

## Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity

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[1] We derive explicit expressions of the Revelle factor and several other buffer factors of interest to climate change scientists and those studying ocean acidification. These buffer factors quantify the sensitivity of CO<sub>2</sub> and H<sup>+</sup> concentrations ([CO<sub>2</sub>] and [H<sup>+</sup>]) and CaCO<sub>3</sub> saturation (Ω) to changes in dissolved inorganic carbon concentration (DIC) and alkalinity (Alk). The explicit expressions of these buffer factors provide a convenient means to compare the degree of buffering of [CO<sub>2</sub>], [H<sup>+</sup>], and Ω in different regions of the oceans and at different times in the future and to gain insight into the buffering mechanisms. All six buffer factors have roughly similar values, and all reach an absolute minimum when DIC = Alk (pH ~ 7.5). Surface maps of the buffer factors generally show stronger buffering capacity in the subtropical gyres relative to the polar regions. As the dissolution of anthropogenic CO<sub>2</sub> increases the DIC of surface seawater over the next century, all the buffer factors will decrease, resulting in a much greater sensitivity to local variations in DIC and Alk. For example, diurnal and seasonal variations in pH and Ω caused by photosynthesis and respiration will be greatly amplified. Buffer factors provide convenient means to quantify the effect that changes in DIC and Alk have on seawater chemistry. They should also help illuminate the role that various physical and biological processes have in determining the oceanic response to an increase in atmospheric CO<sub>2</sub>.

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### 1. Introduction

[2] Understanding the partitioning of carbon dioxide between the atmosphere and the ocean is important for predicting future climate change. The oceans currently remove approximately 30% of the anthropogenic CO<sub>2</sub> released yearly into the atmosphere [Sabine *et al.*, 2004]. This uptake by the ocean has slowed the growth of CO<sub>2</sub> concentrations in the atmosphere and has reduced net atmospheric accumulation by about 55 ppm compared to what it would be with no oceanic CO<sub>2</sub> sink. Eventually, the oceans will remove about 90% of anthropogenic CO<sub>2</sub> emissions [Archer *et al.*, 1998], but this equilibration with the atmosphere will take hundreds of thousands of years. On shorter time scales, the oceanic CO<sub>2</sub> sink will persist as long as atmospheric CO<sub>2</sub> increases; the efficiency of this sink will vary, however, as the chemistry of the ocean changes. In particular, the availability of carbonate ion (CO<sub>3</sub><sup>2-</sup>) will eventually limit how much bicarbonate (HCO<sub>3</sub><sup>-</sup>) can be

formed by reaction with CO<sub>2</sub>, decreasing the total amount of CO<sub>2</sub> that the surface waters can hold.

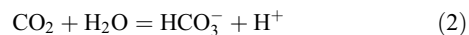
[3] Since the upper waters of the ocean are also where most marine organisms live, changes in surface ocean chemistry could have a profound impact on ecosystem structure. The accumulation of atmospheric CO<sub>2</sub> in the ocean results directly in three changes in seawater chemistry that are particularly interesting from a biological point of view:

[4] 1. The concentration of aqueous CO<sub>2</sub> ([CO<sub>2</sub>(aq)] = [CO<sub>2</sub>] + [H<sub>2</sub>CO<sub>3</sub>]), increases as a result of the dissolution of CO<sub>2</sub> gas:



By itself the increase in [CO<sub>2</sub>] may be important to photosynthetic organisms, which must acquire inorganic carbon for fixation [Badger *et al.*, 1998; Tortell, 2000].

[5] 2. The pH decreases as a result of the proton released from the reaction of CO<sub>2</sub> and water to form bicarbonate, HCO<sub>3</sub><sup>-</sup>:



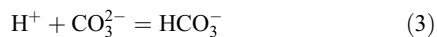
This effect, recently termed ocean acidification, has received a great deal of attention in the scientific and

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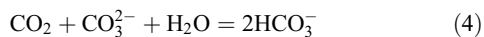
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popular press because of the potential impacts on marine ecosystems. Effects range from changes in the speciation and availability of some essential elements such as iron to direct physiological impacts [e.g., Morel *et al.*, 2003; Michaelidis *et al.*, 2005].

[6] Most of the protons released in reaction (2) are consumed by reaction with the carbonate ion:



such that the main overall reaction ((2) + (3)) is a neutralization of the dissolved  $\text{CO}_2$  by  $\text{CO}_3^{2-}$ :



The consumption of  $\text{H}^+$  and  $\text{CO}_2$  by reaction with  $\text{CO}_3^{2-}$  counteracts much of the  $\text{H}^+$  and  $\text{CO}_2$  increase providing the principal buffering of seawater. A similar but quantitatively less important buffering results from the reactions of  $\text{H}^+$  and  $\text{CO}_2$  with the borate ion,  $\text{B}(\text{OH})_4^-$ .

[7] 3. As reactions (3) and (4) proceed, the carbonate ion concentration decreases, resulting in a decrease in the saturation state of calcium carbonate ( $\Omega$ ):

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}} \quad (5)$$

where  $K_{sp}$  is the solubility constant for calcite or aragonite. The declining saturation state of calcium carbonate in the ocean has been observed to impair the ability of calcifying organisms to form carbonate shells, an important component of the carbon cycle in the ocean [Riebesell *et al.*, 2000; Feely *et al.*, 2002, 2004; Langer *et al.*, 2006; Orr *et al.*, 2005].

[8] At the first order, rising atmospheric  $\text{CO}_2$  concentrations increase the total dissolved inorganic carbon (DIC) of the ocean, without changing its alkalinity (Alk). Alkalinity is a function of riverine inputs, biogenic calcification, ocean floor burial, nitrate and ammonium uptake, and several other minor sources and sinks [Sigman and Boyle, 2000]. Most century-scale projections of future  $\text{CO}_2$  uptake by the ocean assume that alkalinity will stay constant in the short-to-mid-term future [e.g., Orr *et al.*, 2005]. However, biological feedbacks such as a reduction in biogenic calcification or enhanced calcite dissolution in the shallow water column or shallow marine sediments may increase the alkalinity of the upper ocean over the next 100 years. Over longer time scales, increased mineral weathering will provide the oceans with an additional input of alkalinity that will enhance their capacity to store  $\text{CO}_2$ .

