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Multiple regimes of air-sea carbon partitioning identified from constant-alkalinity buffer factors

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[1] Numerical studies have indicated that the steady-state ocean-atmosphere partitioning of carbon will change profoundly as emissions continue. In particular, the globally averaged Revelle buffer factor will first increase and then decrease at higher emissions. Furthermore, atmospheric carbon will initially grow exponentially with emission size, after which it will depend linearly on emissions at higher emission totals. In this article, we explain this behavior by means of an analytical theory based on simple carbonate chemistry. A cornerstone of the theory is a newly defined dimensionless factor, O . We show that the qualitative changes are connected with different regimes in ocean chemistry: if the air-sea partitioning of carbon is determined by the carbonate ion, then the Revelle factor increases with emissions, whereas the buffer factor decreases with emission size, when dissolved carbon dioxide determines the partitioning. Currently, the ocean carbonate chemistry is dominated by the carbonate ion response, but at high total emissions, the response of dissolved carbon dioxide takes on this role.

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1. Introduction

[2] Due to concern about the potentially significant impact of global warming in the foreseeable future, it is of crucial importance to understand how much of the anthropogenic carbon dioxide is likely to accumulate in the atmosphere and how much will be taken up by the oceans. This issue was initially considered by *Revelle and Suess* [1957] who suggested that most of the carbon dioxide would be absorbed by the oceans within decades after emission. The ocean uptake of carbon dioxide is complicated by the fact that it reacts with dissolved carbonate ions to form bicarbonate. Such chemical effects were considered in a thorough analysis by *Bolin and Eriksson* [1959] which led to the conclusion that only a small fraction of anthropogenic carbon can be absorbed on a decadal timescale. Furthermore, *Bolin and Eriksson* [1959] explicitly defined what is now usually referred to as the ‘Revelle buffer factor’: the relative change in atmospheric carbon, given a relative change in oceanic carbon. An explicit expression for this buffer factor in terms of oceanic carbon was given by *Sundquist et al.* [1979]. Further analysis was provided by *Volk and Hoffert* [1985] who introduced the concept of carbon pumps. However, after numerical models of the oceanic carbon cycle

were first used [*Knox and McElroy*, 1984; *Sarmiento and Toggweiler*, 1984; *Siegenthaler and Wenk*, 1984], ocean uptake of carbon has mainly been investigated by means of simulations. Although this approach has provided valuable insights [*Fasham*, 2003], it seems to have diverted the attention from the development of conceptual models and basic, analytical theory.

[3] The analytical approach was taken up again by *Ito and Follows* [2005] who derived a first-order differential equation describing the impact of the organic carbon pump on the atmospheric carbon content, but they assumed a constant Revelle buffer factor. This assumption was relieved by *Goodwin et al.* [2007] who found an approximate solution to the differential equation by introducing a quantity called the ‘buffered carbon’ I_B . Under the assumption that I_B is constant (which is approximately the case over a large range of atmospheric pCO_2), it was shown that the atmospheric carbon content depends exponentially on the total amount of carbon in the ocean-atmosphere system. *Marinov et al.* [2008a, 2008b] then accounted for small variations in I_B , expressing atmospheric pCO_2 as a sum of exponentials.

[4] *Ito and Follows* [2005] and *Marinov et al.* [2008a, 2008b] studied changes in the organic carbon pump that yield relatively modest variations in the atmospheric carbon content. Much larger changes are expected to result from current and future anthropogenic carbon emissions. With respect to the oceanic uptake of anthropogenic carbon, three crucial time periods can be distinguished [*Archer et al.*, 1997]: (1) an initial period where CO_2 emissions are ongoing and air-sea equilibrium has not been reached which is the present situation; (2) a quasi-steady state, where

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emissions have ceased and ocean and atmospheric carbon reservoirs are equilibrated though the fluid system has not yet come into equilibrium with the carbonate sediments. This period would extend for several thousands of years; and (3) a final equilibrium where, after many tens of thousands of years, weathering and sediment interactions have occurred altering the total ocean-atmosphere carbon budget. A recent study by *Goodwin and Ridgwell* [2010] has focused on ocean-atmosphere partitioning of carbon during the last phase; centennial/millennial timescales (phase 2) were investigated by *Goodwin et al.* [2007, 2008, 2009] and by *Egleston et al.* [2010]. The results of the centennial/millennial simulations by Goodwin et al. indicate that large emissions of carbon lead to regime shifts in the air-sea carbon partitioning. To a good approximation, atmospheric pCO_2 turns out to depend exponentially on total carbon emissions up to total emissions of 5000 Gt (consistent with the assumption of a constant I_B); above 10000 Gt, the relationship becomes linear. Furthermore, the globally averaged Revelle buffer factor increases with emission size up to 8000 Gt, reaching a maximum of 18; for higher total emissions, it decreases again.

[5] *Egleston et al.* [2010] defined a number of different buffer factors (some of which are equivalent to factors derived by *Frankignoulle* [1994]), quantifying the change in atmospheric CO_2 , oceanic pH , and carbonate saturation state (Ω) with increasing oceanic DIC concentrations. A regime shift is also suggested by the behavior of these new buffer factors: they all reach an extremum approximately at the point where the DIC concentration becomes equal to the ocean alkalinity.

[6] In this article, we focus on explaining the different regimes identified by Goodwin et al. and Egleston et al. by formulating a complementary theory based on elementary carbonate chemistry. The regimes turn out to be related to the compound dominating the response of the ocean carbon chemistry: at relatively low emissions, this compound is CO_3^{2-} , whereas at higher emissions, dissolved CO_2 becomes more important.

[7] We make the following general assumptions:

[8] (1) Both the ocean and the atmosphere are assumed to be well-mixed boxes. Carbon is fully equilibrated between these compartments, but there has not (yet) been exchange of carbonate with the sediments. This implies that we are concerned with centennial to millennial timescales, or time period (2) as defined above.

