

A complete set of buffer factors for acid/base CO₂ system in seawater

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Abstract

A set of buffer factors is proposed which allows to compute changes of pH and pCO₂ resulting from an input or an output of bicarbonate, carbonate and proton ions in seawater. Results are compared to the well-known buffer factors that describe a dissolved CO₂ change (among which the Revelle factor $\beta = d\ln(p\text{CO}_2)/d\ln|\Sigma\text{CO}_2|$). It is pointed out that the actual β value can be quite different from the usual one (about 10) when other processes than air–sea exchanges are involved. Two examples of application are discussed: (1) A relationship is proposed to estimate $\beta = d\ln(p\text{CO}_2)/d\ln|\Sigma\text{CO}_2|$ by taking into account simultaneous organic and inorganic carbon metabolism: $\beta = -7.02 + 0.186\%C_{\text{org}}$ ($r^2 = 0.9994$), where $\%C_{\text{org}}$ is the percentage of carbon uptake for organic metabolism, (2) A relationship is proposed to calculate the amount of CO₂ that has to be exchanged with the atmosphere when adding strong acid to an equilibrated open seawater system.

1. Introduction

The understanding of the CO₂ system chemical dynamic is of fundamental importance to describe the effect of any biological, geological or chemical oceanic process on the global carbon cycle. Because the penetration of the man-induced atmospheric CO₂ excess into the ocean is of prime importance, some analytical expressions have been developed to describe the effect of dissolved CO₂ input/output to seawater: the chemical buffer factor ($d|\Sigma\text{CO}_2|/dp\text{H}$, Riley and Skirrow, 1975), but mainly the *homogenous Revelle factor* ($d\ln(p\text{CO}_2)/d\ln|\Sigma\text{CO}_2|$, Sundquist and Plummer, 1981). Those buffer factors presume no interaction with the solid carbonated phase (the total alkalinity, T_{alk} , is assumed to be

constant). While they appear to be efficient to describe air–sea CO₂ exchanges in the open ocean, no expression has so far been proposed to calculate the effect on CO₂ dynamics, in the seawater chemical context, of partial exchange with the solid phase. This could help in studying CO₂ dynamics involved during some major oceanic processes as deep sea carbonate dissolution/precipitation as well as calcification occurring during some phytoplanktonic bloom (e.g. coccolithophore) or coral reefs.

In this paper, I propose some equations that allow to calculate changes of both pH and pCO₂ for any input/output of bicarbonate ion (HCO₃⁻), carbonate ion (CO₃²⁻) as well as the so-called proton (H₃O⁺). Those calculations are made by taking into account the buffer effect of borate.

2. Equations

The chemical buffer factor Φ , that describes pH variation related to any input or output of one among the three inorganic carbon species (dissolved CO_2 , bicarbonate and carbonate ions) can be written (see e.g. Riley and Skirrow, 1975):

$$\begin{aligned}\Phi &= \frac{dpH}{d|\Sigma\text{CO}_2|} \\ &= - \left\{ |\text{H}_3\text{O}^+| \ln(10) \frac{d|\Sigma\text{CO}_2|}{d|\text{H}_3\text{O}^+|} \right\}^{-1} \\ &= - \left\{ |\text{H}_3\text{O}^+| \ln(10) \left[\frac{d|\text{CO}_2|}{d|\text{H}_3\text{O}^+|} + \frac{d|\text{HCO}_3^-|}{d|\text{H}_3\text{O}^+|} \right. \right. \\ &\quad \left. \left. + \frac{d|\text{CO}_3^{2-}|}{d|\text{H}_3\text{O}^+|} \right] \right\}^{-1} \quad (1)\end{aligned}$$

where $|\text{CO}_2|$, $|\text{HCO}_3^-|$, $|\text{CO}_3^{2-}|$, $|\Sigma\text{CO}_2|$ and $|\text{H}_3\text{O}^+|$ are respectively the total concentrations of dissolved CO_2 , bicarbonate ion, carbonate ion, total inorganic carbon and proton.

