do this, the model is run to equilibrium after the relative volumes of the two deep-water boxes in the model are changed, while the total volume is of course maintained and while the global chemical inventories and all other model parameters are kept constant.

4 Model experiments

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As noted above, the reconstruction of past changes in the dynamical structure (flow rates) of the ocean remains a major challenge (Wunsch, 2003; Lynch-Steiglitz et al.,

- ¹⁵ 2007). However, proxies for past deep-water composition, such as for example benthic foraminiferal Cd/Ca (Boyle, 1988a), δ^{13} C (Duplessy et al., 1988; Curry and Oppo, 2005) and more recently dispersed ferromanganese oxide ε_{Nd} (Goldstein and Hemming, 2003), more readily allow us to infer past changes in water-mass distribution. Thus for the Atlantic during the last glacial, it would appear that northern-sourced (or at least NADW/like) doop-water should to a dopth of ~ 1.8 to 2.5 km, and was replaced
- ²⁰ least NADW-like) deep-water shoaled to a depth of ~1.8 to 2.5 km, and was replaced at greater depths by southern-sourced (or AABW-like) deep-water (Hodell et al., 2003; Marchitto and Broecker, 2005; Lynch-Steiglitz et al., 2007).

If we take into account the hypsometry of the ocean floor (Menard and Smith, 1966), and if we assume that northern-sourced deep-water can account for up to 50% of

the Circumpolar Deep Water (CDW) that is exported to the deep Indo-Pacific basins (Broecker and Peng, 1982; Matsumoto, 2007), then we can calculate the expected global volume ratio (R_{ns}) of "northern-sourced deep-water" (NDW) *versus* "southern-



sourced deep-water" (SDW) given the depth of a presumed (horizontal) boundary between the two. This is illustrated in Fig. 4, where a rise in the NDW/SDW boundary from 5 km to 2.5 km in the Atlantic is taken to imply a proportionate reduction of the amount of NDW mixed into the Indo-Pacific basins via CDW and hence a global reduction in the

total volume ratio of northern- to southern deep-water (R_{ns}) from 1.43 to 0.5 between the Holocene and the LGM. Using more sophisticated models of the ocean circulation it should be possible to determine this ratio more exactly for a "physically sensible" ocean circulation and water-mass geometry (e.g. Cox, 1989). This could eventually permit a "calibration" of simulated changes in atmospheric pCO_2 to simulated changes in R_{ns} (including perhaps for different causes of R_{ns} change).

In the box model described here, equilibrium atmospheric pCO_2 is found to drop consistently as the R_{ns} value for the box-model geometry decreases (i.e. NDW gives way to SDW). This is shown in Fig. 5, where a shift in the NDW/SDW water-mass boundary from 5 km to 2.5 km (or a change in R_{ns} from 1.43 to 0.5) corresponds to a drop in equilibrium atmospheric pCO_2 of just over 30 ppm. The box model volumes and chemical inventories for the hypothesised "glacial" water-mass geometry (2.5 km NDW/SDW water-mass boundary, R_{ns} =0.5) are summarised in Table 3. As expected, a "standing volume effect" such as described here is not going to account for the entirety of glacial – interglacial pCO_2 change. However, the important and perhaps surprising observation is that this mechanism might account for as much of the glacial – interglacial atmospheric pCO_2 change as has been attributed to other fundamental mechanisms, such as the thermodynamic solubility pump, carbonate compensation, or the biological pump (Sigman and Boyle, 2000; Peacock et al., 2006; Brovkin et al., 2007).

5 Discussion: sustaining a "standing volume" effect

²⁵ The box model experiments illustrated in Fig. 5 appear to confirm the thought experiment described in Sect. 2, whereby (all else being equal) an ocean that is dominated by AABW-like deep-water holds more CO₂. In order to operate effectively however,



this sequestration mechanism requires three conditions: 1) there must be rather large changes in water-mass volumes (in the scenario envisaged here ~60% of the Atlantic and ~30% of the Indo-Pacific is affected by the reduced NADW contribution); 2) the expanding water-mass must have high *TCO*₂ relative to the water it effectively displaces;
 and 3) the expanding southern overturning limb must not "leak" CO₂ to the atmosphere very efficiently. Each of these conditions should be readily testable in the geological archive using palaeoceanographic proxies, and perhaps with sophisticated numerical

A corollary of the third condition above is that any mechanism that would further reduce the extent to which Southern Ocean sub-surface water is allowed to equilibrate with the atmosphere (e.g. Keeling and Stephens, 2001; Toggweiler et al., 2006; Watson and Naveira Garabato, 2006) will enhance the standing volume effect. The same is also true of any mechanism that tends to exacerbate the chemical contrast between the "recycled" abyss and the upper ocean. This includes a more efficient biological pump, especially in the Southern Ocean. These extensions of the proposed standing volume sequestration effect are illustrated in Fig. 6, where the sensitivity of modelled atmospheric CO₂ to changes in deep water-mass geometry (i.e. R_{ns}) is shown for reduced and enhanced gas exchange, and for increased biological uptake rates, in the Southern Ocean. In the simple box model presented here, the sensitivity of the

models.

