An Analytical Framework for the Steady State Impact of Carbonate Compensation on Atmospheric CO₂

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Abstract The deep-ocean carbonate ion concentration impacts the fraction of the marine calcium carbonate production that is buried in sediments. This gives rise to the carbonate compensation feedback, which is thought to restore the deep-ocean carbonate ion concentration on multimillennial timescales. We formulate an analytical framework to investigate the impact of carbonate compensation under various changes in the carbon cycle relevant for anthropogenic change and glacial cycles. Using this framework, we show that carbonate compensation amplifies by 15–20% changes in atmospheric CO₂ resulting from a redistribution of carbon between the atmosphere and ocean (e.g., due to changes in temperature, salinity, or nutrient utilization). A counterintuitive result emerges when the impact of organic matter burial in the ocean is examined. The organic matter burial first leads to a slight decrease in atmospheric CO₂ and an increase in the deep-ocean carbonate ion concentration. Subsequently, enhanced calcium carbonate burial leads to outgassing of carbon from the ocean to the atmosphere, which is quantified by our framework. Results from simulations with a multibox model including the minor acids and bases important for the ocean-atmosphere exchange of carbon are consistent with our analytical predictions. We discuss the potential role of carbonate compensation in glacial-interglacial cycles as an example of how our theoretical framework may be applied.

1. Introduction

The partitioning of carbon between the ocean and the atmosphere is key for understanding glacial-interglacial changes in atmospheric CO₂ (Archer et al., 2000; Menviel et al., 2008; Omta et al., 2006), as well as for predicting the fate of anthropogenic CO₂ (Archer, 2005; Archer et al., 2009; Montenegro et al., 2007). By combining carbon mass balances with carbonate chemistry, analytical expressions have been derived to describe the ocean-atmosphere partitioning of carbon on multiconcentennial to millennial timescales (d’Orgeville et al., 2011; Goodwin et al., 2007, 2008, 2009; Ito & Follows, 2005; Kwon et al., 2011; Marinov, Follows, et al., 2008; Marinov, Gnanadesikan, et al., 2008; Omta et al., 2010, 2011). In our view, the great benefit of this analytical approach is that it leads to a quantitative intuition for the system. With such a quantitative intuition, it is easier to assess which mechanisms have the largest impact on the atmospheric and oceanic carbon budgets, before embarking on time-consuming simulations. Here we apply the analytical approach to mechanisms repartitioning carbon between the ocean and the atmosphere on multimillennial timescales.

On multimillennial timescales, the ocean-atmosphere partitioning of carbon interacts with the ocean alkalinity cycle. Essentially, ocean alkalinity is the concentration of bases (e.g., CO₃²⁻) available to react with CO₂ to form HCO₃⁻. Alkalinity is transported into the ocean as a consequence of continental rock weathering and removed from the ocean through sedimentation and burial of calcifying organisms (see Figure 1). It is generally assumed that the ocean maintains a balance between these input and output fluxes of alkalinity through a mechanism referred to as carbonate compensation, which works as follows. The CO₃²⁻ concentration ([CO₃²⁻]) is lower in the deep ocean than at the surface, mainly because the soft-tissue carbon pump transfers carbon from the upper to the deep ocean (Volk & Hoffert, 1985). Furthermore, the solubility of calcium carbonate (CaCO₃) increases with pressure (Pytkowicz & Conners, 1964). Due to a combination of these effects, much of the deep ocean is undersaturated with respect to calcite (Ridgwell & Zeebe, 2005). At a level named the carbonate compensation depth (CCD), the rates of sedimentation and dissolution of calcite are equal. Below this level, there is no CaCO₃ present in sediments. A decrease of the deep-ocean [CO₃²⁻] leads to an increase in both the dissolution of CaCO₃ from sediments and a decrease in the accumulation of new CaCO₃ sediments.
Figure 1. A schematic depiction of the input and output of alkalinity into and out of the ocean (figure adapted from Omta et al., 2013). Alkalinity is added to the ocean through river runoff and is consumed by calcifiers and removed from the ocean through calcifier sedimentation. Above the carbonate compensation depth (CCD), calcium carbonate accumulates, whereas it dissolves below the CCD. A decrease in deep-ocean \([\text{CO}_2^-]\) leads to a decrease in \(\text{CaCO}_3\) output and, thus, an increase in deep-ocean \([\text{CO}_2^-]\). This carbonate compensation feedback is thought to return the deep-ocean \([\text{CO}_2^-]\) to its equilibrium value on a multimillennial timescale.

This, in turn, leads to an increase in the deep-ocean \([\text{CO}_2^-]\). Overall, the deep-ocean \([\text{CO}_2^-]\) is expected to relax back to its original value, as long as the alkalinity input into the ocean by, for example, rivers does not change (Archer & Maier-Reimer, 1994; Sigman et al., 1998). The increased sediment dissolution and the decreased sediment accumulation mechanisms occur on two different timescales (Archer et al., 1997, 1998; Ridgwell & Hargreaves, 2007). Based on a suite of carbon release experiments with the carbon-centric Grid ENabled Integrated Earth system model (cGENIE), Lord et al. (2016) combined these two timescales into a single response time of 4 – 16 kyr (depending on the total carbon emissions). However, as a result of continuous equilibration and reequilibration of carbon between the atmosphere, ocean, and sediments, the overall relaxation has a long tail stretching tens of thousands of years.

Running numerical simulations for tens of thousands of years until full carbonate compensation has been achieved is very time consuming. Thus, simple analytical expressions for estimating the impact of carbonate compensation on atmospheric \(\text{CO}_2\) are very useful, particularly if various different disturbances are to be investigated. Using the argument that \([\text{CO}_2^-]\) returns to its original value, Goodwin and Ridgwell (2010) derived such an expression for the ocean-atmosphere partitioning of anthropogenic carbon on multimillennial timescales. From this expression, Goodwin and Ridgwell (2010) estimated that between 6% and 10% of anthropogenic carbon will remain in the atmosphere after carbonate compensation has been completed. We extend their work by deriving analytical expressions to estimate the overall impact of carbonate compensation in response to variations in ocean temperature, salinity, and nutrient utilization and the total ocean nutrient inventory (section 2). We compare the main predictions from our analytical framework against simulations with a multibox model including the full set of compounds involved in the ocean-atmosphere exchange of carbon, which is described in detail in Appendix A. We believe that the expressions derived here will be useful both for understanding how future climate change may feed back onto the marine carbon cycle and for understanding glacial-interglacial \(\text{CO}_2\) changes. We provide a more detailed discussion of the potential relevance of our findings for the future and the past carbon cycle in sections 3 and 4.