[9] (2) The oceanic temperature and preformed alkalinity, as well as the strength of the carbon pumps and the land biosphere, are assumed constant. However, any change in either the carbon pumps or carbon in the terrestrial biosphere can simply be formulated as a change in the total carbon inventory and thus, its impact can be predicted.

[10] In the following section, we will introduce a new quantity, analogous to the well-known Revelle factor, which reveals useful insights.

2. Ocean-Atmosphere Carbon Partitioning

[11] The oceanic carbonate chemistry can be characterized by means of two quantities [*Chester*, 2000]: the DIC con-

centration (C) and the total alkalinity (A). Throughout this article, we will consider situations with $pH \approx 6-9$ where the main bases in the ocean are $[HCO_3^-]$ and $[CO_3^{2-}]$ and we will therefore identify A with the carbonate alkalinity. This inevitably leads to imprecision (since bases such as OH^- and $B(OH)_4$ constitute a few percent of total alkalinity), but it will turn out that we can explain well the general features of the ocean-atmosphere carbon partitioning regimes using this approximation. The impact of this and other approximations that we make in the calculations are discussed in section 3. Thus, we define C and A as:

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

and

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

[12] The relationship between the atmospheric pCO_2 and C at the ocean surface is commonly described by means of the Revelle buffer factor (R) defined as:

$$R \equiv \frac{\partial \ln pCO_2}{\partial \ln C} \quad (1)$$

If R is constant, then the relationship between pCO_2 and C is given by a simple power law:

$$pCO_2 \propto C^R$$

Unfortunately, R is not constant: it varies between approximately 8 and 15 at the ocean surface [*Watson and Liss*, 1998]. Furthermore, the globally averaged Revelle buffer factor depends strongly on the total amount of carbon in the ocean-atmosphere system [e.g., *Goodwin et al.*, 2007]. We now derive an alternative index that is more constant than R .

2.1. A New Quantity to Describe Ocean Carbon Chemistry

[13] In the ocean, the main chemical reactions involving carbon are dissolution of carbon dioxide from the atmosphere, the subsequent formation of carbonic acid H_2CO_3 by reaction with water, dissociation of H_2CO_3 into bicarbonate HCO_3^- and H^+ , and dissociation of HCO_3^- into carbonate CO_3^{2-} and H^+ [*Bolin and Eriksson*, 1959; *Broecker and Peng*, 1982]. If the air-sea partitioning of carbon dioxide as well as the carbonate reaction system are at equilibrium, we have:

$$K_H[CO_2] = pCO_2 \quad (2a)$$

$$K_0[H_2CO_3] = [CO_2] \quad (2b)$$

$$K_1[H^+][HCO_3^-] = [H_2CO_3] \quad (2c)$$

$$K_2[H^+][CO_3^{2-}] = [HCO_3^-] \quad (2d)$$

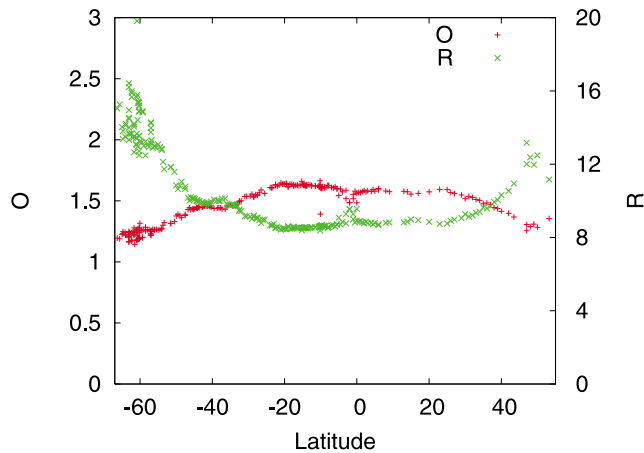


Figure 1. O and R as a function of latitude along a transect at 170°W in the Pacific. Values were calculated using DIC and Alkalinity for the present-day ocean from GLODAP [Key *et al.*, 2004] and temperature and salinity from the World Ocean Atlas [Loncarnini *et al.*, 2006].

where K_H , K_0 , K_1 , K_2 are dissociation constants. Eliminating $[H^+]$ from the above equations, one obtains:

$$pCO_2 = \frac{[HCO_3^-]^2}{K[CO_3^{2-}]} \quad (3)$$

Here, K is a composite chemical equilibrium constant equivalent to $\frac{K_2}{K_1 K_0 K_H}$.

[14] Generally, there are much larger relative variations in $[CO_3^{2-}]$ than in $[HCO_3^-]$. Hence, to a fair approximation, $[HCO_3^-]$ is constant which implies $KpCO_2 \propto [CO_3^{2-}]^{-1}$: a power-law dependence of pCO_2 on $[CO_3^{2-}]$, rather than on C . However, because $[HCO_3^-]$ is not exactly constant, it is suggestive that a more accurate way of formulating the power-law relationship between pCO_2 and $[CO_3^{2-}]$ would be:

$$KpCO_2 \propto [CO_3^{2-}]^{-O} \quad (4)$$

with

$$O \equiv -\frac{\partial \ln(KpCO_2)}{\partial \ln[CO_3^{2-}]} \quad (5)$$

In the situations considered in this paper, K is constant, which means that we can also write:

$$O \equiv -\frac{\partial \ln(pCO_2)}{\partial \ln[CO_3^{2-}]}$$

To find an explicit expression for O , we express relationship (3) in terms of the carbonate alkalinity A and $[CO_3^{2-}]$:

$$KpCO_2 = \frac{(A - 2[CO_3^{2-}])^2}{[CO_3^{2-}]}$$

which can be rewritten as:

$$\ln(KpCO_2) = 2 \ln(A - 2[CO_3^{2-}]) - \ln([CO_3^{2-}]) \quad (6)$$

Alkalinity is conserved when carbon is exchanged between the ocean and the atmosphere. We can thus assume constant A when describing the ocean-atmosphere partitioning of carbon as carbon dioxide is added to the atmosphere. After differentiating equation (6) with respect to $\ln([CO_3^{2-}])$ and resubstituting $[HCO_3^-] + 2[CO_3^{2-}]$ for A , we arrive at:

$$O = 1 + 4 \frac{[CO_3^{2-}]}{[HCO_3^-]} \quad (7)$$

Because $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ is only about 0.1, it can easily be seen that O must be almost constant. O varies between about 1.2 and 1.6 at the surface of the World Ocean. This is illustrated in Figure 1 where we show O and R as a function of latitude along a transect at 170°W in the Pacific. Most notably, R increases, whereas O decreases towards higher latitudes. Moreover, the relative variation as a function of latitude is more than twice as large for R than it is for O : the ratio of the standard deviation of O to its median value equals 0.11, whereas this ratio is 0.25 for R .

[15] Another important advantage of O is that it is a simple function of $[CO_3^{2-}]$ and $[HCO_3^-]$. Therefore, the dependence of O on oceanic carbon and alkalinity is transparent. O decreases monotonically with increasing DIC concentration, because $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ decreases monotonically; O increases monotonically with increasing alkalinity, because $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ increases monotonically. O has a simpler and more transparent behavior than both R and I_B , particularly when a large range of carbon emissions is considered. As mentioned in the Introduction, R changes strongly and non-monotonically if more carbon is added to the ocean-atmosphere system. The buffered carbon, I_B , has the advantage of staying rather constant up to a total emission of 5000 Gt. However, O remains at approximately the same value, even if the total emission far exceeds 5000 Gt: it is about 1.4 in the pre-industrial situation, and it approaches 1, when total carbon emissions become very high.

[16] The perspective of the ocean acidification problem [Feely *et al.*, 2002; Orr *et al.*, 2005; Langer *et al.*, 2006] may lead to an entirely different interpretation of O . The saturation state of calcium carbonate (Ω) is given by:

$$\Omega \equiv \frac{[Ca^{2+}][CO_3^{2-}]}{K_{Ca}}$$

with K_{Ca} a solubility constant. Now, $[Ca^{2+}]$ stays constant when carbon is exchanged between the atmosphere and the ocean, and therefore:

$$\frac{\partial \ln \Omega}{\partial \ln pCO_2} = \frac{\partial \ln [CO_3^{2-}]}{\partial \ln pCO_2} = -\frac{1}{O} \quad (8)$$

Thus, $\frac{1}{O}$ can be interpreted as the relative decrease in the ocean carbonate saturation state with increase of pCO_2 .

2.2. Dependence of the Revelle Factor on Oceanic Carbon

[17] Simulations presented by *Goodwin et al.* [2007] have shown that the Revelle buffer factor R increases as carbon is added to the ocean-atmosphere system up to total emissions of about 8000 Gt C; at higher emissions, it decreases again. We can use O to understand why this is the case. We reformulate R in terms of $[CO_2]$, $[CO_3^{2-}]$, O , and the DIC concentration C :

$$R \equiv \frac{d \ln pCO_2}{d \ln C} = \frac{C}{\frac{dC}{d \ln pCO_2}}$$

Now, we use $C = A - [CO_3^{2-}] + [CO_2]$, so with A constant:

$$\frac{dC}{d \ln pCO_2} = -\frac{d[CO_3^{2-}]}{d \ln pCO_2} + \frac{d[CO_2]}{d \ln pCO_2} = \frac{[CO_3^{2-}]}{O} + [CO_2]$$

and therefore

$$R \equiv \frac{d \ln pCO_2}{d \ln C} = \frac{C}{\frac{[CO_3^{2-}]}{O} + [CO_2]} \quad (9)$$

This expression is essentially a simplified version of expressions derived by *Sundquist et al.* [1979] and *Egleston et al.* [2010] which also take bases such as $B(OH)_4^-$ into account.

[18] Changes in the minor species $[CO_3^{2-}]$ and $[CO_2]$ are relatively much larger than in the total C and therefore, the behavior of R is dominated by the denominator term $\frac{[CO_3^{2-}]}{O} + [CO_2]$. If $\frac{[CO_3^{2-}]}{O} \gg [CO_2]$, then $R \approx \frac{OC}{[CO_3^{2-}]}$. This means that as long as O can be considered constant (i.e., $[CO_3^{2-}] \ll [HCO_3^-]$), R must increase with increasing pCO_2 , since $[CO_3^{2-}]$ decreases with increasing pCO_2 . If, on the other hand, $[CO_2] \gg \frac{[CO_3^{2-}]}{O}$, then $R \approx \frac{C}{[CO_2]}$ which means that R decreases with increasing pCO_2 , because $[CO_2]$ increases with increasing pCO_2 . In the intermediate regime, R must attain a maximum. In this range, most DIC is in the form of $[HCO_3^-]$; thus, $C \approx A$ which suggests that we can write:

$$R \approx \frac{A}{\frac{[CO_3^{2-}]}{O} + [CO_2]} \quad (10)$$

If the denominator reaches a minimum, then R reaches its maximum value. To find the location of the maximum of R , we can therefore write:

$$\frac{d\left(\frac{[CO_3^{2-}]}{O} + [CO_2]\right)}{d \ln pCO_2} \approx \frac{1}{O} \frac{d[CO_3^{2-}]}{d \ln pCO_2} + \frac{d[CO_2]}{d \ln pCO_2} = 0$$

which leads to

$$[CO_3^{2-}] = O^2 [CO_2] \quad (11)$$

Using that $[HCO_3^-] \approx A$ and that $pCO_2 = K_H [CO_2]$, we can rewrite equation (3) into:

$$[CO_2] \approx \frac{A^2}{K_H K [CO_3^{2-}]} \quad (12)$$

Combining equations (11) and (12) then yields:

$$[CO_3^{2-}] = \frac{OA}{\sqrt{K_H K}} \quad (13)$$

from which we can derive

$$[CO_2] = \frac{A}{O \sqrt{K_H K}} \quad (14a)$$

$$pCO_2 = K_H [CO_2] = \frac{A}{O} \sqrt{\frac{K_H}{K}} \quad (14b)$$

$$R_{\max} = \frac{A}{\frac{A}{O \sqrt{K_H K}} + \frac{A}{\sqrt{K_H K}}} = \frac{\sqrt{K_H K}}{1 + \frac{1}{O}} \quad (14c)$$

with R_{\max} the maximum value that R attains. Before we consider the above relationship in a quantitative sense, we need to realize that O is not entirely constant. In fact, at the relatively high carbon concentration for which R reaches its maximum, O must be lower than in the pre-industrial ocean. To estimate O , we use relationships (7) and (13); we again assume that $[HCO_3^-] \approx A$:

$$O \approx 1 + 4 \frac{[CO_3^{2-}]}{A} = 1 + 4 \frac{O}{\sqrt{K_H K}}$$

which yields

$$O = \frac{1}{1 - \frac{4}{\sqrt{K_H K}}} = 1.12 \quad (15)$$

Filling in this value for O in equations (13) and (14), we find that when R is maximized, $R_{\max} = 19$ and $[CO_3^{2-}] = 75 \mu\text{M}$, $[CO_2] = 59 \mu\text{M}$, $pCO_2 = 1540 \text{ ppm}$.

[19] The maximum in R can be understood qualitatively from a change in the relative abundances of carbonate and carbon dioxide which is illustrated in Figure 2. At low total carbon, there is much more carbonate than carbon dioxide in the water; carbon entering the ocean from the atmosphere is essentially used to neutralize carbonate into bicarbonate. The resulting decrease of the carbonate concentration leads to an increase of the Revelle buffer factor. As more carbon is added to the ocean, there are fewer carbonate ions left to be neutralized; at some point, the extra carbon entering the ocean mostly stays in the form of carbon dioxide. In this regime, the Revelle factor decreases because of the increasing $[CO_2]$. The different regimes of R are illustrated in Figure 3a.

[20] Another way of looking at this is by considering the bicarbonate fraction of DIC. According to Figure 2, this fraction attains a maximum at a DIC concentration of about 2.4 mM. Now, $O \approx 1$, therefore:

$$\frac{[CO_3^{2-}]}{O} + [CO_2] \approx [CO_3^{2-}] + [CO_2] = C - [HCO_3^-]$$

and

$$R \approx \frac{C}{C - [HCO_3^-]} = \frac{1}{1 - \frac{[HCO_3^-]}{C}} \quad (16)$$

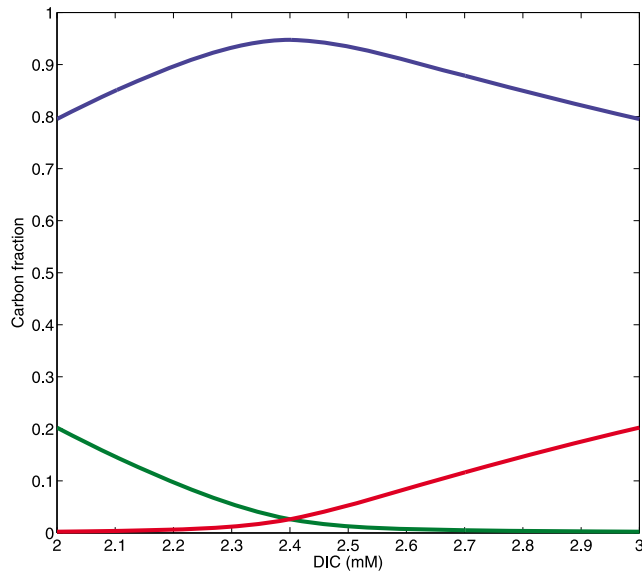


Figure 2. Dissolved carbon dioxide (red), bicarbonate (blue), and carbonate (green) fractions of DIC as a function of DIC concentration calculated from equation (3) with parameter values as in Table 2; as in the calculations in the earlier sections, we have neglected the contributions from non-carbonic bases such as $B(OH)_4^-$ and OH^- to the ocean alkalinity.

If the bicarbonate fraction of DIC, equal to $\frac{[HCO_3^-]}{C}$, reaches a maximum, then $1 - \frac{[HCO_3^-]}{C}$ reaches a minimum which in turn implies that R attains a maximum.

[21] Recently, *Egleston et al.* [2010] defined new buffer factors that behave in a way analogous to R as a function of the oceanic carbon concentration. We discuss some of these factors in Appendix B.

2.3. Carbon Partitioning in the Ocean-Atmosphere System

[22] Now we will apply the theory to derive the dependence of atmospheric pCO_2 on total carbon in the ocean-atmosphere system. We will show that depending on the relative sizes of two different terms, three regimes can be distinguished, of which two were previously identified by *Goodwin et al.* [2007]. We start by writing down a balance equation for carbon in the ocean-atmosphere system (as given by *Ito and Follows* [2005]):

$$MpCO_2 + VC + \int C_{reg}dV = C_t \quad (17)$$

with M the total gas content of the atmosphere (mol), V the volume of the ocean (l), C the average oceanic concentration of preformed dissolved inorganic carbon, C_{reg} the regenerated carbon concentration (M), and C_t the total carbon content of the ocean-atmosphere system (m). Using that $C = A - [CO_3^{2-}] + [CO_2]$ (where A is the preformed alkalinity averaged over the ocean) and that $[CO_2]$ and pCO_2 are

simply related through Henry's law, i.e. $pCO_2 = K_H [CO_2]$, we can write:

$$pCO_2 \left(M + \frac{V}{K_H} \right) + V(A - [CO_3^{2-}]) = C_t - \int C_{reg}dV \quad (18)$$