[9] Roger Revelle and Hans Suess were the first to realize that the amount of  $\text{CO}_2$  the oceans are able to accumulate is limited [Revelle and Suess, 1957]. The fractional change in  $[\text{CO}_2]$  over the fractional change in DIC has since been referred to as the Revelle factor, or R [Broecker *et al.*, 1979]:

$$R = \frac{\partial \ln[\text{CO}_2]}{\partial \ln \text{DIC}} \quad (6)$$

where the partial differentials indicate that other state variables such as alkalinity are kept constant as DIC changes ( $p\text{CO}_2$  and  $[\text{CO}_2]$  being proportional to each other, the Revelle factor can be defined equivalently as  $R = \partial \ln p\text{CO}_2 / \partial \ln \text{DIC}$ ). As formulated, the Revelle factor quantifies the ocean's sensitivity to an increase in atmospheric  $\text{CO}_2$ . Given their understanding of the surface ocean properties in their day, Revelle and Suess calculated that R had a value of about 10. Because of an improved global data set we know that the Revelle factor currently ranges from about 9 in low-latitude tropical waters up to 15 in the southern ocean off Antarctica and is about one unit higher than the preindustrial ocean because of the uptake of anthropogenic  $\text{CO}_2$  [Sabine *et al.*, 2004]. Although the Revelle factor has been invoked in many studies, it is typically reported as a modeled estimate [Goodwin *et al.*, 2007] or calculated from small variations in input parameters in numerical simulations [Sabine *et al.*, 2004]. Surprisingly, to our knowledge, no exact explicit formula for its value has ever been published (see below).

[10] Here we derive not only the Revelle factor, but also several other parameters quantifying the ability of ocean chemistry to resist change. In addition to calculating the sensitivity of  $[\text{CO}_2]$  to changes in DIC, we derive a parameter quantifying its response to changes in alkalinity. We also derive parameters quantifying the sensitivity of  $[\text{H}^+]$  and  $\Omega$  to changes in both DIC and alkalinity. The numerical values of these parameters and their variations upon changes in seawater composition, and thus with time and geographic location, provide insight into the ocean's response to future  $\text{CO}_2$  levels and the regions that may be most sensitive to ocean acidification.

## 2. Buffer Factors

[11] The carbonate and acid-base chemistry of the ocean is defined by two conservative quantities, DIC and alkalinity:

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (7)$$

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] - [\text{H}^+] + [\text{OH}^-] \quad (8)$$

For this application the conjugate bases of other weak acids, which contribute to alkalinity besides bicarbonate, carbonate, borate, and water are negligible in seawater. To derive an analytical solution for the change in  $[\text{CO}_2]$  relative to the change in DIC, we take advantage of the fact that both DIC and Alk can be written as explicit functions of  $[\text{H}^+]$  and  $[\text{CO}_2]$  by introducing the appropriate mass laws for the acid-base reactions of carbonate and borate:

$$\text{DIC} = [\text{CO}_2] + \frac{K_{a1}[\text{CO}_2]}{[\text{H}^+]} + \frac{K_{a1}K_{a2}[\text{CO}_2]}{[\text{H}^+]^2} \quad (9)$$

$$\text{Alk} = \frac{K_{a1}[\text{CO}_2]}{[\text{H}^+]} + 2\frac{K_{a1}K_{a2}[\text{CO}_2]}{[\text{H}^+]^2} + \frac{B_{\text{tot}}K_{\text{hb}}}{(K_{\text{hb}} + [\text{H}^+])} - [\text{H}^+] + \frac{K_w}{[\text{H}^+]} \quad (10)$$

**Table 1.** Buffer Factors<sup>a</sup>

Response to Change in DIC	Response to Change in Alk
$\gamma_{\text{DIC}} = \left( \frac{\partial \ln[\text{CO}_2]}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C^2}{S}$	$\gamma_{\text{Alk}} = \left( \frac{\partial \ln[\text{CO}_2]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2 - \text{DIC} \times S}{\text{Alk}_C}$
$\beta_{\text{DIC}} = \left( \frac{\partial \ln[\text{H}^+]}{\partial \text{DIC}} \right)^{-1} = \frac{\text{DIC} \times S - \text{Alk}_C^2}{\text{Alk}_C}$	$\beta_{\text{Alk}} = \left( \frac{\partial \ln[\text{H}^+]}{\partial \text{Alk}} \right)^{-1} = \frac{\text{Alk}_C^2}{\text{DIC}} - S$
$\omega_{\text{DIC}} = \left( \frac{\partial \ln \Omega}{\partial \text{DIC}} \right)^{-1} = \text{DIC} - \frac{\text{Alk}_C \times P}{[\text{HCO}_3^-]}$	$\omega_{\text{Alk}} = \left( \frac{\partial \ln \Omega}{\partial \text{Alk}} \right)^{-1} = \text{Alk}_C - \frac{\text{DIC}[\text{HCO}_3^-]}{P}$

<sup>a</sup>Where  $S = [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{K_{hb} + [\text{H}^+]}$ ;  $P = 2[\text{CO}_2] + [\text{HCO}_3^-]$ ;  $\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ ;  $\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ; and  $\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] - [\text{H}^+] + [\text{OH}^-]$ . DIC, dissolved inorganic carbon concentration; Alk, alkalinity.