- ²⁰ standing volume effect is broadly independent of Southern Ocean gas exchange rates (although of course absolute atmospheric CO_2 levels do depend on the efficiency of Southern Ocean gas exchange). The same is true for the efficiency of the Southern Ocean biological pump, which helps to set absolute atmospheric CO_2 levels but does not greatly affect the sensitivity of atmospheric CO_2 to a variable standing volume ef-
- fect, even for a ~100% efficient biological pump in the Southern Ocean (phosphate depleted to ~0 μ mol kg⁻¹). As shown in Fig. 6, atmospheric CO₂ drops by ~30 ppm for a decrease in R_{ns} from 1.43 to 0.5, regardless of changes in Southern Ocean gas exchange or biological export efficiency. This means that a "standing volume effect" resulting from a greater volumetric contribution of AABW-like deep-water would com-



bine additively with changes in biological export and/or gas exchange (or upper ocean vertical mixing), and does not appear to depend on a specific formulation of these processes either.

- Previously, it has been suggested on the basis of first order principles and numerical modelling experiments that if global nutrient budgets are maintained while surface nutrients are depleted, either via reduced overturning rates or increased biological export rates, atmospheric pCO_2 will vary in proportion to the resulting average preformed nutrient concentration of the deep sea (Sigman and Haug, 2003; Toggweiler et al., 2003; Ito and Follows, 2005; Marinov et al., 2006). The average deep-sea preformed nutrient concentration is thus suggested to scale with atmospheric pCO_2 , with an estimated ~130–170 ppm change in pCO_2 per 1 μ mol kg⁻¹ change in preformed phosphate (Sigman and Haug, 2003; Ito and Follows, 2005; Marinov et al., 2006). The reason for the positive correlation is that any change that acts to reduce the mean nutrient (i.e. phosphate) concentration at the ocean surface (especially in regions of deepwater formation, Marinov et al., 2006) will result in: 1) a reduction of the advected nutrient flux into the ocean interior (thus lowering the mean preformed nutrient concentration of
- deep sea); and 2) an increase in the mean nutrient concentration of the deep-sea (due to the conservation of ocean nutrients), thus sequestering more carbon in the deep sea.
- ²⁰ The proposed scaling between mean deep-sea preformed nutrient concentrations and atmospheric pCO_2 might be taken to imply that the domination of the deep sea by AABW-like deep water (with a relatively high preformed nutrient concentration) would cause atmospheric pCO_2 to rise, contrary to the hypothesis presented here (Sigman and Haug, 2003; Toggweiler et al., 2003). However, this inference would only be correct ²⁵ under the assumption that an increase in the volume of AABW-like deep-water would result in an increase in the surface nutrient (i.e. phosphate and TCO_2) content, which is in fact impossible as long as AABW has an elevated total nutrient concentration relative to the water-mass it replaces. This becomes obvious when a heterogeneous deep-sea with constant total volume despite variable deep-sea water-mass volumes is



considered. The conservation of the global carbon budget can be stated as follows:

$$MpCO_{2} + V_{surf} \left\{ \overline{C_{surf}} \right\} + V_{d} \left\{ \overline{C_{d}} \right\} = MpCO_{2}$$
$$+ V_{surf} \left\{ \overline{C_{surf}} \right\} + V_{sd} \left\{ C_{sd} \right\} + V_{nd} \left\{ C_{nd} \right\} = B_{tot}$$

- Where M is the total molar content of the atmosphere; V_d , V_{sd} , V_{ad} and V_{surf} are the 5 volumes of the whole deep ocean, southern deep-water component, northern deepwater component, and surface ocean respectively; C_d and C_{surf} are the mean carbon concentrations in the deep- and surface ocean; C_{sd} and C_{nd} are the southern- and northern deep-water carbon concentrations; and B_{tot} is the global carbon budget. In this system, any perturbation to the carbon budget of the deep-sea must be balanced
- by a change in the atmospheric carbon content, which will remain in approximate equi-10 librium with the carbon content of the surface ocean. If we consider a perturbation to the system due only to changing V_s at the expense of V_n (i.e. $\delta V_{sd} = -\delta V_{nd}$), where R_{CP} is the Redfield C:P ratio, then we find that (cf. Ito and Follows, 2005):

$$\frac{\delta \rho \text{CO}_2}{\delta V_{sd}} = \frac{(C_{nd} - C_{sd})}{M\gamma} = \frac{R_{C:P} (P_{nd} - P_{sd})}{M\gamma} = \frac{V_{\text{surf}} R_{C:P} (\Delta P_{\text{surf}})}{\delta V_{sd} M\gamma}$$

where: 15

$$\gamma = 1 + \frac{V_{\text{surf}}C_{\text{surf}}}{M\gamma_{\text{DIC}}\rho\text{CO}_2}$$

In the above equation γ is a dimensionless parameter that accounts for the equilibration between the atmosphere and the surface ocean, and represents the relative magnitudes of the atmospheric and surface ocean carbon reservoirs, via the "Revelle factor" (buffer factor), γ_{DIC} . These relationships, which are based on the framework 20 proposed by Ito and Follows (2005), confirm the intuitive expectation that changes in pCO_2 and in the surface nutrient concentration (ΔP_{surf}) should both be negative for increasing V_s as long as the expanding southern deep-water mass has a higher nutrient content and TCO_2 than the water-mass it replaces $(C_{sd} > C_{nd})$. Otherwise, the