Now, we differentiate equation (18) with respect to C_t , while assuming A and C_{reg} constant and using that $\frac{d[CO_3^{2-}]}{dC_t} = \frac{\partial[CO_3^{2-}]}{\partial pCO_2} \frac{\partial pCO_2}{\partial C_t}$:

$$\frac{\partial pCO_2}{\partial C_t} \left(M + \frac{V}{K_H} \right) - V \frac{\partial[CO_3^{2-}]}{\partial pCO_2} \frac{\partial pCO_2}{\partial C_t} = 1$$

Using the definition of O , we can rearrange to obtain:

$$\frac{\partial \ln pCO_2}{\partial C_t} \left(\left(M + \frac{V}{K_H} \right) pCO_2 + V \frac{[CO_3^{2-}]}{O} \right) = 1 \quad (19)$$

The term $(M + \frac{V}{K_H})pCO_2 + V \frac{[CO_3^{2-}]}{O}$ is equivalent to the 'buffered carbon' I_B introduced by *Goodwin et al.* [2007], so we can write:

$$\frac{\partial \ln pCO_2}{\partial C_t} \equiv \frac{1}{I_B}$$

[23] Pleasingly, I_B can be reinterpreted in this framework. It consists of two terms; one is proportional to the atmospheric and oceanic carbon dioxide concentrations, the other one is proportional to the oceanic carbonate ion concentration. Based on the relative importance of the terms, three regimes can be distinguished, the ranges of which are given in Tables 1 and 2:

[24] 1) The low-carbon ocean-atmosphere system; we do not know of any geological period during which atmospheric and oceanic carbon were so low that this regime was relevant, but we have added it for completeness. In this regime, the atmospheric and oceanic carbon dioxide concentrations are low, the oceanic carbonate concentration is high and the partitioning is determined by the behavior of the carbonate ion. Specifically, $(M + \frac{V}{K_H})pCO_2 \ll V \frac{[CO_3^{2-}]}{O}$, so equation (18) can be written as:

$$V(A - [CO_3^{2-}]) \approx C_t - \int C_{reg}dV$$

which can be rearranged into:

$$[CO_3^{2-}] \approx A + \frac{\int C_{reg}dV}{V} - \frac{C_t}{V}$$

In this regime, we cannot suppose that O is constant, because $4 \frac{[CO_3^{2-}]}{[HCO_3^-]}$ is rather large. However, an alternative quantity $H \equiv \frac{\partial \ln pCO_2}{\partial \ln [H^+]}$ (see Appendix A) remains quite close to 1 and therefore, we will assume that this factor is constant. We now combine the relationships $[CO_3^{2-}] = \frac{A}{K_2[H^+] + 2}$ and $pCO_2 \propto [H^+]^H$ with the above equation to find that

$$pCO_2 \propto \left(\frac{1}{1 + \frac{\int C_{reg}dV}{VA} - \frac{C_t}{VA}} - 2 \right)^H \quad (20)$$

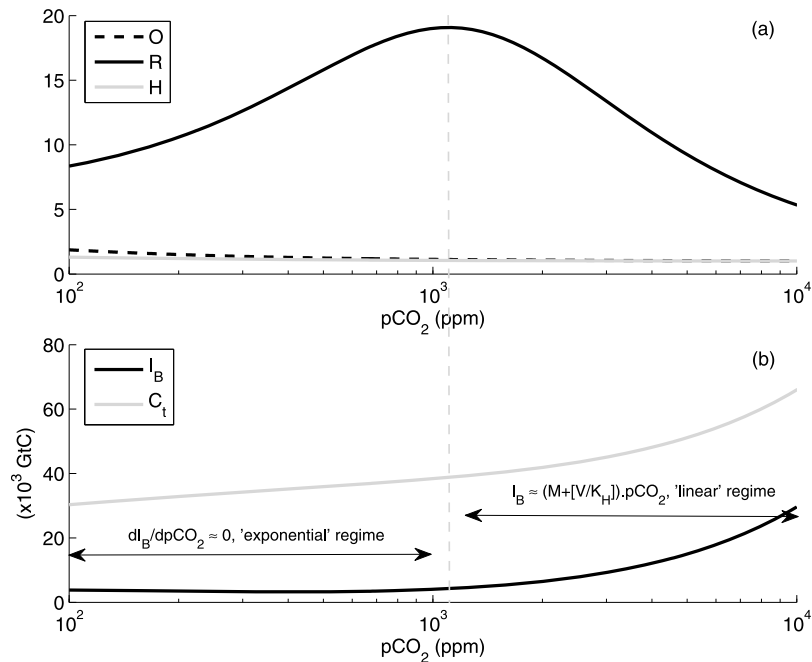


Figure 3. Carbon system quantities versus pCO_2 from a two-box model with a well-mixed abiotic ocean (volume $V = 1.3 \cdot 10^{18} \text{ m}^3$) in equilibrium with a well-mixed atmosphere (containing $M = 1.77 \cdot 10^{20}$ moles of gas). Ocean temperature (5°C), salinity (34.7 psu) and titration alkalinity (2.35 moles eq m^{-3}) are held constant and carbonate chemistry is explicitly solved [Follows *et al.*, 2006] in DIC increments of 0.002 moles m^{-3} . (a) R increases to a maximum of 19 at $pCO_2 \sim 1080$ ppm and then decreases with increasing pCO_2 . O decreases from 1.9 at $pCO_2 = 100$ ppm approaching unity for $pCO_2 > 1000$ ppm. H remains close to unity throughout the range of pCO_2 , continually decreasing from 1.3 at $pCO_2 = 100$ ppm. (b) The buffered carbon inventory I_B remains stable from $100 < pCO_2 < 1000$ ppm and increases when $pCO_2 > 1000$ ppm, while total air-sea carbon, C_t , always increases with increasing pCO_2 . Note that Figure 3 displays the same qualitative behavior as model runs within Goodwin *et al.* [2007], but with slight differences in numerical values. These small numerical differences are primarily because the simulations here were performed using a different ocean temperature.