Where  $K_{a1}$  and  $K_{a2}$  are the first and second acidity constants for  $\text{CO}_2$  in seawater,  $K_{hb}$  is the acidity constant for boric acid,  $K_w$  is the ion product of water, and  $B_{tot}$  is the total concentration of boron in seawater which we take as constant. (To calculate the buffer factors in various oceanic locations, we take into account the variations of  $B_{tot}$  with salinity [Uppström, 1974]; see below.) The partial differentials of these equations with respect to  $[\text{CO}_2]$  and  $[\text{H}^+]$  are easily calculated, yielding the total differentials of DIC and Alk, which can be written in matrix notation:

$$\begin{pmatrix} d\text{DIC} \\ d\text{Alk} \end{pmatrix} = \mathbf{J} \begin{pmatrix} d[\text{CO}_2] \\ d[\text{H}^+] \end{pmatrix} \quad (11)$$

where the Jacobian  $\mathbf{J}$  is defined as

$$\mathbf{J} = \begin{pmatrix} \frac{\partial \text{DIC}}{\partial [\text{CO}_2]} & \frac{\partial \text{DIC}}{\partial [\text{H}^+]} \\ \frac{\partial \text{Alk}}{\partial [\text{CO}_2]} & \frac{\partial \text{Alk}}{\partial [\text{H}^+]} \end{pmatrix} \quad (12)$$

and

$$\begin{pmatrix} d[\text{CO}_2] \\ d[\text{H}^+] \end{pmatrix} = \mathbf{J}^{-1} \begin{pmatrix} d\text{DIC} \\ d\text{Alk} \end{pmatrix} \quad (13)$$

The inverse of the Jacobian is made up of the four partial derivatives:  $\partial[\text{CO}_2]/\partial \text{DIC}$ ,  $\partial[\text{CO}_2]/\partial \text{Alk}$ ,  $\partial[\text{H}^+]/\partial \text{DIC}$ , and  $\partial[\text{H}^+]/\partial \text{Alk}$ . A similar method can be used to derive  $\partial\Omega/\partial \text{DIC}$  and  $\partial\Omega/\partial \text{Alk}$ . These six parameters quantify the differential change in ocean chemistry as a result of small changes in DIC and Alk. To scale these changes, it is practical to express them as fractional change in  $[\text{CO}_2]$ ,  $[\text{H}^+]$ , and  $\Omega$  (e.g.,  $(1/[\text{CO}_2]) \times \partial[\text{CO}_2]/\partial \text{DIC} = \partial \ln[\text{CO}_2]/\partial \text{DIC}$ ). Additionally, for consistency with the traditional expressions of buffer factors, we use here the inverse of these partial derivatives, which, as written, quantify the sensitivity of the chemistry of the system to changes in DIC or Alk. For example, the ocean's capacity to buffer changes in  $[\text{CO}_2]$  due to the accumulation of  $\text{CO}_2$  from the atmosphere (increasing DIC at constant Alk) is quantified by

$$\gamma_{\text{DIC}} = (\partial \ln[\text{CO}_2]/\partial \text{DIC})^{-1} \quad (14)$$

In the same way we define

$$\gamma_{\text{Alk}} = (\partial \ln[\text{CO}_2]/\partial \text{Alk})^{-1} \quad (15)$$

$$\beta_{\text{DIC}} = (\partial \ln[\text{H}^+]/\partial \text{DIC})^{-1} \quad (16)$$

$$\beta_{\text{Alk}} = (\partial \ln[\text{H}^+]/\partial \text{Alk})^{-1} \quad (17)$$

$$\omega_{\text{DIC}} = (\partial \ln \Omega/\partial \text{DIC})^{-1} \quad (18)$$

$$\omega_{\text{Alk}} = (\partial \ln \Omega/\partial \text{Alk})^{-1} \quad (19)$$

[12] Note that since  $[\text{Ca}^{2+}]$  and the solubility products of  $\text{CaCO}_3(\text{s})$  are invariant with changes in DIC or Alk,  $\partial \ln \Omega/\partial \text{DIC} = \partial \ln[\text{CO}_3^{2-}]/\partial \text{DIC}$  and  $\partial \ln \Omega/\partial \text{Alk} = \partial \ln[\text{CO}_3^{2-}]/\partial \text{Alk}$ . The buffer factors, thus defined, have dimensions of moles per liter (or moles per kilogram) and quantify the ability of the system to resist change. Table 1 presents the explicit expressions of the six buffer factors as a function of the concentrations of the hydrogen ion and the carbonate and borate species in solution, calculated from the inversion of the Jacobian given in Text S1.<sup>1</sup> The values of  $\gamma_{\text{Alk}}$  and  $\beta_{\text{Alk}}$  are negative, while  $\omega_{\text{Alk}}$  is positive because the addition of strong base to seawater decreases  $[\text{CO}_2]$  and  $[\text{H}^+]$  but increases  $[\text{CO}_3^{2-}]$ ; likewise,  $\gamma_{\text{DIC}}$  and  $\beta_{\text{DIC}}$  are positive while  $\omega_{\text{DIC}}$  is negative because adding  $\text{CO}_2$  to seawater increases  $[\text{CO}_2]$  and  $[\text{H}^+]$  but decreases  $[\text{CO}_3^{2-}]$ . Note that a simplifying assumption that the total borate concentration is constant reduces the problem to two independent state variables, yielding a  $2 \times 2$  Jacobian matrix. However, the general problem with the total borate concentration as an independent state variable can be solved in exactly the same manner since a  $3 \times 3$  matrix also has a reasonably simple explicit inverse.

[13] Before examining the numerical values of the various buffer factors, a perusal of the formulae of Table 1 yields

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008GB003407.

some useful insights. First, we note that the parameter  $\beta_{\text{Alk}}$ , defined as

$$\beta_{\text{Alk}} = (\partial \ln[\text{H}^+] / \partial \text{Alk})^{-1} \quad (20)$$

measures the resistance to change of the hydrogen ion concentration (or activity) when alkalinity changes at constant DIC, i.e., upon addition of a strong base. It is thus directly related to the traditional buffer capacity of the system,  $\beta_{\text{H}}$ , which quantifies the resistance to change of the pH of a chemical system to additions of strong acid or base, TOTH [Morel and Hering, 1993]:

$$\beta_{\text{H}} = -(\partial \text{pH} / \partial \text{TOTH})^{-1} = -2.3\beta_{\text{Alk}} \quad (21)$$

[14] Second, we note that  $\beta_{\text{DIC}}$  is identical to  $-\gamma_{\text{Alk}}$ :

$$\partial \ln[\text{H}^+] / \partial \text{DIC} = -\partial \ln[\text{CO}_2] / \partial \text{Alk} \quad (22)$$

This curiously simple result is not particularly intuitive but we do not think it is particularly profound either; it just is.