2. Analytical Framework

We start from a balance equation for carbon in the ocean-atmosphere system (Ito & Follows, 2005; Williams & Follows, 2011):

\[
M \text{CO}_2 + V (C_{sat} + C_{reg} + C_{carb}) = I_{oa}
\]  

(1)
with \( M \) the total gas content of the atmosphere (mol), \( V \) the volume of the ocean (m\(^3\)), \( X_{\text{CO}_2} \) the atmospheric \( \text{CO}_2 \) mixing ratio (ppmv), and \( I_{\text{oa}} \) the total carbon inventory of the ocean-atmosphere system (mol). \( C_{\text{sat}}, C_{\text{reg}}, \) and \( C_{\text{carb}} \) (all in mol/m\(^3\)) describe the partitioning of dissolved inorganic carbon (DIC) into the different carbon pumps introduced by Volk and Hoffert (1985). \( C_{\text{sat}} \) is the average oceanic saturated carbon concentration, which is somewhat higher than the average saturated carbon concentration at the ocean surface as a result of the lower temperature of the deep ocean (the solubility pump), \( C_{\text{reg}} \) is the average regenerated carbon concentration (the soft-tissue pump), and \( C_{\text{carb}} \) is the carbon added to the ocean through dissolution of sinking \( \text{CaCO}_3 \) (the carbonate pump).

The process of carbonate compensation leads to a change in the total carbon inventory of the ocean-atmosphere system because of the dissolution and burial of \( \text{CaCO}_3 \). We will refer to such changes in \( I_{\text{oa}} \) as \( \delta I_{\text{oa,calc}} \). Furthermore, carbon can be added or removed from the ocean-atmosphere system in forms other than \( \text{CaCO}_3 \), for example, through anthropogenic carbon emissions and burial of particulate organic carbon (POC). We will refer to such changes in \( I_{\text{oa}} \) as \( \delta I_{\text{oa,noncalc}} \). Equation (1) can be used to relate the changes in the total carbon inventory to changes in \( X_{\text{CO}_2}, C_{\text{sat}}, C_{\text{reg}}, \) and \( C_{\text{carb}} \):

\[
M \delta X_{\text{CO}_2} + V \delta (C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}}) = \delta I_{\text{oa,calc}} + \delta I_{\text{oa,noncalc}} \tag{2}
\]

For every mole of carbon in \( \text{CaCO}_3 \) that is added, the ocean gains two moles of alkalinity. Thus, \( \delta I_{\text{oa,calc}} = \frac{V \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}})}{2} \), with \( A \) the alkalinity. Furthermore, if we neglect the contributions to alkalinity from all acids and bases other than \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \), then \( \delta A \approx \delta[\text{HCO}_3^-] + 2\delta[\text{CO}_3^{2-}] \). Neglecting dissolved \( \text{CO}_2 \), \( \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}}) \approx \delta[\text{HCO}_3^-] + \delta[\text{CO}_3^{2-}] \). Hence, \( \delta A \approx \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}}) + \delta[\text{CO}_3^{2-}] \).

Following earlier analytical work on the impact of carbonate compensation (Goodwin & Ridgwell, 2010), the difference between the whole-ocean and deep-ocean average \( [\text{CO}_3^{2-}] \) is neglected. The underlying assumption is that DIC and alkalinity are vertically homogeneous throughout most of the ocean. This seems a reasonable approximation for the current ocean, in which vertical gradients in DIC and alkalinity are rather small below ~1,000 m (Chester, 2000). With this assumption (discussed in more detail in section 3.1), we can equate the whole-ocean average \( [\text{CO}_3^{2-}] \) to the \( [\text{CO}_3^{2-}] \) at the CCD, relevant for carbonate compensation. Thus, we state that \( \delta[\text{CO}_3^{2-}] = 0 \) after full carbonate compensation, which means that \( \delta A \approx \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}}) \).

Altogether, this gives

\[
M \delta X_{\text{CO}_2} + \frac{V \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}})}{2} = \delta I_{\text{oa,noncalc}} \tag{3}
\]

Essentially, the term \( V \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}}) \) in equation (1) has been replaced in equation (3) by a term \( \frac{V \delta(C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}})}{2} \). The factor \( \frac{1}{2} \) expresses that any transfer of carbon between the atmosphere and ocean will account for the full change in atmospheric carbon but only half of the change in oceanic carbon. This reflects the very nature of the carbonate compensation process: for every \( \text{CO}_2 \) molecule that the ocean takes up, the ocean also needs to take up a \( \text{CO}_3^{2-} \) ion from the sediment to restore the original \( [\text{CO}_3^{2-}] \). This is an approximation, because \( \text{CO}_3^{2-} \) and \( \text{CO}_2 \) also react with minor acids and bases, such as the boron species, \( \text{H}_2^+ \), and \( \text{OH}^- \). However, it appears to be sufficiently accurate for our purposes, as we demonstrate in sections 2.1 and 2.2 through comparisons between our analytical predictions and simulations with a multibox model that includes these minor acids and bases.

In section 2.1, we derive an expression for the change in atmospheric \( \text{CO}_2 \), if carbon is redistributed within the ocean-atmosphere system. In other words, we assume: \( \delta I_{\text{oa,noncalc}} = 0 \). Such a carbon redistribution could be due to a change in ocean temperature or salinity or a change in nutrient utilization. Without carbonate compensation, there would be no change in the total ocean-atmosphere carbon inventory, but the carbonate compensation process leads to input or output of carbon in the form of \( \text{CaCO}_3 \). In section 2.2, we derive an expression for the change in atmospheric \( \text{CO}_2 \), if some POC is buried instead of being remineralized in the water column. In other words: \( \delta I_{\text{oa,noncalc}} = \delta I_{\text{oa,bur}} \). To maintain deep-ocean \( [\text{CO}_3^{2-}] \) at its original value, \( C_{\text{reg}} \) and \( \text{CaCO}_3 \) need to be removed in a 1:1 ratio. The resulting alkalinity decrease then leads to outgassing of \( \text{CO}_2 \) from the ocean to the atmosphere.
2.1. Carbonate Compensation in Response to Redistribution of Carbon in the Ocean-Atmosphere System

If the only changes in the total carbon inventory in the ocean-atmosphere system are due to the carbonate compensation process, then equation (3) becomes

\[ M \delta \Delta X_{CO_2} + \frac{V \delta (C_{sat} + C_{reg} + C_{carb})}{2} = 0 \]  

(4)

The saturated carbon concentration is determined by the atmospheric CO₂ content and by the ocean temperature, salinity, and alkalinity. As in Goodwin and Lenton (2009), we split the dependencies of \( C_{sat} \) into contributions from atmospheric CO₂, temperature, alkalinity, and salinity, with \( B \equiv \frac{\partial \Delta X_{CO_2}}{\partial \Delta A_{sat}} \) the Revelle buffer factor (Bolin & Eriksson, 1959), \( \gamma_T \equiv \frac{\partial C_{sat}}{\partial \Delta T} \), \( \gamma_S \equiv \frac{\partial C_{sat}}{\partial \Delta S} \), and \( \gamma_A \equiv \frac{\partial C_{sat}}{\partial \Delta A_{sat}} \). The change in ocean alkalinity \( (\delta A) \) is divided into a change in preformed alkalinity \( (\delta A_{pref}) \), relevant for the ocean-atmosphere carbon partitioning, a change due to the carbonate pump \( (\delta A_{carb} = 2\delta A_{carb}) \) and a change due to the remineralization of organic matter (Sarmiento & Gruber, 2006) \( \delta A_{reg} = -R_{N, C} \delta C_{reg} \) (with \( R_{N, C} \) the Redfield N:C ratio). The expansion of \( \delta A_{sat} \) gives

\[ \delta C_{sat} = \frac{C_{sat}}{X_{CO_2}} \frac{\delta X_{CO_2}}{B} + \gamma_T \delta T + \gamma_S \delta S + \gamma_A \delta A_{pref} \]