Hence, pCO_2 appears to have a (complicated) power-law type of dependence on total carbon C_t in this regime.

[25] 2) The intermediate regime (the current situation) where both carbon dioxide and carbonate play a role. Specifically, $\frac{dI_B}{dpCO_2} = M + \frac{V}{K_H} - V \frac{[CO_3^{2-}]}{pCO_2 O^2} + V [CO_3^{2-}] \frac{d\frac{1}{O}}{dpCO_2} \approx 0$, so I_B is approximately constant. As derived by [Goodwin *et al.*, 2007], this implies an exponential dependence of pCO_2 on total system carbon:

$$pCO_2 \propto e^{\frac{C_t}{B}} \quad (21)$$

[26] 3) The high-carbon ocean-atmosphere system where the oceanic carbonate ion concentration is negligible. This regime may have been relevant during geological periods

with very high carbon levels such as the Cretaceous and the Eocene [Huber *et al.*, 2000]. Specifically, $(M + \frac{V}{K_H})pCO_2 \gg V \frac{[CO_3^{2-}]}{O}$; hence, $I_B \approx (M + \frac{V}{K_H})pCO_2$. From equation (19), it can be seen that this leads to

$$\frac{\partial pCO_2}{\partial C_t} = \frac{1}{M + \frac{V}{K_H}} \quad (22)$$

which implies a linear relationship between pCO_2 and C_t . According to equation (22), $\frac{\partial pCO_2}{\partial C_t} = 4.35 \cdot 10^{-15} \text{ ppm/mol}$ which corresponds to 0.362 ppm/Gt C. The simulations by Goodwin *et al.* suggest a slope in the linear regime of about

Table 1. Regime Changes From Theory With Modern Titration Alkalinity

Regime	pCO_2 (ppm)	pH	$\frac{[CO_2]}{[CO_3^{2-}]}$
Power-law	<10	>9.7	<0.0005
Exponential	20–1000	7.8–9.5	0.001–0.6
Linear	>2000	<7.5	>1.4

Table 2. Parameter Values

Parameter	Units	Value
A	mM	2.4
V	l	$1.3 \cdot 10^{21}$
M	mol	$1.8 \cdot 10^{20}$
K_H	l atm/mol	26
K	mol $\text{l}^{-1} \text{ atm}^{-1}$	50

0.356 ppm/Gt C [Goodwin *et al.*, 2007, Figure 5]. The exponential and linear regimes are illustrated in Figure 3b.

3. Discussion

[27] In this article, we have developed a simple analytical theory to explain how the Revelle buffer factor (and new buffer factors defined by Egleston *et al.* [2010]) as well as the ocean-atmosphere partitioning of carbon depend on total carbon. It complements earlier developments [Goodwin *et al.*, 2007; Marinov *et al.*, 2008b; Egleston *et al.*, 2010] and it is consistent with the general features found from numerical simulations [Goodwin *et al.*, 2007, 2008, 2009]. Both suggest that the Revelle factor increases with total carbon until it reaches a maximum, after which it starts to decrease. Furthermore, both the simulations and this framework predict that the atmospheric carbon dioxide concentration will first increase exponentially and then linearly with emissions. The maximum in the Revelle factor can be explained from the neutralization of dissolved carbonate into bicarbonate, combined with an increase in dissolved carbon dioxide, as more carbon enters the ocean. Once the carbonate concentration has become negligible, practically all carbon entering the ocean remains in the form of carbon dioxide; at this point, the atmospheric CO_2 concentration starts to increase linearly with emissions. Thus, the anthropogenic carbon emissions can be thought of as driving a regime change in the oceanic carbon chemistry.

[28] There are some minor notable differences between the predictions from this theory and the Goodwin *et al.* [2007] simulation results, especially concerning the behavior of the Revelle buffer factor. In fact, the theory suggests that this factor has its maximum at $pCO_2 = 1540$ ppm, whereas the simulations suggest that the maximum of R rather occurs at $pCO_2 = 1800$ ppm. Furthermore, we predict that $R_{\max} = 19$, whereas it is only 18 according to the simulations. Both these differences may be explained from our assumption that the carbonate alkalinity is equal to the total alkalinity since we did not take bases other than (bi-)carbonate into account (the most important one being $B(OH)_4^-$ throughout the regime that we have considered). If we assume that the concentration of such bases scales linearly with the carbonate concentration, then the $\frac{[CO_3^{2-}]}{O}$ -term in the denominator of R is effectively multiplied by a value larger than 1. This means that R becomes slightly lower at every value of pCO_2 (but especially in the low-carbon regime), and that $[CO_2]$, and thus pCO_2 , must be slightly higher at the maximum of R . In the same vein, one could argue that the $V\frac{[CO_3^{2-}]}{O}$ -term in I_B should effectively be multiplied by a factor larger than 1. The effects on the different regimes defined in section 2.3 would be rather modest: the intermediate-carbon regime (where pCO_2 depends on total carbon exponentially) would begin and end at slightly higher values of pCO_2 . At very high or very low pH (very low and very high pCO_2 , respectively), our assumption that the carbonate alkalinity is equal to the total alkalinity is certainly not valid: at $pH < 5$, $[H^+]$ accounts for a significant portion of total alkalinity, whereas at $pH > 9$, $[OH^-]$ becomes important.