The homogeneous buffer factor β , which depicts relative variations of partial CO_2 pressure and total inorganic carbon can then be given by:

$$\begin{aligned}\beta &= \frac{d \ln(p\text{CO}_2)}{d \ln |\Sigma\text{CO}_2|} \\ &= \frac{|\Sigma\text{CO}_2|}{|\text{CO}_2|} \frac{d|\text{CO}_2|}{d|\text{H}_3\text{O}^+|} \frac{d|\text{H}_3\text{O}^+|}{d|\Sigma\text{CO}_2|} \\ &= -|\text{H}_3\text{O}^+| \ln(10) \frac{|\Sigma\text{CO}_2|}{|\text{CO}_2|} \frac{d|\text{CO}_2|}{d|\text{H}_3\text{O}^+|} \Phi \quad (2)\end{aligned}$$

where $p\text{CO}_2$ is the partial CO_2 pressure in seawater.

According to MacIntyre (1978):

$$\begin{aligned}\frac{d|\text{HCO}_3^-|}{d|\text{H}_3\text{O}^+|} &= \frac{2K_2|A| + |\text{H}_3\text{O}^+|(|\text{H}_3\text{O}^+| + 2K_2) \frac{d|A|}{d|\text{H}_3\text{O}^+|}}{(|\text{H}_3\text{O}^+| + 2K_2)^2}, \\ \frac{d|\text{CO}_3^{2-}|}{d|\text{H}_3\text{O}^+|} &= \frac{-K_2|A| + K_2(2K_2 + |\text{H}_3\text{O}^+|) \frac{d|A|}{d|\text{H}_3\text{O}^+|}}{(|\text{H}_3\text{O}^+| + 2K_2)^2}\end{aligned}$$

and

$$\frac{d|\text{CO}_2|}{d|\text{H}_3\text{O}^+|} = \frac{|A||\text{H}_3\text{O}^+|}{(|\text{H}_3\text{O}^+| + 2K_2)K_1} + \frac{|\text{H}_3\text{O}^+|}{K_1} \frac{d|\text{HCO}_3^-|}{d|\text{H}_3\text{O}^+|} \quad (3)$$

where $|A|$ is the carbonate alkalinity ($|\text{HCO}_3^-| + 2|\text{CO}_3^{2-}|$), K_1 and K_2 are dissociation constants of carbonic acid. The resolution of the above equations is thus possible for input/output of any inorganic carbon species if one can find an expression that describes $d|A|/d|\text{H}_3\text{O}^+|$ during the considered chemical scenario. In the following equations, buffer factors will have subscripts (D, B or C) that will respectively correspond to input/output of dissolved CO_2 , bicarbonate and carbonate. A complete list of used symbols is available at the end of the paper.

2.1. Input/output of dissolved CO_2

Because any input/output of dissolved CO_2 does not change the total alkalinity (Talk), both Φ_D and β_D can be calculated in this case using the constant total alkalinity concept ($|A| + |B(\text{OH})_4^-| + |\text{OH}^-| - |\text{H}_3\text{O}^+| = \text{constant}$, Sundquist and Plummer, 1981):

$$\begin{aligned}\frac{d|A|}{d|\text{H}_3\text{O}^+|} &= - \frac{d|B(\text{OH})_4^-|}{d|\text{H}_3\text{O}^+|} - \frac{d|\text{OH}^-|}{d|\text{H}_3\text{O}^+|} \\ &\quad + \frac{d|\text{H}_3\text{O}^+|}{d|\text{H}_3\text{O}^+|} \quad (4)\end{aligned}$$

whith,

$$\frac{d|B(\text{OH})_4^-|}{d|\text{H}_3\text{O}^+|} = - \frac{K_B|TB|}{(|\text{H}_3\text{O}^+| + K_B)^2}$$

and

$$\frac{d|\text{OH}^-|}{d|\text{H}_3\text{O}^+|} = - \frac{K_H}{|\text{H}_3\text{O}^+|^2}$$

where $|B(\text{OH})_4^-|$, $|TB|$ and $|\text{OH}^-|$ are respectively borate, total borate ($|B(\text{OH})_4^-| + |\text{H}_3\text{BO}_3|$) and hydroxyl concentrations, K_B and K_H are borate and water dissociation constants. When calculated in those conditions, β_D is often called the Revelle factor.