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opposite is true. The mean preformed nutrient concentration of the deep sea can be defined as the total flux of dissolved nutrients into the sub-surface (i.e. the sum of the products of surface phosphate and their associated downward mass transport terms) divided by the net overturning circulation (e.g. Sigman and Haug, 2003). This means that mean preformed nutrients in the deep-sea must also decrease as V_{sd} increases 5 and pCO_2 decreases (again if $C_{nd} < C_{sd}$). Hence as long as the postulated changes in deep water-mass volumes cause the surface nutrient concentration to drop (especially at high latitudes, in regions of deep-water formation), we can expect them to cause a drop in atmospheric pCO_2 and a drop in mean deep-water preformed nutrient concentration, all because of an increase in the total deep-sea nutrient budget. In the 10 box model experiments carried out here, the expected theoretical relationships based on the arguments presented above, and based on previous work (Sigman and Haug, 2003; Toggweiler et al., 2003; Ito and Follows, 2005; Marinov et al., 2006), are borne out: atmospheric pCO_2 drops by almost 100 ppm per 1 μ mol kg⁻¹ drop in the mean preformed nutrient concentration in the ocean interior boxes (calculated from Tables 1, 15 2 and 3). The proposed standing volume effect therefore appears to be consistent with previous conceptualisations of the biological pump and its variable efficiency, although it demonstrates that dissolved- or particulate export rates are not the only parameters controlling the mean surface-to-deep nutrient/carbon concentration gradient in a closed system. 20

6 Conclusions: ocean circulation and the "CO₂ stew"

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The main purpose of the present study is not to attempt a complete simulation or explanation of glacial – interglacial atmospheric CO_2 change, nor is it to suggest that ocean circulation rates and biological export rates are unimportant for glacial – interglacial CO_2 change. Rather, the goal here is to draw a distinction between two separate aspects of the "ocean circulation" (water-mass distribution *versus* water-mass renewal/overturning rates) in terms of their respective roles in glacial – interglacial CO_2

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change. Based on a simple thought experiment and a set of box-model tests, it would appear that a surprisingly large portion of the glacial – interglacial CO_2 change might be explained simply by changes in the volumetric contribution of contrasting deep-water end-members to the deep sea, prior to any changes in overturning-, gas exchange-

- or biological export rates. The proposed "standing volume effect" would arise due to substantial changes in the volume of AABW-like (relatively high *T*CO₂) deep-water filling the ocean basins, and requires only that the expanding overturning loop does not "leak" excess CO₂ to the atmosphere as a result of countervailing changes in biological export rates or gas exchange rates for example. The standing volume effect therefore
 appears to be additive with respect to accompanying changes in the efficiency of the biological pump or of gas exchange around Anterestica, but does not depend on these
- biological pump or of gas exchange around Antarctica, but does not depend on these processes in its operation.

Although previous studies that have simulated glacial atmospheric CO₂ using complex numerical models with accurate bathymetry (e.g. Heinze et al., 1991) may have ¹⁵ already included the proposed standing volume effect implicitly, none so far have tried to identify or quantify its possible impact on glacial CO₂ draw-down. Although one recent exception (Brovkin et al., 2007) has suggested that the expansion of AABW at the

- expense of NADW in the glacial ocean might have caused atmospheric CO₂ to drop by as much as 43 ppm, this estimate includes the effects of changes in deep-water over-
- turning rates (reduced NADW by ~20% and intensified AABW). The proposed standing volume effect therefore remains to be tested adequately using complex numerical model simulations of the glacial ocean circulation.

If the simple standing volume mechanism proposed here for enhancing deep-sea carbon sequestration can be incorporated into the list of "ingredients" that have con-

tributed to glacial – interglacial CO₂ change (Archer et al., 2000; Sigman and Boyle, 2000; Kohler et al., 2005; Peacock et al., 2006), it may help to reduce the CO₂ deficit that remains to be explained by appealing to more equivocal or controversial processes. More importantly however, it may also help us to evaluate more explicitly the role of the "ocean circulation" as an ingredient in the glacial – interglacial "CO₂



stew", as well as the factors that have repeatedly pushed the marine carbon cycle between glacial and interglacial modes (Shackleton, 2000). This is especially true if the mechanisms or timescales for changing the vertical mass transport rate in the ocean differ from those for changing the (vertical) redistribution of contrasting deepwater end-members. Indeed, a de-convolution of the expected impacts of an altered "ocean circulation" into renewal-rate effects and standing-volume effects can only gain importance to the extent that proxy evidence for a large reduction in the net overturning rate of the glacial ocean remains equivocal (Lynch-Steiglitz et al., 2007), and/or theoretical support for such a change continues to be debated (Wunsch, 2003).