(5)

which can be rearranged thus:

\[ \frac{\delta C}{\delta X_{CO_2}} = \frac{C_{sat}}{X_{CO_2}} \frac{\delta X_{CO_2}}{B} + \gamma_T \delta T + \gamma_S \delta S + (1 + R_{N, C}) \delta C_{reg} - 2(1 - \Delta A) \delta C_{carb} \]

(6)

Substituting equation (6) into (4), we obtain

\[ (1 - \gamma_A) M \delta \Delta X_{CO_2} = -\frac{V}{2} \left( \frac{C_{sat}}{X_{CO_2}} B \delta X_{CO_2} + \gamma_T \delta T + \gamma_S \delta S + (1 + R_{N, C}) \delta C_{reg} - 2(1 - \Delta A) \delta C_{carb} \right) \]

(7)

which can be used to calculate the change in atmospheric \( X_{CO_2} \):

\[ \delta X_{CO_2} = \frac{\gamma_T \delta T + \gamma_S \delta S + (1 + R_{N, C}) \delta C_{reg} - 2(1 - \Delta A) \delta C_{carb}}{2(1 - \gamma_A) M \frac{C_{sat}}{X_{CO_2}} B} \]

(8)

This is the change in atmospheric \( X_{CO_2} \) after carbonate compensation resulting from a change in ocean temperature \( \delta T \), salinity \( \delta S \), nutrient utilization \( \delta C_{reg} \), or the carbonate pump \( \delta C_{carb} \). Combining equation (8) with the balance equation (4) and \( \delta A \approx \delta (C_{sat} + C_{reg} + C_{carb}) \), the result can also be expressed in terms of whole-ocean alkalinity:

\[ \delta A = -\frac{2M \delta \Delta X_{CO_2}}{V} = \frac{\gamma_T \delta T + \gamma_S \delta S + (1 + R_{N, C}) \delta C_{reg} - 2(1 - \Delta A) \delta C_{carb}}{1 - \gamma_A + \frac{C_{sat}}{X_{CO_2}} B \frac{V}{2M}} \]

(9)

Without carbonate compensation, the change in \( X_{CO_2} \) would be

\[ \delta X_{CO_2} = \frac{\gamma_T \delta T + \gamma_S \delta S + (1 + R_{N, C}) \delta C_{reg} - 2(1 - \Delta A) \delta C_{carb}}{M \frac{V}{2} + \frac{C_{sat}}{X_{CO_2}} B} \]

(10)
which is essentially a restatement of results derived in various earlier papers (Goodwin et al., 2008, 2011; Marinov, Follows, et al., 2008; Marinov, Gnanadesikan, et al., 2008; Omta et al., 2011).

The ratio of \( \delta X_{\text{CO}_2} \) with carbonate compensation to \( \delta X_{\text{CO}_2} \) without carbonate compensation is thus

\[
\frac{\delta X_{\text{CO}_2} \text{ (carbocomp.)}}{\delta X_{\text{CO}_2} \text{ (nocarbocomp.)}} = \frac{M X_{\text{CO}_2} + \frac{V \gamma A}{B}}{2 \gamma A M X_{\text{CO}_2} + \frac{V \gamma A}{B}}
\]  

(11)

Using \( M = 1.80 \times 10^{20} \text{ mol, } X_{\text{CO}_2} = 300 \text{ ppmv, } V = 1.40 \times 10^{18} \text{ m}^3, \gamma A = 0.90, C_{\text{sat}} = 2.00 \text{ mol/m}^3, \) and \( B = 12.0, \) we get

\[
\frac{\delta X_{\text{CO}_2} \text{ (carbocomp.)}}{\delta X_{\text{CO}_2} \text{ (nocarbocomp.)}} \approx 1.18
\]  

(12)

That is, carbonate compensation enhances the change in atmospheric \( \text{CO}_2 \) by about 18% after a redistribution of carbon between the atmosphere and the ocean. This value must have varied in the geological past, in particular because there have been variations in \( X_{\text{CO}_2} \).

To test this prediction of an \( \sim 18\% \) enhancement of \( \text{CO}_2 \) changes against more precise calculations including the minor acids and bases important for the ocean-atmosphere exchange of carbon (the boron species, \( \text{H}^+, \) and \( \text{OH}^- \)), we use the multibox model described in Appendix A. The response of the ocean-atmosphere carbon partitioning to a perturbation in ocean temperature, salinity, or carbon pumps is expected to occur on three timescales (Lord et al., 2016); (1) a multicentennial equilibration of carbon between the atmosphere and ocean, without significant interaction with the sediments; (2) a multimillennial equilibration with the calcite sediments through the carbonate compensation feedback; and (3) a final equilibration of the ocean alkalinity cycle due to adjustments in the silicate weathering rate on timescales of many hundreds of thousands of years.

In the simulations, we study the \( X_{\text{CO}_2} \) response to perturbations in the ocean on the first two of these timescales, neglecting long-term changes in the silicate weathering rate. First, we let the box model equilibrate on the faster timescale without carbonate compensation, after which we turn on the carbonate compensation to study the slower equilibration through the carbonate compensation feedback. In our multibox model, the carbonate compensation process is formulated as a linear relaxation toward an equilibrium deep-ocean \([\text{CO}_2]^-\) with a 5 kyr time constant.

The model is spun up for 200 kyr to equilibration with carbonate compensation switched on. With the imposed equilibrium deep-ocean \([\text{CO}_2]^-\), ocean temperatures, and carbon and phosphorous inventories, the steady state \( X_{\text{CO}_2} \) settles at 297 ppmv. Subsequently, we run a set of experiments in which the temperature of all the ocean surface boxes is changed, with and without carbonate compensation. As expected, a temperature change has a somewhat stronger impact on atmospheric \( \text{CO}_2 \) with carbonate compensation than without it (Figure 2). The ratio \( \frac{\delta X_{\text{CO}_2} \text{ (carbocomp.)}}{\delta X_{\text{CO}_2} \text{ (nocarbocomp.)}} \) increases from 1.15 to 1.21, as the imposed temperature change increases from \(-5 \) to \(+5 \) °C (Figure 2b), which can be understood as follows. Since \( 2(\gamma A) \) is only about 0.2, equation (11) can be approximated as

\[
\frac{\delta X_{\text{CO}_2} \text{ (carbocomp.)}}{\delta X_{\text{CO}_2} \text{ (nocarbocomp.)}} \approx \frac{M X_{\text{CO}_2} \gamma A}{V} + 1.
\]

As \( X_{\text{CO}_2} \) increases with increasing temperature, \( \frac{V \gamma A}{B} \) remains relatively constant, which leads to the overall increase in the ratio.