2.2. Input / output of carbonate or bicarbonate ions

The seawater chemical dynamics involved by an input/output of carbonate or bicarbonate ions can be described by:

$$\frac{d|\text{Talk}|}{d|\Sigma\text{CO}_2|} = X = \frac{d|A|}{d|\Sigma\text{CO}_2|} + \frac{d|\text{B(OH)}_4^-|}{d|\Sigma\text{CO}_2|} + \frac{d|\text{OH}^-|}{d|\Sigma\text{CO}_2|} - \frac{d|\text{H}_3\text{O}^+|}{d|\Sigma\text{CO}_2|} \quad (5)$$

where $X=2$ for carbonate and $X=1$ for bicarbonate input/output.

By multiplying both terms by $d|\Sigma\text{CO}_2|/d|\text{H}_3\text{O}^+|$, one get:

$$\frac{d|A|}{d|\text{H}_3\text{O}^+|} = X \frac{d|\Sigma\text{CO}_2|}{d|\text{H}_3\text{O}^+|} - \frac{d|\text{B(OH)}_4^-|}{d|\text{H}_3\text{O}^+|} - \frac{d|\text{OH}^-|}{d|\text{H}_3\text{O}^+|} + 1 \quad (6)$$

Because $d|\text{B(OH)}_4^-|/d|\text{H}_3\text{O}^+|$ and $d|\text{OH}^-|/d|\text{H}_3\text{O}^+|$ are known (see above) $d|A|/d|\text{H}_3\text{O}^+|$ can be introduced in Eq. (3) and then combined with Eq. (1) to yield:

$$\frac{d|\Sigma\text{CO}_2|}{d|\text{H}_3\text{O}^+|} = \left[K_2|A| + QV(|\text{H}_3\text{O}^+| + K_2) + \frac{|\text{H}_3\text{O}^+|}{K_1} \right] \times (|A|Q + 2K_2|A| + |\text{H}_3\text{O}^+|QV) / Q \times \left[Q - X \left(|\text{H}_3\text{O}^+| + K_2 + \frac{|\text{H}_3\text{O}^+|^2}{K_1} \right) \right]^{-1} \quad (7)$$

where,

$$Q = |\text{H}_3\text{O}^+| + 2K_2$$

and

$$V = \frac{K_B|TB|}{(|\text{H}_3\text{O}^+| + K_B)^2} + \frac{K_H}{|\text{H}_3\text{O}^+|^2} + 1 \quad (8)$$

Eq. (7) can then be introduced in Eq. (6) to calculate $d|A|/d|\text{H}_3\text{O}^+|$ and then both Φ_C and β_C (carbonate input/output), as well as Φ_B and β_B (bicarbonate input/output), using the suitable X value.

2.3. Input / output of H_3O^+ ion

Any input or output of strong acid (H_3O^+) will, according to the electronegativity condition, correspond respectively to a decrease or an increase of the total alkalinity ($|\text{Talk}| = |A| + |\text{B(OH)}_4^-| + |\text{OH}^-| - |\text{H}_3\text{O}^+|$). The chemical buffer factor, Φ_H , resulting from an input/output of H_3O^+ can thus be written:

$$\Phi_H = - \frac{dpH}{d|\text{Talk}|} = \left\{ |\text{H}_3\text{O}^+| \ln(10) \frac{d|\text{Talk}|}{d|\text{H}_3\text{O}^+|} \right\}^{-1} = \left\{ |\text{H}_3\text{O}^+| \ln(10) \left(\frac{d|A|}{d|\text{H}_3\text{O}^+|} + \frac{d|\text{B(OH)}_4^-|}{d|\text{H}_3\text{O}^+|} + \frac{d|\text{OH}^-|}{d|\text{H}_3\text{O}^+|} - \frac{d|\text{H}_3\text{O}^+|}{d|\text{H}_3\text{O}^+|} \right) \right\}^{-1} \quad (9)$$

