

# Biogeochemical Processes and Inorganic Carbon Dynamics

# 5

Organic matter production and degradation result in the consumption and release of carbon dioxide; oxidation and reduction reactions involve the production or consumption of protons; carbonate mineral formation and dissolution reactions cause consumption or release of carbonate and bicarbonate. All these processes have the potential to increase or decrease proton concentrations, i.e. change the pH, yet marine pH varies over a rather small range (about one unit only). This is due to the buffering of seawater. For a complete understanding of the impact of carbon dioxide on organisms, the role of organisms in carbon dioxide dynamics, and the role of marine systems in climate change (e.g., carbon dioxide uptake and ocean acidification; Box 5.1), we have to understand the chemistry of the carbon dioxide system in water and for this we need to understand what governs pH dynamics.

In this chapter, we will first refresh the basics of inorganic carbon chemistry in water and seawater, then introduce alkalinity and buffering, and discuss how biological processes and mineral formation are impacted and impact carbon dioxide in marine systems.

## 5.1 The Basics

Pure water can dissociate into protons and hydroxide ions:

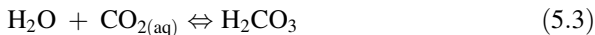


This reaction occurs virtually immediately and one can thus assume equilibrium between the three species ( $[\text{H}_2\text{O}]$ ,  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ):

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad \text{or} \quad K_w = [\text{H}^+][\text{OH}^-] \quad (5.2)$$

where  $K_w$  denotes the equilibrium constant for water self-ionisation. This type of equilibrium relation is also known as a mass-action law. Having two unknowns ( $[H^+]$ ,  $[OH^-]$ ) that are related via the above equilibrium relation, we have one degree of freedom: i.e. if we choose  $[H^+]$ , then  $[OH^-]$  is set to  $\frac{K_w}{[H^+]}$ .

Next, we consider pure water in equilibrium with a gas containing  $CO_2$ . Part of the  $CO_2$  will remain in the atmosphere ( $CO_{2(g)}$ ), but part will dissolve in water ( $CO_{2(aq)}$ ). This dissolved  $CO_{2(aq)}$  will react with water to form carbonic acid ( $H_2CO_3$ ) according to:



This equilibrium is somewhat slow and the equilibrium constant of hydration  $K_h =$

$\frac{[H_2CO_3]}{[H_2O][CO_2]}$  is rather small ( $\sim 0.002$ ); almost all dissolved carbon dioxide remains in the form of  $CO_{2(aq)}$ . Moreover, it is analytically not possible to distinguish between  $CO_{2(aq)}$  and  $H_2CO_{3(aq)}$ ; they are therefore lumped together and usually termed  $CO_2^*$  or  $H_2CO_3^*$ . However, carbonic acid  $H_2CO_{3(aq)}$  is a moderately weak acid ( $K \approx 10^{-3.6}$ ), while the combined  $H_2CO_3^*$  is a weak acid ( $K \approx 10^{-6.3}$ ). For reasons of notational simplicity, we will term it  $H_2CO_3$  from now onwards.

Carbonic acid is a weak diprotic acid and partly dissociates first into a bicarbonate ion ( $HCO_3^-$ ) and a proton, and subsequently, the bicarbonate is dissociated partly into carbonate ion ( $CO_3^{2-}$ ) and a proton. The relevant reactions are:



for which we can write equilibrium relations:

