**Climate
of the Past
Discussions**

Interactive comment on "Glacial – interglacial atmospheric CO$_2$ change: a possible "standing volume" effect on deep-ocean carbon sequestration" *by* L. C. Skinner

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I am very grateful for the referees' detailed and thoughtful comments, which I have now had a chance to consider and which I attempt to address below. I think that after addressing the issues raised by the referees, it is still possible to demonstrate that the proposed 'standing volume' mechanism is indeed a viable one, which could contribute to atmospheric CO2 changes of perhaps 20-30 ppm (i.e. non-negligible). Such changes, which would occur on millennial timescales, could represent not so much a major contribution to glacial – interglacial CO2 change, as a means of coordinating and enhancing marine carbon cycle change via the well-known biological/solubility pump

mechanisms. The implication is that changes in water mass geometry may represent an important impetus and amplifier for marine carbon cycle change, and as such could play an as yet understated role in the glacial/deglacial process.

Below I lay out my response to each referee in turn.

Referee 1

Referee 1 raises three 'major issues' that need to be addressed.

Major issue 1: "It seems that the concept of the standing volume (SV) effect is not used consistently throughout the paper..."

This is true. The intended full definition of the standing volume effect is indeed: the change in the marine carbon budget that arises from relative changes in deep water-mass volumes, prior to any modification of vertical mass transport rates, but including the effects of any redistribution of temperature, salinity, and pre-formed/remineralised nutrients that results from the change in volumes. With this definition more clearly stated, I believe that much of the criticism of Referee 2 can also be addressed (see below). I have modified the text in sections 1, 2 and 5 as suggested by Referee 1 in order to provide a clearer and more consistent definition of the proposed mechanism.

Although Referee 1 is completely right to point out an inconsistent/ambiguous definition of the standing volume effect in the original manuscript, I would plead that it may still be warranted to conduct a preliminary 'thought experiment' that employs only part of the full definition, as I have done in section 2. This seems to be warranted for illustrative/introductory purposes, as long as the predication of the 'standing volume effect' employed is clearly stated, which I believe I do at the end of section. I believe this helps to set a basis for what follows in the manuscript.

Major issue 2: "I think the argument is on the right track in drawing attention to the DIC differences between AABW and NADW, but enters shaky territory when assuming total phosphate is also diagnostic because phosphate and carbon are too easily decoupled

by air-sea exchange…. The key is to articulate why, despite [the] loss of CO2 to the atmosphere [during AABW formation], an expansion of AABW in the Atlantic is expected to cause atmospheric CO2 to decrease. "

This is indeed an important point, but one that I think was already addressed to some extent in the original manuscript. The central contention is that AABW could maintain equilibrium with the atmosphere so effectively (via vertical mixing in the Southern Ocean and/or air-sea gas exchange) that an increase in its representation in the deep-sea would push atmospheric CO2 up, not down. However, the original manuscript specifically noted in Section 5 that the proposed impact on CO2 would only occur under three conditions, including the condition that the DIC concentration of the expanding water-mass were greater than that of the water-mass it displaced ($C_{sd} > C_{nd}^{\r{A}}$). Thus, if the DIC budget of the ocean increases (which it must if a greater volume of the ocean has a higher DIC concentration), that of the atmosphere must decrease as long as the total carbon budget of the ocean/atmosphere system is maintained. The only way around this is if, as Referee 1 suggests, the DIC of the expanding water-mass is actually lower than that of the water-mass it displaces, perhaps due to enhanced gas exchange processes. But this alternative is dealt with by stating that the effect holds true only as long as $C_{sd} > C_{nd}$.

The extent to which phosphate can be taken as diagnostic of DIC in this regard is a slightly separate issue, which ultimately depends on the efficiency of air-sea gas exchange and the relative importance of preformed- and remineralised nutrients in the expanding water-mass. In the original manuscript an attempt was also made to deal with this issue by conducting 'enhanced gas exchange/biological export' experiments (second paragraph, Section 5), which demonstrated that the sensitivity of atmospheric CO2 to the proposed standing volume effect was not greatly impacted on by a doubling of the efficiency of gas exchange in the box-model Southern Ocean or a fully depleted Southern Ocean phosphate pool, even if the overall partitioning of carbon between the atmosphere and the ocean was of course affected by these changes. Therefore, while

higher gas exchange rates and lower biological export rates in the box-model Southern Ocean act to increase equilibrium atmospheric CO2 levels (and vice versa), changes in the relative volumes of the two deep-water masses have a similar impact regardless of gas exchange or biological export rates.

