Analytical relationships between atmospheric carbon dioxide, carbon emissions, and ocean processes

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Carbon perturbations leading to an increase in atmospheric CO₂ are partly offset by the carbon uptake by the oceans and the rest of the climate system. Atmospheric CO₂ approaches a new equilibrium state, reached after ocean invasion ceases after typically 1000 years, given by \( P_{CO2} = P_0 \exp(\delta I_c/I_B) \), where \( P_0 \) and \( P_{CO2} \) are the initial and final partial pressures of atmospheric CO₂, \( \delta I_c \) is a CO₂ perturbation, and \( I_B \) is the buffered carbon inventory of the air-sea system. The perturbation, \( \delta I_c \), includes carbon emissions and changes in the terrestrial reservoir, as well as ocean changes in the surface carbon disequilibrium and fallout of organic soft tissue material. Changes in marine calcium carbonate, \( \delta I_{CaCO3} \), lead to a more complex relationship with atmospheric CO₂, where \( P_{CO2} \) is changed by the ratio \( P_{CO2} = P_0 \{1/(I_{OA} - c) - \delta I_{CaCO3}/I_{OA} - c\} \) and then modified by a similar exponential relationship, where \( I_{OA} - c \) is the difference between the inventories of titration alkalinity and dissolved inorganic carbon. The overall atmospheric \( P_{CO2} \) response to a range of perturbations is sensitive to their nonlinear interactions, depending on the product of the separate amplification factors for each perturbation.


I. Introduction

Atmospheric carbon dioxide concentrations are currently rising from anthropogenic emissions, which are partly offset by the exchange of carbon with the terrestrial biosphere, the ocean and, eventually, through the weathering of rocks. The ocean uptake is particularly important in reducing the impact of emissions on timescales of decades to thousands of years [Archer et al., 1997; Sabine et al., 2004]. Our aim is to elucidate the role of ocean processes in modifying the atmospheric response to carbon emissions by developing a new analytical framework. The analytical relationships provide insight into how the carbon system operates by explicitly revealing the atmospheric CO₂ dependence of different variables and are ideal to investigate parameter space. The analytical relations provide quantitative predictions for long-term atmospheric CO₂ and, thus, provide a simpler reference point to more detailed numerical investigations, such as those by Lenton et al. [2006], Plattner et al. [2001] and Matear and Hirst [1999].

The coupling of the atmosphere and ocean carbon systems is achieved in a rather complex and disjointed manner (Figure 1). While the surface mixed layer is in direct contact with the atmosphere, the timescale for air-sea exchange of carbon dioxide is generally too slow to keep pace with seasonal-forced physical and biological changes [Broecker and Peng, 1982]. Thus, a local equilibrium between the atmospheric and oceanic partial pressure for carbon dioxide is rarely achieved and usually a disequilibrium exists. In turn, the carbon concentrations in the ocean interior are determined by the physical and biological transfer of carbon from the surface mixed layer, which occur in an intermittent manner. The physical transfer is achieved via convection within the mixed layer and then subduction into the stratified thermocline during late winter [Follows et al., 1996]. The biological transfer involves the gravitational fallout of organic matter from the surface sunlit ocean, usually peaking during a spring bloom, with the fallout containing soft tissue, organic carbon and hard tissue, calcium carbonate material. While increased export of organic carbon leads to an increased ocean drawdown of CO₂, increased export of calcium carbonate instead alters the charge balance of dissolved inorganic carbon species in the surface ocean and leads to an ocean outflux of CO₂.

Given the complexity of the ocean processes transferring carbon, this study extends a new analytical framework to address two related questions: 1. What is the effect of separate ocean processes on the long-term atmospheric concentration of carbon dioxide? 2. How do these different ocean processes interact with increasing carbon emissions?
and combine together to effect the long-term atmospheric concentration of carbon dioxide?

[5] In order to illustrate these questions prior to developing our analytical framework, consider a series of separate, carbon perturbations applied to a simple numerical ocean box model (Appendix A; Sarmiento and Toggweiler [1984]): an anthropogenic emission of carbon into the atmosphere (Figure 2a, gray solid line), an increase in biological fallout of soft tissue and calcium carbonate material (Figure 2a, gray dashed and dotted lines, respectively). For the carbon emissions, there is an initial peak in atmospheric concentrations and then a decline to a background state when ocean invasion ceases after typically 1000 years. For the increased fallout of organic carbon, there is a reduction in the atmospheric CO$_2$ from the soft tissue fallout, but a slight increase from the calcium carbonate drawdown. The integrated effect of these different processes differ according to whether each process is treated separately in the model and then linearly summed or, more realistically, allowed to vary together at the same time in the model (Figure 2b, dashed and solid lines, respectively).

[6] This study, extending a new analytical framework to understand long-term carbon cycling, is structured in the following manner. Analytical relations revealing the effects of charge neutral carbon cycle changes upon atmospheric CO$_2$ are derived in section 2, which combine a buffered carbon inventory approach [Goodwin et al., 2007] with a process-driven, carbon storage view [Ito and Follows, 2005]. This framework is extended to incorporate changes in the marine CaCO$_3$ cycle including perturbations in the overall surface charge balance in section 3. The analytical framework is used to demonstrate how the amplifying feedbacks combine between different perturbation mechanisms in section 4 and, finally, the implications of the study are discussed in section 5.

