Dependence of the ocean-atmosphere partitioning of carbon on temperature and alkalinity

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Dependence of the ocean-atmosphere partitioning of carbon on temperature and alkalinity

Anne Willem Omta,1 Stephanie Dutkiewicz,1 and Michael J. Follows1

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[1] We develop and extend a theoretical framework to analyze the impacts of changes in temperature and alkalinity on the ocean-atmosphere carbon partitioning. When investigating the impact of temperature, we assume that there is no change in the global ocean alkalinity. This idealized situation is probably most relevant on intermediate timescales of hundreds to thousands of years. Our results show that atmospheric pCO2 depends approximately exponentially on the average ocean temperature, since the chemical equilibria involved have an exponential (Arrhenius-type) dependence. The dependence of pCO2 on alkalinity is more complicated, and our theory suggests several regimes. The current ocean-atmosphere system appears to have an exponential dependence of pCO2 on global mean ocean alkalinity, but at slightly higher alkalinitites, the dependence becomes a power law. We perform experiments with a numerical physical-biogeochemical model to test the validity of our analytical theory in a more complex, ocean-like system: in general, the numerical results support the analytical inferences.


1. Introduction

[2] Currently, the oceans take up about 30% of the anthropogenically emitted carbon [Orr et al., 2001]. This percentage will most certainly decrease with the ongoing anthropogenic carbon emissions, because the buffering capacity of the oceans diminishes as the oceanic carbon concentration increases [Goodwin et al., 2007; Omta et al., 2010] and carbonate ions at the ocean surface are neutralized by reaction with (anthropogenic) carbon dioxide. In addition, the solubility of carbon dioxide in water decreases with increasing temperature [Lee and Millero, 1995; McKinley et al., 2006; Takahashi et al., 1993]. Hence, a positive feedback is expected: any global warming due to an increasing amount of carbon in the atmosphere leads to a lower oceanic carbon uptake which in turn increases the warming [Plattner et al., 2001; Friedlingstein et al., 2006]. To obtain insight into the (long-term) impact of this temperature feedback, we develop a framework to consider the relationship between temperature and the ocean-atmosphere partitioning of carbon. This is significant not only for the prediction of future carbon partitioning as ocean temperatures rise, but also to gain a deeper understanding of CO2 variations in the geological past.

[3] Several earlier studies have focused on the impact on atmospheric pCO2 of localized perturbations of the ocean temperature [Bacastow, 1996; Broecker et al., 1999; DeVries and Primeau, 2009]. Such perturbations can affect atmospheric pCO2 through impacts on both the carbon solubility and the air-sea disequilibrium of carbon [Toggweiler et al., 2003]. DeVries and Primeau [2009] have shown that the impact of the disequilibrium component scales with the strength of the overturning circulation. And, using their Green-function analysis, it can also be shown that the impact of the solubility component on atmospheric pCO2 approximately scales with the average temperature of the ocean. Here, we instead consider the relation between the mean temperature of the whole ocean and atmospheric pCO2. That is, we study the solubility component in isolation and we do not consider changes in the carbon disequilibrium.

[4] We assume that carbon has equilibrated between the atmosphere and the ocean, but that total global ocean alkalinity remains constant. This idealized situation is probably most relevant on intermediate timescales of thousands of years [Archer et al., 1997]. Further assumptions are that the biological activity does not change and that total carbon in the system is constant.

[5] First, we derive a relationship between the ocean average temperature and atmospheric pCO2 (throughout this article, “pCO2” refers to the volume fraction of CO2 in the atmosphere in ppmv), and show that it accurately predicts the results of three-dimensional physical/biogeochemical model simulations. We then compare specific predictions from our theoretical framework with observations from
Table 1. Variable Parameters Used in the Calculations With Value Ranges Between 0°C and 30°C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value Range</th>
<th>Definition</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O$</td>
<td></td>
<td>1.2–1.6</td>
<td>$-\frac{\partial \ln [K \times pCO_2]}{\partial \ln (\text{DIC})}$</td>
<td>CO$_2$ scaling parameter</td>
</tr>
<tr>
<td>$H$</td>
<td></td>
<td>1.1–1.3</td>
<td>$-\frac{\Delta \ln [K \times pCO_2]}{\Delta \ln (\text{DIC})}$</td>
<td>H$^+$ scaling parameter</td>
</tr>
<tr>
<td>$K$</td>
<td>mol L$^{-1}$ atm$^{-1}$</td>
<td>30–130</td>
<td>$\frac{pCO_2}{[CO_2]}$</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>$K_H$</td>
<td>L atm/mol</td>
<td>16–40</td>
<td>$\frac{pCO_2}{[CO_2]}$</td>
<td>Henry’s law constant</td>
</tr>
<tr>
<td>$a$</td>
<td>°C$^{-1}$</td>
<td>0.041–0.052</td>
<td>$-\frac{\partial \ln [K]}{\partial T}$</td>
<td>Temperature dependence $K$</td>
</tr>
<tr>
<td>$b$</td>
<td>°C$^{-1}$</td>
<td>0.023–0.039</td>
<td>$-\frac{\partial \ln [K]}{\partial T}$</td>
<td>Temperature dependence $K_H$</td>
</tr>
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*From Mehrbach et al. [1973] and Millero [1995].

