Impact of oceanic circulation on biological carbon storage in the ocean and atmospheric $p$CO$_2$

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Abstract. We use both theory and ocean biogeochemistry models to examine the role of the soft-tissue biological pump in controlling atmospheric CO$_2$. We demonstrate that atmospheric CO$_2$ can be simply related to the amount of inorganic carbon stored in the ocean by the soft tissue pump, which we term ($OCS_{soft}$). $OCS_{soft}$ is linearly related to the inventory of remineralized nutrient - which in turn is just the total nutrient inventory minus the preformed nutrient inventory. In a system where total nutrient is conserved, atmospheric CO$_2$ can thus be simply related to the global inventory of preformed nutrient. Previous model simulations have explored how changes in the surface concentration of nutrients in deepwater formation regions change the global preformed nutrient inventory. We show that changes in physical forcing such as winds, vertical mixing, and lateral mixing can shift the balance of deepwater formation between the North Atlantic (where preformed nutrients are low) and the Southern Ocean (where they are high). Such changes in physical forcing can thus drive large changes in atmospheric CO$_2$, even with minimal changes in surface nutrient concentration. If Southern Ocean deepwater formation strengthens, the preformed nutrient inventory and thus atmospheric CO$_2$ increase. An important consequence of these new insights is that the relationship between surface nutrient concentrations, biological export production and atmospheric CO$_2$ is more complex than previously predicted. Contrary to conventional wisdom, we show that $OCS_{soft}$ can increase and atmospheric CO$_2$ decrease, while surface nutrients show minimal change and export production decreases.

1. Introduction

Volk and Hoffert [1985] define an ocean carbon pump as "a process that depletes the ocean surface of dissolved inorganic carbon (DIC) relative to the deep-water DIC." They recognized three such pumps: the soft-tissue pump, the carbonate pump and the solubility pump. While the first two are biological, the third is a response to solubility differences of CO$_2$ in warm and cold water. Of the three, the soft-tissue or organic pump receives the most attention because it is potentially the largest and also seems to exhibit the most variability over time, e.g. glacial-interglacial cycles. Recent work suggests, however, that the biological process causing the surface to deep DIC difference ($DIC_{deep} - DIC_{surf}$) to vary in the real ocean is quite different from the kind of pumping process envisioned by Volk and Hoffert.

Organisms create a DIC difference when they take...
up PO_4 and CO_2 at the surface and create sinking organic particles that are then remineralized back into PO_4 and CO_2 in the deep ocean. In their derivations, Volk and Hoffert defined the soft tissue pump as a function of the mean oceanic vertical gradient of PO_4, i.e.

\[ \Delta \text{DIC} = r_{C,P} \cdot \Delta \text{PO}_4, \]

where \( r_{C,P} \) is a stoichiometric ratio. Similarly, Broecker and Peng [1992] and Gruber and Sarmiento [2002] determine the soft tissue contribution from the difference between local and mean surface PO_4.

However, as emphasized recently by Ito and Follows [2005] (henceforth IF), there are two components to \( \Delta \text{PO}_4 \), the preformed and the remineralized components. The preformed PO_4 are the biologically unutilized nutrients which are subducted into the ocean interior. As shown in the three-box models of Sarmiento and Toggweiler [1984] and Siegenthaler and Wenk [1984], it is the preformed component, rather than the total PO_4, that is most likely to vary over time. Hence, Volk and Hoffert's pump metaphor and its emphasis on fluxes of organic matter and surface-to-deep gradients of total phosphate seems to us to be pointing in the wrong direction.

The preformed PO_4 in the three-box model is set in the model's polar box, which is generally taken to represent the high-PO_4 surface waters of the Southern Ocean (Figure 1a). Utilization (or underutilization) of PO_4 by organisms in the polar box can lower (or raise) the preformed PO_4 and make \( \text{DIC}_{\text{deep}} - \text{DIC}_{\text{surf}} \) large (or small). However, the polar box in the three-box model is really a combination of the ocean’s two areas of deep-water formation, the low-PO_4 North Atlantic and the high-PO_4 Southern Ocean. As pointed out by Toggweiler et al. [2003], the spread or difference in preformed PO_4 between the low-PO_4 north and the high-PO_4 south gives \( \text{DIC}_{\text{deep}} - \text{DIC}_{\text{surf}} \) an additional degree of freedom to vary, and the spread owes more to the distinctive circulations in the north and south than to differences in end-member nutrient utilization. So, while it is possible for organisms to alter \( \text{DIC}_{\text{deep}} - \text{DIC}_{\text{surf}} \) by changing polar PO_4 concentrations it is also possible that changes in circulation alter \( \text{DIC}_{\text{deep}} - \text{DIC}_{\text{surf}} \) by changing the mix of northern and southern water that fills the ocean interior.

Hence, we propose in Section 3 of this paper a less biased terminology, Ocean Carbon Storage (\( \text{OCS}_{\text{soft}} \)), to describe how \( \text{DIC}_{\text{deep}} - \text{DIC}_{\text{surf}} \) varies in the ocean. We also show that a theory based on the weighting of northern and southern components does an excellent job of predicting the \( \text{OCS}_{\text{soft}} \) in models with different circulations. Changes in \( \text{OCS}_{\text{soft}} \) directly affect atmospheric pCO_2. We show in Section 4, along the lines of IF, that atmospheric pCO_2 is exponentially related to \( \text{OCS}_{\text{soft}} \) and the global inventory of preformed PO_4 at the limit where gas exchange rates are artificially fast enough to suppress ocean-atmosphere pCO_2 differences. The relationship becomes more complicated if we take into account the surface disequilibrium of CO_2 (Section 5).

2. Methods: Model Simulations

We perform long equilibrium simulations for eight versions of a GCM with different oceanic circulations produced by different mixing or winds. The total ocean-atmospheric carbon inventory is identical among all models. Because the partitioning of inorganic carbon between ocean and atmosphere depends on circulation, atmospheric pCO_2 at equilibrium is different in the different models.

The GCM we use is the Geophysical Fluid Dynamics Laboratory Modular Ocean Model version 3 [Pacanowski...
and Griffies, 1999] with a biogeochemistry component consistent with OCMIP-2 specifications [Najjar and Orr, 1998, Najjar et al. 2007]. New biological production is calculated by forcing surface PO$_4$ towards observed seasonal Levitus values PO$_4$$_{obs}$, at each time step $t$, whenever

$$J_{prod}(x, y, z, t) = (PO_4(x, y, z, t) - PO_4_{obs}(x, y, z, t))/\tau,$$

(1)

for $z < 75$ m. $\tau$ is the biological time scale. $x$, $y$, $z$ are model longitude, latitude and depth. Globally integrated PO$_4$ is set constant in all experiments.

Two sets of simulations are performed: a standard, realistic set with $\tau$=30 days and one with extremely inefficient biology ($\tau$=1 year). For simplicity we turn off the solubility and carbonate pumps by setting surface ocean temperature and salinity constant everywhere in the CO$_2$ gas exchange calculations, and by setting alkalinity constant everywhere. This soft-tissue model configuration was used in Marinov et al. [2006].

In addition to the standard biogeochemical tracers from previous versions of this model (O$_2$, PO$_4$, dissolved inorganic carbon (DIC), particulate organic phosphate, dissolved organic phosphate), we add “preformed phosphate” as a new tracer. The preformed tracer is set equal to the model PO$_4$ concentration at each surface ocean point. In the ocean interior the preformed tracer is advected and mixed without biological sources or sinks.

Mixing is parameterized in terms of a diapycnal diffusion coefficient $K_v$ and an isopycnal coefficient $A_i$. The latter coefficient is used both for along-isopycnal stirring and for representing advective fluxes associated with mesoscale eddies [Gent and McWilliams, 1990]. Several different model versions are designed as follows.

- In the standard or LL model, $K_v$ varies hyperbolically in the ocean from 0.15 cm$^2$/s at the surface to 1.3 cm$^2$/s at 5000 m with a hyperbolic tangent transition at 2500 m [Bryan and Lewis, 1979]. Isopycnal mixing $A_i$ coefficient is set to 1000 m$^2$/s everywhere in the ocean.

- In the high $K_v$ model, $K_v$ varies hyperbolically from 0.6 cm$^2$/s at the surface to 1.3 cm$^2$/s at 5000 m everywhere in the ocean. $A_i$ is set to 1000 m$^2$/s as above.