2. Developing an Analytical Framework for CO$_2$ Perturbations

[7] Consider an atmosphere, with atmospheric partial pressure $P_{CO_2}$, for carbon dioxide in a global equilibrium with an ocean with an average dissolved inorganic carbon (DIC) concentration $C_{DIC}$. The total amount of carbon in the system, $\Sigma C$, is given by

$$\Sigma C = I_A + I_O = MP_{CO_2} + VM_{DIC},$$

(1)

where $I_A$ and $I_O$ are the atmospheric and oceanic carbon inventories respectively, $M$ is the molar volume of the atmosphere, $V$ is the volume of the ocean, and $C_{DIC} = [CO_2] +$...
[H$_2$CO$_3$] + [HCO$_3^-$] + [CO$_3^{2-}$]. The effective $P_{CO2}$ of the ocean is only dependent upon the uncharged constituents of C$_{DIC}$ (Appendix B), but the speciation of DIC in seawater makes calculating this new steady state nontrivial.

Ocean DIC concentrations, C$_{DIC}$, can be separated into component concentrations due to different processes [Brewer, 1978],

$$C_{DIC} = C_{sat} + C_{dis} + C_{bio} + C_{CaCO3}. \tag{2}$$

In order to understand this separation, consider a parcel of water, initially at the surface of the ocean in contact with the atmosphere (Figure 1). If the water is in equilibrium with the atmosphere, the DIC concentration is equal to the saturation concentration, $C_{sat}$. More typically, if there is an air-sea exchange of CO$_2$, then the concentration of DIC is equal to the saturation concentration plus the disequilibrium concentration, $C_{dis}$. If the water parcel is subducted, no further exchange with the atmosphere is possible and so the disequilibrium concentration of the parcel is fixed until the water parcel resurfaces. While the water parcel is in the deep ocean, remineralization of biological soft tissue increases the DIC concentration by $C_{bio}$. Finally, dissolution of falling CaCO$_3$ from the hard tissue of an organism increases C$_{DIC}$ of the water parcel further by C$_{CaCO3}$, as well as increasing the titration alkalinity of the water parcel.

This mechanistic view can now be expressed in terms of a global inventory equation, combining (1) and (2) [Ito and Follows, 2005]:

$$I_A + I_O = MP_{CO2} + V(\frac{C_{sat} + C_{dis} + C_{bio} + C_{CaCO3}}{C_{DIC}}) = \Sigma C, \tag{3}$$

where an overbar represents a global average. If small perturbations to the inventory equation (3) are now considered:

$$\delta I_A + \delta I_O = M\delta P_{CO2} + V(\delta C_{sat} + \delta C_{dis} + \delta C_{bio} + \delta C_{CaCO3}) = \Sigma \delta C, \tag{4}$$

where, for example, $\delta C_{bio}$, represents a change in the ocean storage of carbon due to a change in biological nutrient utilization. Changes in the total air-sea carbon inventory ($\Sigma \delta C$) on the right-hand side of (4) may be due to anthropogenic carbon emissions ($I_{em}$) and exchanges with the terrestrial carbon reservoir ($I_{ter}$):

$$M\delta P_{CO2} + V(\delta C_{sat} + \delta C_{dis} + \delta C_{bio} + \delta C_{CaCO3}) = I_{em} - I_{ter}. \tag{5}$$

There is a minus sign for the $I_{ter}$ term, since an expansion of the terrestrial carbon reservoir decreases the total amount of carbon in the air-sea system.

In order to solve for the atmospheric $P_{CO2}$ on a millennial timescale, (5) can be rearranged (ignoring changes to C$_{CaCO3}$, which are addressed in section 3) to yield:

$$M\delta P_{CO2} + V\delta C_{sat} = \delta I_{em} - I_{ter} - V(\delta C_{dis} + \delta C_{bio}). \tag{6}$$

where the right-hand side of (6) represents perturbations imparted upon the system, and the left-hand side represents the response of the system on a millennial timescale. Using $\delta I_A$ to represent the combined effects of $\delta I_{em}, -\delta I_{ter}, -V\delta C_{dis}$ and $-V\delta C_{bio}$, (6) is rewritten as

$$\frac{\delta P_{CO2}}{P_{CO2}} = \frac{M\delta P_{CO2} + V\delta C_{sat}}{P_{CO2}} = \frac{\delta I_A}{I_B}. \tag{7}$$

During the response to a imposed perturbation, $\delta I_A$, the only term in DIC (2) that changes is $C_{sat}$ with $\delta C_{sat} = \delta C_{DIC}$. Thus, the term $(P_{CO2}\delta C_{sat})/(C_{DIC}\delta P_{CO2})$ can be reexpressed as $(P_{CO2}\delta C_{DIC})/C_{DIC}\delta P_{CO2} = V_{global}$, where $B_{global}$ is the globally averaged Revelle buffer factor of seawater. Hence, (7) can be rewritten in terms of the buffered carbon inventory of the air-sea system, $I_B$ [Goodwin et al., 2007], where $I_B = MP_{CO2} + (V_{DIC}/B_{global}) = I_A + (I_B/B_{global})$, giving

$$\delta \frac{\ln P_{CO2}}{P_{CO2}} = \frac{\delta I_A}{I_B}, \tag{8}$$

which relates an infinitesimal perturbation in $\delta I_A$ to the air-sea system response in $P_{CO2}$ after ocean invasion. Integrating (8), assuming that $I_B$ is unchanged as the system is perturbed, $\delta I_A \ll I_B$, [Goodwin et al., 2007], gives

$$P_{CO2} = P_0 \exp\left(\frac{\delta I_A}{I_B}\right), \tag{9}$$

where $\delta I_A$ again represents either $\delta I_{em}, -\delta I_{ter}, -V\delta C_{dis}$ and $-V\delta C_{bio}$. This relationship is now employed to predict how atmospheric $P_{CO2}$ will rise exponentially on a millennial timescale if carbon is added into the atmosphere through (1) an emission of fossil fuels ($\delta I_{em} > 0$) or a contraction of the terrestrial carbon reservoir ($\delta I_{ter} < 0$), (Figure 3a, dashed line); and (2) a reduction in air-sea disequilibrium ($\delta C_{dis} < 0$) or a reduction in the carbon stored in the deep ocean due to weakening in biological drawdown ($\delta C_{bio} < 0$) (Figure 3b, dashed line).