To give an idea of the transient dynamics with and without carbonate compensation, we show full time series of \( X_{\text{CO}_2} \) as well as DIC and alkalinity in the Antarctic Bottom Water (AABW) box. First, the sea surface temperatures (SST) are decreased by 5 °C without carbonate compensation (Figure 3). The temperature change leads to a repartitioning of carbon between the atmosphere and the ocean: \( X_{\text{CO}_2} \) decreases by 48 ppmv (green line in Figure 3a), while DIC increases by 7 μM (green line in Figure 3b). The alkalinity remains constant, as long as there is no carbonate compensation (green line in Figure 3c). After 10 kyr, the system has equilibrated and we switch the carbonate compensation on, while the low SST are maintained. The carbonate compensation process leads to a further decrease in atmospheric \( X_{\text{CO}_2} \) of just over 7 ppmv (blue line in Figure 3a), an increase in DIC of 9 μM (blue line in Figure 3b), and an increase in alkalinity of 16 μM (blue line in Figure 3c). This is slightly more than the alkalinity change expected from our framework: \( \delta A = \frac{2M X_{\text{CO}_2} \gamma A}{V} = 14 \) μM, which is likely due to the contributions from minor acids and bases such as the boron species. The carbonate compensation takes place on a timescale much longer than the imposed 5 kyr response time because of the asymptotic nature of the overall equilibration process. That is, a certain change in temperature leads to a certain change
in $X_{CO_2}$ and deep-ocean DIC. This leads to CaCO$_3$ dissolution or burial, which in turn leads to a change in atmospheric $X_{CO_2}$, which in turn leads to CaCO$_3$ dissolution or burial, which in turn leads to a change in atmospheric $X_{CO_2}$, etc.

2.2. Carbonate Compensation in Response to Organic Matter Burial
If organic carbon and phosphorus are buried instead of being remineralized, then there is a decrease in the inventory of regenerated carbon equal to the decrease in the total carbon inventory: $\delta I_{oa,noncalc} = \delta I_{oa,bur} = V \delta C_{reg}$. In this case, equation (3) becomes

\[ M \delta X_{CO_2} + \frac{V \delta (C_{sat} + C_{reg} + C_{carb})}{2} = V \delta C_{reg} \]

or

\[ M \delta X_{CO_2} + \frac{V \delta (C_{sat} - C_{reg} + C_{carb})}{2} = 0 \]

We use an expansion analogous to equation (5) but ignoring any changes in the temperature and salinity, because the focus is on changes in the nutrient inventory:

\[ \delta (C_{sat} - C_{reg} + C_{carb}) = \frac{C_{sat}}{X_{CO_2} B} \delta X_{CO_2} \]

\[ + \gamma_A \delta (C_{sat} + C_{reg} + C_{carb}) + \gamma_A (R_W C \delta C_{reg} - 2 \delta C_{carb}) - \delta C_{reg} + \delta C_{carb} \]
Figure 3. Multibox model simulation: after the spin-up (red line), the sea surface temperature is decreased by 5 °C everywhere, first without carbonate compensation (green line) and finally with carbonate compensation (blue line); (a) atmospheric CO2, (b) dissolved inorganic carbon (DIC) in the Antarctic Bottom Water box, and (c) total alkalinity in the Antarctic Bottom Water box.

Collecting \( \delta \left( C_{\text{sat}} - C_{\text{reg}} + C_{\text{carb}} \right) \) terms on the left-hand side and dividing by \( 1 - \gamma_A \) gives

\[
\delta \left( C_{\text{sat}} - C_{\text{reg}} + C_{\text{carb}} \right) = \frac{\frac{\delta C_{\text{CO}_2}}{X_{\text{CO}_2} B} \left( 2\gamma_A - 1 + R_{N:C} \right) \delta C_{\text{reg}} - \left( 2\gamma_A - 1 \right) \delta C_{\text{carb}}}{1 - \gamma_A}
\]  \quad (16)

Combining equations (14) and (16) then leads to

\[
\delta X_{\text{CO}_2} = -\frac{\left( 2\gamma_A - 1 + R_{N:C} \right) \delta C_{\text{reg}} - \left( 2\gamma_A - 1 \right) \delta C_{\text{carb}}}{2 \left( 1 - \gamma_A \right) \frac{M}{V} + \frac{C_{\text{sat}}}{X_{\text{CO}_2} B}}
\]  \quad (17)

Equation (17), which describes the impact of burial of POC on \( \delta X_{\text{CO}_2} \), is identical to equation (8), which applies to a change in nutrient utilization (setting \( \delta T \) and \( \delta S \) equal to 0), except that the factor \( 1 + R_{N:C} \) in front of \( \delta C_{\text{reg}} \) is replaced by \( 2\gamma_A - 1 + R_{N:C} \). Given that \( \frac{2\gamma_A - 1 + R_{N:C}}{1 + R_{N:C}} \approx 0.8 \), the change in atmospheric CO2 after carbonate compensation is \( \sim 20% \) smaller if it is caused by POC burial than if it is caused by a decreased nutrient utilization, for a given decrease in the regenerated carbon \( \delta C_{\text{reg}} \).

Using equation (13) and \( \delta A \approx \delta \left( C_{\text{sat}} + C_{\text{reg}} + C_{\text{carb}} \right) \), equation (17) can also be cast as an expression for the whole-ocean alkalinity change:

\[
\delta A = 2 \left( -\frac{M\delta X_{\text{CO}_2}}{V} + \delta C_{\text{reg}} \right) = \frac{\left( 2\gamma_A - 1 + R_{N:C} \right) \delta C_{\text{reg}} - \left( 2\gamma_A - 1 \right) \delta C_{\text{carb}}}{1 - \gamma_A + \frac{C_{\text{sat}}}{X_{\text{CO}_2} B} \frac{V}{2M}} + 2\delta C_{\text{reg}}
\]  \quad (18)

The sinkings of POC and CaCO3 are intimately connected with each other (Klaas & Archer, 2002). Consistently, we assume that the whole-ocean average strengths of the carbonate pump and the soft-tissue pump
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Figure 4. Atmospheric CO₂ as a function of the total amount of buried particulate organic carbon (POC), after a 250-kyr equilibration with carbonate compensation (blue diamonds). The green diamond indicates the spin-up simulation; the black cross stands for the simulation experiment shown in Figure 5. The red line indicates the slope predicted by relation (19), using $M = 1.80 \times 10^{25}$ mol, $X_{\text{CO}_2} = 300$ ppmv, $V = 1.40 \times 10^{18}$ m$^3$, $\gamma_A = 0.90$, $C_{\text{sat}} = 2.00$ mol/m$^3$, $B = 12.0$, and $R_{\text{calc}} = 0.100$. In calculating this slope, the alkalinity change directly resulting from the remineralization of organic matter ($\delta A_{\text{reg}} = -R_{N,C} \delta C_{\text{reg}}$) was neglected, because this effect is not included in our multibox model.

\[
\delta X_{\text{CO}_2} = -\frac{(2\gamma_A - 1)(1 - R_{\text{calc}}) + R_{N,C} \delta C_{\text{reg}}}{2(1 - \gamma_A) M V + C_{\text{sat}} X_{\text{CO}_2} B}
\]  

Figure 5. Multibox model simulation: after the spin-up (red line), organic carbon and phosphorus are buried (green line). Most of the carbonate compensation takes place after the burial has been halted (blue line). (a) Atmospheric CO₂, (b) dissolved inorganic carbon (DIC) in the Antarctic Bottom Water (AABW) box, (c) total alkalinity in the AABW box, and (d) dissolved inorganic phosphorus (DIP) in the AABW box.