- In the high $A_i$ model, $A_i$ is set to 2000 m$^2$/s everywhere while $K_v$ has LL model values.

- In the high $A_i$-high $K_v$ model, $A_i$ is set to 2000 m$^2$/s everywhere while $K_v$ is as in the high $K_v$ model.

- In a high south $K_v$ model, vertical mixing coefficient $K_v$ is set to 1 cm$^2$/s throughout the water column south of 50$^\circ$S. Elsewhere in the ocean, $K_v$ has the same hyperbolic profile as the LL model. $A_i$ is set to 1000 m$^2$/s everywhere as in LL.

The above five models are based on Gnanadesikan et al. [2002, 2003, 2004] and use seasonal wind stresses of Hellerman and Rosenstein [1983].

To explore the effect of extreme Southern Ocean wind stress we design three other models where winds are set to Hellerman and Rosenstein everywhere except south of 30$^\circ$S where wind stress is either increased three fold (windx3 model), increased two fold (windx2 model) or decreased by 50% (windx0.5 model) relative to the LL model (Figure 1h). $K_v$ and $A_i$ have LL model values.

The windx2 model has wind stresses comparable to the ECMWF stresses of Trenberth et al. [1989].

Each of the above models is run for a few thousand years to equilibrium with both regular gas exchange and fast gas exchange (where surface pCO$_2$ at each time step is set equal to atmospheric pCO$_2$ calculated at the pre-
vious time step). In an infinitely fast gas exchange scenario, CO₂ at the ocean surface is in equilibrium with the atmosphere above, and surface DIC disequilibrium is zero. This assumption is fundamental both in deriving theoretical models of the ocean carbon cycle (section 4.1) and making sense of model results (section 4.2-4.3). However, as we will see in section 5 and has already been pointed out by others (e.g., Toggweiler et al., 2003), the surface DIC disequilibrium can have a sizable impact on the amount of carbon stored in the ocean, causing departures from simple theories.

The standard (LL) model with fast gas exchange is run to equilibrium from an arbitrary dissolved inorganic carbon (DIC) distribution with a fixed preindustrial atmospheric CO₂ concentration of 278 ppm by allowing CO₂ to invade the ocean until the absolute value of the global, annual mean air-sea CO₂ flux is less than 0.01 PgC/yr. This model is then run further with constant global ocean-atmospheric carbon inventory, while atmospheric CO₂ is allowed to vary. After bringing the LL model to a new equilibrium, we calculate the total inorganic carbon inventory (total ocean DIC plus total atmospheric CO₂). We then run simulations for all other circulation models while keeping the total ocean-atmosphere carbon inventory constant and identical with the LL inventory. Since this inventory is kept constant, atmospheric pCO₂ is different between simulations with different physical models, as well as between fast and regular gas exchange simulations in the same physical model.

3. Model Results

The present section discusses results from equilibrium simulations using the eight different models described above. We show that export production and surface nutrients are not good indicators for atmospheric pCO₂. By contrast, the global volume-averaged preformed nutrients are excellent indicators for atmospheric pCO₂.

3.1. Oceanic circulation and biological export production

The simulated oceanic circulation relevant for the carbon cycle can be summarized as follows. Wind forces deep water rich in nutrients and DIC to upwell as Circumpolar Deep Water (CDW) to the south of the Antarctic Polar Front. The lower circulation (schematically shown in blue in Figure 1b) consists of the upwelling Southern Ocean water which moves southward and is subducted to the deep ocean south of the Polar Front as Antarctic Bottom Water (AABW). The upper circulation (in red in Figure 1b) comprises the upwelling Southern Ocean water which moves northward and eventually returns to the Southern Ocean via North Atlantic Deep Water (NADW).

Changes in diapycnal diffusivity $K_v$ and Southern Ocean winds have a large impact on both the lower and upper simulated circulations. As diapycnal diffusivity $K_v$ increases, both the meridionally integrated zonal mass transport and the zonally integrated meridional mass transport increase [Gnanadesikan, 2003 and Figure 2a-b], resulting in stronger upper and lower circulations, i.e., stronger vertical exchange around 60°S and stronger sinking of dense water south of 60°S.

Larger zonal wind magnitude at Drake Passage latitudes (55°S to 63°S) results in larger northward Ekman volume transport and forces stronger southward geostrophic flow at depth and more Southern Ocean upwelling in the windx3 compared to the LL run (Fig-
ure 2a,c). At the same time, stronger westerlies or stronger $K_v$ drive an increase in Southern Ocean convective mixing (Figure 2d-f). Since the overturning circulation is partly driven by deep convection in the models, this results in a stronger lower circulation cell and thus more vigorous deep ocean ventilation via the Southern Ocean.

Examination of $^{14}$C distributions show that the variations in deep ocean $^{14}$C due to changes in winds or mixing emanate primarily from the Southern Ocean via AABW or convection. Less negative $\Delta^{14}$C below the thermocline in both the high $K_v$ and windx3 runs relative to the LL run indicates younger deep waters and more vigorous deep water ventilation (Figure 2g). Conversely, smaller Southern Ocean winds or larger $A_i$ result in a weaker Southern Ocean deep overturning cell and thus in less deep water ventilation relative to the standard LL model, as indicated by more negative $\Delta^{14}$C values.

Based on our analysis of the oceanic circulation and $^{14}$C in the models, we can broadly divide our models into low Southern Ocean ventilation models (LL, windx0.5, high $A_i$) and high Southern Ocean ventilation models (high $K_v$, high $A_i$-high $K_v$, windx2, windx3), depending on the strength of the Southern Ocean overturning or "lower" circulation.

Oceanic circulation and convective mixing impact the distribution of biological export production (Figure 3a). Larger vertical mixing or larger Southern Ocean winds increase convection and upwelling of deep waters in Drake Passage latitudes. This implies a larger supply of deep ocean nutrients to the surface and higher global export production in the high mixing models relative to the standard (LL) model, with largest increases in convective regions such as the Weddell Sea. Conversely, lower Southern Ocean winds decrease convection and upwelling, slightly decreasing Southern Ocean biological production.

Figure 3a shows that stronger biological export production is associated with higher $pCO_2$ and therefore with lower (not higher, as one might be tempted to think) oceanic accumulation of carbon across our seven models. Biological export production alone cannot be used to explain variations in $pCO_2$. When biology is inefficient ($\tau = 1$ year), a slow removal of surface PO$_4$ results in weaker export production and less $pCO_2$ drawdown compared to an efficient biology case ($\tau = 30$ days; compare open and full symbols in Fig 3a). While the spread in export production is smaller when biology is inefficient, it is still the case that high ventilation models have higher export production.

Biological export production alone is not a good indicator for $pCO_2$ in our models. In order to understand atmospheric $pCO_2$ variations we need to understand what controls the CO$_2$ storage in the ocean.

### 3.2. Preformed and Remineralized nutrients

High surface nutrient concentrations, particularly in high latitudes, are a sign that biology is inefficient at these latitudes. The biologically unutilized nutrients which are subducted and transported into the interior ocean are called preformed nutrients.

The total nutrient pool in the ocean can be divided into a preformed pool and a remineralized pool,

$$PO_4 = PO_{4\text{pref}} + PO_{4\text{remin}},$$

where an overline denotes global volume averages. Previous studies inferred preformed PO$_4$ from the concentra-
tion of apparent oxygen utilization or \( AOU \):

\[
PO_4^{pref} = PO_4 - r_{O_2} \cdot AOU = r_{O_2} \cdot (O_2 - O_2^{sat}),
\]

where \( PO_4 \) and \( O_2 \) are model tracers and the saturation concentration \( O_2^{sat} \) is a function of local temperature and salinity. This method assumes that surface \( O_2 \) is in equilibrium with the atmosphere, an assumption which does not always hold and results in errors in \( AOU \) estimates (Ito et al. [2004]). It is precisely to circumvent these problems that we introduce preformed \( PO_4 \) as an actual model tracer.

Since surface preformed \( PO_4 \) is highest in the Southern Ocean, high Southern Ocean ventilation models (e.g., high \( K_v \), windx3) have higher preformed phosphate concentration in the deep ocean compared to the low ventilation models (LL, windx0.5, high \( A_i \)), as indicated by Fig. 4 and by the nice \( \Delta^{14}C - PO_4^{pref} \) correlation (Fig. 2g, Table 1).