Why can the buffered carbon inventory, $I_B$, be considered constant in the integration of (8)? In preindustrial ocean conditions the majority of DIC exists in the bicarbonate form, with carbonate dominating over the uncharged forms (collectively labeled CO$_2^*$) among the minor constituents (Figure 4a). If a charge neutral carbon perturbation is imparted on the system, $\delta I_A$, such that $P_{CO2}$ (and therefore $I_A$) increases, the proportion of DIC in the form CO$_2^*$ increases and the carbonate proportion decreases, while the majority of DIC remains in the bicarbonate form. These DIC constituent changes cause the globally averaged buffer factor of ocean waters, $B_{global}$, to increase from a preindustrial value of around 12 to a maximum of around 20 when $[CO_2^*] \approx [CO_3^{2-}]$ (Figure 4b). An increase in $P_{CO2}$ acts to increase the atmospheric inventory, $I_A$, but at the same time acts to increase $B_{global}$, thus leading to relatively small changes in the buffered carbon inventory $I_B$ (Figure 4c, up to 4000 GtC).
However, further emissions in excess of 4000 GtC leads to both a further increase in $I_A$, as well as a decrease in $B_{\text{global}}$, thus leading to an eventual increase in $I_B$ (Figure 4c).

These analytical relations for $P_{\text{CO}_2}$ (9) not only provide insight as to the effect of CO$_2$ perturbations when ocean invasion ceases, they also provide quantitative skill. In order to illustrate this predictive ability, the analytical relations are compared against a numerical 3 ocean box model (Appendix A) based on Sarmiento and Toggweiler [1984]. The numerical box model includes crude representations of meridional overturning, ocean exchanges and ocean biological fallout and remineralization, but does not contain representations of sediment or weathering interactions. The box model is perturbed by additions of carbon and changes to biological nutrient utilization. The final $P_{\text{CO}_2}$ predicted by the analytical relations (9) are in close agreement with the numerical calculations of the box model [Goodwin et al., 2007].

Given the skill of the analytical relationship for CO$_2$ perturbations, the more complex problem of the calcification cycle is considered.

### 3. Effect of Calcium Carbonate Cycling and Changes in Alkalinity

Changes in the marine calcification cycle alter the charge balance of ocean waters, where the formation or dissolution of CaCO$_3$ in seawater is given by,

$$\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq). \quad (10)$$

On the left-hand side, there is 1 unit of DIC which carry 0 units of charge, while on the right-hand side, there is 2 units of DIC which collectively carry 2 units of charge. Therefore, as dissolution of CaCO$_3$ occurs and (10) proceeds to the right, the DIC concentration increases by...
[16] The analytical framework for \( P_{CO2} \) is now extended to include perturbations in the marine calcification cycle with changes in alkalinity and DIC incorporated in a 2:1 ratio and allowing air-sea \( CO2 \) exchange.

### 3.1. Effect of a CaCO_3 Perturbation on Seawater \( P_{CO2} \)

[17] Approximating titration alkalinity with carbonate alkalinity, equations for the carbonate alkalinity system (Appendix B) can be combined to form a quadratic in \([CO_3^2-]\):

\[
a[CO_3^2-]^2 + b[CO_3^2-] + c = 0,
\]

where \( a, b, \) and \( c \) are terms containing \( C_{DIC} \), the carbonate alkalinity, \( A_C \), and the first and second dissociation constants of \( CO2 \) in seawater, \( K_1 \) and \( K_2 \) (Appendix B). Implicitly differentiating this quadratic (11) assuming constant temperature, \( T \), and salinity, \( S \), leaves an expression relating infinitesimal changes to \( A_C \) and \( C_{DIC} \) to the resulting change in \([CO_3^2-]\) of the form:

\[
2a[CO_3^2-]\delta_{TS} [CO_3^2-] + [CO_3^2-]^2\delta_{TS} a + b[CO_3^2-] \delta_{TS} [CO_3^2-] + [CO_3^2-] \delta_{TS} b + c = 0,
\]

where \( \delta_{TS} \) indicates a small change with \( T \) and \( S \) held constant. Performing this implicit differentiation loses the information required to analytically approximate an initial \( P_{CO2} \) value, but keeps the information required to calculate a change in \( P_{CO2} \). Assuming \( \delta A_C = 2\delta C_{DIC} \), this relation (12) can be rearranged for \( CaCO_3 \) perturbations to give

\[
\delta [CO_3^2-] = -\frac{(\delta A_C - \delta C_{DIC} + 2(1 - \frac{4K_2}{K_1})\delta[CO_3^2-])}{A_C - C_{DIC} - \frac{4K_2}{K_1}(A_C - 2C_{DIC})}.
\]

This relationship can be simplified in the following manner. First, \( K_2/K_1 \) is small, implying that

\[
\frac{4K_2}{K_1}(A_C - 2C_{DIC}) \ll |A_C - C_{DIC}|,
\]

and, second, \([CO_3^2-]\) is very small in relation to \( C_{DIC} \) implying

\[
2\left(1 - \frac{K_2}{K_1}\right)\delta[CO_3^2-] \ll |\delta A_C - \delta C_{DIC}|.
\]

which approximates to \( |\delta[CO_3^2-]| \ll |\delta C_{DIC}| \), since for a \( CaCO_3 \) perturbation \( \delta A_C = 2\delta C_{DIC} \). Thus, whenever conditions (14) and (15) are met, (13) can be simplified, as well as combined with seawater \( P_{CO2} \) being proportional to \([CO_3^2-]\), to relate an infinitesimal \( CaCO_3 \) perturbation to the resulting infinitesimal change in seawater \( P_{CO2} \):