The ratio $R_{\text{calc}}$ determines to what extent the carbonate compensation in the deep ocean is communicated to the ocean surface. If this ratio were 1:1, then the weakening of the soft-tissue carbon pump and the associated carbonate compensation would be offset exactly by a weakening of the carbonate pump, and $[\text{CO}_2^-]$ at the ocean surface (and thus atmospheric CO₂) would remain constant. However, the average ratio of CaCO₃:POC added to the water column is believed to be in the 0.1–0.2:1 range (Boyle, 1988; Yamanaka & Tajika, 1996). Hence, a large fraction of the alkalinity output in the deep ocean is communicated to the surface ocean, because less carbon is added to the deep ocean through the carbonate pump than through the soft-tissue carbon pump.
off and the system is left to equilibrate. The carbonate compensation is switched on at all times. To vary the output of organic phosphorus and POC, we run a set of simulations where the burial fraction is increased from 0.2% to 2.0% in 0.2% increments. The total amount of phosphorus buried in the model experiments varied between 0.05 \times 10^{15} and 0.50 \times 10^{15} mol, out of a total initial inventory of 2.41 \times 10^{15} mol; the total amount of POC buried varied between 70 Pg C and 630 Pg C. In Figure 4, we show atmospheric CO₂ as a function of the total amount of buried POC, after full equilibration (250 kyr) with carbonate compensation, along with the slope predicted by relation (19). As can be seen, there is excellent agreement between the analytical theory and the box model simulations.

In Figure 5, we show the time series of \( X_{\text{CO}_2} \), as well as DIC, alkalinity, and dissolved inorganic phosphorus in the AABW box for one of the simulations. During the burial phase, there are two competing effects: the removal of phosphorus weakens the soft-tissue carbon pump and therefore increases atmospheric CO₂, whereas the removal of carbon decreases atmospheric CO₂. In our box model, the combined removal of carbon and phosphorus under the Redfield ratio before significant carbonate compensation leads to a minor decrease in \( X_{\text{CO}_2} \) (green line in Figure 5a). (This reflects that there is not full nutrient utilization. With full nutrient utilization across the ocean (\( C_{\text{reg}} = R_{\text{C,µP}} \)) and a removal of carbon and phosphorus according to the Redfield ratio (\( \delta_{\text{a,noncalc}} = R_{\text{C,µP}} \)), then \( I_{\text{al,noncalc}} = \delta C_{\text{reg}} \). That is, equation (2) becomes: \( \delta X_{\text{CO}_2} + V \delta (C_{\text{sat}} + C_{\text{carb}}) = 0 \). If \( C_{\text{carb}} \) does not change, then the net effect on atmospheric CO₂ is 0, as \( C_{\text{sat}} \) depends only on \( X_{\text{CO}_2} \), temperature, salinity, and alkalinity.) During the burial phase, the major changes are in the ocean carbon and phosphorus inventories: DIC decreases by 27 \( \mu M \) (green line in Figure 5b), while the dissolved inorganic phosphorus concentration decreases by 0.22 \( \mu M \) (green line in Figure 5d). The alkalinity decrease is still relatively minor (green line in Figure 5c), because the carbonate compensation process responds to changes in the deep ocean \([\text{CO}_2^2+]\) with a lag of many thousands of years. After the burial phase, the carbonate compensation leads to a rather large increase in \( X_{\text{CO}_2} \) (blue line in Figure 5a), as well as major decreases in DIC and alkalinity (blue lines in Figures 5b/c), while the dissolved inorganic phosphorus concentration remains constant (blue line in Figure 5d). The overall increase in \( X_{\text{CO}_2} \) equals 24 ppmv, whereas the overall alkalinity decrease equals 57 \( \mu M \) eq. Based on \( \delta A = 2 \left( \frac{\delta X_{\text{CO}_2}}{V} + \delta C_{\text{reg}} \right) \), one would expect an alkalinity decrease of 61 \( \mu M \) eq, under the assumption that \( \delta C_{\text{reg}} = R_{\text{C,µP}} \). Again, the final state is only achieved after many tens of thousands of years, during which there is continuous equilibration and reequilibration between the different reservoirs.

3. Discussion

As in section 2, we first discuss carbonate compensation under a constant nutrient inventory (section 3.1), before moving to the potential combined impact of POC burial and carbonate compensation (section 3.2). Finally, we discuss how CaCO₃ preservation and production may impact the timescale at which deep-ocean \([\text{CO}_2^2+]\) is restored (section 3.3).

3.1. Constant Nutrient Inventory

Our analytical framework (as well as our multibox model) predicts that carbonate compensation increases by 15–20% the impact of changes in atmospheric CO₂ resulting from a redistribution of carbon between the atmosphere and ocean. The full changes in atmospheric CO₂ due to variations in the ocean temperature and the soft-tissue carbon pump can thus be inferred from coupled ocean-atmosphere-biogeochemistry models that do not include carbonate compensation and are therefore cheaper to run, because they equilibrate in multcentennial timescales rather than multimillennial timescales. The rule of thumb is then to multiply the model’s predicted CO₂ changes by 1.15–1.20 to account for carbonate compensation.

The most important application of the 15–20% rule of thumb will likely be in the study of glacial-interglacial cycles. Ice core measurements suggest that atmospheric CO₂ dropped by 80–100 ppmv during glacial climates compared to interglacials (Lüthi et al., 2008; Petit et al., 1999). These drops may have involved various disturbances of the ocean carbon system (Chikamoto et al., 2012; Peacock et al., 2006; Wallmann, 2014), for example, changes in the whole-ocean temperature, salinity, alkalinity, and nutrient utilization. However, it remains unclear whether the net impact of all these ocean changes can amount to the total 80–100 ppmv swings in atmospheric CO₂ (Brovkin et al., 2012; Sigman & Boyle, 2000; Sigman et al., 2010). Our study suggests that changes in ocean temperature, salinity, alkalinity, and nutrient utilization need explain only 70–85 ppmv changes, because an additional 15–20% can be attributed to carbonate compensation.
Another important application of our result is to predict the long-term fate of anthropogenic carbon emissions, for which Goodwin and Ridgwell (2010) previously developed an analytical framework. They focused on the chemical processes (air-sea carbon partitioning and carbonate compensation) in isolation, without considering the impact of the changing climate on the ocean-atmosphere partitioning of CO$_2$. However, temperature is expected to change under global warming. Furthermore, it has been suggested that the soft-tissue carbon pump will strengthen in a high CO$_2$ world (Bernardello et al., 2014; Oschlies et al., 2008; Riebesel et al., 2007). All these hypothesized mechanisms essentially involve a redistribution of carbon between the ocean and the atmosphere, which means that their impacts on atmospheric CO$_2$ will be enhanced by 15–20% after carbonate compensation.