[29] In addition, we made two further assumptions impacting our calculation of R_{\max} : we implicitly supposed

that C is constant by assuming $C \approx A$ (equation 10) and we took O constant when calculating derivatives with respect to $\ln pCO_2$ in (11). Both these assumptions primarily affect the value of pCO_2 for which R reaches its maximum. In section 2.2, we basically analyzed the denominator of R instead of R itself and we assumed that when the denominator reaches its minimum, R has its maximum. The fact that C increases with increasing pCO_2 implies that when the denominator of R reaches its minimum, R will still be increasing. Therefore, R must actually have its maximum at a slightly higher pCO_2 than we estimated. The fact that O decreases with increasing

pCO_2 implies that $\frac{\partial \frac{[CO_3^{2-}]}{O}}{\partial pCO_2}$ is less negative than if O were constant which in turn means that the denominator of R reaches its minimum for a lower value of pCO_2 . Hence, the effects of these two assumptions work in different directions: the constant C tends to give a too low estimate of pCO_2 at R_{\max} , whereas the constant O tends to yield a too high value of pCO_2 at R_{\max} .

4. Conclusion

[30] Overall, the ocean-atmosphere partitioning of carbon appears to be described well across a very wide range of regimes by a theory based on simple carbonate chemistry. The quantity O has turned out to be particularly useful for a number of reasons. First of all, it is much more constant than the Revelle buffer factor that has been extensively applied in theories of the ocean-atmosphere carbon partitioning. Second, O behaves transparently as a function of the total carbon in the ocean-atmosphere system: if total carbon increases, then O decreases, because the ratio $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ goes down. Even at very high total emissions, the order of magnitude of this quantity remains the same: in the pre-industrial situation, O is about 1.4, whereas it approaches 1, if total carbon becomes exceedingly high. Hence, the framework presented appears to have a number of advantages: relative simplicity, transparency and applicability to different regimes. Therefore, we expect that it will turn out useful for obtaining a deeper understanding of various topics in ocean biogeochemistry, first of all the dependence of pCO_2 on temperature and alkalinity. The framework presented here may also be useful for determining which carbon regime (exponential or linear) the system displayed during past geological periods, by using atmospheric pCO_2 [Royer *et al.*, 2001] and carbonate chemistry [Ridgwell, 2005] considerations.

Appendix A: Factor H

[31] We define the quantity H as follows:

$$H \equiv \frac{\partial \ln pCO_2}{\partial \ln [H^+]} \quad (A1)$$

The above definition implies that if H can be considered constant, then:

$$pCO_2 \propto [H^+]^H \quad (A2)$$

To evaluate (A1), we rewrite the expression for pCO_2 (3) in terms of A and $[H^+]$, using relationship (2) between $[H^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$:

$$pCO_2 = \frac{AK_2}{K} \frac{[H^+]^2}{[H^+] + \frac{2}{K_2}} \quad (A3)$$

and therefore:

$$\frac{\partial \ln pCO_2}{\partial \ln [H^+]} = 2 - \frac{[H^+]}{[H^+] + \frac{2}{K_2}} \quad (A4)$$

restitution then leads to:

$$H = 1 + 2 \frac{[CO_3^{2-}]}{A} \quad (A5)$$

As long as $[CO_3^{2-}] \ll [HCO_3^-]$, H behaves qualitatively very similar to O : it is slightly above 1, approaching 1 as total carbon increases. However, in the low-carbon regime, O becomes large, whereas H remains close to 1, approaching 2, if $[CO_3^{2-}] \gg [HCO_3^-]$. Thus, H is more constant than O which can be considered as an advantage for using H over using O . On the other hand, O is more directly related to the most important compounds in the oceanic carbon system which makes analysis based on O more straightforward than analysis based on H .

Appendix B: Behavior of Other Buffer Factors

[32] Egleston et al. [2010] defined six buffer factors: $\frac{\partial C}{\partial \ln pCO_2}$ (γ_{DIC}), $\frac{\partial C}{\partial \ln [H^+]}$ (β_{DIC}), $\frac{\partial C}{\partial \ln \Omega}$ (ω_{DIC}) at constant alkalinity, and $\frac{\partial A}{\partial \ln [CO_3^{2-}]}$ (γ_{Aik}), $\frac{\partial A}{\partial \ln [H^+]}$ (β_{Aik}), $\frac{\partial A}{\partial \ln \Omega}$ (ω_{Aik}) at constant DIC. Because our paper is concerned with what happens to the ocean carbon system as carbon is added to the ocean-atmosphere system, but alkalinity stays constant, we will only consider the constant-alkalinity buffer factors γ_{DIC} , β_{DIC} , and ω_{DIC} . In fact, γ_{DIC} is equal to the denominator term of R which we already analyzed. Furthermore, because of the definition of Ω :

$$\omega_{DIC} = \frac{\partial C}{\partial \ln [CO_3^{2-}]} = \frac{\partial C}{\partial \ln pCO_2} \frac{\partial \ln pCO_2}{\partial \ln [CO_3^{2-}]} = -O\gamma_{DIC} \quad (B1)$$

As can be seen in Figure 2 of Egleston et al. [2010], $-\omega_{DIC} \approx \gamma_{DIC}$ at high oceanic DIC concentrations which can be understood from the fact that $O \approx 1$ in that regime. With decreasing C , the ratio of $-\omega_{DIC}$ to γ_{DIC} becomes larger, because O increases with decreasing C . To relate β_{DIC} to γ_{DIC} , we will use H , defined in (A1):

$$\beta_{DIC} = \frac{\partial C}{\partial \ln [H^+]} = \frac{\partial C}{\partial \ln pCO_2} \frac{\partial \ln pCO_2}{\partial \ln [H^+]} = H\gamma_{DIC} \quad (B2)$$

The relationship between β_{DIC} and γ_{DIC} is qualitatively very similar to the relationship between γ_{DIC} and ω_{DIC} : at high DIC, $\beta_{DIC} \approx \gamma_{DIC}$, since $H \approx 1$; as DIC decreases, H increases and therefore, the ratio of β_{DIC} to γ_{DIC} increases. However, β_{DIC} is always smaller than $-\omega_{DIC}$, because H is always smaller than O .