[15] Third, the traditional Revelle factor,  $R$ , can be calculated directly from  $\gamma_{\text{DIC}}$ :

$$R = \text{DIC} / \gamma_{\text{DIC}} \quad (23)$$

Since Revelle and Suess first introduced the concept of an oceanic carbon buffer, several methods have been used for calculating or estimating  $R$  [Broecker et al., 1979; Sarmiento and Gruber, 2006]. Broecker et al. stated that the Revelle factor is a function of the ratio of DIC to alkalinity. By examining the explicit expression of  $R$ , we can demonstrate that this is mathematically true under the assumption that the minor species borate, proton, and hydroxide can be neglected compared to bicarbonate. In that case the formula for  $\gamma_{\text{DIC}}$  simplifies to

$$R = \frac{\text{DIC}}{\gamma_{\text{DIC}}} = \frac{\text{DIC}}{\text{DIC} - \frac{\text{Alk}_C^2}{[\text{HCO}_3^-] + 4[\text{CO}_3^{2-}]}} \quad (24)$$

The DIC term then cancels out in the expression of  $R$  (for example, by expressing all the concentrations as a function of  $[\text{CO}_2]$  and  $[\text{H}^+]$  and factoring out  $[\text{CO}_2]$ ). The remaining expression for  $R$  is only a function of  $[\text{H}^+]$ :

$$R = \frac{\left(1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2}\right)}{\left(1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2}\right) - \frac{\left(\frac{K_{a1}}{[\text{H}^+]} + \frac{2K_{a1}K_{a2}}{[\text{H}^+]^2}\right)}{\left(\frac{K_{a1}}{[\text{H}^+]} + \frac{4K_{a1}K_{a2}}{[\text{H}^+]^2}\right)}} \quad (25)$$

Since  $[\text{H}^+]$  is only a function of DIC/Alk when the carbonate terms dominate the expression of alkalinity,  $R$  is also only a function of DIC/Alk when the borate, proton, and hydroxide concentrations can be neglected. More recently, Sarmiento and Gruber used several simplifying

assumptions to derive an explicit expression of the Revelle factor, and of  $\partial \ln[\text{CO}_2] / \partial \ln \text{Alk}$  [Sarmiento and Gruber, 2006]. The results of their derivation provide approximate values of the parameters over the pH range 7.9 to 8.6 with errors on the order of 20–30%. Unfortunately, these two formulae are not applicable under conditions where  $\text{Alk} \approx \text{DIC}$  (i.e., in the neighborhood of  $\text{pH} = 7.5$ ), because the term (Alk-DIC) appears in the denominator of the approximate expressions of both  $\gamma_{\text{DIC}}$  and  $\gamma_{\text{Alk}}$ .

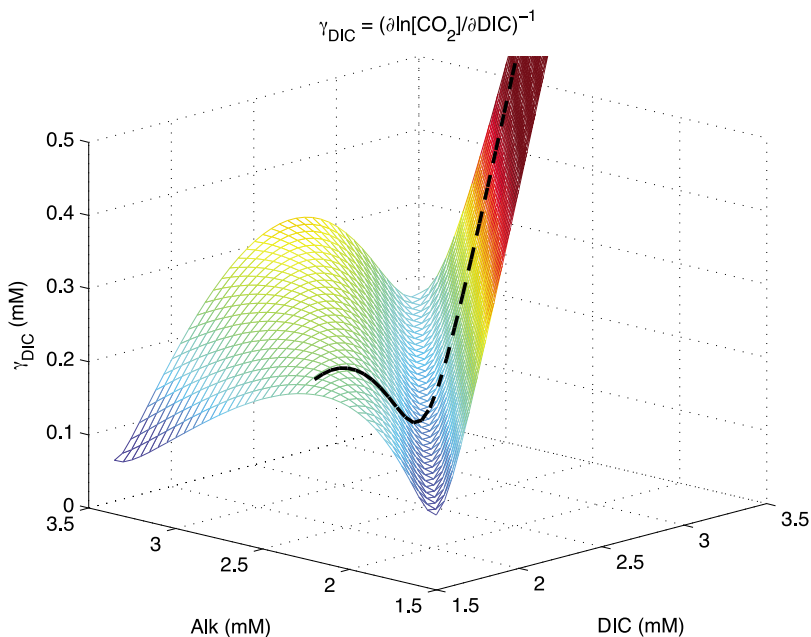
[16] Broecker et al. [1979] as well as Sarmiento and Gruber [2006] neglected borate in their approximations of the Revelle factor. At first glance this is understandable since borate only accounts for a few percent of seawater alkalinity. However, we shall see that borate actually contributes nearly a quarter of the buffering of seawater for pH above 7.5. Finally, an exact derivation of the Revelle factor was provided by Zeebe and Wolf-Gladrow [2001]; unfortunately, their final formula is made unusable by a ruinous typographical error.

### 3. Variations in Buffering With DIC and Alkalinity

[17] A three-dimensional representation of the value of  $\gamma_{\text{DIC}}$  as a function of DIC and Alk (Figure 1) shows two starkly different trends separated by a conspicuous trough near the  $\text{DIC} = \text{Alk}$  line. Low  $\gamma_{\text{DIC}}$  values imply low buffering capacity and larger changes in  $[\text{CO}_2]$  for a given change in DIC. When Alk is larger than DIC,  $\gamma_{\text{DIC}}$  varies between 0.1 and 0.3 mM with a broad shoulder at midvalues of Alk and DIC. When DIC is larger than Alk,  $\gamma_{\text{DIC}}$  increases sharply with DIC with a lesser dependence on Alk.