Derivation

Carbon in the ocean exists as multiple species: aqueous carbon dioxide (CO$_2$), carbonic acid (H$_2$CO$_3$), the bicarbonate ion (HCO$_3^-$), and the carbonate ion (CO$_3^{2-}$). The sum of all these compounds is called dissolved inorganic carbon (DIC) which we will denote as $C$:

$$C \equiv [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

The ocean has a high buffering capacity for CO$_2$, as it reacts with bases such as CO$_3^{2-}$ to form HCO$_3^-$. A measure for this buffering capacity is given by the total titration alkalinity [Chester, 2000] which is the sum of the concentrations of all the conjugate bases of weak acids. In the ocean, HCO$_3^-$ and CO$_3^{2-}$ account for 95% of the total titration alkalinity [Zeebe and Wolf-Gladrow, 2001]. We will neglect other bases and approximate the total titration alkalinity by the carbonate alkalinity (which we will call $A$):

$$A \equiv [HCO_3^-] + 2 \times [CO_3^{2-}]$$

[7] For all values of $C$ and $A$, the relationship between atmospheric $pCO_2$, [HCO$_3^-$], and [CO$_3^{2-}$] is given by [Broecker and Peng, 1982]:

$$pCO_2 = \frac{[HCO_3^-]^2}{K \times [CO_3^{2-}]}$$

In this equation, $K$ is a composite chemical equilibrium constant, consisting of a Henry’s law solubility constant and equilibrium constants for the dissociation of carbonic acid into bicarbonate and the dissociation of bicarbonate into carbonate. As long as $[HCO_3^-] \gg [CO_3^{2-}]$, $K \times pCO_2$ and $[CO_3^{2-}]$ are approximately inversely related which suggests that $K \times pCO_2 \propto [CO_3^{2-}]^{-1}$. Or slightly more accurately:

$$K \times pCO_2 \propto [CO_3^{2-}]^{-O}$$

where we have used the quantity $O$, defined by Omta et al. [2010]:

$$O \equiv -\frac{\partial \ln (K \times pCO_2)}{\partial \ln (\text{DIC})}$$

Under constant alkalinity, $O$ is given by:

$$O = 1 + 4 \times \frac{[CO_3^{2-}]}{[HCO_3^-]} \approx 1.4$$

$O$ provides a useful conceptual tool because:

[8] 1. $O$ is almost constant. $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ is small (only about 0.1) which means that $O$ varies between 1.2 and 1.6 at the surface of the world’s oceans, considerably less than the commonly used Revelle buffer factor [Bolin and Eriksson, 1959] which varies between 8 and 15 [Watson and Liss, 1998].

[9] 2. The dependence of $O$ on oceanic carbon and carbonate alkalinity is transparent, because it is a simple function of $[CO_3^{2-}]$ and $[HCO_3^-]$. $O$ decreases monotonically with increasing DIC concentration: as CO$_2$ is added to the ocean, it reacts with CO$_3^{2-}$ to form HCO$_3^-$, and therefore, the ratio $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ decreases. Similarly, $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ goes up with carbonate alkalinity, and therefore, $O$ increases monotonically with increasing carbonate alkalinity.

2. Analysis

Carbon in the ocean exists as multiple species: aqueous carbon dioxide (CO$_2$), carbonic acid (H$_2$CO$_3$), the bicarbonate ion (HCO$_3^-$), and the carbonate ion (CO$_3^{2-}$). Finally, we derive an expression for the dependence of the atmospheric CO$_2$ content on (carbonate) alkalinity.

2.1. Temperature Dependence of the Air–Sea Partitioning of Carbon

2.1.1. Air–Sea Carbon Partitioning: Analytical Derivation

[10] We now use the properties of $O$ to derive the dependence of atmospheric $pCO_2$ on the water temperature averaged over the global ocean. The derivation is quite long, but the basic idea is relatively simple: we differentiate a global conservation equation for carbon with respect to temperature and collect the terms, so that we are left with an expression for $\frac{\partial pCO_2}{\partial T}$. Throughout the derivation, different parameters are introduced, the value ranges of which are given in Table 1.
The parameter \( f \) remains approximately constant. A temperature increase leads to an increase in \( pCO_2 \) which tends to increase \( f \), but also to an increase of \([CO_3^{2-}]\) which tends to decrease \( f \). Furthermore, with \( pCO_2 = 280 \) ppmv, \([CO_3^{2-}] = 0.2 \text{ mM}\), \( O = 1.4\), \( K_H = 27 \text{ L atm/mol} \) and values for \( M \) and \( V \) from Table 2, \( f \) is only about 0.3, so small variations in \( f \) will not have a strong impact on the term \( 1 + f \).