Our framework is built on an assumption that DIC and alkalinity are more or less vertically homogeneous throughout most of the ocean, which holds in the present-day ocean. The framework needs to be modified if there is a strong vertical heterogeneity in DIC at intermediate depths and in the abyss. In fact, this has already been demonstrated by earlier box model simulations (Hain et al., 2010). In these simulations, carbonate compensation enhanced the impact of changes in nutrient utilization on atmospheric CO$_2$ by 16% (i.e., within our predicted 15–20%) under the present-day ocean circulation. However, under an inferred glacial circulation, carbonate compensation enhanced the impact of changes in nutrient utilization on atmospheric CO$_2$ by 32%. This stronger carbonate compensation feedback was likely due to the “focusing” of regenerated nutrients and carbon in a water mass around the CCD. In the future, we plan to expand our framework with multiple water masses, so that, for example, the impact of nutrient focusing in an isolated reservoir can be considered.

### 3.2. Organic Matter Burial

Our analytical framework (as well as our multibox model) predicts that the combination of organic matter burial and carbonate compensation lead to an increase in atmospheric CO$_2$. Although this result may seem counterintuitive, it can be understood intuitively as follows. After a mole of phosphorus has first become available for biological production, it provides for a net uptake of CO$_2$ from the atmosphere at two points in time: (1) the first time the mole of phosphorus is incorporated into organic matter and (2) the first time the mole of phosphorus, incorporated in organic matter, is remineralized in the deep ocean. At this point, DIC is released into the deep ocean, leading to a decrease in deep-ocean [CO$_2$], since $\delta$[CO$_2$] $\approx \delta A - \delta C$. This, in turn, leads to a net dissolution of CaCO$_3$ and an ocean alkalinity increase. Once the ocean-atmosphere system has equilibrated, the alkalinity increase will have led to an uptake of CO$_2$ from the atmosphere into the ocean.

When the mole of phosphorus is finally buried, the CO$_2$ uptake achieved in step (1) is made permanent, while the step (2) CO$_2$ uptake is reversed. The carbonate compensation proceeds in the other direction, leading to a decrease in ocean alkalinity and an outgassing of CO$_2$ from the ocean into the atmosphere. This outgassing is expected to take place on the ~4–16 kyr timescales associated with the equilibration of the sediments (Lord et al., 2016), with a long tail due to the continuing equilibration and reequilibration between the ocean and the atmosphere. Thus, the impact of organic matter burial depends on the timescale that one considers. The residence time of phosphorus in the ocean is estimated to be 10–40 kyr (Filippelli, 2011; Ruttenberg, 2003), which means that uptake in step (2) and its reversal can safely be neglected on timescales of millions of years but not on timescales of tens of thousands of years.

Could this mechanism have played a role in glacial-interglacial CO$_2$ changes? Broecker (1982) suggested that at the end of glacial-interglacial transitions, enhanced organic matter burial may have occurred on newly flooded continental shelves. However, Peacock et al. (2006) argued that this mechanism can only be responsible for a small portion of the deglacial weakening of the soft-tissue carbon pump, based on the thickness of the deglacial sediment cover on the Sunda Shelf—the world’s largest shallow shelf (Hanebuth et al., 2000). Moreover, Kohfeld and Ridgwell (2009) suggested that the deglacial sea level rise occurred too late for this mechanism to have played a major role in the deglacial rise in atmospheric CO$_2$. The continental shelves only flooded toward the end of the deglaciation, after the main Northern Hemisphere ice sheets had melted, and the carbonate compensation process would have taken place even later. In response to both these objections, we wish to point out that recent observations suggest that enhanced deglacial productivity may have occurred in the open ocean, rather than on newly flooded continental shelves. In fact, deglacial maxima in productivity proxies such as opal accumulation and biogenic Ba have been found at deep-sea sites in the Atlantic (Gil et al., 2009; Meckler et al., 2013; Romero et al., 2008), the Pacific (Galbraith et al., 2007; Hayes et al., 2011; Jaccard et al., 2005; Kohfeld & Chase, 2011), and the Southern Ocean (Anderson et al., 2009; Jaccard et al., 2013). Although it remains difficult to quantify from these observations the total amount of organic matter
buried, together they suggest that the deglacial decrease of the ocean nutrient inventory could have been more significant than generally recognized.

### 3.3. Restoring Deep-Ocean \([\text{CO}_2^-_{3}]\): Preservation Versus Production

The assumption that the deep-ocean \([\text{CO}_2^-_{3}]\) returns to its original value after a disturbance is key to the application of our framework. The geological record provides strong evidence for this assumption. Focusing on glacial-interglacial cycles, the B/C proxy indicates only small changes in the deep-ocean \([\text{CO}_2^-_{3}]\) (in particular if averaged over different locations; Doss & Marchitto, 2013; Kerr et al., 2017; Raitzsch et al., 2011; Rickaby et al., 2010; Yu et al., 2010, 2014). That said, a study of 31 cores from the Pacific, Atlantic, and Indian Oceans specifically focused on CaCO₃ dissolution proxies (Mekik et al., 2012) did not find strong evidence for a global deglacial carbonate preservation maximum, which presents somewhat of a mystery from the conventional carbonate compensation perspective.

Perhaps, the focus has been too much on CaCO₃ dissolution and preservation: a large net deglacial CaCO₃ accumulation could also be achieved through an increase in CaCO₃ production. For example, a deglacial maximum in organic matter production would likely have been accompanied by a deglacial maximum in CaCO₃ production. Due to POC being remineralized at faster rates than CaCO₃, the global average CaCO₃:POC ratio of material collected in sediment traps at depths below ∼1,000 m is close to 1:1 (Figure 4c in Archer, 1996), which implies an output of carbon and alkalinity in a ∼1:1 ratio. If this ratio applied during a deglacial burial event, then the organic matter burial and the alkalinity output needed to maintain a constant whole-ocean \([\text{CO}_2^-_{3}]\) would have occurred simultaneously (since \(\delta[\text{CO}_2^-_{3}] \approx \delta A - \delta C\)). Thus, a combined burial of POC and CaCO₃ would have accelerated the carbonate compensation process. From this perspective, it is interesting that the deglacial oceanic productivity maximum appears to be accompanied by a maximum in the CaCO₃ fraction of the sediments (Brunelle et al., 2010; Flores et al., 2003; Gebhardt et al., 2008; Jaccard et al., 2005; Jaccard et al., 2013; Rickaby et al., 2010). Enhanced CaCO₃ production is a particularly viable explanation for deglacial CaCO₃ maxima at locations with continuous CaCO₃ accumulation, such as the Cape Basin (Flores et al., 2003) and the Weddell Sea (Rickaby et al., 2010). However, even at locations without continuous CaCO₃ accumulation (e.g., the deep North Pacific, Jaccard et al., 2005; and the deep Southern Ocean, Jaccard et al., 2013) where deglacial CaCO₃ spikes represent transient deepenings of the CCD, these CCD deepenings could ultimately be driven by CaCO₃ production. The CCD is the level where the supply and dissolution of CaCO₃ are equal. Hence, the CCD deepens when the CaCO₃ supply increases, even if the CaCO₃ dissolution rate remains constant.