[18] A convenient comparison among the buffer factors is shown in Figure 2 where the absolute values for all six parameters are plotted as a function of DIC for a constant Alk (= 2.25 mM, a value relevant for much of the surface ocean today), along the track indicated in Figure 1. Remarkably, all the buffer factors have roughly similar absolute values and similar qualitative behavior, all reaching a minimum when  $\text{DIC} \approx \text{Alk}$  ( $\text{pH} \sim 7.5$ ). In this region of low buffer capacity, all six buffer factors have nearly the same absolute value ( $\approx 0.12$  mM), signifying that  $[\text{CO}_2]$ ,  $[\text{H}^+]$ , and  $\Omega$  all experience roughly the same percentage change in response to similar changes in DIC or Alk. At low DIC all six parameters have distinct values while at higher DIC,  $\gamma_{\text{DIC}}$ ,  $\gamma_{\text{Alk}}$ ,  $\beta_{\text{DIC}}$ , and  $\omega_{\text{DIC}}$  are effectively identical. A close examination of the values of these six parameters and of why they vary with pH as they do provides insight into the buffering mechanisms in seawater.

[19] First consider  $\gamma_{\text{Alk}}$ ,  $\beta_{\text{Alk}}$ , and  $\omega_{\text{Alk}}$ . Why should a small addition of strong base, or acid, yield relative changes of the same magnitude in the absolute values of  $[\text{CO}_2]$ ,  $[\text{H}^+]$ , and  $\Omega$  (or equivalently  $[\text{CO}_3^{2-}]$ )? Over the pH range of Figure 2,  $\text{HCO}_3^-$  is the dominant carbonate species, such that a small addition of base or acid, which has a substantial effect on  $[\text{H}^+]$ , can have only a small effect on  $[\text{HCO}_3^-]$ . For a fixed  $[\text{HCO}_3^-]$ ,  $[\text{CO}_2]$  is proportional to  $[\text{H}^+]$ , and  $[\text{CO}_3^{2-}]$  inversely proportional to it. All three parameters thus experience nearly the same relative change when base or acid is added and  $\gamma_{\text{Alk}}$ ,  $\beta_{\text{Alk}}$ , and  $\omega_{\text{Alk}}$  have similar magni-

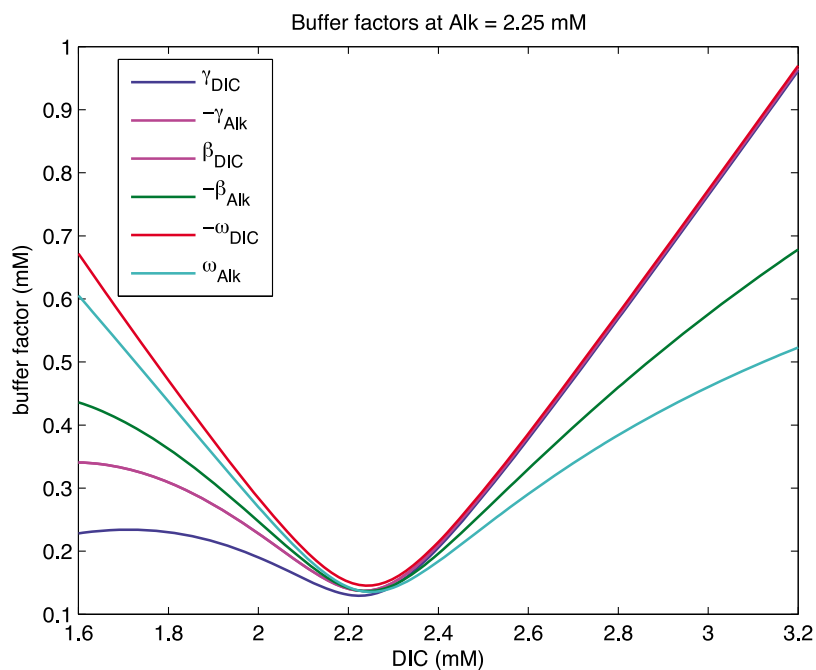


**Figure 1.** Three-dimensional surface of dissolved inorganic carbon concentration (DIC) values across a range of DIC and alkalinity (Alk) values with relevance to the natural environment. The dashed line indicates an Alk of 2.25 mM, across which Figure 2 shows values for all six buffer factors.

tudes. The reason why  $\beta_{\text{DIC}}$ ,  $\gamma_{\text{DIC}}$ , and  $\omega_{\text{DIC}}$  also have similar magnitudes in that pH range is that the addition of a small concentration of  $\text{CO}_2$  (which increases DIC without changing Alk) is equivalent to adding bicarbonate and a strong acid simultaneously. The added bicarbonate has a relatively small effect on the  $\text{HCO}_3^-$  concentration, but the

strong acid has a substantial effect on  $[\text{H}^+]$ . Thus, a  $\text{CO}_2$  addition is nearly the same as a strong acid addition.

[20] The reason for the minimum buffering capacity when  $\text{DIC} \approx \text{Alk}$  is easiest to understand in terms of the traditional acid-base buffer capacity of a chemical system. Recall that  $\beta_{\text{Alk}} = -\beta_{\text{H}}/2.3$ , the buffer capacity of the system, which measures its ability to resist changes in



**Figure 2.** Absolute values of the six buffer factors at Alk = 2.25 mM, across a range of DIC from 1.6 mM to 3.2 mM.

$[H^+]$  upon the addition of strong acid or base. As is well-known, the buffer capacity of a weak acid solution is largest when the pH is close to the  $pK_a$  of the weak acid and is smallest farthest from the  $pK_a$ . In seawater, the minimum buffer capacity due to the carbonate system occurs at a pH of about 7.5, halfway between the two  $pK_a$ 's. (Because of the presence of borate, the actual minimum occurs at a slightly lower pH, when  $DIC = Alk$ .) Near this pH,  $CO_2$ ,  $CO_3^{2-}$ , and  $B(OH)_4^-$  are all present at very low concentrations, and even a small addition of acid or base reacting with  $HCO_3^-$  produces a significant change in concentration of  $CO_2$  or  $CO_3^{2-}$  and markedly changes the pH. According to the minor species theorem [Morel and Hering, 1993], a good approximation of the buffer capacity of a system at a pH away from the  $pK_a$ 's of the weak acids it contains is given by the sum of the species that are either protonated or deprotonated compared to the dominant species at that pH (times a factor of 2.3). In our system the approximate value of  $\beta_{Alk}$  is thus given by

$$\beta_{Alk} = -\beta_H/2.3 = -([CO_2] + [CO_3^{2-}] + [B(OH)_4^-]) \quad (26)$$

Tedious but trivial algebra shows that indeed the formulae of all the buffer factors of Table 1 are approximated by equation (26) (with the appropriate sign) when  $[CO_2]$  and  $[CO_3^{2-}]$  are small compared to  $[HCO_3^-]$ , and  $[B(OH)_4^-]$  is small compared to  $[B(OH)_3]$ . Equation (26) provides a convenient approximate value of all buffer factors when  $DIC \sim Alk$  and shows clearly why they increase at both lower and higher DIC/Alk ratio (higher and lower pH).