Remineralized nutrients are nutrients added to the ocean interior through organic matter remineralization, and are calculated here as the difference between two model tracers: total \( PO_4 \) and preformed \( PO_4 \). Since globally averaged total \( PO_4 \) is constant in our experiments, a smaller nutrient fraction in the remineralized pool is equivalent to a larger nutrient fraction in the preformed pool and vice-versa (Figure 4, Figure 5a-b).

Much oceanographic literature has been devoted to the connection between surface nutrients levels and atmospheric \( pCO_2 \) [e.g., Archer et al., 2000]. Do we see a causal correlation between surface nutrients and \( pCO_2 \) in our GCMs?

A cursory look at Figure 3b would seem to indicate a relationship between \( pCO_2 \) and surface nutrients. However, this is an indirect result of changes in circulation—higher vertical exchange results in more productivity which (because of our parameterization of productivity in terms of nutrient restoring) must be associated with higher surface nutrients. The idea that surface nutrient concentrations can be simply related to \( pCO_2 \) is undermined by the different linear relationships seen for the different restoring times. In the Supplementary material we present further evidence undermining the idea that there is a simple mapping from surface nutrients to \( pCO_2 \), based on simulations in which the surface nutrients in the Southern Ocean are restored to zero.

By contrast, the global volume average of preformed \( PO_4 \) is an excellent indicator of \( pCO_2 \) (Figure 3c), with all simulations lying on a single line. In Section 4.4 we ask whether intermodel changes in global preformed \( PO_4 \) are due to the observed changes in surface nutrients versus changes in ventilation, and conclude that the latter are critically important. We next analyze what determines the preformed \( PO_4 - pCO_2 \) relationship.

4. Discussion

4.1. Ocean Carbon Storage, preformed nutrients and atmospheric \( pCO_2 \)—a theoretical analysis

At every point in the ocean \( DIC \) can be decomposed into its equilibrium contribution and components due to the soft tissue, carbonate and solubility pumps:

\[
DIC = DIC_{eq} + DIC_{soft} + DIC_{carb} + DIC_{solub} + DIC_{diseq}.
\]

In its most general form, the total amount of carbon
in the atmosphere-ocean system can be written as:

\[
TC_{atm, oc} = M_{atm} \cdot pCO_2a + V_{oc} \cdot DIC_{eq} + OCS_{soft} + OCS_{carb} + OCS_{solub} + OCS_{diseq},
\]

where \( M_{atm} \) is the mass of the atmosphere; \( V_{oc} \) is the ocean volume and overline denotes global volume average. The Ocean Carbon Storages due to the soft tissue, carbonate and solubility pumps are \( OCS_{soft} = V_{oc} \cdot DIC_{soft}, OCS_{carb} = V_{oc} \cdot DIC_{carb}, OCS_{solub} = V_{oc} \cdot DIC_{solub} \). The equilibrium (saturated) and the disequilibrium component of the carbon inventory are \( V_{oc} \cdot DIC_{eq} \) and \( OCS_{diseq} = V_{oc} \cdot DIC_{diseq} \). For a soft tissue only model in which surface \( CO_2 \) is in equilibrium with the atmosphere, the carbon inventory simplifies to:

\[
TC_{atm, oc} = M_{atm} \cdot pCO_2a + V_{oc} \cdot DIC_{eq} + OCS_{soft}. \quad (3)
\]

The total amount of remineralized carbon in the ocean due to the soft tissue pump (\( OCS_{soft} \)) is exactly the remineralized \( PO_4 \) inventory scaled by a stoichiometric ratio:

\[
OCS_{soft} = r_{C:P} \cdot PO_4_{rem} \cdot V_{oc} = r_{C:P} \cdot (PO_4 - PO_4_{pref}) \cdot V_{oc}, \quad (4)
\]

where \( V_{oc} \) is ocean volume and \( r_{C:P} = 117 \). As pointed out by IF, for a constant total ocean \( PO_4 \) (true by design in all our experiments), a decrease in global preformed \( PO_4 \) inventory results in an increase in global remineralized \( PO_4 \) inventory and in the ocean carbon storage. Disregarding for now the role of the equilibrium term, Eq. 3 suggests that a larger ocean carbon storage (and a smaller preformed \( PO_4 \)), should result in smaller \( pCO_2a \). Our model results demonstrate (Figure 5a-c) that \( OCS_{soft} \), the preformed \( PO_4 \) inventory and the remineralized \( PO_4 \) inventory all correlate well to \( pCO_2a \). A high preformed \( PO_4 \) inventory means that there are low concentrations of remineralized phosphate and carbon in the deep ocean, low carbon storage and therefore high atmospheric \( pCO_2 \). Conversely, the oceanic carbon storage is at a maximum and atmospheric \( pCO_2 \) is at a minimum- when all the nutrients in the deep ocean are in remineralized form and preformed nutrients are zero. In order to quantitatively predict the relationship between atmospheric \( pCO_2 \) and preformed nutrients, we now need to consider the role of the disequilibrium term. Our theoretical analysis assumes that gas exchange at the ocean surface is infinitely fast; section 5 will comment on the role of disequilibrium.

Let us perturb the system (Eq.3) by changing the soft tissue pump. Since \( TC_{atm, oc} \) is assumed constant,

\[
\delta TC_{atm, oc} = M_a \cdot \delta pCO_2a + V_{oc} \cdot \delta DIC_{eq} + \delta OCS_{soft} = 0. \quad (5)
\]

The goal is to find a simple relationship between \( pCO_2a \) and \( OCS_{soft} \). The change in equilibrium carbon, \( \delta DIC_{eq} \), can be written as a function of the atmospheric carbon change, \( \delta pCO_2a \). For each point at the ocean surface, the Revelle (buffer) factor is given by:

\[
R = \frac{\delta lnpCO_2a}{\delta lnDIC_{eq}}
\]

IF showed that to a good approximation one can replace
DIC\textsubscript{eq} above by its surface mean DIC\textsubscript{eq} such that:

\begin{equation}
R \geq \frac{\delta \ln p\text{CO}_2}{\delta \ln \text{DIC}\textsubscript{eq}} = \frac{\delta p\text{CO}_2}{\delta \text{DIC}\textsubscript{eq}} \frac{\text{DIC}\textsubscript{eq}}{p\text{CO}_2} \tag{6}
\end{equation}

We note that in our fast gas exchange models surface temperature and salinity are kept constant throughout the ocean for the purpose of the gas exchange calculation, such that equilibrium DIC is the same everywhere at the surface and (6) is exact.

Replacing \(\frac{\delta \text{DIC}\textsubscript{eq}}{\delta p\text{CO}_2}\) from (6) in (5) we get:

\begin{equation}
\frac{\delta p\text{CO}_2}{\delta\text{OCS}\textsubscript{soft}} = -\frac{p\text{CO}_2}{M\cdot p\text{CO}_2 + V\text{oc} \cdot \text{DIC}\textsubscript{eq}} R \tag{7}
\end{equation}

This equation was previously analyzed by IF, who proposed that for small changes in \(p\text{CO}_2\) the right hand side of the equation is approximately constant. With this assumption \(p\text{CO}_2\) varies linearly with the soft tissue carbon storage. Below we present a more accurate, exponential approximation to the differential Eq. (7).

I. New exponential approximation.

In a recent paper, Goodwin et al. [2007] suggested that under certain conditions the air-sea buffered carbon inventory, defined as “the total carbon inventory of the atmosphere plus the total buffered carbon inventory of the ocean” is approximately constant. Table 1 shows that their approximation holds reasonably well for the models presented in this paper. We note that

\[ C\text{buffered} = M\cdot p\text{CO}_2 + V\text{oc} \cdot \frac{\text{DIC}\textsubscript{eq}}{R} \simeq \text{constant}, \]

holds in our models because as \(p\text{CO}_2\) increases, \(R\) also increases in such a way as to restore \(C\text{buffered}\). The solution to (7) then becomes:

\begin{equation}
p\text{CO}_2 \simeq c_1 \cdot e^{-\frac{\text{OCS}\textsubscript{soft}}{C\text{buffered}}} = c_1 \cdot e^{-\frac{r_C \cdot p\text{CO}_2 \cdot \text{OCS}\textsubscript{soft} - p\text{CO}_2}{C\text{buffered}}} \tag{8}
\end{equation}

This approximate solution holds since in our models changes in the ratio \(\frac{\text{OCS}\textsubscript{soft}}{C\text{buffered}}\) are dominated by changes in \(\text{OCS}\textsubscript{soft}\). The constant \(c_1\) is the \(p\text{CO}_2\) value for the limit in which \(\text{OCS}\textsubscript{soft} = 0\) and is 601 ppm for LL model. The exponential fit (8) approximates well the dependence of \(p\text{CO}_2\) on \(\text{OCS}\textsubscript{soft}\) observed in the model results (Figure 6).