[12] Next, we differentiate equation (8) with respect to \( T \), assuming that \( A, C_r \), and \( C_{reg} \) are constant:

\[
M \times \frac{dpCO_2}{dT} + V \times \left( -\frac{d[CO_3^{2-}]}{dT} + \frac{d[CO_2]}{dT} \right) = 0
\]  

(9)

\([CO_3^{2-}]\) depends on \( T \) ‘directly’, i.e., because the carbonate system depends on temperature, and ‘indirectly’, because \([CO_3^{2-}]\) depends on \( pCO_2 \) which in turn depends on temperature. We need to take both effects into account when determining \( \frac{d[CO_3^{2-}]}{dT} \):

\[
\frac{d[CO_3^{2-}]}{dT} = \frac{\partial[CO_3^{2-}]}{\partial pCO_2} \times \frac{dpCO_2}{dT} + \frac{\partial[CO_3^{2-}]}{\partial T} \times \frac{dT}{dT} = \frac{\partial[CO_3^{2-}]}{\partial pCO_2} \times \frac{dpCO_2}{dT}
\]  

(10)

From the definition of \( O \) (equation 5), it can be shown that when \( pCO_2 \) is kept constant

\[
\frac{\partial[CO_3^{2-}]}{\partial pCO_2} = \frac{[CO_3^{2-}]}{O} \times a
\]  

(11)

The parameter \( a = -\frac{\partial \ln K}{\partial pCO_2} \) (calculated from Mehrbach et al. [1973] and Millero [1995]) decreases from 0.052°C\(^{-1}\) at 0°C to 0.041°C\(^{-1}\) at 30°C. Furthermore,

\[
\frac{\partial[CO_3^{2-}]}{\partial pCO_2} = -\frac{[CO_3^{2-}]}{O \times pCO_2}
\]  

(12)

which yields

\[
\frac{d[CO_3^{2-}]}{dT} = \left( \frac{[CO_3^{2-}]}{O} \times a \right) \frac{dpCO_2}{dT} \]  

(13)

The solubility of \( CO_2 \) in water follows Henry’s law:

\[
pCO_2 = K_H \times [CO_2]
\]  

(14)

with \( K_H \) a Henry’s law constant. Analogous with equation (13), we obtain:

\[
\frac{d[CO_2]}{dT} = \left( \frac{[CO_2]}{O} \times a \right) \frac{dpCO_2}{dT}
\]  

(15)

Collecting all the terms with \( \frac{dpCO_2}{dT} \) on the left-hand side yields:

\[
\frac{dpCO_2}{dT} \times \left( M + V \times \left( \frac{[CO_3^{2-}]}{O} + [CO_2] \right) \right)
\]

\[
= V \times \left( \frac{[CO_3^{2-}]}{O} \times a + b \times [CO_2] \right)
\]  

(17)

and with

\[
f = \frac{M \times pCO_2 \times \frac{[CO_3^{2-}]}{[CO_2]} \times V}{O \times [CO_2]}
\]

\[
\frac{dpCO_2}{dT} = \frac{\left( a + \frac{b \times [CO_2]}{[CO_2]} \right) \times pCO_2}{1 + f}
\]  

(18)

which we can simplify to:

\[
\frac{dpCO_2}{dT} = \frac{pCO_2}{T_B}
\]  

(19)

where \( T_B = \frac{f + 1}{a + \frac{b \times [CO_2]}{[CO_2]}} \). Although it appears to be a rather complex quantity, \( T_B \) actually remains approximately constant when the ocean temperature changes, because:

[13] 1. \( f \) remains approximately constant. A temperature increase leads to an increase in \( pCO_2 \) which tends to increase \( f \), but also to an increase of \([CO_3^{2-}]\) which tends to decrease \( f \). Furthermore, with \( pCO_2 = 280 \) ppmv, \([CO_3^{2-}] = 0.2 \text{ mM}\), \( O = 1.4\), \( K_H = 27 \text{ L atm/mol} \) and values for \( M \) and \( V \) from Table 2, \( f \) is only about 0.3, so small variations in \( f \) will not have a strong impact on the term \( 1 + f \).

[14] 2. Variations in \( a \) are relatively modest: \( a \) decreases from 0.052°C\(^{-1}\) at 0°C to 0.041°C\(^{-1}\) at 30°C; variations in
the term $\frac{\delta x_{\text{DIC}}}{[\text{DIC}]}$ have little impact, as this term is only about $0.002\,\text{C}^{-1}$.

[15] Since $T_B$ is to a first approximation independent of $T$, equation (19) suggests an exponential dependence of atmospheric $pCO_2$ on the temperature of the ocean. With the parameters from Table 1, $T_B \approx 27\,\text{C}$ which means that an increase in the ocean temperature of $1\,\text{C}$ leads to an increase in atmospheric $pCO_2$ of about $4\%$. Thus, a very simple equation relates global ocean temperature and atmospheric $pCO_2$, with a single parameter, quantifiable from basic knowledge of the carbonate system. We will further analyze the validity of this relationship by comparing predicted values with actual ocean biogeochemistry simulation outputs.