[21] Away from  $pH \sim 7.5$ , the effects on  $[H^+]$  of adding a strong acid or  $CO_2$  are not exactly the same:  $[H^+]$  is less sensitive to DIC increases (i.e.,  $CO_2$  addition) than to Alk decreases (i.e., strong acid addition) (Figure 2, right) ( $pH < 7.5$ ;  $|\beta_{DIC}| > |\beta_{Alk}|$ ) and more sensitive to DIC increases than to Alk decreases (Figure 2, left) ( $pH > 7.5$ ;  $|\beta_{DIC}| < |\beta_{Alk}|$ ). This reflects the weak diprotic acid character of  $CO_2$ , which releases less than one proton per molecule at  $pH < 7.5$  and more at  $pH > 7.5$ . In fact, a  $CO_2$  addition affects the pH of seawater in exactly the same way as the addition of any diprotic acid with the same  $pK_a$ . This reasonably intuitive result can be demonstrated mathematically by examination of the formulae in Table 1 which yield the relation

$$\beta_{Alk} = -\beta_{DIC} \times (Alk_C/DIC) \quad (27)$$

where the term  $Alk_C/DIC = ([HCO_3^-] + 2 [CO_3^{2-}])/DIC$  quantifies the number of protons released by  $CO_2$  at a given pH.

[22] At high pH (Figure 2, left), the differences among the buffer factors result in part from the larger than stoichiometric proton release from  $CO_2$  and in part from the fact that an addition of  $CO_2$ , unlike that of an acid, changes the DIC along with the pH. At low pH (Figure 2, right), there is very little  $CO_3^{2-}$  or  $B(OH)_4^-$  present for  $CO_2$  to react with, such that an addition of  $CO_2$  leads to a quantitative increase in  $[CO_2]$  (i.e.,  $\gamma_{DIC} = [CO_2]$ ). In other words, the buffering of a  $CO_2$  addition does not come from a chemical reaction but simply from its dilution into the existing  $CO_2$  pool. This process leaves  $[HCO_3^-]$  essentially unchanged so that  $[H^+]$

increases and  $[CO_3^{2-}]$  decreases proportionally ( $\beta_{DIC} = -\omega_{DIC} = \gamma_{DIC}$ ). For the same reason the bulk of the protons released by addition of a strong acid react with  $HCO_3^-$  rather than  $CO_3^{2-}$  or  $B(OH)_4^-$  and result also in a quantitative increase in  $[CO_2]$  ( $-\gamma_{Alk} = \gamma_{DIC}$ ). The concomitant decrease in  $[HCO_3^-]$  is the reason the corresponding increase in  $[H^+]$  and decrease in  $[CO_3^{2-}]$  are proportionally larger ( $-\beta_{Alk}$  and  $-\omega_{Alk} < \beta_{DIC}$ ).

#### 4. Buffer Capacity of the Contemporary Ocean

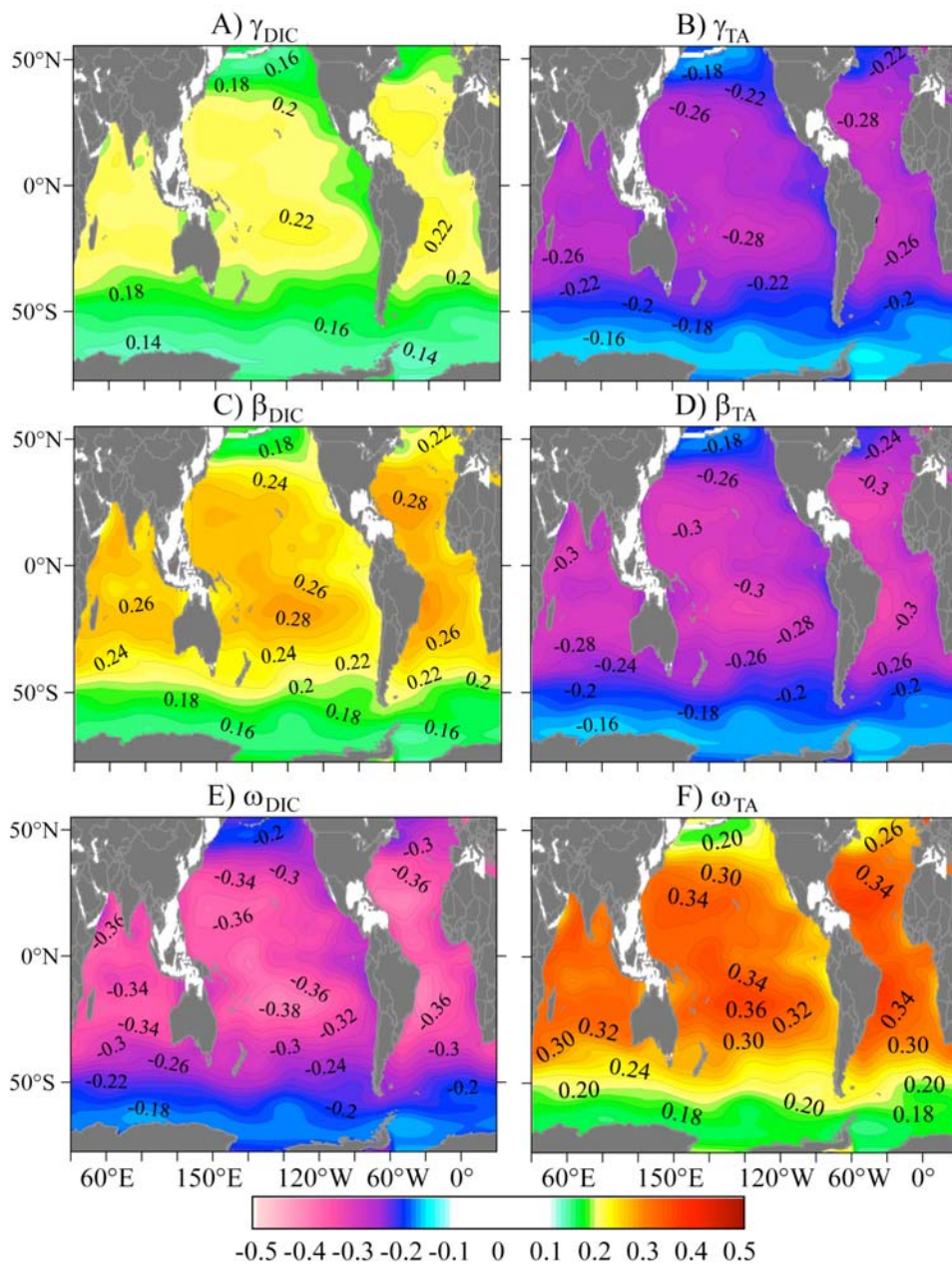
[23] Using the  $1^\circ \times 1^\circ$  gridded alkalinity and DIC fields from the GLODAP project [Key et al., 2004] together with annual mean temperature, salinity, and nutrient climatologies from the World Ocean Atlas 2005 [Locarnini et al., 2006; Antonov et al., 2006; Garcia et al., 2006], we can examine the buffer factor distributions for the contemporary ocean. The carbonate species needed for the equations in Table 1 were calculated using the CO2SYS computer program [Lewis and Wallace, 1998].