10 References

20

- Archer, D. and Maier-Reimer, E.: Effect of deep-sea sedimentary calcite preservation on atmospheric CO2 concentration, Nature, 367, 260–263, 1994.
- Archer, D., Winguth, A., Lea, D. W., and Mahowald, N.: What caused the glacial/interglacial atmospheric *p*CO2 cycles?, Rev. Geophys., 38(2), 159–189, 2000.
- ¹⁵ Bard, E.: Correction of accelerator mass spectrometry 14C ages measured in planktonic foraminifera: Paleoceanographic implications, Paleoceanography, 3(6), 635–645, 1988.
 - Boyle, E.: Cadmium and d13C paleochemical ocean distributions during the Stage 2 glacial maximum, Ann. Rev. Earth Planet. Sci., 20, 245–287, 1992.

Boyle, E. A.: Cadmium: chemical tracer fro deepwater paleoceanography, Paleoceanography, 3, 471–489, 1988a.

Boyle, E. A.: The role of vertical fractionation in controlling late Quaternary atmospheric carbon dioxide, J. Geophys. Res., 93(C12), 15701–15714, 1988b.

Broecker, W. S.: Glacial to interglacial changes in ocean chemistry, Prog. Oceanogr., 11, 151– 197, 1982a.

- ²⁵ Broecker, W. S.: Ocean chemistry during glacial time, Geochim. Cosmochim. Ac., 46, 1698– 1705, 1982b.
 - Broecker, W. S. and Peng, T. H.: Tracers in the Sea, Eldigio Press, Palisades, New York, USA, 1982.

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5, 1259–1296, 2009

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- Broecker, W. S. and Peng, T.-H.: The cause of the glacial to interglacial atmospheric CO2 change: a polar alkalinity hypothesis, Global Biogeochem. Cy., 3(3), 215–239, 1989.
- Brovkin, V., Ganopolski, A., Archer, D., and Rahmstorf, S.: Lowering glacial atmospheric CO₂ in response to changes in oceanic circulation and marien biogeochemistry, Paleoceanography, 22, PA4202, 1–14, 2007.
- Cox, M. D.: An idealized model of the world ocean. Part I: The global-scale water masses, J. Phys. Oceanogr., 19, 1730–1752, 1989.

5

10

25

- Curry, W. B., Duplessy, J. C., Labeyrie, L. D., and Shackleton, N. J.: Changes in the distribution of d13C of deep water sigma-CO₂ between the last glaciation and the Holocene, Paleoceanography, 3(3), 317–341, 1988.
- Curry, W. B. and Oppo, D. W.: Glacial water mass geometry and the distribution of d13C of Sigma-CO₂ in the western Atlantic Ocean, Paleoceanography, 20, PA1017, doi:10.1029/2004PA001021, 2005.

Denman, K. L., Brasseur, G., Chidthaisong, A., Ciasis, P., Cox, P. M., Dickinson, R. E., Hauglus-

- taine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P. L., Wofsy, S. C., and Zhang, X.: Couplings between changes in the climate system and biogeochemistry, in: Climate Change 2007: The Physical Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Combridge University Press, Combridge New York, USA, 0007.
- Miller, H. L., Cambridge University Press, Cambridge, New York, USA, 2007. Dugdale, R. C.: Nutrient limitation in the sea: dynamics, identification, and significance, Limnol. Oceanogr., 12, 685–695, 1967.
 - Duplessy, J.-C., Shackleton, N. J., Fairbanks, R. G., Labeyrie, L., Oppo, D., and Kallel, N.: Deep water source variations during the last climatic cycle and their impact on global deep water circulation, Paleoceanography, 3, 343–360, 1988.
 - Ganachaud, A. and Wunsch, C.: Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data, Nature, 408, 453–457, 2000.
 - Gildor, H. and Tziperman, E.: Physical mechanisms behind biogeochemical glacial-interglacial CO₂ variations, Geophys. Res. Lett., 28(12), 2421–2424, 2001.
- ³⁰ Gnanadesikan, A., de Boer, A. M., and Mignone, B. K.: A simple theory of the pycnocline and overturning revisited, in: Ocean circulation: mechanisms and impacts, edited by: Schmittner, A., Chiang, C. H., and Hemming, S. R., Geophysical Monograph, AGU, Washington DC, 19– 32, 2007.

5, 1259-1296, 2009 Standing volume role in CO₂ change L. C. Skinner **Title Page** Abstract Introduction Conclusions References Figures Tables Back Close Full Screen / Esc Printer-friendly Version Interactive Discussion



Goldstein, S. L. and Hemming, S. R.: Long-lived isotopic tracers in oceanography, paleoceanography and ice-sheet dynamics, in: Treatise on Geochemistry, edited by: Elderfield, H., Elsevier, 453–489, 2003.

Gordon, A. L.: Comment on the South Atlantic's role in the global circulation, in: The South

Atlantic: Present and Past Circulation, edited by: Wefer, G., Berger, A., Siedler, G., and Webb, D. J., Springer-Verlag, Berlin Heidelberg, Germany, 121–124, 1996.

Heinze, C., Maier-Reimer, E., and Winn, K.: Glacial pCO_2 reduction by the world ocean: Experiments with the Hamburg carbon cycle model, Paleoceanography, 6, 395–430, 1991.