2.1.2. Air-Sea Carbon Partitioning: Numerical Simulations

[16] To test the validity of relationship (19) between ocean temperature and atmospheric $pCO_2$ in a more realistic three-
dimensional ocean-atmosphere system, we perform a set of experiments with a numerical ocean-atmosphere carbon cycle model using parameter values given in Table 2. Similar to Follows et al. [2002] and Ito and Follows [2003], we use the MIT ocean circulation model [Marshall et al., 1997] configured in a sector extending from 24°S to 69° N, and sixty degrees wide at 3° × 3° horizontal resolution. There are fifteen levels from 50 m thick (uppermost) increasing downward to 690 m, with the ocean floor at 5000 m. Sea surface temperature is restored to monthly fields [Levitus et al., 1994]. The biogeochemical cycles of carbon, phosphorus, oxygen and total titration alkalinity are coupled to the circulation model. The full carbonate chemistry is solved explicitly [Follows et al., 2006] and the air-sea exchange of CO$_2$ is parameterized with a gas transfer coefficient assuming a constant uniform wind speed. A well-mixed atmospheric box is coupled to the ocean carbon cycle such that the partitioning of carbon between the atmosphere and the ocean is explicitly calculated; the model conserves total carbon. The atmospheric mixing ratio of CO$_2$ adjusts according to the net air-sea CO$_2$ flux at each time step. There is an explicit but idealized representation of the biological carbon pump following Dutkiewicz et al. [2005]. Further details about the model setup are given in Appendix A.

[17] In a suite of model experiments, we change the target to which sea surface temperature is being restored in steps of 2°C and reequilibrate the model, thus changing the global mean ocean temperature. We have chosen to investigate an (unrealistically) large range of global mean ocean temperatures to test the theoretical relationship (19). In general, the experiments are close to equilibrium with respect to the partitioning of carbon between the atmosphere and the ocean after 1000 years, but small drifts persist for over 10,000 years; for thoroughness we spun the physical model up for 20,000 years without the biogeochemical module and then for another 20,000 years with biogeochemistry. We maintain the latitudinal temperature gradients, the seasonality and, for simplicity, we do not allow freezing of the ocean water. The initial total titration alkalinity distribution is the same in each run.

[18] The overturning stream function and vertical distributions of DIC and total titration alkalinity for the ‘standard’ simulation at an average ocean temperature of 2.7°C are shown in Figure 1. The model reproduces the observed vertical gradients of DIC and total titration alkalinity [Sarmiento and Gruber, 2006]. The structure of the overturning circulation changes very little with altered global mean ocean temperature, because the meridional SST gradients are the same in all of the simulations and we do not allow for freezing. Because $T_B \approx 27°C$, the simulated values of ln(pCO$_2$) as a function of the average temperature of the ocean should lie on a straight line with a slope of $(27°C)^{-1}$. In Figure 2, we show such a slope, along with the simulated atmospheric pCO$_2$ plotted on a log scale as a function of the average temperature, integrated over the entire ocean. There is a very good agreement between the analytical theory and the simulations, even though many additional complexities of the ocean biogeochemistry are included in the numerical model (e.g., the impact of the biology and of temperature gradients in the ocean). We have also performed four simulations in which we allowed the seawater to freeze and...
we used a nonlinear equation of state. As can be seen in Figure 2, these simulations show slightly less agreement with the analytical prediction, but the overall trend is well reproduced. A comparison with earlier simulations by Goodwin and Lenton [2009] and with observations of Takahashi et al. [1993] is provided in Appendix B.

2.2. Alkalinity Dependence

[19] On geologic timescales, neither the carbonate alkalinity nor the total titration alkalinity can be considered constant, as various alkali salts are added to the ocean through rock weathering and the ocean loses alkalinity through carbonate sedimentation. We use the same framework to investigate the relationship between the ocean-atmosphere partitioning of carbon and ocean carbonate alkalinity. The details of the derivation are given in Appendix C, but the procedure is analogous to the derivation of the temperature dependence. We start from the global carbon conservation equation (8), take the derivative with respect to carbonate alkalinity, and collect the different terms in such a way that we find the derivative of pCO₂ with respect to carbonate alkalinity. The resulting relationship is:

\[
\frac{dpCO₂}{dA} = \frac{-pCO₂ \times (O + 1)}{2 \times [CO₃⁻] + 2 \times pCO₂ \times (M + \frac{V}{K_W})} \tag{20}
\]

We can define \(A_B = \frac{2 \times O}{V \times (M + \frac{V}{K_W})} \times \left(\frac{V \times [CO₃⁻]}{O} + pCO₂ \times (M + \frac{V}{K_W})\right)\), such that:

\[
\frac{dpCO₂}{dA} = \frac{-pCO₂}{A_B} \tag{21}
\]

\(A_B\) is analogous to \(T_B\) and the factor \(I_B\) that was introduced by Goodwin et al. [2007, 2008] to describe the dependence of atmospheric \(pCO₂\) on total carbon emissions (after full equilibration between the atmospheric and oceanic reservoirs).