II. Linear approximation

For small deviations in \(p\text{CO}_2\) from a reference state, a Taylor series expansion of Eq. 8 gives:

\begin{equation}
p\text{CO}_2 \simeq c_2 - \frac{p\text{CO}_2\textsubscript{ref}}{C\text{buffered}} \cdot \text{OCS}\textsubscript{soft} \tag{9}
\end{equation}

where \(c_2\) is 537 ppm (LL model) and \(p\text{CO}_2\) varies linearly with the ocean carbon storage. This formulation can be reconciled with the linear approximation proposed by IF.

Figure 6 shows that equation (8) is a better fit than (9) to our model results. Follow up work not shown here suggests that for large changes in ocean carbon storage (i.e., a broader spectrum of \(\text{OCS}\textsubscript{soft}\) on the x axis of figure 6), the exponential (8) holds increasingly better.
than the linear fit (9). Our results confirm that \( OCS_{soft} \), which measures the ability of the soft tissue pump to store \( pCO_2 \) in the deep ocean, is the right norm for atmospheric \( pCO_2 \). Assuming that \( P_4 \) is constant, circulation-induced changes in global mean preformed \( P_4 \) predict changes in \( pCO_2a \). In the linear approximation,

\[
\Delta pCO_2a \approx \frac{pCO_{2a\,ref}}{C_{buf\,ered}} \cdot \tau_{C,P} \cdot V_{oc} \cdot \Delta P_4\,pref
\]

\[
= 179 \, \text{ppm} \cdot \frac{\mu mol/kg}{\Delta P_4\,pref} (\mu mol/kg) \quad (10)
\]

where our reference point is the LL model and 179 is the linear slope in Figure 3c. A global increase in \( P_4\,pref \) by 1 \( \mu mol/kg \) corresponds to a decrease in \( OCS_{soft} \) of 1935 PgC and an increase of about 179 ppm in \( pCO_2a \).

### 4.2. What controls global preformed phosphate-Lessons from the 3 box-model

Having linked atmospheric \( pCO_2 \) to preformed nutrient, we now turn to the question of what controls preformed nutrient concentrations. The global preformed nutrient inventory is approximately given by the deep ocean preformed inventory. The three box model (3BM) in Figure 1a offers us the most basic way of understanding what controls the deep preformed nutrients. Assuming zero low latitude \( P_4 \) values, the deep ocean and high latitude preformed \( P_4 \) values are identical:

\[
Pref_d = Pref_h = P_4\,dh.
\]

where by definition the high latitude surface preformed \( P_4 \) equals the (total) \( P_4 \) at the respective surface. Thus, in the three box model, the only way to change the global integral of preformed nutrients is to change surface nutrients in the high latitude box. One can analytically derive \( P_4\,dh \) as in Sarmiento and Toggweiler [1984] (see their equation 9), such that:

\[
pCO_2a \propto \frac{Pref_d = P_4\,dh = \frac{M_{total} \cdot P_4\,total - M_d \cdot Prod_d/f_{hd}}{M_h + M_d \cdot (1 + T/f_{hd})}}{M_h + M_d \cdot (1 + T/f_{hd})}.
\quad (11)
\]

where \( M \) is the mass of a given reservoir; \( h \) and \( d \) are the high and deep ocean boxes, respectively; \( Prod_d \) is the high latitude export production; \( T \) is an advective term representing deep water formation; and \( f_{hd} \) is mixing between the \( h \) and \( d \) boxes. The symbol \( \propto \) shows, in the spirit of the linear approximation (9), that \( pCO_2a \) is proportional to the deep preformed \( P_4 \) inventory.

The 3BM suggested that changes in deep preformed nutrients and \( pCO_2a \) are driven entirely by changes in high latitude surface nutrients, and inspired oceanographers to use surface nutrients as a metric for the biological pump impact on atmospheric \( pCO_2 \) [e.g., Archer et al., 2000]. Surface nutrients in the high latitudes (and therefore deep preformed \( P_4 \) and atmospheric \( pCO_2 \)) depend very strongly on biological export production \( Prod_d \) and \( f_{hd} \).

Let us assume \( Prod_d \) is fixed in Eq. 11. Since \( f_{hd} \) supplies nutrients to the high latitude surface, a larger \( f_{hd} \) increases \( P_4\,dh \) and deep preformed \( P_4 \). A larger \( f_{hd} \) also brings more carbon from the deep, increasing surface \( CO_2 \) and outgassing more \( CO_2 \) to the atmosphere. This is consistent with the way the problem is often viewed in the paleoceanographic literature. Increased high latitude stratification (smaller \( f_{hd} \)) is one of the classical hypotheses explaining the lower \( pCO_2a \) during glacials.
Conversely, let us assume high latitude mixing \( f_{hd} \) is fixed in Eq. 11. In this case there is a cause effect relationship between biological production and \( p\text{CO}_2 \). Larger export production results in smaller \( \text{PO}_4 \), smaller \( \text{Pref}_{hd} \) and smaller atmospheric \( \text{pCO}_2 \). Intuitively this makes sense: larger export production lowering surface \( \text{CO}_2 \), allowing more \( \text{CO}_2 \) ingassing into the ocean and lower atmospheric \( \text{pCO}_2 \). This strong link implied by the 3BM resulted in much paleoceanographic work using biological export production as the implicit metric for the impact of biological pump on atmospheric \( \text{pCO}_2 \).

Let us consider by comparison surface nutrients in our GCM suite. In our GCM we notice that:

a. No unique functional relationship between surface \( \text{PO}_4 \) and \( p\text{CO}_2,a \) can be established (see Fig. 3b and Supplementary material). This contrasts with the exponential relationship found between global preformed \( \text{PO}_4 \) inventory and \( p\text{CO}_2,a \) (Fig. 3c). Unlike the 3BM, changes in surface nutrients (due to changes in mixing) explain at most half of the observed changes in deep preformed \( \text{PO}_4 \) and \( p\text{CO}_2,a \) changes (Section 4.4).

b. Higher export production is associated with higher \( p\text{CO}_2,a \) (Figure 3a). This is contrary to the predictions of Eq. 11.

Furthermore, Marinov et al. [2006] showed that export production is controlled by the Subantarctic while atmospheric \( \text{pCO}_2 \) is controlled primarily by the Antarctic region of the Southern Ocean. This suggests that the link between \( p\text{CO}_2,a \) and export production is much more complex than implied by a simple reading of equation 11. What mechanisms is the 3BM missing?

A first clue is given by Eq. 11, which shows that high latitude nutrients, and therefore atmospheric \( \text{pCO}_2 \), depend on the ratio \( \text{Prod}_b / f_{hd} \). \( \text{Prod}_b \) and \( f_{hd} \) have opposite effects on \( \text{PO}_4h \) and atmospheric \( \text{pCO}_2 \). This makes perfect physical sense: the surface \( \text{CO}_2 \) concentration depends both on export production (\( \text{Prod}_b \)) - which acts to remove preformed nutrients and \( \text{CO}_2 \) from the surface - and on the vertical supply of nutrients and \( \text{CO}_2 \) to the ocean surface (\( f_{hd} \)). Furthermore, changes in high latitude mixing affect biological production, such that \( \text{Prod}_b \) and \( f_{hd} \) tend to be linked to each other. Thus, it is possible for larger \( \text{Prod}_b \) not to be associated with smaller surface \( \text{CO}_2 \) if \( f_{hd} \) also changes.

This is exactly what happens in our GCM. Larger \( K_v \) or Southern Ocean winds act to (1) increase \( f_{hd} \) and thus the supply of nutrients to the surface (which acts to increase \( p\text{CO}_2,a \) ) and (2) increase biological export production \( \text{Prod}_b \), acting to decrease \( p\text{CO}_2,a \).