The key point then (which I believe Referee 1 is driving at), is whether or not there is a countervailing change in gas exchange rate in the Southern Ocean at the same time as a change in the volumes of the water-masses, thus counteracting the standing volume effect (the same holds for countervailing changes in biological export rates). But this was already stated in the original manuscript, for example in the first paragraph of section 5 and again in section 6 (page 22, lines 5-9): "The proposed 'standing volume effect' would arise due to substantial changes in the volume of [LCDW]-like (relatively high TCO2) 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."

However, there are also practical problems with inferring a better 'ventilated' deep Southern Ocean during glacials, and during the last glacial maximum (LGM) in particular. I have modified the text in Section 2 and in Section 5 in order to underline the fact that radiocarbon evidence (e.g. Marchitto et al., Science, 2007), benthic δ13C (e.g. Ninneman et al., EPSL, 2002) and pore-water temperature/salinity estimates (Adkins et al., Science, 2002) all tend to suggest that deep-water in the Southern Ocean probably represented an isolated repository for carbon that was rather poorly equilibrated with the atmosphere. Indeed, recent evidence has now confirmed this, indicating that glacial LCDW had a very low carbonate ion concentration (hence presumably an elevated TCO2) (Barker et al., 2009; Barker et al., submitted), as well as a very depleted radiocarbon concentration (Skinner et al., submitted), indicating that glacial LCDW was very poorly equilibrated with the atmosphere relative to today.

In an attempt to make the above points clearer in the revised manuscript, section 5 has been rewritten so as to state more clearly how the standing volume effect works, what

it requires, and that it represents a means of triggering small but significant changes in the biological and solubility pumps, as well as a means of enhancing additional imposed changes in the biological/solubility pumps due to extraneous factors such as ocean fertilization, buoyancy stratification or sea-ice expansion.

Major issue 3: "Certainly, one should not lump together AABW and CDW."

I absolutely agree. The reference to AABW throughout the manuscript was not only unhelpful but also incorrect. There is perhaps an unfortunate tendency to refer colloquially to southern sourced deep-water that is exported to the Atlantic and Indo-Pacific as 'AABW', which I fell prey to – mea culpa! Accordingly I have revised the manuscript to make clearer the distinction between AABW and CDW. Furthermore, in order to avoid the confusion between southward/eastward flowing CDW and the denser water that is exported to the Atlantic and Indo-Pacific basins, I have revised the text to refer specifically to 'lower circumpolar deep-water' (LCDW), which does flow predominantly northwards in every sector of the deep Southern Ocean (e.g. Sloyan and Rintoul, JPO, 2001), and with a relatively elevated DIC concentration (e.g. Key et al., GBC, 2004). AABW is therefore replaced with LCDW throughout the revised text. As pointed out by Referee 1, LCDW should not be confused with UCDW, which flows predominantly southwards in all sectors of the Southern Ocean, and is mixed downwards into LCDW and mixed upwards into Antarctic sub-polar mode/surface water where it is modified by air-sea exchange (Sloyan and Rintoul, JPO, 2001). It is this water-mass that introduces NADW into the ACC in the Atlantic sector of the Southern Ocean, and which outcrops directly in the Southern Ocean.

The key question, with regard to the third 'major issue' of Referee 1, is the extent to which the removal of the influence of NADW on the composition of upper- and lower CDW would cause the DIC concentration of the Indo-Pacific to increase or decrease. As Referee 1 points out, if it was AABW replacing LCDW, the DIC concentration of the Indo-Pacific could indeed decrease slightly, due to the effects of air-sea exchange during AABW formation (especially if air-sea exchange was enhanced dur-

ing the last glacial, which I argue above is unlikely). However, what was envisaged in the manuscript was an expansion of LCDW in the Atlantic basin, along with a modification of the composition of LCDW that is exported downstream of the Atlantic sector of the Southern Ocean, which would arise from a reduction in the contribution of NADW to UCDW. The manuscript text (in particular Section 2) has been modified in order to make this proposition clearer. In this scenario, with the removal of the low-DIC NADW end-member from UCDW and LCDW, it is hard to imagine that the DIC of LCDW/AABW exported northwards into the Indo-Pacific would not increase. If this is granted, the basic premise of the model experiments described in the manuscript should remain valid, even if the extent of the DIC increase achievable in the Indo-Pacific by this process could be debated.

Minor Issues (Referee 1):

1. Section 1 and Abstract: The notion that prior work on the glacial CO_2 drawdown focused only "dynamical or kinetic" processes is perhaps a bit misleading. The idea that CO_2 is largely controlled by pre-formed nutrients has a very long history. This idea also transcends the notion of exclusively dynamical or kinetic control.