Since \(I_B = (M + \frac{V}{K_W}) \times pCO₂ + V \times \frac{[CO₃⁻]}{O}\) [Omta et al., 2010], there exists a relatively simple relationship between \(A_B\) and \(I_B\):

\[
A_B = \frac{2 \times O \times pCO₂}{V \times (M + \frac{V}{K_W})} \times \left(\frac{V \times [CO₃⁻]}{O} + pCO₂ \times (M + \frac{V}{K_W})\right)\tag{20}
\]

[20] \(A_B\) consists of two terms, \(\frac{V \times [CO₃⁻]}{O}\) and \(pCO₂ \times (M + \frac{V}{K_W})\); the relative sizes of these terms give rise to three different regimes (analogous to those given by Omta et al. [2010] when changing the carbon in the ocean-atmosphere system) in which it is possible to approximate equation (20) by simpler relationships:

[21] 1. High carbonate alkalinity: \(\frac{V \times [CO₃⁻]}{O} \gg pCO₂ \times (M + \frac{V}{K_W})\). For the ocean-atmosphere system, this is the case, if \(A > 2.6\) mM. Though the average value of \(A\) at the ocean surface is about 2.2 mM, there are regions where \(A\) is much higher (e.g., in the Black Sea, surface carbonate alkalinity is around 3.2 mM [Hiscock and Millero, 2006]). In this regime, we cannot expect \(O\) to be constant, as \(4 \times \frac{[CO₃⁻]}{[HCO₃⁻]}\) is rather large. However, in the work of Omta et al. [2010], we defined the constant-alkalinity factor \(H\):

\[
H ≡ \frac{\partial \ln(K \times pCO₂)}{\partial \ln[H^₇]} = 1 + 2 \times \frac{[CO₃⁻]}{A} \tag{22}
\]

As long as \([CO₃⁻] \ll [HCO₃⁻]\), \(H\) behaves qualitatively very similar to \(O\); it is slightly above 1, approaching 1 as carbonate alkalinity decreases. However, if \([CO₃⁻] \gg [HCO₃⁻]\), \(O\) approaches infinity, whereas \(H\) approaches 2; that is, \(H\) remains much more constant. Assuming that \(H\) is constant implies that \(pCO₂ ∝ [H^7]^H\). At equilibrium, \([H^7]^H = \frac{[HCO₃⁻]}{K_W[CO₃⁻]^2}\) (with \(K_W\) an equilibrium constant). Using \(A ≡ [HCO₃⁻] + 2 \times [CO₃⁻]^2\), we find that \([H^7]^H = \frac{[CO₃⁻]^2}{4A^2} - 2\), from which we obtain:

\[
pCO₂ ∝ \left(\frac{A}{[CO₃⁻]^2} - 2\right)^H \tag{23}
\]

Furthermore, if we neglect atmospheric carbon and oceanic carbon in the form of \(CO₂\) (which are both very low in this regime) in the carbon conservation equation, then rearranging equation (8) leads to:

\[
[CO₃⁻] ≈ A + \left(\frac{C_{ocean}dV}{V}\right) - \left(\frac{C_I}{V}\right) \tag{24}
\]

Combining equations (23) and (24), we find

\[
pCO₂ ∝ \left(\frac{A}{A - \frac{C_{ocean}dV}{V} - \frac{C_I}{V}} - 2\right)^H \tag{25}
\]

Hence, \(pCO₂\) appears to have a (rather complicated) power law dependence on carbonate alkalinity in this regime.

[22] 2. Intermediate regime: \(\frac{V \times [CO₃⁻]}{O} \approx pCO₂ \times (M + \frac{V}{K_W})\). With increasing alkalinity, \([CO₃⁻]\) goes up and \(pCO₂\) goes down which makes \(A_B\) approximately constant. If \(A_B\) is constant, then the solution of equation (21) is an exponential relationship between \(pCO₂\) and \(A\):

\[
pCO₂ ∝ e^{\frac{-A}{V + \frac{V}{K_W}}} \tag{26}
\]

Judging from Figure 4, this is the case for 1.9 mM < \(A < 2.3\) mM. Today’s ocean is in this situation, as \(A ≈ 2.2\) mM.

[23] 3. Very low carbonate alkalinity: \(\frac{V \times [CO₃⁻]}{O} \ll pCO₂ \times (M + \frac{V}{K_W})\). This is the case, if \(A < 1.8\) mM (e.g., in the Baltic Sea, \(A ≈ 1.5\) mM [Hjalmarsson et al., 2008]). Since \(O ≈ 1\) in this regime, we can write

\[
\frac{dpCO₂}{dA} \approx -\frac{1}{V + \frac{V}{K_W}} \tag{27}
\]

which implies a linear relationship between \(pCO₂\) and \(A\).

[24] Similar to section 2.1.2, we have performed numerical simulations with the physical biogeochemical model to test relationship (21). In each of the simulations, we changed the global average total titration alkalinity by 0.1 mM when initializing the three-dimensional total titration alkalinity distribution, although we maintained the same latitudinal and vertical gradients. With \(pCO₂ = 280\) ppmv, \([CO₂^+] = 0.2\) mM and parameter values from Table 1, we expect that \(A_B ≈ 0.21\) mM. In Figure 4, we show the simulated \(\ln(pCO₂)\) as a function of average ocean total titration alkalinity, along with a line with a slope corresponding to \(A_B = 0.21\) mM. As can be seen, the
simulations start to diverge from the straight line just above the current-day total titration alkalinity. This is the transition from an exponential to a power law type of dependence.