From the point of view of \( p\text{CO}_2,a \), the first mechanism wins. Larger mixing or winds result in larger \( p\text{CO}_2,a \) despite stronger export production. Changes in ocean circulation decouple \( p\text{CO}_2,a \) from export production. We note however that in the absence of changes in ocean physics there would be a cause-effect relationship between the two variables and larger export would mean lower \( p\text{CO}_2,a \).

From the point of view of surface nutrients, the two mechanisms above balance closely and surface nutrients change little. Unlike the 3BM, we will show next that a significant percent of the observed change in \( p\text{CO}_2,a \) in our GCMs cannot be explained by changes in surface \( \text{PO}_4 \). Sections 4.3-4.4 discuss an additional circulation mechanism - not present in a 3BM - which can explain the complex relationship between nutrients and \( p\text{CO}_2,a \) observed in the GCM.
4.3. What controls global preformed PO$_4$? Lessons from the 4-box-model

Because the 3BM in Figure 1a allows only one way of forming deep water, deep preformed nutrients are entirely determined by surface nutrients in the high latitude box. In the real ocean, preformed PO$_4$ is advected and mixed into the deep by the watermasses which ventilate the deep ocean: AABW, NADW, Antarctic Intermediate Water and the Subantarctic Mode Water, the first two being the most important.

To a good approximation, the ocean is dominated by a northern ($T$) and a southern source ($f_{hd}$), corresponding to the North Atlantic and Southern Ocean, respectively. Let us consider a four box model (4BM) in which the generic high latitude box is replaced by two distinct high latitude boxes (Figure 1b). The net upwelling now takes place in the Southern Ocean, the net sinking in the north Atlantic.

Since preformed PO$_4$ is conserved in the deep ocean, one can write:

$$\frac{dP_{ref}}{dt} = (P_{ref}^s - P_{ref}^d) \cdot f_{hd} + T \cdot (P_{ref}^n - P_{ref}^d),$$

such that at steady state:

$$pCO_2 a \propto P_{ref}^d = \frac{P_{ref}^s \cdot f_{hd} + P_{ref}^n \cdot T}{T + f_{hd}}$$

This is the equivalent of Eq.11 for the 3BM. This equation shows clearly that the deep preformed nutrient concentration, a driver for $pCO_2 a$, can be modified though changes in the relative contributions of the NADW ($T$) and AABW ($f_{hd}$) to the deep ocean. Significantly, a change in $P_{ref}^d$ does not require a change in surface nutrients, as in the simpler 3BM.

The net preformed PO$_4$ relevant for $pCO_2 a$ is now a linear combination of the surface preformed PO$_4$ in each deep water formation area, weighted by the net ventilation of the deep reservoir by each water source. Since surface nutrients are higher in the Southern Ocean compared to the North Atlantic, $P_{ref}^s - P_{ref}^n > 0$. Assuming fixed $P_{ref}^s$, $P_{ref}^n$, and $T$, a larger southern ventilation rate $f_{hd}$ results in a larger $P_{ref}^d$ and higher $pCO_2 a$.

4.4. Analyzing our GCM as a four box model

As already noted, changes in circulation can both increase the surface nutrient concentrations and change the balance of waters ventilating the deep ocean. Which effect is most important in the GCMs? We begin our analysis by rewriting Eq 12 as follows:

$$P_{ref}^d = f_s \cdot P_{ref}^s + f_n \cdot P_{ref}^n$$

where $f_s = f_{hd}/(T + f_{hd})$ and $f_n = T/(T + f_{hd})$ are the relative contributions of the Southern Ocean and North Atlantic, respectively, to the deep ocean.

For a small circulation induced perturbation around a control state (e.g., the LL equilibrium state) and since $\Delta f_s = -\Delta f_n$ we approximate:

$$\Delta P_{ref}^d \simeq \Delta f_s \cdot (P_{ref}^{ctrl} - P_{ref}^{ctrl}) + \Delta P_{ref}^s \cdot f^{ctrl}_s + \Delta P_{ref}^n \cdot f^{ctrl}_n$$

Note that if we could somehow hold $P_{ref}^s$ and $P_{ref}^n$ fixed while $f_s$ increased we would still see a $P_{ref}^d$ increase. We now use Eq.14 to evaluate which terms are
most important in changing deep preformed phosphate in the GCMs. This task is nontrivial, since deep water formation in our models happens seasonally in isolated convective areas. However, because we distinguish preformed and remineralized phosphate, we can isolate regions which have not had time to accumulate remineralized phosphate and are thus representative of the surface endmember. We defined $P_{ref}$ as averaged preformed PO$_4$ everywhere south of 60° in waters where remineralized phosphate was less than 0.05 µmol/kg. $P_{ref}$ was defined using the same conditions on the nutrients for the Atlantic basin north of 40°N. $P_{ref}$ and $P_{ref}$ are therefore the effective surface preformed nutrients as seen by the deep ocean. We note that $P_{ref}$ is different from $P_{surf}$, which is the preformed PO$_4$ averaged only over the Southern Ocean surface south of 60°S (Table 2).

A simple analysis of four of our models is summarized in Table 2, where we calculate $f_s$ based on our end member approximations and on Eq.13. Table 3 breaks the separate impacts of the changes in $f_s$, $P_{ref}$, and $P_{ref}$.

We isolate the effect of vertical mixing by comparing the high $K_v$ model to the LL model. The increase in vertical mixing $K_v$ increases the fraction of the deep water originating in the Southern Ocean ($f_s$) from 52% to 74%, a 42% increase. At the same time, the Southern Ocean preformed nutrients increase from 1.66 to 1.86 µmol/kg, a 12% increase. In Table 3, we calculate exactly the relative magnitudes of all terms in Eq.14. Thus, we see that the increase in $f_s$ accounts for 55% of the changes in $P_{ref}$, while the increases in $P_{ref}$ and $P_{ref}$ account for 27% and 17%, respectively, of the $P_{ref}$ change. Finally, we note that changes in $P_{surf}$ are smaller than the changes in $P_{ref}$. This shows that increasing vertical mixing in the ocean changes the deep ocean preformed PO$_4$ and therefore $p_{CO_2}$, primarily through increasing the ventilation of the deep ocean via the Southern Ocean relative to the ventilation via NADW, equivalent to increasing $f_{vd}$ in the 4BM.

Changes in the isopycnal mixing coefficient $A_i$ - which also corresponds to the so-called GM [Gent McWilliams, 1990] coefficient - have a more complicated impact on atmospheric $p_{CO_2}$. Larger $A_i$ increases the Southern Ocean eddy overturning (which tends to decrease net residual mean overturning) and decreases convection [Danabasoglu and McWilliams, 1995; Gnanadesikan et al., 2004]. In the models with low vertical mixing (LL and high $A_i$), increasing $A_i$ results in a $f_s$ drop from 0.52 to 0.37. Less deep ocean ventilation via the Southern Ocean implies less contribution of Southern Ocean nutrients to the deep ocean and smaller $P_{ref}$. This results in more oceanic carbon storage and lower $p_{CO_2}$, as shown in Figure 5c, with the change in $f_s$ accounting for 80% of the change in deep preformed nutrients. In the runs with high vertical mixing, by contrast, increasing $A_i$ has a bigger impact on the northern overturning than on the Southern overturning, so that $f_s$ actually increases. This change in circulation is key to explaining why $p_{CO_2}$ goes up in the high $A_i$-high $K_v$ relative to the high $K_v$ model despite a decrease in surface preformed nutrients. Finally, comparing the high $A_i$-high $K_v$ and LL models (right-hand column of Table 3) we see that circulation changes explain 79% of the difference in deep preformed nutrients.

We do not claim that the direct effect of circulation changes in altering the mix of preformed waters is always more important than the indirect effect of changing the end-member preformed nutrient content. In fact, when we examined the impact of tripling the winds, we found that changes in $f_s$ are less important than changes in
end-member preformed nutrients. Nonetheless, changes in $f_s$ (which varied from 0.42 to 0.55) still account for an important fraction of the changes in $pCO_2_a$ in these runs, with higher winds producing higher deep preformed nutrients and higher $pCO_2_a$.

Intuitively, our results make sense. Larger Southern Ocean winds or $K_v$ result in larger vertical supply of $CO_2$ in the Southern Ocean through mixing or CDW upwelling. Because biology is highly inefficient in the Southern Ocean, much of this upwelled $CO_2$ escapes to the atmosphere, increasing atmospheric $pCO_2$. Conversely, an increase in eddy activity due to larger $A_i$ results in less upwelling of $CO_2$ via the CDW and therefore lower atmospheric $pCO_2$.