\[
\frac{\delta[CO_3^2-]}{CO_3^2-} = \frac{\delta P_{CO2}}{P_{CO2}} \approx -\frac{\delta(A_C - C_{DIC})}{A_C - C_{DIC}}.
\]
\[ \Delta \ln P_{CO_2} \approx -\Delta \ln A_C - \Delta C_{DIC}, \]  

relating the change in the \( P_{CO_2} \) of a water parcel due to a 2:1 change in \( A_C \) and \( C_{DIC} \) from \( CaCO_3 \) changes. As \( CaCO_3 \) is dissolved, \( C_{DIC} \) increases, but \( P_{CO_2} \) decreases because of the greater addition of alkalinity (Figure 5; dots); the log change in \( P_{CO_2} \) being given by the negative of the log change in \( A_C - C_{DIC} \).

This relationship (17) is valid for surface ocean conditions with \( P_{CO2} \) typical of the present-day, Holocene or last glacial maximum levels (as illustrated in the model test in Figure 5), while conditions (14) and (15) are met and titration alkalinity is approximated by carbonate alkalinity, \( A_C \); eventually, (17) breaks down when there is very high \( P_{CO2} \), \( C_{DIC} \) approaches \( A_C \), and (15) becomes invalid.

In comparison, Broecker and Peng [1982] derived an analytical prediction for the value of \( P_{CO2} \) of ocean waters at given values of \( C_{DIC} \) and \( A_C \), but their prediction requires knowledge of \( T \) and \( S \) and ignores the \( CO_2^* \) component of DIC in the carbonate chemistry equations. In this alternative relation (17), the \( CO_2^* \) component of DIC is retained in its derivation, and knowledge of \( T \) and \( S \) is not required (as the terms in (13) containing the dissociation constants of \( CO_2 \) are insignificant), but (17) does require a known initial value of \( P_{CO2} \) in order to approximate analytically the change due to a \( CaCO_3 \) perturbation.

### 3.2. Closed System Perturbations: Reorganization of the Vertical Alkalinity Gradient

The analytical framework is now applied to examine the effects of two types of perturbation to the ocean calcium carbonate cycle: Closed system changes, where the oceanic calcium ion budget is fixed, but its distribution rearranged (this section), and open system changes where external sources and sinks of calcium ions are included (section 3.3). Closed system changes are relevant for internal ocean changes, such as a global change in phytoplankton community structure affecting the amount of calcium carbonate.
production and export. For example, it has been hypothesized that glacial periods may have been characterized by a leakage of silica from the Southern Oceans enhancing diatom production globally and reducing coccolithophore production [Brzezinski et al., 2002; Matsumoto et al., 2002]. The effects of such a perturbation (on a submillennial timescale) can be viewed as a closed system response, with a reduction in the rain ratio of CaCO₃ to organic tissue in falling matter, a decrease in the mean vertical gradient of alkalinity, and a global increase in surface alkalinites.

[22] The impact of such closed system changes are now considered in terms of the analytical framework. In reality, when the calcium carbonate cycle is perturbed, changes in deep ocean storage of alkalinity and DIC occur simultaneously with an air-sea exchange in CO₂. However, for simplicity, consider this adjustment process to occur in two separate hypothetical stages.

[23] 1. In the first stage, the system is assumed to be at a steady state with a partial pressure of P₀, and ocean saturation concentration of C_sat, with the carbon inventory given by

\[ MP₀ + V(C_{sat}(P₀) + C_{dis} + C_{bio} + C_{CaCO₃}) = ΣC. \]  

(18)

When C_{CaCO₃} is perturbed, assume that the deep ocean storage of alkalinity and DIC and the effective P_{CO₂} of the ocean adjusts, but no air-sea exchange of CO₂ is yet permitted. At this transient stage, atmospheric P_{CO₂} remains at P₀ while the saturation carbon concentration of the ocean is altered to C_sat(P_{ocean}). For this state, P₀ and P_ocean can be related using (17) with the globally averaged concentrations of preformed DIC, C_{pre}, and preformed alkalinity, A_{pre},

\[ P_{ocean} = P₀ \left( \frac{A_{pre} - C_{pre} + \delta(A_{pre} - C_{pre})}{A_{pre} - C_{pre} - \delta(C_{CaCO₃})} \right). \]  

(19)

where an increase in C_{CaCO₃} reduces A_{pre} and C_{pre} in a 2:1 ratio by redistributing alkalinity and DIC away from the surface ocean and into the ocean interior. This hypothetical stage creates a charge neutral carbon anomaly of \( 6I_{X} = M(P₀ - P_{ocean}) \) with the ocean now saturated at C_sat = C_sat(P_{ocean}), but the atmosphere still having a CO₂ partial pressure of P₀.

[24] 2. In the second stage, air-sea exchange of CO₂ proceeds until the charge neutral carbon anomaly is removed and there is no further net annual air-sea carbon exchange. Once stage 2 has completed the system reaches a final steady state with the atmospheric CO₂ partial pressure equal to P_{final} and C_sat reaching C_sat(P_{final}). The resulting charge neutral carbon anomaly, P_{final}, can be related to P_{ocean} by (9),

\[ P_{final} = P_{ocean} \exp \left( \frac{M(P₀ - P_{ocean})}{I_B} \right). \]  

(20)

Combining (19) and (20) then allows the change in atmospheric P_{CO₂} to be related to a small perturbation in global average C_{CaCO₃},

\[ P_{final} = P₀ \left( \frac{A_{pre} - C_{pre} - \delta(C_{CaCO₃})}{A_{pre} - C_{pre} - \delta(C_{CaCO₃})} \right) \cdot \exp \left( \frac{-MP₀\delta(C_{CaCO₃})}{(A_{pre} - C_{pre} - \delta(C_{CaCO₃}))I_B} \right). \]  