Assuming $d|\Sigma\text{CO}_2|/d|\text{H}_3\text{O}^+| = 0$ in this chemical context, and using Park (1969) expressions for $|\text{CO}_2|$ and $|\text{CO}_3^-|$, one can calculate $d|A|/d|\text{H}_3\text{O}^+|$ from:

$$\frac{d|\text{HCO}_3^{2-}|}{d|\text{H}_3\text{O}^+|} = \frac{K_1(K_1K_2 - |\text{H}_3\text{O}^+|^2)|\Sigma\text{CO}_2|}{(|\text{H}_3\text{O}^+|^2 + |\text{H}_3\text{O}^+|K_1 + K_1K_2)^2}$$

and

$$\frac{d|\text{CO}_3^{2-}|}{d|\text{H}_3\text{O}^+|} = \frac{-K_1K_2(2|\text{H}_3\text{O}^+| + K_1)|\Sigma\text{CO}_2|}{(|\text{H}_3\text{O}^+|^2 + |\text{H}_3\text{O}^+|K_1 + K_1K_2)^2} \quad (10)$$

To calculate the effect of strong acid on seawater $p\text{CO}_2$, one can define the buffer factor Π_{H} from the above calculated Φ_{H} :

$$\begin{aligned} \Pi_{\text{H}} &= -\frac{d p\text{CO}_2}{d |\text{Talk}|} = -\frac{\frac{d p\text{CO}_2}{d\text{pH}}}{\frac{d |\text{Talk}|}{d\text{pH}}} \\ &= \frac{-|\text{H}_3\text{O}^+|}{K_0} \ln(10) \frac{d |\text{CO}_2|}{d |\text{H}_3\text{O}^+|} \\ &= \frac{\Phi_{\text{H}}}{\Phi_{\text{H}}} \end{aligned} \quad (11)$$

where, assuming $d |\Sigma\text{CO}_2| / d |\text{H}_3\text{O}^+| = 0$:

$$\begin{aligned} \frac{d |\text{CO}_2|}{d |\text{H}_3\text{O}^+|} &= \frac{|\text{H}_3\text{O}^+| K_1 (|\text{H}_3\text{O}^+| + 2K_2) |\Sigma\text{CO}_2|}{(|\text{H}_3\text{O}^+|^2 + |\text{H}_3\text{O}^+| K_1 + K_1 K_2)^2} \end{aligned} \quad (12)$$

In order to compare the effect of a strong acid input/output to those one induces by one among the three inorganic carbon species, one can also write:

$$\Pi_{\text{D,B,C}} = \frac{d p\text{CO}_2}{d |\Sigma\text{CO}_2|} = \frac{|\text{CO}_2|}{K_0 |\Sigma\text{CO}_2|} \beta_{\text{D,B,C}} \quad (13)$$

where both Π and β refer to the same inorganic species.

3. Results and discussion

Fig. 1 gives calculated values of the chemical buffer factors Φ_{D} , Φ_{B} and $\Phi_{\text{C}} = d\text{pH}/d |\Sigma\text{CO}_2|$,

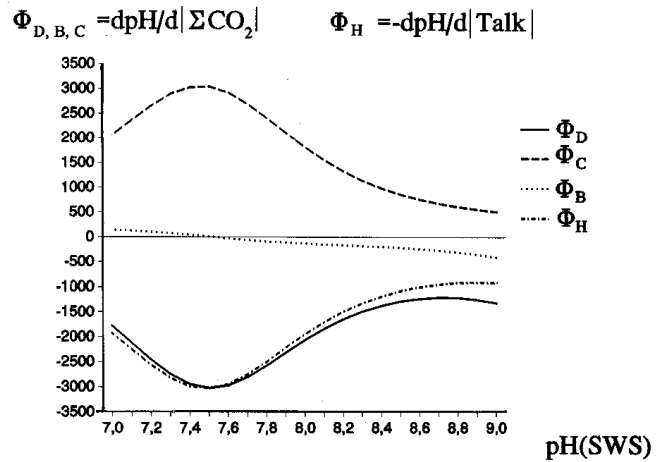


Fig. 1. Evolution versus pH of the chemical buffer factors, in kg/mol, that describe the effect of input/output of dissolved CO_2 (Φ_{D}), of bicarbonate (Φ_{B}), of carbonate (Φ_{C}) and of strong acid (Φ_{H}). $S = 35$, $t = 15^\circ\text{C}$ and $|\text{Talk}| = 2.4 \text{ meq.kg}^{-1}$.