In summary, our GCM results show that one can have dramatic changes in deep preformed $PO_4$ and $pCO_2_a$ that cannot be fully accounted for by the smaller changes in mean surface nutrients (Figure 3b-c and Supplementary Material). The presence of two deep water formation regions effectively decouples deep preformed nutrients and $pCO_2_a$ changes from surface nutrient changes, as first observed by Toggweiler [1999]. Because it has only one deep-water formation region, the 3BM misses this mechanism. By contrast, a 4BM is the simplest box model that can allow the decoupling mechanism and can explain to first order our GCM results. In Eqs.13-14 one can change deep preformed $PO_4$ by changing $f_s$, even if surface preformed $PO_4$ does not change.

The importance of oceanic circulation for atmospheric $pCO_2$ becomes clear when analyzing the terms in the atmosphere-ocean carbon inventory (Eq. 3) for both the fast gas exchange and regular gas exchange simulations (Table 1 and Figure 7). For each model used the oceanic equilibrium component, $V_e \cdot [DIC_{eq}]$, is about 17 times larger than $OCS_{soft}$, the next largest term, and about 50 times larger than the atmospheric carbon content. The atmospheric carbon content is only about 1.5-2% of the total air-sea carbon budget. In panels a-c of Figure 7 and Table 1, models are arranged from left to right in order of increasing deep water ventilation. As deep ventilation increases, deep preformed $PO_4$ increases and $OCS_{soft}$ decreases. In fast gas exchange models, this decrease in soft tissue carbon storage is exactly compensated by increases in both the carbon dioxide content of the atmosphere (Figure 7b) and in the equilibrium carbon content of the ocean (via an increase in surface $DIC$). In regular gas exchange models, circulation changes also induce changes in surface $DIC$ disequilibrium, which in turn have an impact on atmospheric $pCO_2$. This disequilibrium is the topic for section 5.

5. The role of surface $CO_2$ disequilibrium in the carbon inventory

The critical assumption in our discussion so far has been that $CO_2$ exchange at the ocean surface happens infinitely fast, such that $CO_2$ at the ocean surface is permanently in equilibrium with the atmosphere. Under this assumption, we concluded that the global preformed nutrient inventory determines the ocean biological carbon storage and atmospheric $pCO_2$.

In reality, we know that $CO_2$ at the ocean surface takes about nine months to equilibrate with the atmosphere, longer than typical mixed layer circulation time scales, such that $CO_2$ is out of equilibrium with the atmosphere. The degree of disequilibrium depends on both the circulation time scale (which determines how fast $CO_2$ is upwelled, transported and downwelled) and on the bio-
logical time scale (at which biology incorporates carbon into organic matter).

Let us consider a water parcel in a deep water formation area with a disequilibrium contribution to its inorganic carbon content given by \( DIC_{diseq} \). As the water parcel sinks into the deep ocean, it will continue to reflect the initial surface disequilibrium but it will also accumulate \( DIC \) from the soft tissue pump, i.e., from the remineralization of organic matter through the water column. Disregarding the carbonate and the solubility pumps, \( DIC \) at each point in the ocean is the sum of the equilibrium, soft-tissue and disequilibrium components:

\[
DIC = DIC_{eq} + DIC_{soft} + DIC_{diseq}. \tag{15}
\]

Since \( DIC_{diseq} \) is a conserved tracer in the ocean interior, we can write the deep ocean \( DIC_{diseq} \) by analogy with Eq.13 as:

\[
DIC_{diseq} = DIC_{diseq}^s \cdot f_s + DIC_{diseq}^n \cdot f_n, \tag{16}
\]

where \( DIC_{diseq}^s \), \( DIC_{diseq}^n \), \( DIC_{diseq} \) are the disequilibrium contributions of the Southern Ocean, North Atlantic and deep ocean. Deep ocean disequilibrium \( DIC \) is a linear combination of surface disequilibrium signatures modulated by the respective value of deep ocean ventilation. Is this 4BM picture reflected by the GCM results?

Let us consider results from our regular gas exchange simulations in which surface \( CO_2 \) equilibration is slow. Figure 8 shows the zonally averaged disequilibrium \( DIC \) for the standard LL model, high \( K_v \), and windsx3 models with regular gas exchange. Disequilibrium \( DIC \) at each point in the ocean is calculated as the difference between total \( DIC \), \( DIC_{eq} \), and \( DIC_{soft} = r_{C, P} \cdot (PO_4 - PO_4^{pref}) \).

Upwelling and convection bring large quantities of \( CO_2 \) to the Southern Ocean surface. Slow gas exchange and a biology inefficient at taking up \( CO_2 \) result in a large positive Southern Ocean surface disequilibrium. This signal is subducted by the Southern Ocean lower circulation to the deep ocean. Larger \( K_v \) or Southern Ocean winds increase this circulation \((f_s \text{ in Eq. 16})\), and increase the positive average value of deep ocean \( DIC_{diseq} \). Disequilibrium \( DIC \) is a useful tracer of oceanic circulation; its broad large scale structure is similar to that of preformed \( PO_4 \) (compare Figures 8 and 4).

The total carbon inventory of the atmosphere-ocean system becomes:

\[
TC_{atm oc} = M_{atm} \cdot pCO_2_a + V_{oc} \cdot (\overline{DIC_{eq}} + \overline{DIC_{soft}} + \overline{DIC_{diseq}}),
\]

\[
= M_{atm} \cdot pCO_2_a + OCS_{eq} + OCS_{soft} + OCS_{diseq}, \tag{17}
\]

where \( OCS_{eq} = V_{oc} \cdot \overline{DIC_{eq}}, \)

\( OCS_{soft} = V_{oc} \cdot r_{C, P} \cdot (PO_4^4 - PO_4^{pref}) \),

and the oceanic carbon storage due to the surface disequilibrium is \( OCS_{diseq} = V_{oc} \cdot \overline{DIC_{diseq}} \).

Table 1 and Figure 7c-d illustrate the terms in the above carbon budget for regular gas exchange simulations in our models. Though significant, the contribution of \( OCS_{diseq} \) to the total carbon inventory is smaller than the contribution of all other terms in Eq. 17 (Figure 7c). Consistent with Figure 8, the total ocean carbon content due to disequilibrium increases with larger vertical mixing \( K_v \) or stronger Southern Ocean winds. Conversely, larger isopycinal mixing \( A_i \) decreases the AABW forma-
tion and Southern Ocean convection. This decreases the contribution of Southern Ocean disequilibrium to the deep ocean, decreasing $OCS_{diseq}$.

The impact of surface disequilibrium on atmospheric $pCO_2$ becomes clear when we compare results from the fast gas exchange or FGE simulations (instantaneous CO$_2$ surface equilibration, zero CO$_2$ disequilibrium) and regular gas exchange or RGE simulations (slow surface equilibration, non-zero disequilibrium).

Figure 5c shows oceanic carbon storage versus atmospheric $pCO_2$ in our eight circulation models. Changing the gas exchange equilibration time scale has a significant impact on atmospheric $pCO_2$ for a fixed ocean-atmosphere DIC inventory. Figure 5c shows that for a given circulation model (and therefore for a given biological pump and $OCS_{soft}$), the presence of disequilibrium considerably decreases $pCO_2$.

Water upwelling in the Southern Ocean brings large amounts of CO$_2$ from the deep. While in the FGE runs most of this CO$_2$ is instantaneously lost to the atmosphere, this is not the case in the RGE runs, where much of the additional CO$_2$ moves southward with the currents and is subducted to the deep. As a consequence, the presence of surface disequilibrium results in more ocean carbon storage and smaller atmospheric $pCO_2$ in the RGE compared to the FGE runs (Figure 5c, 7d).

To further complicate things, the impact of disequilibrium on $pCO_2$ varies among models with different circulations; it is -30 ppm in the wind$^{0.5}$ and low $A_i$, -43 ppm in the LL and about -65 ppm in the wind$^{3}$ model.