### 4. Conclusions

We have created an analytical framework for quantifying the impacts on atmospheric CO₂ of various carbon cycle disturbances after carbonate compensation has been completed. We think that a few points are crucial:

1. Carbonate compensation amplifies by ∼15–20% changes in atmospheric CO₂ resulting from redistribution of carbon within the ocean-atmosphere system (due to changes in temperature, salinity, and nutrient utilization).

2. Counterintuitively, the combination of organic matter burial in the ocean and carbonate compensation leads to an increase in atmospheric CO₂. According to our framework, changes in the soft-tissue carbon pump have very similar impacts on atmospheric CO₂ after carbonate compensation, regardless of their origin. That is, burial of 10% of the nutrient inventory has almost the same impact as a 10% decrease in the nutrient utilization.

3. The impact of carbonate compensation on atmospheric CO₂ predicted from our analytical theory is consistent with multibox model calculations involving the full set of reactions involved in the ocean-atmosphere exchange of carbon, including the boron species, H⁺, and OH⁻.

In the near future, we intend to apply our framework to investigate hypotheses about the glacial-interglacial CO₂ changes quantitatively. However, our framework can also be used to assess the long-term fate of anthropogenic CO₂.

### Appendix A: Multibox Setup

The multibox model was modified from an earlier version used in Omta et al. (2013, 2016). The initial tracer concentrations are listed in Table A1, along with their respective values at the end of the spin-up. In Table A2, the model parameters (e.g., box volumes and transport rates) and their respective values are listed.
Table A1

<table>
<thead>
<tr>
<th>Variables</th>
<th>Units</th>
<th>Meaning</th>
<th>Initial value</th>
<th>Value after spin-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$</td>
<td>mol eq/m³</td>
<td>Southern Ocean alkalinity</td>
<td>2.200</td>
<td>2.260</td>
</tr>
<tr>
<td>$A_l$</td>
<td>mol eq/m³</td>
<td>Low-latitude alkalinity</td>
<td>2.200</td>
<td>2.227</td>
</tr>
<tr>
<td>$A_n$</td>
<td>mol eq/m³</td>
<td>North Atlantic alkalinity</td>
<td>2.200</td>
<td>2.221</td>
</tr>
<tr>
<td>$A_i$</td>
<td>mol eq/m³</td>
<td>NADW alkalinity</td>
<td>2.400</td>
<td>2.235</td>
</tr>
<tr>
<td>$A_d$</td>
<td>mol eq/m³</td>
<td>AABW alkalinity</td>
<td>2.400</td>
<td>2.363</td>
</tr>
<tr>
<td>$C_s$</td>
<td>mol/m³</td>
<td>Southern Ocean DIC concentration</td>
<td>2.160</td>
<td>2.095</td>
</tr>
<tr>
<td>$C_l$</td>
<td>mol/m³</td>
<td>Low-latitude DIC concentration</td>
<td>2.160</td>
<td>1.958</td>
</tr>
<tr>
<td>$C_n$</td>
<td>mol/m³</td>
<td>North Atlantic DIC</td>
<td>2.160</td>
<td>2.040</td>
</tr>
<tr>
<td>$C_i$</td>
<td>mol/m³</td>
<td>NADW DIC concentration</td>
<td>2.350</td>
<td>2.249</td>
</tr>
<tr>
<td>$C_d$</td>
<td>mol/m³</td>
<td>AABW DIC concentration</td>
<td>2.350</td>
<td>2.353</td>
</tr>
<tr>
<td>$P_s$</td>
<td>mol eq/m³</td>
<td>Southern Ocean phosphorus</td>
<td>$5.00 \times 10^{-5}$</td>
<td>$8.338 \times 10^{-5}$</td>
</tr>
<tr>
<td>$P_l$</td>
<td>mol eq/m³</td>
<td>Low-latitude phosphorus</td>
<td>$5.00 \times 10^{-5}$</td>
<td>$0.9059 \times 10^{-5}$</td>
</tr>
<tr>
<td>$P_n$</td>
<td>mol eq/m³</td>
<td>North Atlantic phosphorus</td>
<td>$5.00 \times 10^{-5}$</td>
<td>$4.564 \times 10^{-5}$</td>
</tr>
<tr>
<td>$P_i$</td>
<td>mol eq/m³</td>
<td>NADW phosphorus</td>
<td>$2.00 \times 10^{-3}$</td>
<td>$1.934 \times 10^{-3}$</td>
</tr>
<tr>
<td>$P_d$</td>
<td>mM</td>
<td>AABW phosphorus</td>
<td>$2.00 \times 10^{-3}$</td>
<td>$2.068 \times 10^{-3}$</td>
</tr>
<tr>
<td>$X_{CO_2}$</td>
<td>ppmv</td>
<td>Atmospheric CO₂ mixing ratio</td>
<td>200.0</td>
<td>296.6</td>
</tr>
</tbody>
</table>

Notes. NADW = North Atlantic Deep Water; AABW = Antarctic Bottom Water; DIC = dissolved inorganic carbon.