Hodell, D. A., Venz, K. A., Charles, C. D., and Ninneman, U. S.: Pleistocene vertical carbon iso-

- tope and carbonate gradients in the South Atlantic sector of the Southern Ocean, Geochem. Geophy. Geosy., 4(1), GC1004, doi:10.1029/2002GC000367, 2003.
 - Ito, T. and Follows, M. J.: Preformed phosphate, soft tissue pump and atmospheric CO₂, J. Mar. Res., 63, 813–839, 2005.

Keeling, R. F. and Stephens, B. B.: Antarctic sea ice and the control of Pleistocene climate instability, Paleoceanography, 16(1), 112–131, 2001.

15

30

Keigwin, L. D.: Radiocarbon and stable isotope constraints on Last Glacial Maximum and Younger Dryas ventilation in the western North Atlantic, Paleoceanography, 19, PA4012, 1–15, 2004.

Keigwin, L. D. and Lehmann, S. J.: Deep circulation change linked to Heinrich event 1 and

- Younger Dryas in a mid-depth North Atlantic core, Paleoceanography, 9(2), 185–194, 1994.
 Key, R. M., Kozyr, A., Sabine, C., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T.-H.: A global ocean carbon climatology: Results from the Global Data Analysis Project (GLODAP), Global Biogeochem. Cy., 18, GB4031, 1–23, 2004.
- Kim, S.-J., Flato, G. M., and Boer, G. J.: A coupled climate model simulation of the Last Glacial Maximum, Part 2: approach to equilibrium, Clim. Dynam., 20, 635–661, 2003.
 - Knox, F. and McElroy, M.: Changes in atmospheric CO₂: influence of marine biota at high latitude, J. Geophys. Res., 89, 4629–4637, 1984.
 - Kohler, P., Fischer, H., Munhoven, G., and Zeebe, R. E.: Quantitative interpretation of atmospheric carbon records over the last glacial termination, Global Biogeochem. Cy., 19, 1–24, 2005.
 - Lynch-Steiglitz, J., Adkins, J. F., Curry, W. B., Dokken, T., Hall, I. R., Heguera, J. C., Hirschi, J. J.-M., Ivanova, E. V., Kissel, C., Marchal, O., Marchitto, T. M., McCave, I. N., McManus, J. F., Mulitza, S., Ninneman, U. S., Peeters, F. J. C., Yu, E.-F., and Zahn, R.: Atlantic meridional

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overturning circulation during the last glacial maximum, Science, 316, 66-69, 2007

Marchal, O. and Curry, W. B.: On the abyssal circulation in the glacial Atlantic, J. Phys. Oceanogr., 38, 2014–2037, 2008.

Marchal, O., Stocker, T. F., and Joos, F.: A latitude-depth, circulation-biochemical ocean model for paleoclimate studies. Development and sensitivities, Tellus, 50B(3), 290–316, 1998.

for paleoclimate studies. Development and sensitivities, Tellus, 50B(3), 290–316, 1998.
 Marchitto, T. M. and Broecker, W.: Deep water mass geometry in the glacial Atlantic Ocean: A review of constraints from the paleonutrient proxy Cd/Ca, Geochem. Geophy. Geosy., 7(12), 1–16, 2005.

Marchitto, T. M., Oppo, D. W., and Curry, W. B.: Paired benthic foraminiferal Cd/Ca and Zn/Ca

- evidence for a greatly increased presence of Southern Ocean Water in the glacial North Atlantic, Paleoceanography, 17(3), 10.11–10.16, 2002.
 - Marinov, I., Gnadesikan, A., Toggweiler, J. R., and Sarmiento, J. L.: The Southern Ocean biogeochemical divide, Nature, 441, 964–967, 2006.

Martin, J. H., Knauer, G. A., Karl, D. M., and Broenkow, W. W.: VERTEX: carbon cycling in the northeast Pacific. Deep Sea Res., 34, 267–286, 1987.

15

25

- Matsumoto, K.: Radiocarbon-based circulation age of the world oceans, J. Geophys. Res., 112(C), 1–7, 2007.
 - Menard, H. W. and Smith, S. M.: Hypsometry of ocean basin provinces, J. Geophys. Res., 71(18), 4305–4325, 1966.
- Michel, E., Labeyrie, L., Duplessy, J.-C. and Gorfti, N.: Could deep Subantarctic convection feed the worl deep basins during last glacial maximum?, Paleoceanography, 10(5), 927–942, 1995.
 - Müller, S. A., Joos, F., Edwards, N. R., and Stocker, T. F.: Water mass distribution and ventilation time scales in a cost-efficient, three-dimensional ocena model, J. Climate, 19, 5479–5499, 2006.
 - Najjar, R. G., Sarmiento, J. L., and Toggweiler, J. R.: Downward transport and fate of organic matter in the ocean: simulations with a general circulation model, Global Biogeochem. Cy., 6, 45–76, 1992.

Naviera Garabato, A. C., Polzin, K. L., King, B. A., Heywood, K. J., and Visbeck, M.: Widespread intense turbulent mixing in the Southern Ocean, Science, 303, 210–213, 2004.