(21a)

where the initial value is P₀ and the final value after air-sea exchange is P_{final}. This equation can be written more succinctly by defining I_{O(A-C)} as the initial difference between global inventories of preformed alkalinity and DIC, and by writing P_{CO₂} = P_{final}:

\[ P_{CO₂} = P₀ \left( \frac{I_{O(A-C)}}{I_{O(A-C)}} \right) \exp \left( -I_{ter}I_B\delta(C_{CaCO₃}) \right). \]  

(21b)

An increase in C_{CaCO₃} acts to raise atmospheric P_{CO₂} (Figure 3c, dashed line) due to the 2:1 reduction in preformed alkalinity and DIC, from the ratio term, \([I_{O(A-C)}(I_{O(A-C)} - Vδ(C_{CaCO₃}))]/(I_{O(A-C)} - Vδ(C_{CaCO₃})) \) in (21b); there is larger increase in P_{CO₂} when the inventory I_{O(A-C)} is small. This increase in P_{CO₂} is partly opposed by the resulting air-sea exchange with a damping though the exponential term. Thus, in contrast to perturbations in I_{ter}, I_{ter}s C_{bio} and C_{dis} a given perturbation in C_{CaCO₃} causes a larger change in P_{CO₂} if I_B is large, because the damping due to air-sea exchange is decreased.

[26] To exploit this analytical relationship (21b) to understand how the sensitivity of P_{CO₂} to CaCO₃ perturbations varies, consider two air-sea systems in steady state, both with CaCO₃ weathering and sediment cycles in equilibrium and with the same deep sea carbonate ion concentration: (1) The system that has a higher vertical gradient of DIC, e.g., because of having a stronger biological drawdown of carbon, will have a larger value of I_{O(A-C)} and its atmospheric carbon levels will be correspondingly less sensitive to changes in C_{CaCO₃}. (2) The system that has a lower vertical gradient of DIC, because of having a weaker biological drawdown of carbon, will have a smaller value of I_{O(A-C)} and its atmospheric carbon levels will be correspondingly more sensitive to changes in C_{CaCO₃}.

[27] Hence, the analytical framework suggests that a more efficient drawdown of carbon by biological soft tissue can make atmospheric CO₂ levels less sensitive to changes in the marine calcification cycle.

[28] This analytical relationship (21b) provides reasonable quantitative skill with predictions in close agreement (with a typical accuracy of 4%) with the final P_{CO₂} reached by the box ocean model (Figure 3c and Appendix A).

3.3. Open System Perturbations: Sources and Sinks of Alkalinity to the Global Ocean

[29] On geological timescales of many millennia and longer, the combined ocean-atmosphere cannot be considered a closed system with respect to carbon and alkalinity
due to weathering and interactions with the carbonate sediments [Ridgwell and Zeebe, 2005]. Dissolved CaCO$_3$ is constantly being added to the ocean from the weathering of rocks on land, which adds titration alkalinity and DIC. This source is offset by a deposition of precipitated CaCO$_3$ on the ocean floor, which removes titration alkalinity and DIC. An imbalance between weathering and deposition of CaCO$_3$ can alter the ocean inventories of titration alkalinity and DIC over many thousands of years. For example, the long-term response to anthropogenic emissions implies an acidification of the ocean and a reduced rate of calcium carbonate being buried in sediments. This reduction in burial rate in turn leads to an imbalance between supply and removal of dissolved CaCO$_3$, resulting in a 2:1 increase in the whole ocean titration alkalinity and DIC inventories until carbonate ion concentrations are restored [Archer, 2005; Archer et al., 1997]. The analytical framework is now extended to account for such “open system” perturbations.

Now extend the analytical framework to include marine calcification changes for an open system with an increase in the DIC inventory, $\Delta I_{\text{open}}$, from reduced precipitation or enhanced weathering input of CaCO$_3$. Following the same method as for the closed system, the hypothetical change in ocean partial pressure of CO$_2$ with no air-sea exchange is given by

$$P_{\text{ocean}} = P_0 \left( \frac{A_{\text{pre}} - C_{\text{pre}}}{A_{\text{pre}} - C_{\text{pre}} + \beta (A_{\text{pre}} - C_{\text{pre}})} \right)$$

$$= P_0 \left( \frac{I_{O(A-C)}}{I_{O(A-C)} + \Delta I_{\text{open}}} \right),$$

and the final change to atmospheric CO$_2$ with air-sea exchange included is given by

$$P_{\text{CO}_2} = P_0 \left( \frac{I_{O(A-C)}}{I_{O(A-C)} + \Delta I_{\text{open}}} \right) \exp \left( \frac{+I_{\text{bio}} \Delta I_{\text{open}}}{I_{O(A-C)} + \Delta I_{\text{open}}} \right) I_B,$$

These relations (22) and (23) are modified from (19) and (21) by the inclusion of the additional inventory source of DIC, $\Delta I_{\text{open}}$, from the global dissolution of CaCO$_3$ exceeding global precipitation (also equal to half the titration alkalinity inventory change). In addition, the sign of the term $-V \delta \beta$ in (21) is changed to $+\delta I_{\text{open}}$ in (23), since adding 2 units of titration alkalinity and 1 unit of DIC increases the difference between preformed concentrations.

The analytical theory (23) predicts that increasing the titration alkalinity and DIC inventories, due to total global CaCO$_3$ dissolution exceeding precipitation, ($\Delta I_{\text{open}} > 0$) will decrease steady state $P_{\text{CO}_2}$ (Figure 3d, dashed line). Within the range $-1000 < \Delta I_{\text{open}} < +3000$ GtC, the analytical theory predicts steady state $P_{\text{CO}_2}$ to within 10% of a numerical box model comparison (Figure 3d).