I completely agree with the statement that the idea that CO_2 is largely controlled by pre-formed nutrients has a very long history, and one might think that this would imply that consideration had been given to the effects of changing water-mass volumes. Nevertheless, as far as I can tell, all of the experiments that have been performed to explore the impacts of changes in preformed nutrient budgets, or changes in the efficiency of the biological- or solubility pumps, have done so via changes in air-sea gas exchange rates or water/mass fluxes. This is neatly summed up in Figure 8 from the review article of Sigman & Haug (2003), where in order to effect changes in the efficiency of the biological pump, either the flux of water into the ocean interior is changed or the nutrient concentration of that water is changed (only obtainable via biological export changes, all else being constant). As a reflection of this, Watson & Naviera-Garabato (2006), Brovkin et al. (2007), Peacock et al. (2006) and Köhler et al. (2005) all modify fluxes

([M][T]-1) in their experiments. Toggweiler et al (2003) did propose changes based on volumetric dominance of 'AABW' versus 'NADW', however this was not explicitly evaluated in the model by weighting the DIC of each grid cell (for example in their Fig. 5) by the volume of that grid cell, and thus calculating the budgets attributable to each water mass, regardless of their peak DIC values.

2. Page 1268, line 4: Why is it relevant to consider nitrogen in the box model? Unless the model tracks nitrogen sources and sinks (e.g. fixation and denitrification) there is no reason to mention nitrogen here. Better to clarify that this is a single-nutrient model, based on phosphate alone.

Agreed; the reference to nitrogen has been removed from the text.

3. Page 1269: The equations defining the box model need to be presented in a more orderly fashion. The second Equation on page 1269 contains a factor Rns which is not defined until much later. Does this equation perhaps have a spurious factor of C*/P* on the last term?

The C*/P* is not a spurious term, since this refers to the ratio of species concentration (C*, for phosphate, TCO2 etc. . .) to organic carbon (P*).

4. It would be better to write this Equation in terms of the variable Pi(sd) shown in Figure 1, followed by the Equations clarifying how Pi(sd) and Pi(nd) vary with box volume (these critical equations are currently buried in the caption to Figure 1).

This has been changed (thus removing the factor Rns that was not defined).

5. Why are two Equations given for dCn/dt? This seems unnecessary. The quantity (CO2)SOL-n is not defined. There is no need to present the equation for the temperature dependence of CO2 solubility since there are many suitable versions in the literature that could just be cited. Housekeeping of this sort is needed to make model details clearly understandable.

The solubility coefficient has been referenced instead. One equation for dCn/dt is now

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used; in fact the second reference to Cn was an error. Thus the use of (CO2)SOL-n was also mistake. This equation was supposed to refer to the southern surface box, and (CO2)SOL-s instead, which is defined in the next equation down. This has been corrected.

6. Figure 1: The fluxes Pi(sd) and Pi(nd) are drawn as originating from intermediate depth. This looks odd. I think it would probably be better to draw multiple arrows from the surface box, each terminating in a different subsurface box.

The figure has been modified accordingly.

7. Figures 2 and 3: The text in these figures is rendered too small to be clearly legible.

This has been corrected.

Referee 2

Referee 2 raises two main issues: 1) that the CO2 drawdown in the box model arises in part due to a questionable increase in the degree of nutrient utilization (in the low latitudes in particular); and 2) that the bulk of the CO2 drawdown actually arises due to the solubility pump, via the cooling of the deep sea through the expansion of a relatively cold deep-water mass. In addition, given that the mechanisms by which CO2 is reduced in the box-model stem from the biological- and solubility pumps, Referee 2 contends that no new corner of parameter space has been identified for glacial – interglacial CO2 change.

Referee 2 is certainly correct in stating that the standing volume effect identified in the box model arises via changes in the biological- and solubility pumps. This fact has been clarified in the manuscript by rewriting section 5 and the abstract to state this explicitly. Indeed, the main aim of the manuscript was not to identify new 'vectors' for carbon transport in the ocean or between ocean and atmosphere. Rather the intention was to identify a novel mechanism for motivating changes in the well-known biological-

and solubility pumps. As described in response to Referee 1, the revised text tries to make it more clear that the envisaged standing volume effect includes (indeed depends on) changes in the distribution of water properties/chemistry that arise from changes in the relative volumes of contrasting deep-water masses. The volumetric changes are thus seen as a way to cause 'nutrient deepening', which I argue has not yet been examined in sufficient detail in the literature.