Widespread intense turbulent mixing in the Southern Ocean, Science, 303, 210–213, 2004.
 Oppo, D. and Fairbanks, R. G.: Atlantic ocean thermohaline circulation of the last 150,000 years: Relationship to climate and atmospheric CO₂, Paleoceanography, 5, 277–288, 1990.
 Oppo, D. W., Fairbanks, R. G., Gordon, A. L., and Shackleton, N. J.: Late Pleistocene Southern

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Ocean d^{13} C variability, Paleoceanography, 5, 43–54, 1990.

20

30

- Orsi, A. H., Johnson, G. C., and Bullister, J. L.: Circulation, mixing and production of Antarctic Bottom Water, Prog. Oceanogr., 43, 55–109, 1999.
- Peacock, S., Lane, E., and Restrepo, M.: A possible sequence of events for the generalized glacial interglacial cycle, Global Biogeochem. Cy., 20, GB2010, 1–17, 2006.
- ⁵ glacial interglacial cycle, Global Biogeochem. Cy., 20, GB2010, 1–17, 2006. Piotrowski, A., Goldstein, S. L., Hemming, S. R., and Fairbanks, R. G.: Temporal relationships of carbon cycling and ocean circulation at glacial boundaries, Science, 307, 1933–1938, 2005.

Piotrowski, A. M., Goldstein, S. L., Hemming, S. R., and Fairbanks, R. G.: Intensification and variability of ocean thermobaline circulation through the last deglaciation. Earth Planet, Sci.

variability of ocean thermohaline circulation through the last deglaciation, Earth Planet. Sci. Lett., 225, 205–220, 2004.

Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of sea water, in: The Sea, edited by: Hill, M. N., Wiley-Interscience, New York, USA, 26–77, 1962.

- Robinson, L. F., Adkins, J. F., Keigwin, L. D., Southon, J., Fernandez, D. P., Wang, S.-L., and Scheirer, D. S.: Radiocarbon variability in the western North Atlantic during the last deglaciation, Science, 310, 1469–1473, 2005.
 - Rutberg, R. L., Heming, S. R., and Goldstein, S. L.: Reduced North Atlantic Deep Water flux to the glacial Southern Ocean inferred from neodymium isotope ratios, Nature, 405, 935–938, 2000.
 - Sabine, C., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The oceanic sink for anthropogenic CO₂, Science, 305, 367–371, 2004.

Sarmiento, J. L. and Toggweiler, R.: A new model for the role of the oceans in determining atmospheric *p*CO₂, Nature, 308, 621–624, 1984.

 Schulz, M., Seidov, D., Sarnthein, M., and Stattegger, K.: Modeling ocean-atmosphere carbon budgets during the Last Glacial Maximum-Heinrich 1 meltwater event-Bolling transition, Int. J. Earth Sci. (Geol. Rundsch.), 90, 412–425, 2001.

Shackleton, N. J.: The 100 000-year ice-age cycle identified and found to lag temperature, carbon dioxide and orbital eccentricity, Science, 289, 1897–1902, 2000.

Shin, S. I., Liu, Z., Otto-Bliesner, B. L., Brady, E. C., Kutzbach, J. E., and Harrison, S. P.: A simulation of the last glacial maximumclimate using the NCAR-CCSM, Clim. Dynam., 20, 127–151, 2003.

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Siegenthaler, U., Stocker, T. F., Monnin, E., Luthi, D., Schwander, J., Stauffer, B., Raynaud, D., Barnola, J.-M., Fischer, H., Masson-Delmotte, V., and Jouzel, J.: Stable carbon cycle - climate relationship during the Late Pleistocene, Science, 310, 1313–1317, 2005.

Siegenthaler, U. and Wenk, T.: Rapid atmospheric CO₂ variations and ocean circulation, Nature, 308, 5960, 624–625, 1984.

Sigman, D. M. and Boyle, E. A.: Glacial/interglacial variations in atmospheric carbon dioxide, Nature, 407, 859–869, 2000.

Sigman, D. M. and Haug, G. H.: The biological pump in the past, in: Treatise on Geochemistry, edited by: Elderfield, H., Elsevier, 491–528, 2003.

¹⁰ Skinner, L. C. and Shackleton, N. J.: Rapid transient changes in Northeast Atlantic deep-water ventilation-age across Termination I, Paleoceanography, 19, 1–11, 2004.

Speer, K., Rintoul, S. R., and Sloyan, B.: The diabatic deacon cell, J. Phys. Oceanogr., 30, 3212–3222, 2000.

Stuiver, M. and Polach, H. A.: Reporting of 14C data, Radiocarbon, 19(3), 355–363, 1977.