4. Generalizing the Analytical Framework for the Carbon System

The simultaneous effect of a set of perturbations on atmospheric $P_{\text{CO}_2}$ is now considered, rather than treat each perturbation in isolation. Combining together the generic exponential relation (9), the closed (21) and open system (23) relations for calcium carbonate changes gives:

$$P_{\text{CO}_2} = P_0 \exp \left( \frac{\beta I_{\text{bio}} - \beta I_{\text{ter}} - V \delta \beta \text{CaCO}_3}{I_B} \right)$$

$$\cdot \left( \frac{I_{O(A-C)}}{I_{O(A-C)} + \Delta I_{\text{open}}} \right) \exp \left( \frac{+I_{\text{bio}} \Delta I_{\text{open}}}{I_{O(A-C)} + \Delta I_{\text{open}}} \right) I_B$$

(24)

This combined relationship for atmospheric $P_{\text{CO}_2}$ provides a concise summary of how carbon system responds to a range of perturbations. Atmospheric $P_{\text{CO}_2}$ increases if carbon is added to the atmosphere by emissions or a contraction of the terrestrial carbon reservoir, while there is a decrease in $P_{\text{CO}_2}$ for an increase in organic biological drawdown (Figure 6a, dashed lines). Atmospheric $P_{\text{CO}_2}$ is also increased through an increase in the marine drawdown of CaCO$_3$ (Figure 6b, dashed lines) or a removal of titration alkalinity and DIC in a 2:1 ratio by a net precipitation of CaCO$_3$ within the ocean (Figure 6c, dashed lines).

In terms of quantitative skill, the analytical predictions for $P_{\text{CO}_2}$ are in reasonable accord with the numerical calculations from the simplified box model (Figure 6). While $P_{\text{CO}_2}$ remains below 1080 ppm, or ~4 times preindustrial levels, the analytically predicted $P_{\text{CO}_2}$ agrees with model output to within 4% within the ranges of $\delta I_{\text{bio}}$, $\delta I_{\text{ter}}$, $\delta C_{\text{dis}}$, $\delta C_{\text{bio}}$ and $\delta C_{\text{CaCO}_3}$ tested. In the extreme limit when atmospheric $P_{\text{CO}_2}$ begins to exceed 4 times preindustrial levels, then the buffered carbon inventory can no longer be considered constant, and (24) is no longer valid. When considering “open system” effects, errors become significant when both $\delta I_{\text{bio}} - \delta I_{\text{ter}}$ exceeds 3000 GtC and $\Delta I_{\text{open}}$ exceeds 2000 GtC (Figure 6c) for a combination of reasons: $I_B$ cannot be assumed constant with such large combined changes to titration alkalinity and carbon inventories (and also then the extra assumptions made when altering titration alkalinity, (14) and (15), become invalid).

In reality, $P_{\text{CO}_2}$ is affected by the combination of the multiple carbon processes considered, rather than by a single carbon perturbation acting alone. The overall change in $P_{\text{CO}_2}$ is not accurately given by a linear summation of the individual perturbations acting in isolation, as revealed at the outset in the box model illustration in Figure 2b. The analytical relationship for the combined perturbations (24) can be expanded to reveal how the separate perturbations $\delta I_{\text{bio}}$, $\delta C_{\text{bio}}$, $\delta C_{\text{dis}}$, $\delta C_{\text{CaCO}_3}$, $\delta I_{\text{ter}}$ and $\Delta I_{\text{open}}$ combine to alter $P_{\text{CO}_2}$
and after dividing by $P_0$ can be equivalently written as

\[
\left( \frac{P_{CO_2}}{P_0} \right)_{overall} = \left( \frac{P_{CO_2}}{P_0} \right)_{em} \times \left( \frac{P_{CO_2}}{P_0} \right)_{bio} \times \left( \frac{P_{CO_2}}{P_0} \right)_{dis} \\
\times \left( \frac{P_{CO_2}}{P_0} \right)_{CaCO_3} \times \left( \frac{P_{CO_2}}{P_0} \right)_{ir} \times \left( \frac{P_{CO_2}}{P_0} \right)_{open},
\]

where the terms labeled by $P_{CO_2}/P_0$ for the changes in $I_{em}$, $I_{ter}$, $C_{bio}$ and $C_{dis}$ are given by (9), the change in $C_{CaCO_3}$ is given by (21) and the change in $I_{open}$ is given by (23). Therefore, the overall amplification of $P_{CO_2}$ above the initial value $P_0$ is given by multiplying together each of the separate amplifications of $P_{CO_2}$ when each carbon perturbation acts separately.

These analytical predictions for the final equilibrium state are supported by the numerical box model calculations (Table 1 and Figure 7, gray and black solid lines, respectively), explaining the nonlinear interaction. In addition, this framework allows the changes in $P_{CO_2}$ from a single model integration to be attributed to each of the separate perturbations considered.

5. Discussion

This study provides an analytical framework to understand how the ocean modifies the atmospheric response to carbon emissions on a millennial timescale. The final and initial atmospheric partial pressure of carbon dioxide are connected by a generic exponential relationship, $P_{CO_2} = P_0 \exp \left( \frac{\delta I_{c}}{T_B} \right)$, depending on the size of the carbon perturbation, $\delta I_{c}$, divided by the atmosphere and ocean buffered carbon inventory, $I_B$. This relationship reveals how atmospheric $P_{CO_2}$ will rise exponentially on a millennial timescale if carbon is added into the atmosphere by an emission of fossil fuels, a contraction of the terrestrial carbon reservoir, a reduction in the carbon stored in the deep ocean due to weakening in biological drawdown or a reduction in local air-sea disequilibrium. This relationship becomes more complicated when...
calcium carbonate cycling is incorporated, altering the surface charge balance, with \( P_{CO_2} \) increasing following either an increased export of calcium carbonate into the deep ocean or a global net precipitation of CaCO\(_3\).