The larger the oceanic carbon accumulation due to disequilibrium $OCS_{diseq}$, the smaller atmospheric $pCO_2$; the fit is almost linear (Figure 7d). Larger $K_i$ or Southern Ocean winds result in a smaller $OCS_{soft}$ (due to more accumulation of preformed PO$_4$ in the deep) and a larger $OCS_{diseq}$ (due to more accumulation of DIC$_{diseq}$ in the deep ocean). Surface CO$_2$ disequilibrium therefore interferes with the simple theoretical relationship between $pCO_{2a}$ and $OCS_{soft}$ derived in Section 4.1. Our theoretical fit is not as good in the RGE runs as in the FGE runs and the slope of a linear fit is smaller in the former runs (Figure 5).

6. Conclusions

This paper has focused on understanding in depth the mechanisms relating the soft tissue pump and atmospheric $pCO_2$. Atmospheric $pCO_2$ is inversely related to the oceanic carbon storage which, in a soft-tissue only model, is a simple function of the ocean preformed inventory. For a soft-tissue only model with fast gas exchange we derive a simple exponential relationship between $pCO_{2a}$ and $OCS_{soft}$. Our new theoretical fit compares favorably with model results and improves on the linear fit of IF.

We have shown that the relative magnitudes of deep water ventilation via the lower circulation (which includes AABW and Southern Ocean convection) and via NADW are critical in setting atmospheric $pCO_2$ because they impact the global preformed nutrients. Larger diapycnal mixing or stronger Southern Ocean winds considerably increase the deep ocean ventilation via the Southern Ocean and result in a larger fraction of deep ocean nutrients in the preformed pool, smaller oceanic carbon storage and higher atmospheric $pCO_2$. By contrast, increasing isopycnal mixing (in a weakly ventilated model) decreases the deep ocean ventilation via the Southern Ocean and decreases atmospheric $pCO_2$.

Our findings agree with recent research demonstrating
smaller atmospheric $pCO_2$ with reduced communication
between Southern Ocean deep water formation regions
and the atmosphere, either through increased stratifica-
tion (Archer et al. [2003], Gildor and Tziperman [2001],
Sigman and Boyle [2000], Toggweiler [1999]) or a shift in
wind patterns (Toggweiler et al. [2006]).

The relationship between $pCO_2$ and preformed $PO_4$
is complicated by the fact that surface $CO_2$ is out of equi-
librium with the atmosphere. The impact of this disequi-
librium on $pCO_2$ depends in a complex way on oceanic
circulation. Future work should attempt to incorporate
this disequilibrium signature in theoretical derivations.

The present work shows that biological export produc-
tion, usually associated in the literature with the strength
of the biological pump, is not always a good predictor for
atmospheric $pCO_2$. It is possible to have larger export
with higher atmospheric $pCO_2$ in cases when both ex-
port and $pCO_2$ are affected by changes in ocean physics
(which affect the supply rate of nutrients and carbon to
the ocean surface).

We have shown that the global inventory of preformed
$PO_4$ is an excellent indicator for atmospheric $pCO_2$. By
contrast, surface nutrients are not reliable predictors for
atmospheric $pCO_2$ if oceanic circulation changes. In our
model with simple OCMIP type biogeochemistry, we are
able to produce large changes in atmospheric $pCO_2$ by
changing oceanic circulation in such a way that the sur-
face nutrient change is small, therefore effectively "de-
coupling" surface nutrients from atmospheric $pCO_2$. As
first observed by Toggweiler [1999] and as discussed in
the present paper, this decoupling does not happen in a
3 box-model but is present in a 4 box-model (and other
more complicated models) of the ocean, which allow mul-
tiple deep water sources. The extent of decoupling de-
pends on the model circulation and on the parameteriza-
tion of biological production. The decoupling must hold
but might be weaker in a full ecological model.

Deep ocean ventilation, and the related supply of pre-
formed nutrients to the deep ocean, did not remain con-
stant in the past and will likely change in the future.
Without constraints on changes in circulation and nutri-
ent supply, changes in export production or surface nu-
trients are not sufficient to explain changes in the total
oceanic storage of carbon and in atmospheric $pCO_2$. Fu-
ture studies that attempt to explain atmospheric $pCO_2$
changes must focus on changes in the preformed nutrient
supply to the deep ocean.

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Table 1. Results from eight different soft tissue models

<table>
<thead>
<tr>
<th>Model</th>
<th>high $A_t$</th>
<th>windx1.5</th>
<th>std (LL)</th>
<th>high south Kv</th>
<th>high $K_v$ - high $A_t$</th>
<th>high $K_v$</th>
<th>windx3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^{14}C$</td>
<td>-254.7</td>
<td>-231.7</td>
<td>-196.7</td>
<td>-170.6</td>
<td>-127.0</td>
<td>-112.2</td>
<td>-101.9</td>
</tr>
<tr>
<td>$P_{O_2}^{pref}$ (µmol/kg)</td>
<td>0.97</td>
<td>1.02</td>
<td>1.12</td>
<td>1.27</td>
<td>1.39</td>
<td>1.46</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Fast Gas Exchange

<table>
<thead>
<tr>
<th>$pCO_2$ (ppm)</th>
<th>321.0</th>
<th>328.3</th>
<th>334.3</th>
<th>372.4</th>
<th>395.9</th>
<th>410.9</th>
<th>408.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_a$ $pCO_2$ (ppm)</td>
<td>680.1</td>
<td>696.3</td>
<td>728.02</td>
<td>789.9</td>
<td>840.6</td>
<td>871.5</td>
<td>895.6</td>
</tr>
<tr>
<td>$OCS_{soft}$ (PgC)</td>
<td>2350</td>
<td>2266</td>
<td>2072</td>
<td>1773</td>
<td>1534</td>
<td>1388</td>
<td>1433</td>
</tr>
<tr>
<td>$V_{oc}DIC_{eq}$ (PgC)</td>
<td>3543</td>
<td>3550</td>
<td>35635</td>
<td>35874</td>
<td>36050</td>
<td>36154</td>
<td>36186</td>
</tr>
<tr>
<td>$R$</td>
<td>11.64</td>
<td>11.72</td>
<td>11.95</td>
<td>12.38</td>
<td>12.72</td>
<td>12.93</td>
<td>13.10</td>
</tr>
<tr>
<td>$C_{buffered}$ (PgC)</td>
<td>3733.8</td>
<td>3725.7</td>
<td>3710.4</td>
<td>3687</td>
<td>3674</td>
<td>3667</td>
<td>3667.9</td>
</tr>
</tbody>
</table>

Regular Gas Exchange

<table>
<thead>
<tr>
<th>$pCO_2_{atm}$ (ppm)</th>
<th>288.3</th>
<th>294.2</th>
<th>299.0</th>
<th>329.2</th>
<th>335.3</th>
<th>361.2</th>
<th>352.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_a$ $pCO_2_{atm}$ (PgC)</td>
<td>611</td>
<td>624</td>
<td>635</td>
<td>698</td>
<td>711</td>
<td>766</td>
<td>748</td>
</tr>
<tr>
<td>$OCS_{soft}$ (PgC)</td>
<td>2350</td>
<td>2266</td>
<td>2072</td>
<td>1773</td>
<td>1534</td>
<td>1388</td>
<td>1433</td>
</tr>
<tr>
<td>$OCS_{dis}$ (PgC)</td>
<td>362</td>
<td>368</td>
<td>306</td>
<td>446</td>
<td>628</td>
<td>493</td>
<td>557</td>
</tr>
<tr>
<td>$V_{oc}DIC_{eq}$ (PgC)</td>
<td>35011</td>
<td>35078</td>
<td>35126</td>
<td>35420</td>
<td>35463</td>
<td>35689</td>
<td>35617</td>
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</tbody>
</table>

$^a$ Shown are global mean preformed $P_{O_2}$ and the terms in the air-sea carbon budget equation (Eq. 17) for both fast gas exchange and regular gas exchange simulations. For the fast gas exchange simulations, the sum of $OCS_{soft}$, $M_a$ $pCO_2_{atm}$, $V_{oc}DIC_{eq}$ equals 38340 PgC for all models. Models are arranged in order of increasing deep ocean ventilation as measured by their mean ocean $\Delta^{14}C$ at 1500m. For the regular gas exchange simulations, the sum of the above three terms and of the disequilibrium component $OCS_{dis}$ equals 38340 PgC. Note that the presence of surface disequilibrium changes both the atmospheric carbon budget and the oceanic equilibrium contribution. See also Figure 7 for a visual display of the different terms. Also shown for the fast gas exchange case are the Revelle Buffer factor R and the total buffered carbon in the ocean, $C_{buffered}$ defined in section 4.1.