together with $\Phi_{\text{H}} = -d\text{pH}/d |\text{Talk}|$ as a function of pH (total concentration molality scale, see further) in a range from 7 to 9 and suggests the following comments:

- the maximum Φ value, around $\text{pH}(\text{SWS}) = 7.5$, does correspond to the first equivalence point characterized by a lower buffering capacity,
 - the amphoteric behaviour of bicarbonate ion is responsible for an inversion of the Φ_{B} sign at the equivalence point,
 - Φ_{D} , Φ_{C} and Φ_{H} have the same order of magnitude while Φ_{C} has obviously opposite sign.
- In the seawater pH range, pH change induced by a dissolved CO_2 variation is slightly higher than the one induced by a H_3O^+ change. This was already observed by Stumm and Morgan (1981) when they calculated the chemical buffer factors by neglecting borate buffering effect. The differ-

Table 1

Buffer factors obtained from speciation changes (Spec) and calculated according to the proposed analytical expressions (Calc) applied on initial conditions ($|\text{Talk}| = 2400 \mu\text{eq.kg}^{-1}$, $|\Sigma\text{CO}_2| = 2130 \mu\text{mol.kg}^{-1}$, $S = 35$ and $t = 15^\circ\text{C}$). See text for symbols used

Input 10^{-4} mol.kg $^{-1}$	Final Talk	Final Σ	Φ		β		Π	
			Spec	Calc	Spec	Calc	Spec	Calc
CO_2	2400	2230	-2000	-2025	+11.82	+12.24	+2.52	+2.65
HCO_3^-	2500	2230	-120.0	-139.5	+1.85	+1.76	+0.31	+0.030
CO_3^{2-}	2600	2230	+1330	+1328	-6.23	-6.32	-0.87	-0.91
H_3O^+	2300	2130	-1890	-1920	/	/	+2.10	+2.21

ence between Φ_D and Φ_H is equal to Φ_B . When Φ_B has a positive sign, below the equivalence point, Φ_H is higher than Φ_D . according to the classical equilibrium equation, $\text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^-$, any chemical buffer factor associated to a bicarbonate change should have a value equal to half the sum of those associated to carbonate and dissolved CO_2 . So, at $\text{pH}(\text{SWS}) = 8.2$ (cf. Fig. 1), one calculates $\Phi_B = -154.91$, $\Phi_C = 1331.68$ and $\Phi_D = -1641.51$.

In the same way, according to the equation $\text{H}_3\text{O}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3 + \text{H}_2\text{O}$, the chemical buffer factors associated to a CO_2 (i.e. H_2CO_3) change should be equal to the sum of those related to H_3O^+ and HCO_3^- . At $\text{pH}(\text{SWS}) = 8.2$ (cf. Fig. 1), one calculates $\Phi_H = -1486.60$, which agrees with Φ_B and Φ_D given here above.

The validity of the proposed equations can also be checked by comparing results obtained when calculating the derivatives numerically from Talk and ΣCO_2 changes. Table 1 gives some examples and shows that difference between both methods is in the range 0-3%, due to fact that buffer factors are not constant from initial to final conditions chosen to perform numerical calculation.

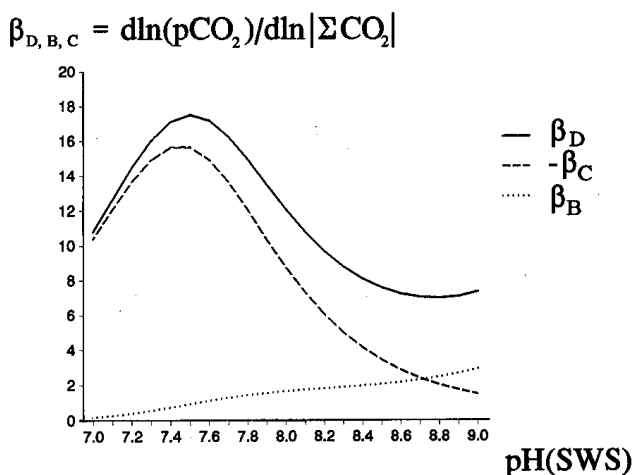


Fig. 2. Evolution versus pH of the homogeneous buffer factors that describe the effect of input/output of dissolved CO_2 (β_D), of bicarbonate (β_B) and of carbonate (β_C). β_C is illustrated with opposite sign. $S = 35$, $t = 15^\circ\text{C}$ and $|\text{Talk}| = 2.4 \text{ meq.kg}^{-1}$.