[38] These analytical relationships provide insight as to how different processes operate in the carbon system when ocean invasion ceases, as well as quantitative predictions for atmospheric \( P_{CO_2} \). The relationships are ideal to explore a large range of parameter space and, thus, an ideal complement to more sophisticated numerical studies of the carbon system, which are often computationally restricted to a smaller range. Thus, the analytical relationships are a useful tool to explore the long-term response of carbon perturbations for a wide range of carbon problems.

[39] The analytical relations support the following speculations as to how the carbon system may be likely to change. Anthropogenic carbon emissions will cause \( P_{CO_2} \) to be higher on a millennial timescale according to (9) \((\delta I_{em} > 0)\). However, the long-term response of the terrestrial carbon inventory to climate change remains uncertain [Lenton et al., 2006]. Ocean acidification due to emissions will make the precipitation of CaCO\(_3\) in surface waters less favorable, and could reduce marine calcification \((\delta C_{CaCO_3} < 0)\) [Ridgwell and Zeebe, 2005], which will tend to dampen the \( P_{CO_2} \) increase, (21). Changes in wind-forcing due to climate change are also highly uncertain; however if wind-forcing of the surface ocean increases, ocean DIC is likely to become further from saturation and the \( C_{dis} \) pool will become more negative \((\delta C_{dis} < 0)\) [Ito and Follows, 2003, 2005], amplifying the increase in \( P_{CO_2} \), (9). Changes in global ocean nutrient utilization in response to anthropogenic forcing are also highly uncertain; however if the Southern Ocean ventilation intensifies, increasing the supply of nutrients which remain unutilized, then the biological soft tissue carbon pool will decrease \((C_{bio} < 0)\), further amplifying the increase in \( P_{CO_2} \), (9). In addition on timescales of tens of thousands of years, ocean acidification due to emissions is predicted to cause a net addition of dissolved CaCO\(_3\) to the ocean \((\delta I_{open} > 0)\), which will dampen the anthropogenic increase in \( P_{CO_2} \), (23), until carbonate ion concentrations are restored.

[40] While each carbon perturbation can be understood and quantified in isolation, using (9), (21), and (23), in reality a range of carbon perturbations are occurring at the same time. Our framework predicts that the \( P_{CO_2} \) after ocean invasion is accurately estimated by multiplying the amplification factors for each process using (26), rather than linearly combining the sum of each separate process. While a reasonable estimate of the carbon response from our box model studies is initially obtained by linearly combining the effects of different processes, an accurate estimate of the final equilibrium state is only obtained by accounting for the nonlinear amplification between the feedback processes implied by our analytical framework (Figure 7). Thus, our analytical framework can be used to provide insight into the nonlinear interactions between carbon perturbations.

[41] There are more complicated feedback processes that are not included in the analytical relationships, which ultimately need to be considered for a complete prediction. For example, temperature changes alter the solubility of CO\(_2\) and feedback on atmospheric concentrations, which is estimated to provide a \( \sim10\% \) amplification for \( P_{CO_2} \) [Archer, 2005]. The sensitivity of the ocean circulation to anthropogenic forcing remains poorly understood and

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**Table 1. Model Output After 2000 Years for Three Carbon Perturbations Applied Separately and Together**

<table>
<thead>
<tr>
<th>Forcing</th>
<th>Carbon Cycle Response</th>
<th>Perturbation (GtC)</th>
<th>Model ( \Delta P_{CO_2} ) (ppm)</th>
<th>Error (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft tissue fallout change</td>
<td>( \delta I_{bio} )</td>
<td>(+767)</td>
<td>(-53)</td>
<td>0.81</td>
</tr>
<tr>
<td>CaCO(_3) fallout change</td>
<td>( \delta I_{CaCO_3} )</td>
<td>(+154)</td>
<td>(+9)</td>
<td>1.03</td>
</tr>
<tr>
<td>Carbon emission</td>
<td>( \delta I_{em} )</td>
<td>(+2000)</td>
<td>(+219)</td>
<td>1.78</td>
</tr>
<tr>
<td>Emission + soft tissue + CaCO(_3)</td>
<td>Model prediction combined</td>
<td>–</td>
<td>(+175^b)</td>
<td>1.49(^c)</td>
</tr>
<tr>
<td>Emission + soft tissue + CaCO(_3)</td>
<td>Model output combined</td>
<td>–</td>
<td>(+132)</td>
<td>1.47</td>
</tr>
<tr>
<td><strong>ERROR</strong></td>
<td></td>
<td>(-)</td>
<td>(+44ppm)</td>
<td>(+6ppm)</td>
</tr>
</tbody>
</table>

*Scenarios as in Figures 2 and 7. Linearly adding the effects of multiple carbon cycle changes does not accurately predict the overall \( P_{CO_2} \) change. Instead, applying the analytical framework using the amplification factors for each carbon perturbation leads to a much smaller error in \( P_{CO_2} \).

\(^{b}\)The numerical model \( \Delta P_{CO_2} \) values for the separate forcings are added linearly.

\(^{c}\)The numerical model \( \Delta P_{CO_2}/P_0 \) values are multiplied according to (26).