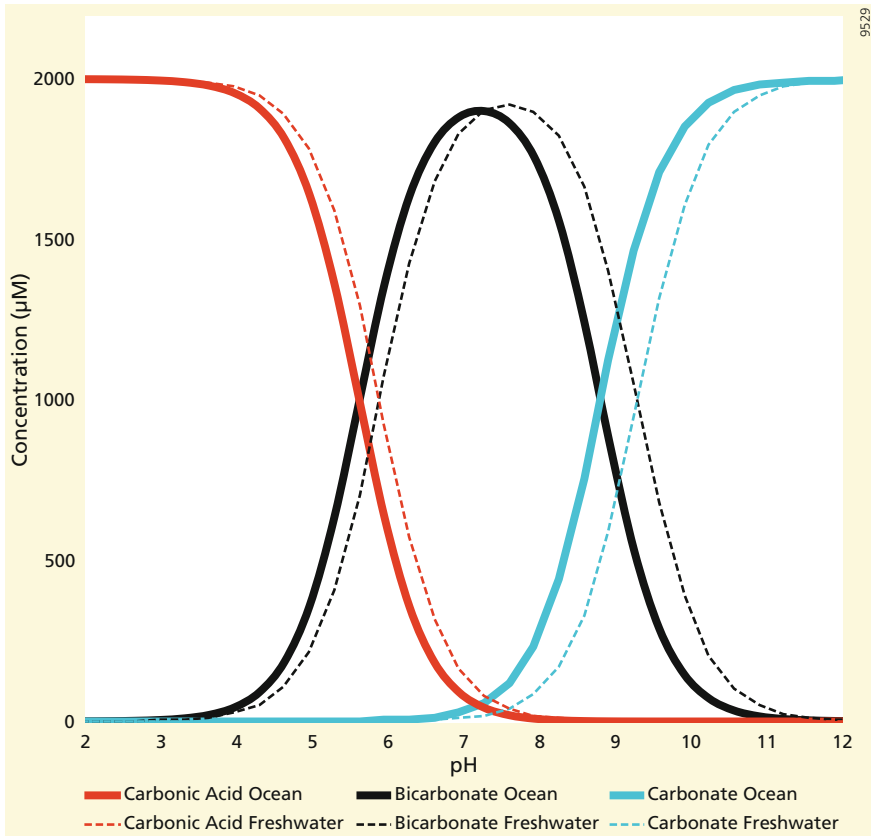
$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (5.6)$$

and

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (5.7)$$

where  $K_1$  and  $K_2$  are the first and second equilibrium constants ( $10^{-6.35}$  and  $10^{-10.3}$  in freshwater at 25 °C). The relative concentrations of  $[H_2CO_3]$ ,  $[HCO_3^-]$  and  $[CO_3^{2-}]$  are governed by the pH ( $-\log_{10}[H^+]$ ) of the solution as depicted by a Bjerrum plot (Fig. 5.1). Carbonic acid is the dominant species at pH values below the  $pK_1$  ( $-\log_{10}K_1$ ), bicarbonate dominates between the  $pK_1$  and  $pK_2$  values and the carbonate ion dominates at pH values above the  $pK_2$ .

The carbonic acid in solution and carbon dioxide in the atmosphere are related via Henry's law:



**Fig. 5.1** Bjerrum plot showing the distribution of carbonic acid (red), bicarbonate (black) and carbonate (blue) ions as a function of pH in freshwater (dashed line) and seawater (solid lines). DIC = 2000  $\mu\text{M}$

$$[\text{H}_2\text{CO}_3] = K_H \times p\text{CO}_2 \quad (5.8)$$

where  $K_H$  is the Henry constant for  $\text{CO}_2$  solubility in water ( $\text{mol kg}^{-1} \text{atm}^{-1}$ ) and  $p\text{CO}_2$  is the partial pressure of  $\text{CO}_2$  (atm). The equilibrium constants  $K_w$ ,  $K_1$ ,  $K_2$  and  $K_H$  are functions of temperature, pressure and salinity in seawater.

Accordingly, for the  $\text{CO}_2\text{-H}_2\text{O}$  system, we have five unknown concentrations ( $[\text{H}_2\text{CO}_3]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ,  $[\text{OH}^-]$  and  $[\text{H}^+]$ ) and four equilibrium relations: water self-ionisation (5.2), Henry's law (5.8) and the first and second equilibria of carbonic acid dissociation (5.6, 5.7). To solve the system, we need one additional relation. Natural waters are uncharged, and we can thus use the charge balance equation for this system: the positive charge of protons should be balanced by the negative charge of hydroxide, bicarbonate and carbonate ions.