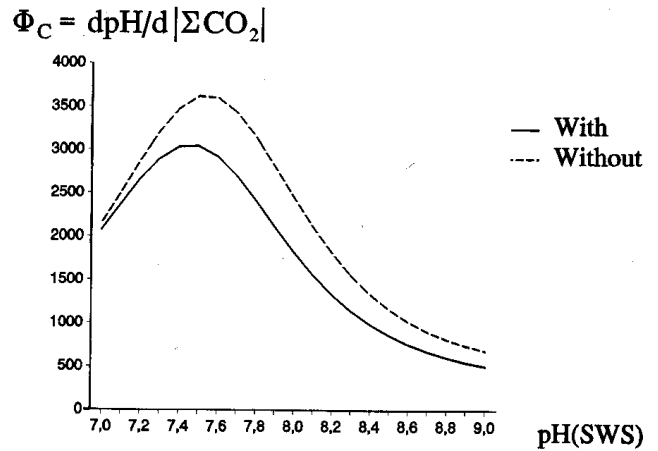


Fig. 3. The chemical buffer factor Φ_C , in kg/mol , describing input/output of carbonate ion calculated with and without the borate contribution. $S = 35$, $t = 15^\circ\text{C}$ and $|\text{Talk}| = 2.4 \text{ meq.kg}^{-1}$.

Fig. 2 gives calculated values for the homogeneous buffer factor $\beta = \text{dln}(\text{pCO}_2)/\text{dln}|\Sigma\text{CO}_2|$ that describes the relative variations of P and ΣCO_2 for any input/output of dissolved CO_2 , bicarbonate and carbonate ions (respectively β_D , β_B and β_C). As expected, dissolved CO_2 has a preponderant effect on pCO_2 and the homogeneous buffer factor related to carbonate input/output is about 60%, with opposite sign, the one of CO_2 .

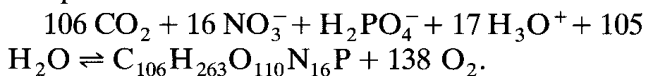
Calculations presented in this paper have been made as suggested by Millero (1979) using CO_2 constants from Goyet and Poisson (1989) (pH on the total hydrogen ion concentration scale, Sea Water Scale), borate constant from Hansson (1973) and dissolved CO_2 solubility coefficient from Weiss (1974). The total borate concentration is calculated from the Culkin (1965) ratio.

To discuss the importance of borate contribution to the global buffering effect of seawater, Fig. 3 shows Φ_C values calculated with and without (according to Stumm and Morgan, 1981), the borate contribution. One can see that the borate contribution to the buffer effect is about 30% of the global buffering effect in the seawater pH range. Taking borate into account is then quite important when studying buffering capacity of seawater media.

4. Application of buffer factors to biogeochemical processes

The usual homogenous Revelle factor value [$\beta_D = \text{dln}(p\text{CO}_2)/\text{d}|\Sigma\text{CO}_2| \approx 10$] would only be observed for input/output of dissolved CO_2 alone (e.g. air–sea CO_2 exchanges). When carbonate, bicarbonate or proton ions are involved in the biogeochemical process, the homogeneous buffer factor β could display quite different value. Equations proposed in this paper can be applied to calculate the homogeneous buffer factor β associated to any biological, geological or chemical reaction, or simultaneous processes, which induce input/output of proton and any species of inorganic carbon.