---

**Figure 7.** Modeled atmospheric \( P_{CO_2} \) (ppm) versus time (years) for three carbon perturbations, including a 2000 GtC emission and an increase in organic marine and CaCO\(_3\) fallout (as in Figure 2a): when the perturbations are numerically modeled separately and the \( P_{CO_2} \) changes linearly combined (black dashed line), and when the perturbations are numerically modeled separately and the results combined according to the analytical prediction (26) (gray solid line), compared with numerical model output when the perturbations are applied simultaneously (black solid line).
any changes in ventilation or overturning can feedback and alter $P_{CO_2}$.
[42] While numerical models provide more detailed information about spatial and temporal variability, our analytical relations provide a transparent view of how the final equilibrium is controlled. Increasingly model hierarchies are needed to provide insight into how the climate system operates [Held, 2005], by revealing how the climate system changes as sources of complexity are added or removed. In the same way, the analytical relations presented here should form part of that model hierarchy for the carbon system.

Appendix A: Numerical Box Model Description
[41] To illustrate the predictive power of the analytical relations derived in this paper, the analytical relations are compared with a numerical model of the air-sea system based on Sarmiento and Toggweiler [1984]. The numerical model contains a well mixed atmosphere attached to a 3-box representation of the ocean, containing cold high-latitude surface ocean, warm low-latitude surface ocean and deep ocean boxes. A meridional overturning circulation is applied, where water sinks from the high-latitude surface ocean to the deep ocean, upwells in the low-latitude surface ocean and is transported back into the high-latitude surface ocean. An additional exchange is applied between the high-latitude surface ocean and the deep ocean boxes. The ocean carbonate system is solved after Follows et al. [2006]. Biological production occurs in the surface ocean boxes as a function of supplied phosphate, marine production of CaCO$_3$ also occurs, removing dissolved inorganic carbon and titration alkalinity in a 1.2 ratio. All organic and marine CaCO$_3$ fallout is dissolved in the deep ocean box, there is no sedimentation or weathering interactions. The preindustrial spin up is achieved by forcing the atmospheric $P_{CO_2}$ to 280 ppm, air-sea exchange of $CO_2$ is then allowed. The perturbations applied to the model consist of adding carbon into the atmosphere, changing the biological phosphate utilization and/or changing the marine CaCO$_3$ fallout. The model reaches a steady state ~1000 years after perturbation. The relevant parameter values used for the 3 box model are given in Table A1.

Appendix B: Carbonate Alkalinity System
[44] In the ocean, carbon dioxide exists as dissolved inorganic carbon, DIC, defined with concentration $C_{DIC}$:

$$ C_{DIC} = [CO^2_3] + [HCO^3_3] + [CO_2^-]. $$

(B1)

where $[CO^2_3]$ is the combined concentration of aqueous $CO_2$ and carbonic acid. The total charge of dissolved inorganic carbon species, the carbonate alkalinity, is defined by the concentration $A_C$:

$$ A_C = [HCO^3_3] + 2[CO_2^-]. $$

(B2)

[45] The constituents of $C_{DIC}$ and $A_C$ at steady state are partitioned according to the dissociation equations:

$$ K_1 = \frac{[H^+][HCO^3_3]}{[CO^2_3]}, $$

(B3)

and

$$ K_2 = \frac{[H^+][CO_2^-]}{[HCO^3_3]}, $$

(B4)

where $K_1$ and $K_2$ are functions of temperature ($T$) and salinity ($S$).

[46] The effective partial pressure of $CO_2$, $P_{CO_2}$, within a water parcel is determined by the concentration of uncharged constituents of $C_{DIC}$ by:

$$ k_0P_{CO_2} = [CO^2_3], $$

(B5)
where $k_0$ is a function of temperature and salinity. Thus, the charged species of DIC do not directly interact with the atmosphere. Locally, there will be no air-sea transfer of CO$_2$ when the $P_{CO2}$ of the air is equal to the $P_{CO2}$ of the seawater.

[47] If carbonate alkalinity is used to approximate titration alkalinity, equations (B1) to (B5) describe a closed carbonate system. The equations can be combined, along with additional constraints, such as borate and silicate concentrations and the dissociation constant of water, to explicitly solve the system numerically [e.g., see Follows et al., 2006].

[48] Equations (B1) to (B4) can be combined to form a quadratic in [CO$_2^*$] by eliminating terms in [CO$_2^2$], [HCO$_3^-$] and [H$^+$] [Goodwin, 2007]

$$\left(1 - \frac{K_2}{K_1}\right)[CO_2^*]^2 + \left(A_C - C_{DIC} - 4 \frac{K_2}{K_1} A_C + 8 \frac{K_2}{K_1} C_{DIC}\right) [CO_2^*]$$

$$- \frac{K_2}{K_1} (A_C^2 - 4 A_C C_{DIC} + 4 C_{DIC}^2) = 0.$$  \hspace{1cm} \text{(B6)}

Implicitly differentiating this quadratic (B6) assuming constant temperature and salinity, and thus a constant $K_1$ and $K_2$, leaves an expression relating infinitesimal changes to $A_C$ and $C_{DIC}$ to the resulting change in [CO$_2^*$]:

$$\left(1 - \frac{4 K_2}{K_1}\right) 2[CO_2^*] \delta[CO_2^*]$$

$$+ \left(A_C - C_{DIC} - 4 \frac{K_2}{K_1} A_C + 8 \frac{K_2}{K_1} C_{DIC}\right) \delta[CO_2^*]$$

$$+ \left(\delta A_C - \delta C_{DIC} - 4 \frac{K_2}{K_1} \delta A_C + 8 \frac{K_2}{K_1} \delta C_{DIC}\right) [CO_2^*]$$

$$- \frac{K_2}{K_1} (2A_C \delta A_C - 4 A_C \delta C_{DIC} - 4 C_{DIC} \delta A_C + 8 C_{DIC} \delta C_{DIC}) = 0.$$  \hspace{1cm} \text{(B7)}

This relation is equivalent to (12), with the coefficients $a$, $b$, and $c$ explicitly stated in terms of $K_1$, $K_2$, $A_C$, and $C_{DIC}$.

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