- ¹⁵ Toggweiler, J. R.: Variation of atmospheric CO₂ by ventilation of the ocean's deepest water, Paleoceanography, 14(5), 571–588, 1999.
 - Toggweiler, J. R., Murnane, R., Carson, S., Gnanadesikan, A., and Sarmiento, J. L.: Representation of the carbon cycle in box models and GCMs: 2. Organic pump, Global Biogeochem. Cy., 17(1), 27.21–27.13, 2003.
- Toggweiler, J. R., Russell, J. L., and Carson, S. R.: Midlatitude westerlies, atmospheric CO2, and climate change during the ice-ages, Paleoceanography, 21, 1–15, 2006.
 - Toggweiler, J. R. and Sarmiento, J. L.: Glacial to interglacial changes in atmospheric carbon dioxide: the critical role of ocean surface water in high latitudes, in: The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present, Geophysical Monograph American Geophysical Union, 163–184, 1985.
 - Tziperman, E. and Gildor, H.: On the mid-Pleistocene transition to 100-kyr glacial cycles and the asymmetry between glaciation and deglaciation times, Paleoceanography, 18(1), 1001, doi:10.1029/2001PA000627, 2003.

Watson, A. J. and Naveira Garabato, A. C.: The role of Southern Ocean mixing and upwelling

³⁰ in glacial – interglacial atmospheric CO₂ change, Tellus, 58B(1), 73–87, 2006. Webb, D. J. and Suginohara, N.: Vertical mixing in the ocean, Nature, 409, p. 37, 2001.

25

Wunsch, C.: Determining paleoceanographic circulations, with emphasis on the Last Glacial Maximum, Quaternary Sci. Rev., 22, 371–385, 2003.

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- Yu, J. and Elderfield, H.: Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, Earth Planet. Sci. Lett., 258, 73–86, 2007.
- Zeebe, R. E. and Wolf-Gladrow, D.: CO2 in seawater: Equilibrium, Kinetics, Isotopes, Elsevier, Amsterdam, The Netherlands, 2001.

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Table 1. Input parameterisation for "baseline" model run. Only R_{ns} is varied in subsequent model runs.

Parameter	Label	Value	Source	Parameter	Label	Value	Source
Fluxes				Temperature, Salinity			
Northern overturning	Fn	28 Sv	-	Northern temperature	T_n	5°C	-
Southern overturning	F_s	16.5 Sv	-	Southern temperature	T _s	1°C	-
Low lat. vertical mixing	f_{II}	5 Sv	-	Low lat. Temperature	T_{I}	21.5°C	-
Northern high lat. vertical mixing	f _{ni}	10 Sv	-	Northern salinity	S_m	35.0‰	-
Southern high lat. vertical mixing	f _{si}	10 Sv	-	Southern salinity	S_s	34.7‰	-
Deep mixing	f _{ns}	5 Sv	-	Low lat. Salinity	S_{l}	36.0‰	-
Volumes, Areas				Restoring phosphate			
Total ocean volume	V_o	1.3×10 ¹⁸ m ³	а	Southern PO ₄	P_s	$1.9\mu molkg^{-1}$	е
Total ocean area	A_o	3.5×10 ¹⁴ m ²	а	Low lat. PO ₄	P_l	0.1 μ mol kg ⁻¹	е
Volume of atmosphere	$V_{\rm atm}$	1.773×10 ²⁰ mol	b	Northern PO ₄	Pn	$0.5 \mu mol kg^{-1}$	е
N. high lat. box area/Total area	A_n/A_o	0.07	С	Redfield Ratios			
S. high lat. box area/Total area	A_s/A_o	0.17	С	Carbon/phosphate	C/P	130	b
Vol. NDW/Vol. SDW	R _{ns}	1.43	a (see text)	Nitrogen/phosphate	N/P	16	b
Global budgets				Oxygen/phosphate	O ₂ /P	138	f
Phosphate	P_{glob}	2.769×10 ¹⁵ mol	b	Southern CaCO ₃ /TCO ₂	S-Ca/CO ₂	0.2	g
Alkalinity	Alkglob	3.12×10 ¹⁸ mol	d	Low lat. CaCO ₃ /TCO ₂	L-Ca/CO ₂	0.2	g
Total dissolved CO ₂	TCO _{2glob}	2.98×10 ¹⁸ mol	d	Northern CaCO ₃ /TCO ₂	N-Ca/CO ₂	0.25	g
Radiocarbon (¹⁴ C)	¹⁴ C _{glob}	3.01×10 ⁶ mol	d				

^a (Menard and Smith, 1966); ^b (Toggweiler and Sarmiento, 1985); ^c estimates for globe>50° S and 40% of >50° N; ^d (Key et al., 2004); ^e (Najjar et al., 1992; Marchal et al., 1998); ^f (Redfield et al., 1962); ^g derived from Alk/P in ref^b.

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		E	BOX CONCEN	TRATIO	NS		BOX BUDGETS		
R _{ns} =1.43 Box	Box budget (10 ¹⁹ kg)	TCO_2 (μ mol kg ⁻¹)	Alkalinity $(\mu mol kg^{-1})$	∆ ¹⁴ C (‰)	Phosphate (µmol kg ⁻¹)	7CO ₂ (mol)	Alkalinity (mol)	¹⁴ C (mol)	Phosphate (mol)
South high latitude	1.523	2142	2306	-132	1.921	3.26E+16	3.51E+16	3.33E+04	2.926E+13
Low latitude	2.725	1875	2226	-9	0.2836	5.11E+16	6.07E+16	5.95E+04	7.728E+12
North high latitude	0.627	1987	2229	-65	0.4963	1.25E+16	1.40E+16	1.37E+04	3.112E+12
North deep	52.44	2120	2280	-123	1.34	1.11E+18	1.20E+18	1.15E+06	7.027E+14
Intermediate depth	40.87	2253	2326	-174	2.33	9.21E+17	9.51E+17	8.94E+05	9.523E+14
South deep	36.67	2323	2356	-199	2.929	8.52E+17	8.64E+17	8.02E+05	1.074E+15
Atmosphere 1.7	1.77E+20 (mol)	279.7 (ppm)	-	0	-	-	-	5.83E+04	-
					Total budgets:	2.98E+18	3.12E+18	3.01E+06	2.769E+15

Table 2. Box concentrations and budgets for "baseline" run (R_{ns} =1.43).