Primary production is a fundamental oceanic process that induced uptake of both dissolved CO_2 and H_3O^+ in proportions that can be estimated using the Redfield et al. (1963) equation related to the mean oceanic algal protoplasm composition:



Moreover, this organic carbon metabolism can be coupled to an inorganic carbon metabolism (i.e. calcification process of e.g. coccolithophore or coral reefs) which results in an uptake of carbonate ion ($\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$) or bicarbonate ion ($\text{Ca}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$). Because both stoichiometries proposed for calcification have the same meaning in terms of chemical equilibria, it is possible to calculate a global homogeneous buffer factor, $\beta_{\text{Prim.Prod}}$, using the Redfield et al. (1963) estimation, associated to any simultaneous organic and inorganic metabolisms:

$$\beta_{\text{Prim.Prod}} = \left(\frac{1}{R+1} \right) [R(\Pi_D + 0.16\Pi_H) + \Pi_C] \cdot \frac{\left(1.16 + \frac{1}{R} \right)}{\left(1 + \frac{1}{R} \right)} \cdot \frac{|\Sigma\text{CO}_2|}{p\text{CO}_2} \quad (14)$$

where R is the ratio between the carbon uptake for organic metabolism (dissolved CO_2 uptake)

and the one for inorganic metabolism (carbonate ion uptake). The computation of this equation has yielded a linear relationship for $\beta_{\text{Prim.Prod}}$ versus the percentage of organic carbon metabolism: $\beta_{\text{Prim.Prod.}} = -7.02 + 0.186\%C_{\text{org}}$ ($r^2 = 0.9994$, $p\text{CO}_2 = 350 \text{ ppmV}$, $|\text{Talk}| = 2400 \mu\text{eq.kg}^{-1}$, $S = 35$ and $t = 15^\circ\text{C}$). The so obtained β values range from -7.02 (no organic production, $\%C_{\text{org}} = 0$, i.e. chemical CaCO_3 dissolution/precipitation) to $+11.58$ (no calcification during organic production, $\%C_{\text{org}} = 100$). The homogenous Revelle factor (β_D) is calculated to be 10.45 in similar conditions. By considering oceanic distribution of both total inorganic carbon and total alkalinity, Broecker and Peng (1982) have proposed that for a global production of 4 organic carbon, 1 is produced in the inorganic pool and this 80% of organic carbon uptake from dissolved CO_2 would then corresponds to a global homogeneous buffer factor β equal to 7.86. More recently, Robertson et al. (in press) have discussed Talk and ΣCO_2 patterns obtained in the North Atlantic with and without predominant coccolithophore activity. Their results suggest that, during coccolithophore bloom, organic and inorganic metabolisms have the same magnitude ($R = 1$ and $\%C_{\text{org}} = 50$). According to the above equation, the associated homogeneous buffer factor β should be 2.28. They are unable to provide an experimental β estimate for high coccolithophore abundance due to the smaller number of data points, but they did estimate $\text{dln}(p\text{CO}_2)/\text{dln}|\Sigma\text{CO}_2|$ to be about 8.98 for diatoms bloom, which is consistent with a low calcifying rate ($\%C_{\text{org}} = 86\%$, according to the proposed equation).

Equations proposed in this paper can also be used to describe quantitatively the equilibrium dynamics involved in consecutive reactions such as the ones that occur in open system (in contact with the atmosphere). In such a system, any input/output in the water bulk of dissolved CO_2 , bicarbonate, carbonate or H_3O^+ will induce a change of the water partial CO_2 pressure and then further exchange with the gas phase to go back to equilibrium condition. To describe the involved CO_2 dynamics, the buffer factors $\Pi_{\text{D,B,C}} = \text{dpCO}_2/\text{d}|\Sigma\text{CO}_2|$ and $\Pi_{\text{H}} = -\text{dpCO}_2/$

$d|\text{Talk}|$ can be used to calculate the amount of total inorganic carbon that should be exchanged with the atmosphere to keep the seawater $p\text{CO}_2$ constant. So, acid rains are a net input of strong acid (H_3O^+) to seawater that results in an increase of the surface partial CO_2 pressure and a potential source of atmospheric CO_2 . Using the proposed equations, it is possible to give an analytical expression to calculate the *released CO_2 /added H_3O^+* ratio the value of which depends on the buffering capacity of the considered water masse:

$$\frac{\text{released } \text{CO}_2}{\text{added } \text{H}_3\text{O}^+} = \frac{-\Pi_{\text{H}}}{\Pi_{\text{D}}} = \frac{\frac{d|\text{Talk}|}{dp\text{CO}_2}}{\frac{d|\Sigma\text{CO}_2|}{d|\Sigma\text{CO}_2|}} = \frac{d|\Sigma\text{CO}_2|}{d|\text{Talk}|} \quad (15)$$