2.3. Comparison Between Analytical Predictions and Observations

2.3.1. Carbon Dioxide Variations at Constant DIC

Concerned with seasonal variations in the fluxes of CO₂ across the air-sea interface, Takahashi et al. [1993] measured pCO₂ as a function of temperature in water samples each with the same DIC concentration. They found that 

\[ \frac{\partial \ln(pCO_2)}{\partial T} \approx 0.0423 \degree C^{-1} \]

To derive this relationship, we use that any 'direct' change in DIC as a consequence of a change in temperature must be offset by an 'indirect' change in DIC, resulting from a different pCO₂:

\[ \frac{dC}{dT} = \frac{\partial C}{\partial T} + \frac{\partial C}{\partial \ln(pCO_2)} \frac{\partial \ln(pCO_2)}{\partial T} = 0 \]  

(28)

which leads to

\[ \frac{\partial \ln(pCO_2)}{\partial T} = - \frac{(\frac{\partial C}{\partial T})}{(\frac{\partial C}{\partial \ln(pCO_2)})} = \frac{[CO^+_2]}{[CO_2]} \times a + b \times [CO_2] \]

(29)

With pCO₂ = 280 ppmv, [CO₂⁺] = 0.2 mM and parameter values from Table 1, we find \( \frac{\partial \ln(pCO_2)}{\partial T} \approx 0.045 \degree C^{-1} \), slightly higher than observed by Takahashi et al. [1993]. It is worth noting that this value is close to \( \frac{1}{T_b} \approx 0.037 \degree C^{-1} \). Hence, if we had calculated \( T_b \) by simply assuming that the average oceanic preformed carbon concentration stays constant when the average temperature of the ocean changes, we would still have obtained a quite good estimate. The reason for this is that the oceanic carbon inventory is much larger than the atmospheric inventory: any change in the atmospheric pCO₂ corresponds with an almost negligible change in the oceanic DIC concentration.

2.3.2. Carbon Disequilibrium at the Ocean Surface

The carbonate distribution at the ocean surface determines the preformed DIC and, in part, the strength of the solubility carbon pump. One important issue is how well the carbon system at the ocean surface is equilibrated with the atmosphere, particularly at high latitudes. The bottleneck in the equilibration of the system is the air-sea exchange of CO₂, taking place on a time scale of weeks, whereas the acid-base reactions within water equilibrate on a time scale of seconds [Zeebe and Wolf-Gladrow, 2001]. Therefore, the equilibrium theory can be applied to derive relationships between the concentrations of the dissolved carbon species, even if their concentrations are far from equilibrated with respect to atmospheric pCO₂. Equilibrium of the associated acid-base reactions implies:

\[ [CO_2] = \frac{[HCO_3^-]^2 \times K_0 \times K_1}{[CO_3^{2-}] \times K_2} \]

(30)
with $K_0$, $K_1$ and $K_2$ the respective reaction constants for the formation of carbonic acid from carbon dioxide and water, the dissociation of carbonic acid into bicarbonate, and the dissociation of bicarbonate into carbonate. This means that regardless of whether the oceanic and atmospheric carbon are at equilibrium, we have:

$$\frac{K_2}{K_0 \times K_1} \propto [CO_3^{2-}]^{-O}$$

and therefore:

$$\frac{[CO_2]}{[CO_3^{2-}]_{eq}} = \left( \frac{[CO_2]}{[CO_3^{2-}]_{eq}} \right)^{-O}$$

with the subscript $eq$ denoting the equilibrium concentration. This, for example, means that if $[CO_3^{2-}]$ is 8% above its equilibrium value, then $[CO_2]$ is about 10% below equilibrium. Thus, the extent to which $[CO_3^{2-}]$ is equilibrated at the ocean surface does provide a good measure of the equilibration of oceanic and atmospheric carbon.

[27] If the carbonate system is equilibrated with respect to atmospheric $pCO_2$ everywhere, then there should be a very simple relationship between $[CO_3^{2-}]$ at the ocean surface and the local (annually averaged) SST given by equation (11): $\frac{\partial [CO_3^{2-}]}{\partial T} = \frac{\partial [CO_2]}{\partial T} \approx 6.6 \mu M/°C$. This derivative is almost constant over a large range of temperatures, because $[CO_3^{2-}]$ and $O$ increase and $a$ decreases with increasing temperature. Thus, the theory predicts an approximately linear variation of $[CO_3^{2-}]$ with temperature. This relationship is observed in the surface ocean (using WOA and GLODAP: Figure 3), suggesting that the carbon system is indeed well equilibrated across the World Ocean.

### 3. Discussion and Conclusion

[28] We have derived analytical relationships for the air-sea partitioning of carbon as a function of ocean temperature and carbonate alkalinity. In general, the relative amount of carbon in the atmosphere with respect to the ocean increases with increasing ocean temperature and decreases with increasing carbonate alkalinity. The impact of temperature on the carbon partitioning generates a positive feedback: global warming resulting from the increasing amount of carbon in the atmosphere leads to a decreased oceanic carbon uptake which in turn increases the global warming. The relationship (19) between average ocean temperature and atmospheric $pCO_2$ suggests that this feedback is of moderate strength compared to the change in $pCO_2$ itself. For instance, an increase in the global average temperature by 3°C (which many models suggest with doubling of atmospheric $pCO_2$ [Intergovernmental Panel on Climate Change, 2007]) would lead to less carbon taken up by the oceans, eventually leading to around 10% higher atmospheric $pCO_2$.