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			BOX CONCEN	ITRATIO	NS	BOX BUDGETS			
R _{ns} =1.43 Box	Box budget (10 ¹⁹ kg)	TCO_2 (μ mol kg ⁻¹)	Alkalinity $(\mu mol kg^{-1})$	∆ ¹⁴ C (‰)	Phosphate (µmol kg ⁻¹)	7CO ₂ (mol)	Alkalinity (mol)	¹⁴ C (mol)	Phosphate (mol)
South high latitude	1.523	2110	2292	-117	1.63	3.21E+16	3.49E+16	3.34E+04	2.484E+13
Low latitude	2.725	1838	2213	13	0.02	5.01E+16	6.03E+16	5.97E+04	4.589E+11
North high latitude	0.627	1947	2216	-44	0.22	1.22E+16	1.39E+16	1.37E+04	1.402E+12
North deep	29.7	2074	2265	-102	1.03	6.16E+17	6.73E+17	6.51E+05	3.056E+14
Intermediate depth	40.87	2214	2312	-158	2.04	9.05E+17	9.45E+17	8.96E+05	8.333E+14
South deep	59.4	2298	2345	-189	2.70	1.36E+18	1.39E+18	1.30E+06	1.603E+15
Atmosphere 1.7	1.77E+20 (mol)	246 (ppm)	-	25.54	-	-	-	5.26E+04	-
					Total budgets:	2.98E+18	3.12E+18	3.01E+06	2.769E+15

Table 3. Box concentrations and budgets for "glacial" run (R_{ns} =0.5).



Fig. 1. Box-model schematic (*S*, southern surface; *L*, low-latitude surface; *N*, northern surface; *ND*, north deep; *Int*, intermediate; *SD*, south deep). The vertical dashed line is intended to suggest an alternative hypothetical box geometry, where southern sourced water dominates the deep ocean. Heavy black lines indicate thermohaline circulation (F_n =northern overturning; F_s =southern overturning). Red arrows indicate two-way exchange (i.e. mixing) terms. Blue arrows indicate gas exchange. Grey arrows indicate particle fluxes. The particle fluxes $P_{i(sd)}$ and $P_{i(nd)}$ that by-pass the intermediate box from the low-latitude box are calculated in proportion to the volume of each deep box relative to the total deep ocean in the model, such that if $V_{nd}/V_d = f$, $P_{i(nd)} = f \times 0.1 \times P_i$ and $P_{i(sd)} = (1-f) \times 0.1 \times P_i$. Approximate box depths are indicated at left (surface areas are given in Table 1).





Fig. 2. Sensitivity of modelled atmospheric ρCO_2 (**A**) and average deep ocean $\Delta^{14}C$ (**B**) to changes in the box-model physical mixing terms, expressed here as percentages relative to the baseline values given in Table 1. The crossed circles indicate results for experiments where both the total overturning strength ($F_n + F_s$) and the surface-box biological uptake rates (i.e. export efficiency) were varied in order to maintain prescribed modern surface box phosphate concentrations.

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Fig. 4. Illustration of how the volume ratio (R_{ns}) of "northern" (NDW) to "southern" (SDW) water-masses is hypothesised to change based on water-mass boundary shoaling and given the hypsometry of the sea floor. The left hand panel shows changing water-mass ratio R_{ns} *versus* the water depth of a presumed horizontal water-mass boundary. Solid dots indicate estimated values for "modern" and last glacial maximum (LGM) hydrography. The right hand panel shows how the sea floor area varies with water depth in the Atlantic and Indo-Pacific basins. Shading illustrates how R_{ns} is calculated, by assuming that SDW fills the abyssal ocean up to the presumed water-mass boundary, while NDW fills only half of the Indo-Pacific basin and all of the Atlantic basin above this. The volume ratio R_{ns} for a given fill depth is thus estimated as the volume above the fill depth in the Atlantic, plus half the volume above the fill depth in the Indo-Pacific. This tempers the exaggeration in volume change that would otherwise result from treating the whole ocean as analogous to the Atlantic.

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Fig. 6. Sensitivity of the modelled change in atmospheric pCO_2 to changes in R_{ns} when Southern Ocean gas exchange efficiency is enhanced/reduced and Southern Ocean biological export efficiency is enhanced to 100%. Although these change affect absolute levels of atmospheric pCO_2 , the same sensitivity of ΔpCO_2 to R_{ns} results in each case.