Table 2. Preformed end-members and Southern Ocean ventilation in four GCMs

<table>
<thead>
<tr>
<th>Model</th>
<th>$Pref_a$</th>
<th>$Pref_s$</th>
<th>$Pref_{d}$</th>
<th>$f_s$</th>
<th>$Pref_{surf S60S}$</th>
<th>$Pref_{surf S30S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>high $A_t$</td>
<td>0.65</td>
<td>1.01</td>
<td>1.01</td>
<td>0.57</td>
<td>1.64</td>
<td>1.06</td>
</tr>
<tr>
<td>LL</td>
<td>0.76</td>
<td>1.06</td>
<td>1.20</td>
<td>0.32</td>
<td>1.67</td>
<td>1.08</td>
</tr>
<tr>
<td>high $K_v$</td>
<td>0.84</td>
<td>1.10</td>
<td>1.10</td>
<td>0.74</td>
<td>1.16</td>
<td>1.13</td>
</tr>
<tr>
<td>high $A_t$-high $K_v$</td>
<td>0.79</td>
<td>1.01</td>
<td>1.01</td>
<td>0.81</td>
<td>1.72</td>
<td>1.13</td>
</tr>
</tbody>
</table>

$^a$ Shown are the deep preformed $P_{O_4}$ below 1500 m ($Pref_d$), the relative contribution of the Southern ocean to the deep ($f_s$), surface preformed $P_{O_4}$ south of 60ºS ($Pref_{surf S60S}$), surface preformed $P_{O_4}$ south of 30ºS ($Pref_{surf S30S}$) for four models. End-members $Pref_a$ and $Pref_s$ are defined as the volume averages of preformed $P_{O_4}$ south of 60ºS and north of 40ºN, respectively.

Table 3. Processes responsible for changes in deep preformed $P_{O_4}$ (in µmol/kg)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta Pref_d$</th>
<th>$\Delta f_s$</th>
<th>$\Delta Pref\cdot Pref_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>high $A_t$ - LL</td>
<td>-0.19</td>
<td>0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>high $K_v$ - LL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(high $A_t$-high $K_v$) - LL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The terms in Eq. 14: comparing the LL model with three other models. Percents refer to contributions of the three terms to $\Delta Pref_d$. "ctrl" refers to the LL model values from Table 2. Most of the $Pref_d$ difference induced by sub-gridscale mixing can be ascribed to changes in $f_s$, the fraction of deep water of Southern Ocean origin. Increasing vertical mixing $K_v$ increases $f_s$, which increases $Pref_d$ and atmospheric $pCO_2$. Increasing horizontal mixing $A_t$ decreases $f_s$, $Pref_d$ and thus atmospheric $pCO_2$. 

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Figure 1. a. Simplified 3BM of oceanic circulation as discussed for example by Sarmiento and Toggweiler [1984]. b. 4BM captures the first order processes relevant for the carbon cycle. Deep preformed PO$_4$, $Pref_d$, determines atmospheric $pCO_2$. $Pref_d$ depends on both NADW strength (represented here by $T$) and AABW strength ($f_{hd}$). Relative changes in these ventilation rates explain observed changes in atmospheric $pCO_2$ in our GCMs.
Figure 2. (a-c): Overturning streamfunction in Sv calculated as the zonal and depth integral of the meridional velocity for the LL model, high $K_v$ - LL model difference, high Southern Ocean wind - LL difference. Shown streamfunctions are the sum between the GM and Euler streamfunctions. (d-f): Zonally averaged convective indices. Convective index is 1 when convection is on. A value of 0.5 can mean that half of the points at a given location are convecting all the time, that all points convect half of the time, or a scenario in between these two. (g-h) Covariation of $\Delta^{14}C$ (globally averaged at 1500 m) with globally averaged Preformed PO$_4$ ($\mu$mol/kg) and OCS$_{soft}$ in the control simulations. The ocean carbon storage due to the soft tissue pump (PgC) is calculated as $\text{OCS}_{soft} = V_{oc} \cdot r_{C,P} \cdot (\text{PO}_4 - \text{PO}_4\text{pref})$. Deep waters in the high $K_v$ and windx3 models are the youngest, best ventilated water masses while deep waters in the high $A_i$ and windx0.5 models are oldest, least ventilated. Annual mean results shown in all cases. (h) Annually and zonally averaged wind stresses for three of the models. Westerlies are positive.
Figure 3. Atmospheric $pCO_2$ (ppm) versus (a) total globally averaged export Production (PgC/yr), (b) average surface PO$_4$ south of 30°S ($\mu$mol/kg), (c) global volume averaged preformed PO$_4$ ($\mu$mol/kg). Fast gas exchange simulations. Models have biological time scale $\tau$=30 days (open symbols) or $\tau$= 1 year (full symbols). Shown are the LL (black circle), \textbf{high $A_i$} (green circle), \textbf{windx0.5} (blue circle), \textbf{high south $K_v$} (red circle), \textbf{high $K_v$-high $A_i$} (green triangle) \textbf{high $K_v$} (red triangle), \textbf{windx2} (black triangle), and \textbf{windx3} (blue triangle) models. Circles denote lower Southern Ocean ventilation models, triangles higher ventilation models.
Figure 4. Global zonal averages of remineralized PO$_4$ (top panels) and preformed PO$_4$ (bottom panels) in the LL, high $K_v$ and winds x3 GCM simulations. Units are $\mu$mol/kg. Larger vertical mixing $K_v$ or larger Southern Ocean winds result in stronger Southern Ocean overturning circulation (see arrows), and larger deep preformed PO$_4$. 
Figure 5. Atmospheric pCO₂ (ppm) versus (a) globally averaged preformed PO₄ (µmol/kg), (b) globally averaged remineralized PO₄ (µmol/kg) and (c) ocean carbon storage due to the soft tissue pump (PgC) calculated as $OCS_{soft} = V_{oc} \cdot r_{C:P} \cdot ([PO_4] - [PO_4_{pref}])$. Biological time scale $\tau = 30$ days. Results in panels a-b are for fast gas exchange simulations. Panel c shows both fast gas exchange and regular gas exchange simulations.
Figure 6. Variation of atmospheric $pCO_2$ (ppm) with the soft tissue ocean carbon storage (PgC), $OCSS_{soft} = V_{oc} \cdot rC_{o} \cdot ([PO_4] - [PO_4_{pref}])$. The exponential fit given by equation 8 and the linear fit given by equation 9 are shown on top of model results from eight different models. Fast gas exchange simulations shown for all models. Biological time scale $\tau$ is either 30 days (open symbols) or 1 year (full symbols). Model notation as in figure 3.
Figure 7. (a) Carbon budget contributions due to the atmosphere ($M_{atm} \cdot pCO_2_{atm}$) and soft tissue ocean carbon storage ($OCS_{soft}$) in the FGE simulations for seven of our models. Units are PgC. Oceanic equilibrium/saturation contribution not shown (about 20-50 times larger than the others). Models arranged from left to right in order of increasing deep water ventilation as indicated by $\Delta ^{14}C$. (b) Carbon contributions - differences relative to the LL model for FGE simulations. Total air-sea carbon budget is identical for all models used. The change in $OCS_{soft}$ relative to LL is compensated by changes in the atmospheric (blue) and oceanic equilibrium contributions (black). (c) Budget contributions in the RGE simulations. The ocean carbon storage due to surface disequilibrium ($OCS_{diseq}$) is smaller than all other components. (d) The decrease in atmospheric pCO$_2$ in ppm due to surface disequilibrium (i.e., the difference between regular and fast gas exchange pCO$_2$) plotted against the disequilibrium oceanic carbon storage from the RGE simulations, $OCS_{diseq}$, in Pg C.
Figure 8. Global zonal averages of disequilibrium DIC in the LL, high $K_v$ and winds x3 GCMs. Results shown for the regular gas exchange (RGE) models. Disequilibrium DIC (µmol/kg) at each point calculated as the difference between total DIC, surface equilibrium DIC, and $DIC_{soft} = r_{C,P} \cdot (PO_4 - PO_4^{pref})$. Increasing ventilation via the Southern Ocean results in more accumulation of deep disequilibrium DIC.