[29] The theoretically predicted trend of atmospheric $pCO_2$ with temperature is consistent with numerical simulations of a more complex “ocean-like” system. In essence, the relationship is exponential because all the chemical equilibria involved (ocean-atmosphere partitioning of carbon)
bon dioxide as well as the chemical reactions that constitute the carbonate chemistry) have an Arrhenius-type (exponential) temperature dependence [Weiss, 1974]. However, the exponential relationship between ocean temperature and atmospheric pCO$_2$ will probably break down, once the composite factor $f = \frac{M_p}{[CO_2]^p} \times \frac{D_p}{[CO_2]^p}$ (see equation (18)) becomes larger than 1. This will be the case after high (anthropic) carbon emissions: for instance, at $pCO_2 = 1000$ ppmv and current alkalinity, $f \approx 2$.

Throughout this article, we have assumed that the carbon system in the ocean is at equilibrium with atmospheric pCO$_2$. As was pointed out by Toggweiler et al. [2003], localized disequilibria can strongly impact atmospheric pCO$_2$. A compilation of results from various Ocean GCMs [DeVries and Primeau, 2009] suggests that the effect of disequilibria scales with the strength of the Atlantic Meridional Overturning Circulation, but that these effects are generally rather modest. Furthermore, the fact that the ocean-surface carbonate distribution as a function of temperature is predicted well by the theory (Figure 3) indicates that the carbonate system at the ocean surface is well-equilibrated with the atmospheric pCO$_2$.

Between our experiments, the biological parametrization does not change. Changes in the biology can affect atmospheric pCO$_2$ primarily by impacting the ratio of preformed to remineralized nutrients [Ito and Follows, 2005]. Again, such effects are correlated with the strength of the Overturining Circulation, but they appear relatively modest [Schmittner et al., 2007].

The different regimes that emerge when carbonate alkalinity is changed are strikingly similar to the regimes that were identified under changing total carbon [Omta et al., 2010]. Both carbonate alkalinity and total carbon affect the ocean pH: it increases with increasing carbonate alkalinity and decreasing total carbon. However, the power law regime seems much more relevant under varying carbonate alkalinity than under varying carbon. In fact, the theory and the simulations suggest that the current ocean with $A \approx 2.3$ mM is right at the edge of the exponential regime, near the transition to the power law regime. The anthropogenic carbon emissions will initially push the system into the exponential regime, but higher alkalinitities due to increased emissions will initially push the system into the exponential regime, near the transition to the power law regime. The anthropogenic carbon emissions will initially push the system into the exponential regime, near the transition to the power law regime. The anthropogenic carbon emissions will initially push the system into the exponential regime, near the transition to the power law regime.

Appendix A: Detailed Description of the Model Setup

The model density distribution is entirely determined by temperature using a linear equation of state; salinity is constant. Sea surface temperature is restored to monthly fields. In the control run, these fields are based on Atlantic Ocean climatological zonal means [Levitus et al., 1994]. Similarly, the wind stress field is the zonal mean across the Atlantic taken from Trenberth et al. [1989]. The large-scale effects of mesoscale eddy transfers are parameterized following Gent and McWilliams [1990] and a globally uniform background vertical mixing rate of $5 \times 10^{-3}$ m$^2$/s is imposed for tracers (salt, temperature and biogeochemical). There is no explicit mixed-layer parametrization, but convective adjustment occurs when the water column is statically unstable.

Initial fields of the tracers are given as depth-mean values for the Atlantic from GLODAP [Key et al., 2004] and the World Ocean Atlas [Locarnini et al., 2006], A crude representation of the biological pump is included to maintain a gradient in inorganic carbon from surface to deep and a reasonable latitudinal surface distribution of DIC. Community production in the euphotic layer is based on the availability of light and macronutrients as in the works of Dukiewicz et al. [2005], Goodwin et al. [2007], and McKinley et al. [2004]. Two thirds of net production are assumed to enter a semilabile dissolved organic pool which has a remineralization time scale of 6 months; the remaining fraction of organic production is exported to depth as sinking particles where it is remineralized according to an empirical power law [Martin et al., 1987]. Transformations of carbon and oxygen to and from the organic form are linked to those of phosphorus assuming fixed Redfield stoichiometry; the calcium carbonate cycle is parameterized using a fixed rain ratio.

Appendix B: Comparison Between Analytical Predictions and Goodwin and Lenton Simulation Results

To obtain insight into the impact of temperature on the ocean carbon system, Goodwin and Lenton [2009] used the scheme proposed by Follows et al. [2006] to calculate numerically that $\frac{\partial f}{\partial T} \approx 0.10$ g/m$^2$ per °C, with pCO$_2$ held constant. Using our framework, an analytical expression for $\frac{\partial f}{\partial T}$ can be derived in a straightforward fashion:

$$\frac{\partial C}{\partial T} = -\frac{\partial [CO_2^+]}{\partial T} + \frac{\partial [CO_2]}{\partial T} = -\frac{[CO_2^+]}{O} - b \times [CO_2]$$

(B1)

With pCO$_2$ = 280 ppm, [CO$_2^+$] = 0.2 mM, and parameter values as in Table 1, we find that $\frac{\partial f}{\partial T} \approx -0.007$ mol m$^{-3}$C$^{-1}$ which translates into a decrease of the (saturated) surface DIC of 0.08 g/m$^2$ per °C which is slightly lower than sug-
gested by Goodwin and Lentons [2009]. Since \( \frac{[CO_2]}{O} \gg b \times [CO_2] \), the main reason for this decrease of DIC with increasing temperature is the fact that \([CO_2^+]\) increases with increasing temperature.