[24] In today's oceans, alkalinity is higher than DIC everywhere, with a ratio DIC/Alk ranging from 0.84 to 0.95 in the mixed layer. The values of  $\gamma_{DIC}$  in the surface ocean thus fall along the leading edge of the flat region to the left of the minimum in Figure 1. Lower in the mixed layer, where the ratio DIC/Alk approaches unity, the buffer factors, including  $\gamma_{DIC}$ , are near their minimum, signifying that the chemistry of these intermediate waters is particularly sensitive to increases in  $[CO_2]$ . The geographical variations in  $\gamma_{DIC}$  in surface waters (30 m) are illustrated in Figure 3a showing a contour map for the mid-1990s. The highest values ( $>0.22$  mM) are observed in the warm, stable, subtropical regions. These are areas where biological production has used up the macronutrients to draw down surface DIC resulting in low DIC/Alk ratios. High- $\gamma_{DIC}$  regions have the strongest buffering capacity and therefore the smallest change in dissolved  $CO_2$  concentration for a given change in DIC. Looking at it the other way, a high  $\gamma_{DIC}$  also implies that the subtropics have the greatest ability to take up carbon for a given atmospheric  $CO_2$  increase. The lowest buffer values ( $<0.15$ ) are observed in the Southern Ocean, south of  $50^\circ S$ , and in the subpolar North Pacific where biology is not able to use up the available macronutrients and upwelling/mixing processes bring up relatively high DIC/Alk waters from below. Buffer values are generally higher in the Atlantic relative to the Pacific and Indian because alkalinity concentrations are higher.

[25] The other five buffer factors show patterns similar to that of  $\gamma_{DIC}$  with low absolute values in the polar regions and high absolute values near the tropics (Figures 3a–3f). So the pH and  $\Omega$  of high-latitude waters are generally more susceptible to changes as a result of atmospheric  $CO_2$  uptake or decrease in calcification. The importance of these variations is best illustrated by calculating the relative variations in  $[CO_2]$ ,  $[H^+]$ , and  $\Omega$  upon change in DIC and Alk at particular locations. For example, the change in  $CO_2$  concentration can be estimated by the formula:

$$\frac{\Delta[CO_2]}{[CO_2]} = \frac{\Delta DIC}{\gamma_{DIC}} + \frac{\Delta Alk}{\gamma_{Alk}} \quad (28)$$





**Figure 3.** Maps of (a)  $\gamma_{\text{DIC}}$ , (b)  $\gamma_{\text{Alk}}$ , (c)  $\beta_{\text{DIC}}$ , (d)  $\beta_{\text{Alk}}$ , (e)  $\omega_{\text{DIC}}$ , and (f)  $\omega_{\text{Alk}}$  in the surface ocean (30 m) for a nominal year 1994.

Similar formulae quantify the relative variations in  $[\text{H}^+]$  and  $\Omega$ . If we consider, for example, an increase in DIC of  $10 \mu\text{M}$  resulting from the uptake of anthropogenic  $\text{CO}_2$  ( $\Delta\text{Alk} = 0$ ),  $[\text{CO}_2]$  and  $[\text{H}^+]$  would increase by about 4.6% and 3.7%, respectively, at the BATS station in the North Atlantic ( $64^\circ \text{W}$ ,  $31^\circ \text{N}$ ) or the HOT station in the North Pacific ( $158^\circ \text{W}$ ,  $22^\circ \text{N}$ ), while  $\Omega$  would decrease by about 2.7%. As is evident from Figure 2,  $[\text{CO}_2]$  is thus the most sensitive of the three parameters, and  $\Omega$  is the least sensitive. In comparison, the same DIC increase at a Southern Ocean site ( $135^\circ \text{E}$ ,  $60^\circ \text{S}$ ) would lead to increases of 6.8% and 6.1% in  $[\text{CO}_2]$  and  $[\text{H}^+]$ , respectively, and a decrease of 5.4% in  $\Omega$ .