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References

- Archer, D. E., H. Keshgi, and E. Maier-Reimer (1997), Multiple time-scales for neutralization of fossil fuel CO_2 , *Geophys. Res. Lett.*, *24*, 405–408.
- Bolin, B., and E. Eriksson (1959), Distribution of matter in the sea and the atmosphere, in *The Atmosphere and the Sea in Motion*, edited by B. Bolin, Rockefeller Inst. Press, New York.
- Broecker, W. S., and T. H. Peng (1982), *Tracers in the Sea*, Lamont-Doherty Geol. Observ., Palisades, N. Y.
- Chester, R. (2000), *Marine Geochemistry*, 2nd ed., Blackwell, Oxford, U. K.
- Egleston, E. S., C. L. Sabine, and F. M. M. Morel (2010), Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity, *Global Biogeochem. Cycles*, *24*, GB1002, doi:10.1029/2008GB003407.
- Fasham, M. J. R. (Ed.) (2003), *Ocean Biogeochemistry*, Springer, Heidelberg, Germany.
- Feeley, R. A., et al. (2002), In situ calcium carbonate dissolution in the Pacific Ocean, *Global Biogeochem. Cycles*, *16*(4), 1144, doi:10.1029/2002GB001866.
- Follows, M. J., T. Ito, and S. Dutkiewicz (2006), On the solution of the carbonate system in biogeochemistry models, *Ocean Modell.*, *12*, 290–301.
- Frankignoulle, M. (1994), A complete set of buffer factors for acid/base CO_2 system in sea water, *J. Mar. Syst.*, *5*, 111–118.
- Goodwin, P., and A. Ridgwell (2010), Ocean-atmosphere partitioning of anthropogenic carbon dioxide on multimillennial timescales, *Global Biogeochem. Cycles*, *24*, GB2014, doi:10.1029/2008GB003449.
- Goodwin, P., R. G. Williams, M. J. Follows, and S. Dutkiewicz (2007), Ocean-atmosphere partitioning of anthropogenic carbon dioxide on centennial timescales, *Global Biogeochem. Cycles*, *21*, GB1014, doi:10.1029/2006GB002810.
- Goodwin, P., M. J. Follows, and R. G. Williams (2008), Analytical relationships between atmospheric carbon dioxide, carbon emissions, and ocean processes, *Global Biogeochem. Cycles*, *22*, GB3030, doi:10.1029/2008GB003184.
- Goodwin, P., R. G. Williams, A. Ridgwell, and M. J. Follows (2009), Climate sensitivity to the carbon cycle modulated by past and future changes in ocean chemistry, *Nat. Geosci.*, *2*, 145–150.
- Huber, B. T., K. G. MacLeod, and S. L. Wing (2000), *Warm Climates in Earth History*, Cambridge Univ. Press, Cambridge, U. K.
- Ito, T., and M. J. Follows (2005), Preformed phosphate, soft-tissue pump and atmospheric CO_2 , *J. Mar. Res.*, *63*, 813–839.
- Key, R. M., et al. (2004), A global ocean carbon climatology: Results from global data analysis project (GLODAP), *Global Biogeochem. Cycles*, *18*, GB4031, doi:10.1029/2004GB002247.
- Knox, F., and M. McElroy (1984), Change in atmospheric CO_2 : Influence of the marine biota at high latitude, *J. Geophys. Res.*, *89*, 4629–4637.
- Langer, G. L., M. Geisen, K. H. Baumann, J. K. Klas, U. Riebesell, S. Thomas, and J. R. Young (2006), Species-specific responses of calcifying algae to changing seawater carbonate chemistry, *Geochim. Geophys. Geosyst.*, *7*, Q09006, doi:10.1029/2005GC001227.
- Loncrardini, R. A., V. Mishonov, J. I. Antonov, T. P. Boyer, and H. E. Garcia (2006), *World Ocean Atlas 2005*, vol. 1, NOAA, Washington, D. C.
- Marinov, I., M. Follows, A. Gnanadesikan, J. L. Sarmiento, and R. D. Slater (2008a), How does ocean biology affect atmospheric pCO_2 ? Theory and models, *J. Geophys. Res.*, *113*, C07032, doi:10.1029/2007JC004598.
- Marinov, I., A. Gnanadesikan, J. L. Sarmiento, J. R. Toggweiler, M. Follows, and B. K. Mignone (2008b), Impact of oceanic circulation on biological carbon storage in the ocean and atmospheric CO_2 , *Global Biogeochem. Cycles*, *22*, GB3007, doi:10.1029/2007GB002958.
- Orr, J. C., et al. (2005), Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, *437*, 681–686.
- Revelle, R., and H. E. Suess (1957), Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades, *Tellus*, *9*, 18–27.

- Ridgwell, A. (2005), A mid-Mesozoic revolution in the regulation of ocean chemistry, *Mar. Geol.*, 217, 339–357.
- Royer, D. L., R. A. Berner, and D. J. Beerling (2001), Phanerozoic CO₂ change: Evaluating geochemical and paleobiological approaches, *Earth Sci. Rev.*, 54, 349–392.
- Sarmiento, J. L., and J. R. Toggweiler (1984), A new model for the role of the oceans in determining atmospheric pCO₂, *Nature*, 308, 621–624.
- Siegenthaler, U., and T. Wenk (1984), Rapid atmospheric CO₂ variations and ocean circulation, *Nature*, 308, 624–626.
- Sundquist, E. T., L. N. Plummer, and T. M. L. Wigley (1979), Carbon dioxide in the ocean surface: The homogeneous buffer factor, *Science*, 204, 1203–1205.
- Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, edited by E. T. Sundquist and W. S. Broecker, pp. 99–110, AGU, Washington, D. C.
- Watson, A. J., and P. S. Liss (1998), Marine biological controls on climate via the carbon and sulphur geochemical cycles, *Philos. Trans. R. Soc. London B*, 353, 41–51.
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