[37] Goodwin and Lentons also investigated how \( \frac{dC}{dT} \) changes as a function of atmospheric carbon content: their calculations suggest that \( \frac{dC}{dT} \approx 0.03 \text{ g/m}^3 \text{ per } ^\circ \text{C} \) [see Goodwin and Lentons, 2009, Figure 2b]. Differentiating equation (B1) with respect to \( \ln(pCO_2) \) (assuming \( O \) constant), we obtain:

\[
\frac{\partial (\frac{dC}{dT})}{\partial \ln(pCO_2)} = \frac{[CO_2^+]}{O^2} - b \times [CO_2] \tag{B2}
\]

Filling in the numbers, we find \( \frac{\partial (\frac{dC}{dT})}{\partial \ln(pCO_2)} \approx 0.05 \text{ g/m}^3 \text{ per } ^\circ \text{C} \), considerably higher than reported by Goodwin and Lentons. Here, the decrease of \([CO_2^+]\) with increasing \( pCO_2 \) turns out to be responsible for the fact that \( \frac{\partial C}{dT} \) increases with increasing \( pCO_2 \).

### Appendix C: Alkalinity Dependence Derivation

[38] To derive the dependence of \( pCO_2 \) on ocean carbonate alkalinity, we differentiate equation (7) with respect to \( A \):

\[
\frac{dpCO_2}{dA} + \frac{V}{M} \times \left(1 - \frac{d[CO_2^+]}{dA} + \frac{d[CO_2^-]}{dA}\right) = 0 \tag{C1}
\]

Because \([CO_2] \) obeys Henry’s law, we simply have: \( \frac{d[CO_2^-]}{dA} = \frac{1}{K_{HI}} \times \frac{dpCO_2}{dA} \), with \( K_{HI} \) the Henry’s law constant. For \( \frac{d[CO_2^+]}{dA} \), we get:

\[
\frac{d[CO_2^+]}{dA} = \frac{\partial [CO_2^+]}{\partial A} + \frac{\partial [CO_2^+]}{\partial pCO_2} \times \frac{dpCO_2}{dA} \tag{C2}
\]

To find an explicit expression for \( \frac{\partial [CO_2^+]}{\partial A} \), we use the relationship between atmospheric \( pCO_2 \), \([HCO_3^-]\), and \([CO_2^+]\) [Broecker and Peng, 1982]:

\[
pCO_2 = \frac{[HCO_3^-] K [CO_2^+]^2}{K [CO_2^+]^2} = \frac{(4 - 2 \times [CO_2^+])^2}{K [CO_2^+]^2} \tag{C3}
\]

Solving equation (C3) for \([CO_2^+]\), we obtain:

\[
[CO_2^+] = \frac{A}{2} + \frac{K \times pCO_2}{8} \times \left(1 - \sqrt{\frac{8 \times A}{K \times pCO_2} + 1}\right) \tag{C4}
\]

By differentiating the above equation, we get:

\[
\frac{\partial [CO_2^+]}{\partial A} = \frac{1}{2} \times \left(1 - \frac{8A}{K \times pCO_2 + 1}\right) \tag{C5}
\]

and filling in the right-hand side of relationship (3) for \( pCO_2 \), we obtain:

\[
\frac{\partial [CO_2^+]}{\partial A} = \frac{1}{2} \times \left(1 - \frac{[HCO_3^-]}{[HCO_3^-] + 4 \times [CO_2^+]}\right)
\]

\[
= \frac{1}{2} \times \left(1 - \frac{1}{O}\right) \tag{C6}
\]

[39] Combining equations (C2) and (C6), we find:

\[
\frac{d[CO_2^+]}{dA} = \frac{1}{2} \times \left(1 - \frac{1}{O}\right) - \frac{[CO_2^+]}{O \times pCO_2} \times \frac{dpCO_2}{dA}
\]

\[
+ \frac{1}{K_{HI} \times e^{pCO_2(T-T_{ref})/C}} \times \frac{dpCO_2}{dA} = 0
\]

which after some algebra leads to

\[
\frac{dpCO_2}{dA} = -\frac{pCO_2 \times (O + 1)}{2 \times [CO_2^+] + 2 \times pCO_2 \times O \times \left(\frac{1}{K_{HI} \times e^{pCO_2(T-T_{ref})/C}}\right)}
\]

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### References


Friedlingstein, P., et al. (2006), Climate–carbon cycle feedback analysis: Results from the C4MIP model intercomparison, J. Clim., 19, 3337–3353.


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