Despite this clarification of the manuscript aims and the definition of the standing volume effect, there remains the question of how much the nutrient pool of the surface ocean, and in particular the low-latitude surface ocean, can actually be reduced by the changes invoked in the box model. Referee 2 contends that a drop of ~ 0.2 μmolkg-1 in the phosphate concentration of the 'low-latitude' box is unreasonable because the low-latitudes are already essentially nutrient deplete today. However, we must bear in mind that in the box-model, the 'low-latitude' box reaches from 50oS to 50oN (and is 100m thick). Today, this region of the ocean includes large areas with phosphate concentrations greater than zero. Indeed, World Ocean Atlas 2005 data indicate that the mean phosphate concentration between 45oS and 45oN (i.e. excluding most of the nutrient-rich fringes of the sub-polar fronts) is ~ 0.2 μmolkg-1 near the sea surface and ~ 0.6 μmolkg-1 at 100m. Therefore I would argue that there is some scope for nutrient drawdown in what corresponds to the 'low-latitude' box, and that this must be at least ~ 0.2 μmolkg-1. If the box-model is modified so that low-latitude phosphate can change by a smaller amount (by changing the initial amount of low-latitude phosphate), the standing volume effect on atmospheric CO2 is diminished accordingly (this is also the reason why the sensitivity of atmospheric CO2 to changing Rns is diminished with extremely high Southern Ocean biological export, as shown in Figure 6). Therefore, although Referee 2 is absolutely right that nutrient drawdown in the surface ocean is crucial to the proposed standing volume effect (as discussed in Section 5 of the original manuscript) I would argue that the extent of nutrient drawdown effected in the box-model is not completely unreasonable, or indeed impossible in reality. He main point is again that changing water-mass geometry may be another way to affect the

efficiency of the biological pump, as discussed at the end of Section 5.

Referee 2 makes two final comments: the first is regarding the extrapolation of 'Atlantic' hydrographic changes to the Indo-Pacific; and the second is regarding the inherent 'strangeness' of attributing significance to box volumes in a box-model rather than their filling rates.

The first of these comments may stem from a misreading of the manuscript. Instead of extrapolating Atlantic hydrographic changes directly to the Indo-Pacific, a rough estimate of Indo-Pacific hydrographic change was derived from the modern contribution of NADW to the Indo-Pacific, with the additional assumption that if NADW does not affect the Atlantic sector of the Southern Ocean below a given depth, then water exported to the Indo-Pacific below this depth would also be without NADW influence. An attempt has been made to make this clearer in section 4 of the revised manuscript. Admittedly, this is a very rough method for predicting the NADW/LCDW mixing ratio of the Indo-Pacific basins at various water depths, however it is supported by LGM benthic δ13C, which show a shoaling of low-δ13C deep-water in the Atlantic sector of the Southern Ocean (Hodell et al., G3, 2003) in parallel with a large drop in the δ13C of LCDW exported to the deep Pacific (McCave et al., QSR, 2008). New εNd results (Piotrowski et al., EPSL 2008; 2009) also indicate a significant reduction in the NADW contribution to LCDW exported to the Cape Basin and the deep Indian Ocean. Although the method of prescribing Indo-Pacific changes on the basis of Atlantic ones is very rough (as I indicate in the second paragraph of section 4), I would argue that it is defensible as an approximation.

The second of Referee 2's final comments illustrates perfectly the need for a study that investigates the impacts of water-mass volume changes on 'average' deep ocean chemistry. The main point of the manuscript is precisely that it is perhaps not strange or absurd to attribute importance to box-volumes, over and above their filling rates for three reasons: 1) the volume occupied by a water-mass directly sets its chemical budget (in relation to its concentration), as well as its mean residence time (in rela-

tion to its overturning rate); 2) palaeoceanographic evidence compels us to at least evaluate the impacts of changes in water-mass volumes, as distinct from changes in mass-transport rate; and 3) conceptual tidiness (and the search for viable 'triggers' for carbon cycle change) requires that we distinguish between kinetic- versus potential energy adjustments in the ocean. As stated in the second to last paragraph in Section 1, 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.

A final important note: It may be noted that the numbers included in the plots have changed in the revised manuscript. This is due to an error that was identified in the way that the global budget correction scheme was implemented for carbon. The error was that the global carbon budget was being normalized to the marine budget, rather than the marine and atmospheric budgets combined. This had then effect of tending to exacerbate changes in atmospheric CO2 that resulted from changes in the marine carbon budget. With this mistake corrected, the modeled changes are slightly reduced (while nevertheless remaining of broadly similar magnitude), but the sense of change and the mechanisms at work are not affected in any way.

In I sincerely hope that my response and revisions will prove adequate to satisfy both Referees.

LCS