[26] The differences among the buffer factors become important when both DIC and Alk change. For example, a hypothetical decrease in calcification, resulting effectively in a  $10 \mu\text{M}$  increase in DIC and a  $20 \mu\text{M}$  increase in Alk at BATS and HOT would lead to practically identical magnitude of changes of about 2.9% in all three parameters,  $[\text{CO}_2]$ ,  $[\text{H}^+]$  (which would decrease), and  $\Omega$  (which would increase). The smaller differences between  $\omega_{\text{DIC}}$  and  $\omega_{\text{Alk}}$  compared to that between  $\gamma_{\text{DIC}}$  and  $\gamma_{\text{Alk}}$  effectively compensates for the larger absolute values of  $\omega_{\text{DIC}}$  and  $\omega_{\text{Alk}}$  compared to  $\gamma_{\text{DIC}}$  and  $\gamma_{\text{Alk}}$ . Note that the decrease in  $[\text{CO}_2]$  is only 2/3 of what it would be if the two buffer factors  $\gamma_{\text{DIC}}$  and  $\gamma_{\text{Alk}}$  had equal absolute values. At the Southern Ocean

site the corresponding changes in the three parameters would be uniformly greater, at about 5.6%.

## 5. Buffer Factors in the Past and Future

[27] The buffer values for the preindustrial ocean were calculated by subtracting the anthropogenic  $\text{CO}_2$  values of Sabine *et al.* [2004] from the GLODAP measured DIC values. Buffer factors for the oceans in a world with double preindustrial atmospheric  $\text{CO}_2$  (560 ppm) and triple atmospheric  $\text{CO}_2$  (840 ppm) were estimated by assuming that the surface ocean would increase at approximately the same rate as the atmosphere [Takahashi *et al.*, 2002]. The modern surface (30 m level in the GLODAP data set) DIC and Alk were used to calculate surface water  $p\text{CO}_2$  for a nominal year 1994 when atmospheric  $\text{CO}_2$  was 358 ppm. The 1994 surface water  $p\text{CO}_2$  was then increased by  $560 - 358 = 202$  ppm for the  $2\times$  case or  $840 - 358 = 482$  ppm for the  $3\times$  case and used with Alk to calculate the  $2\times$  and  $3\times$  DIC values.

[28] Not surprisingly, buffer factors in the preindustrial ocean were only slightly lower than at present (see Text S1). However, as the ratio DIC/Alk in the oceans increases in response to the uptake of atmospheric  $\text{CO}_2$ , the buffer factors will decrease rapidly, essentially falling into the trough of Figure 1. The net result will be a less efficient absorption of  $\text{CO}_2$  from the atmosphere and a greater sensitivity of  $[\text{CO}_2]$ ,  $[\text{H}^+]$  and  $\Omega$  to environmental changes. For  $p\text{CO}_2 = 2\times$  preindustrial, the buffer factors will decrease by 20–40% and again as much for  $p\text{CO}_2 = 3\times$  preindustrial, but the decreases are not the same for all the buffer factors, and they also vary with location (see Text S1).

[29] In general, as shown in Figure 2, the larger buffer factors decrease the most in magnitude as the ratio DIC/Alk increases. For example, at BATS and HOT, for a  $p\text{CO}_2 = 3\times$  preindustrial,  $\gamma_{\text{DIC}}$  would decrease by some 22% compared to present,  $\beta_{\text{DIC}}$  would decrease by 30%, and  $\omega_{\text{DIC}}$  would decrease by about 40% in absolute value (see Text S1). At high latitudes, where the ratio DIC/Alk is already high, the buffer factors reach their minimum values (all  $\sim 0.12$  mM) when  $p\text{CO}_2 = 3\times$  preindustrial. So in such an ocean, the chemistry of surface seawater becomes much more sensitive to local variations in DIC and Alk. For example diurnal and seasonal variations in pH and  $\Omega$  caused by photosynthesis and respiration would be increased by more than 40% and 60%, respectively, compared to present. For the same reason, export production would play an increasingly efficient role in controlling  $[\text{CO}_2]$  at the surface. As a result, if global change were to either increase [Hein and Sand-Jensen, 1997; Levitan *et al.*, 2007] or decrease [Behrenfeld *et al.*, 2006] ocean productivity, it might result in a significant negative or positive feedback for  $\text{CO}_2$  concentration in surface seawater and ultimately have a large effect on oceanic  $\text{CO}_2$  storage.

## 6. Use of Buffer Factors

[30] Buffer factors provide a convenient means to calculate changes in water chemistry under a variety of experimental and natural conditions. For example, the changes in  $[\text{CO}_2]$  and pH due to the growth of phytoplankton in a culture medium or in onboard incubations can be readily

calculated, for either calcifying or noncalcifying organisms. They can also be used to design experiments in which the variations in  $[\text{CO}_2]$ , pH or  $\Omega$  are minimized [Shi *et al.*, 2009].

[31] Buffer factors may also be useful in conjunction with model simulations such as global circulation models. To test the range of uncertainty in GCM simulations requires many runs, since there are typically at least several adjustable parameters, the effects of which need to be explored in various combinations. A quantitative understanding of the sensitivity of ocean chemistry to changes in DIC and Alk provided by the buffer factors may help guide the choices of combinations of parameters most likely to yield differences in the results of the simulations. Likewise, the buffer factors can be useful for developing simplified models where simplifications and predefined relationships are needed to make the models run efficiently.

[32] Finally, buffer factors provide information on the relative sensitivities of different carbon parameters to future climate change. The sharp decrease in all the buffer factors as we approach a world where  $\text{DIC} \approx \text{Alk}$  means that ocean chemistry changes will continue to accelerate in the foreseeable future. As the scientific community considers how to deal with the issues of ocean acidification, it is helpful to understand the differences in the sensitivities of  $[\text{CO}_2]$ , pH, and  $\Omega$  to future changes in DIC and Alk. Properly used, this information can help guide the development of ocean acidification experiments as well as a proper ocean carbon monitoring program.

[33] **Note added in proof.** After implementing the final corrections of this paper, we have been made aware of relevant prior publications that foreshadow some of our results. One by Sundquist *et al.* [1979] gives a correct formula for the Revelle factor and discusses its variations with temperature based on GEOSECS data. Another by Frankignoulle [1994] derives complex formulae of buffer factors that are essentially equivalent to those presented here and discusses their sensitivity to pH.

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