The so-calculated ratio is equal to 0.84 ($|\text{Talk}| = 2400 \mu\text{eq.kg}^{-1}$, $p\text{CO}_2 = 350 \text{ ppmV}$, $S = 35$ and $t = 15^\circ\text{C}$.) and each input of one mole of H_3O^+ in a bulk of seawater open to the atmosphere will produce the escape of 0.84 mole of CO_2 to keep the system equilibrated. Zehnder and Zinder (1980) have estimated that the amount of acid, produced by man use of sulphur compounds, which reaches the ocean is about $2.8 \cdot 10^{11}$ moles. y^{-1} and then results in a source of CO_2 from the sea of about $2.8 \cdot 10^6 \text{ t of C.y}^{-1}$ ($2.4 \cdot 10^{11}$ moles of $\text{CO}_2.\text{y}^{-1}$).

Frankignoulle et al. (in press) have recently used the same approach to calculate the released dissolved CO_2 occurring during calcification process. This is of special importance to determine the final CO_2 budget of ecosystems that are sites of important calcification (e.g. coral reefs, see Frankignoulle and Gattuso, 1993; Gattuso et al., 1993). For present condition ($p\text{CO}_2 = 350 \text{ ppmV}$), they compute a *released CO_2 /precipitated carbonate* ratio equal to 0.6, in good agreement with the one obtained by Ware et al. (1992) using classical speciation. They have also shown that the *released CO_2 /precipitated carbonate* ratio increases together with the dissolved CO_2 level in seawater and that calcification thus present a

positive feedback to the increasing atmospheric CO_2 level.

In conclusion, equations presented in this paper allow to compute any pH and $p\text{CO}_2$ changes resulting from input/output in seawater of HCO_3^- , CO_3^{2-} and H_3O^+ ions. Calculations are carried out by taking into account the borate buffer effect which accounts for about 30% in the seawater media. Equations can easily be computed to avoid time consuming numerical iterative calculation. Buffer factors can be combined to describe the global CO_2 dynamics resulting from simultaneous or consecutive changes of the studied species, as it is most often the case in natural processes.

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List of symbols used

K_1 , K_2 , K_{B} and K_{H} are dissociation constants of carbonic acid, of boric acid, and of water in seawater,

$K = K_1/K_2$,

K_0 is the CO_2 solubility coefficient in seawater, $|\text{H}_3\text{O}^+|$ and $|\text{OH}^-|$ are total concentrations of proton and hydroxyl ion,

$|\text{CO}_2|$, $|\text{HCO}_3^-|$ and $|\text{CO}_3^{2-}|$ are the total concentrations in dissolved CO_2 , bicarbonate and carbonate ions,

$|\Sigma\text{CO}_2|$ is the total inorganic carbon,

$p\text{CO}_2$ is the partial seawater CO_2 pressure,

$|\text{TB}|$ and $|\text{B(OH)}_4^-|$ are total borate and borate concentrations,

$|Talk|$ and $|A|$ are total and carbonate alkalinities,

Φ_D , Φ_B , and Φ_C are the chemical buffer factors ($dpH/d|\Sigma CO_2|$) that describe the effect of input/output of dissolved CO_2 , bicarbonate and carbonate,

Φ_H is the chemical buffer factor ($-dpH/d|Talk|$) that describes the effect of input/output of strong acid,

β_D , β_B and β_C are the homogeneous buffer factors ($dln(pCO_2)/dln|\Sigma CO_2|$) that describe the effect of input/output of dissolved CO_2 , bicarbonate and carbonate.

Π_D , Π_B and Π_C are the chemical buffer factors ($dpCO_2/d|\Sigma CO_2|$) that describe the effect of input/output of dissolved CO_2 , bicarbonate and carbonate,

Π_H is the buffer factor ($-dpCO_2/d|Talk|$) that describes the input/output of strong acid.

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