Table A2

<table>
<thead>
<tr>
<th>Par</th>
<th>Units</th>
<th>Meaning</th>
<th>Standard value</th>
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</thead>
<tbody>
<tr>
<td>$Vol_s$</td>
<td>m³</td>
<td>Southern Ocean surface box volume</td>
<td>$4.2 \times 10^{16}$</td>
</tr>
<tr>
<td>$Vol_l$</td>
<td>m³</td>
<td>Low-latitude surface box volume</td>
<td>$6.0 \times 10^{16}$</td>
</tr>
<tr>
<td>$Vol_n$</td>
<td>m³</td>
<td>North Atlantic surface box volume</td>
<td>$1.8 \times 10^{16}$</td>
</tr>
<tr>
<td>$Vol_i$</td>
<td>m³</td>
<td>NADW box volume</td>
<td>$6.0 \times 10^{17}$</td>
</tr>
<tr>
<td>$Vol_d$</td>
<td>m³</td>
<td>AABW box volume</td>
<td>$6.0 \times 10^{17}$</td>
</tr>
<tr>
<td>$M$</td>
<td>mol</td>
<td>Amount of gas in atmosphere</td>
<td>$1.8 \times 10^{20}$</td>
</tr>
<tr>
<td>$V_p$</td>
<td>m/s</td>
<td>Piston velocity</td>
<td>$5.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$m_{sl}$</td>
<td>Sv</td>
<td>Bidirectional mixing between Southern Ocean and low-latitude boxes</td>
<td>20.0</td>
</tr>
<tr>
<td>$m_{lb}$</td>
<td>Sv</td>
<td>Bidirectional mixing between low-latitude and North Atlantic boxes</td>
<td>20.0</td>
</tr>
<tr>
<td>$m_{nl}$</td>
<td>Sv</td>
<td>Bidirectional mixing between NADW and North Atlantic boxes</td>
<td>10.0</td>
</tr>
<tr>
<td>$m_{ld}$</td>
<td>Sv</td>
<td>Bidirectional mixing between NADW and AABW boxes</td>
<td>2.0</td>
</tr>
<tr>
<td>$m_{ni}$</td>
<td>Sv</td>
<td>Bidirectional mixing between NADW and low-latitude boxes</td>
<td>2.0</td>
</tr>
<tr>
<td>$m_{si}$</td>
<td>Sv</td>
<td>Bidirectional mixing between Southern Ocean and NADW boxes</td>
<td>5.0</td>
</tr>
<tr>
<td>$q_n$</td>
<td>Sv</td>
<td>NADW overturning transport</td>
<td>15.0</td>
</tr>
<tr>
<td>$q_l$</td>
<td>Sv</td>
<td>AABW overturning transport</td>
<td>15.0</td>
</tr>
<tr>
<td>$R_{C:P}$</td>
<td></td>
<td>Carbon:phosphorus ratio soft tissue</td>
<td>106</td>
</tr>
<tr>
<td>$R_{calc}$</td>
<td></td>
<td>Inorganic:organic carbon ratio of remineralization</td>
<td>0.1</td>
</tr>
<tr>
<td>$T_s$</td>
<td>°C</td>
<td>Southern Ocean temperature</td>
<td>3</td>
</tr>
<tr>
<td>$T_l$</td>
<td>°C</td>
<td>Low-latitude box temperature</td>
<td>20</td>
</tr>
<tr>
<td>$T_d$</td>
<td>°C</td>
<td>North Atlantic temperature</td>
<td>5</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>s⁻¹</td>
<td>Southern Ocean export rate</td>
<td>$1.07 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\lambda_l$</td>
<td>s⁻¹</td>
<td>Low-latitude export rate</td>
<td>$6.43 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\lambda_n$</td>
<td>s⁻¹</td>
<td>North Atlantic export rate</td>
<td>$2.14 \times 10^{-8}$</td>
</tr>
<tr>
<td>$[CO_2^+]_{eq}$</td>
<td>mol/m³</td>
<td>Equilibrium $[CO_2^+]$ in the AABW box</td>
<td>0.01</td>
</tr>
<tr>
<td>$\tau$</td>
<td>kyr</td>
<td>Carbonate compensation time</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Notes. NADW = North Atlantic Deep Water; AABW = Antarctic Bottom Water.
Figure A1. A schematic depiction of the multibox setup; box volumes, transport rates, and tracer concentrations before and after the spin-up are listed in Tables A1 and A2.

There are well-mixed atmospheric, low-latitude surface ocean, North Atlantic surface ocean, Southern Ocean surface, North Atlantic Deep Water (NADW), and Antarctic Bottom Water (AABW) boxes (Figure A1). A terrestrial biosphere compartment is also included in the model, but the size of this compartment is kept constant in the simulations. For the oceanic boxes, tracer concentrations are calculated through three modules: ocean-atmosphere carbon exchange, carbon isotope partitioning, and oceanic transport. For each surface ocean box, the carbon exchange module calculates the oceanic $X_{CO2}$ using DIC, alkalinity, and the water temperature of the box by solving the full carbonate system with the Follows et al. (2006) scheme. Then, the air-sea flux of carbon $\phi$ between the box and the atmosphere is calculated from the difference between $X_{CO2, oce}$ and $X_{CO2, atm}$:

$$\phi = V_p a_k (X_{CO2, atm} - X_{CO2, oce})$$

(A1)

with $V_p$ the piston velocity and $a_k$ an equilibrium constant. Tracers are exchanged between the oceanic boxes through bidirectional mixing between boxes $j$ and $k$ with volumes $Vol_j$ and $Vol_k$ at rates $m_{jk}$ and through overturning transports $q_n$ (NADW) and $q_s$ (AABW). For each tracer $Y$, it consists of the following equations (with the subscripts $n, l, s, i$, and $d$ indicating the North Atlantic surface, low-latitude surface, Southern Ocean surface, NADW, and AABW boxes, respectively):

$$\frac{\partial Y_n}{\partial t} = \frac{-(q_n + m_{ik})(Y_n - Y_i) - m_{ik}(Y_n - Y_k)}{Vol_n}$$

(A2)

$$\frac{\partial Y_l}{\partial t} = \frac{-(q_n + m_{li})(Y_l - Y_i) - m_{li}(Y_l - Y_n) - m_{li}(Y_l - Y_s)}{Vol_l}$$

(A3)

$$\frac{\partial Y_s}{\partial t} = \frac{-(q_s(Y_s - Y_d) - m_{is}(Y_s - Y_i) - m_{is}(Y_s - Y_l))}{Vol_s}$$

(A4)

$$\frac{\partial Y_i}{\partial t} = \frac{-(q_n + m_{ik})(Y_i - Y_k) - m_{ik}(Y_i - Y_n) - m_{ik}(Y_i - Y_s)}{Vol_i}$$

(A5)

$$\frac{\partial Y_d}{\partial t} = \frac{-(q_s(Y_d - Y_i) - m_{id}(Y_d - Y_s))}{Vol_d}$$

(A6)
We assume that dissolved inorganic phosphorus is the limiting nutrient. To represent the soft-tissue carbon pump, phosphorus is taken out of the surface boxes at rates $A_j$ from the surface boxes (as in Zhang et al., 2001), along with carbon through a constant Redfield ratio ($R_{C:P} = 106$). The carbonate pump is represented through a constant CaCO$_3$:POC ratio of the exported carbon ($R_{\text{calc}} = 0.1$). The exported phosphorus, carbon, and alkalinity are added to the deep boxes, with one third going to the AABW box and two thirds going to the NADW box; no burial of organic matter takes place in the standard setup. Following various earlier studies (Boudreau, 2013; Boyle, 1983; Broecker & Peng, 1982; Köhler et al., 2010), the carbonate compensation feedback is formulated as a linear relaxation toward an equilibrium carbonate ion concentration ([CO$_3^{2-}$]$_{eq}$) in the deep (AABW) box:

$$\frac{dC_d}{dt} = - \frac{A_d - C_d - [\text{CO}_3^{2-}]_{eq}}{\tau} \quad (A7)$$

$$\frac{dA_d}{dt} = -2 \frac{A_d - C_d - [\text{CO}_3^{2-}]_{eq}}{\tau} \quad (A8)$$

in which [CO$_3^{2-}$]$_{eq}$ is approximated as $A_d - C_d$. We choose a response time $\tau = 5$ kyr, because recent simulations with the Grid Enabled Integrated Earth system model (GENIE) have indicated that the effective carbonate compensation timescale is ~5 kyr for relatively small total carbon emissions of ~1,000 Pg (Lord et al., 2016). These emissions are of a similar order of magnitude as the amounts of carbon that are exchanged between different reservoirs before carbonate compensation in the situations under consideration (0–100 Pg in the temperature change experiments and 0–700 Pg in the carbon burial experiments).

### References


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