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (5.9)$$

Note that the carbonate ion is counted twice in a charge balance because of its double charge. Alternatively, one can define a proton balance equation, a mass balance for protons (Butler 1982):

$$[\text{H}^+] = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{H}_2\text{CO}_3} \quad (5.10a)$$

or its equivalent

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}], \quad (5.10b)$$

This proton conservation equation balances excess protons on the left-hand side with the recipe on the right-hand side. Proton mass balances are always relative to a proton reference level, e.g. Equation (5.10a, b) is relative to  $\text{H}_2\text{CO}_3$  and in this case, it is identical to the charge balance. Mathematically, the system is now fully defined with 5 unknown species linked via 5 equations. Moreover, the system remains fully determined if another component is added for which the total concentration and equilibrium distribution among species is known.

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## 5.2 The Thermodynamic Basis

So far, we have ignored non-ideal behaviour of gases, liquids and solutes that have an impact on equilibria. Although the name equilibrium constant suggests that it is a constant, it is in fact not, because of its dependence on temperature, pressure and the composition of the solution. This dependence relates to the effect of temperature, pressure and mixture composition on the Gibbs Free energy. Formally, at equilibrium, the change in Gibbs free energy  $\Delta G^{react}$  ( $\text{J mol}^{-1}$ ) is related to the thermodynamic equilibrium constant ( $K_x^{\text{therm}}$ ) via  $\Delta G^{react} = -RT \ln K_x^{\text{therm}}$ , where  $T$  is in Kelvin and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

There are two generic pathways towards obtaining equilibrium constants for complex natural solutions. The first approach involves calculating thermodynamic constants from the well-documented and tabulated standard Gibbs free energies of formation and correcting these for temperature and pressure of the system. The thermodynamic equilibrium constant is then expressed in activities of the molecules involved, rather than concentrations. For example, equilibrium relation (5.3) for the thermodynamic  $K_1^{\text{therm}}$  should formally be written as:

$$K_1^{\text{therm}} = \frac{\{\text{HCO}_3^-\}\{\text{H}^+\}}{\{\text{H}_2\text{CO}_3\}}$$

where the  $\{\}$  indicate that activities, rather than concentrations  $[\ ]$  are used. Concentrations and activities are linked via activity coefficients ( $\gamma$ ), which account for both electrostatic interactions, as well as formation of ion-pairs among the various ions in solution:

$$K_1^{therm} = \frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3\}} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \times \frac{\gamma_{HCO_3^-}\gamma_{H^+}}{\gamma_{H_2CO_3}}$$

These activity coefficients are usually calculated using the Pitzer model (Millero 2007) that can be applied to highly complex media, such as brines.

The alternative way of estimating equilibrium constants, used by most chemical oceanographers and marine biogeochemists, is to experimentally determine stoichiometric constants as a function of temperature, pressure and salinity and represent this dependency by a polynomial function. The underlying idea is that the relative composition of seawater is rather constant, that the reaction as such does not change the composition of seawater and that direct measurements in seawater provide more accurate results than using thermodynamic data with activity coefficient corrections:

$$K_{1,(T,S,P)}^* = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

where the \* superscripts indicates that it is a stoichiometric quantity, rather than thermodynamic constant and the subscripts T, S and P stand for temperature, salinity and pressure. The temperature, salinity and pressure dependence of stoichiometric constants result in rather complex and cumbersome expressions (Table 5.1), but there are many computer programs available to facilitate their determination.

Figure 5.2 shows the stoichiometric constant expressed as  $pK_1^*$  as a function of temperature and salinity.  $pK_1^*$  values decrease with increasing temperature and salinity, or in other words, carbonic acid is more dissociated with increasing temperature or salinity. The ratio of the stoichiometric equilibrium constant ( $K_1^*$ ) at salinity 35 to the thermodynamic equilibrium constant ( $K_1^{therm}$ ) in pure water is about 4.4–5. This salinity effect has consequences for the speciation of dissolved inorganic carbon in seawater (Fig. 5.1). Similar dependencies apply to other stoichiometric constants. Moreover, this stoichiometric approach can also be used to accurately quantify the solubility of minerals in seawater and will be used from now on (while dropping the \* superscript).

The solubility of gases, including  $CO_2$ , is also a function of temperature, salinity and pressure (increasing salinity and temperature lower the solubility of gases). Thermodynamically, the fugacity of carbon dioxide is linked via the Henry constant to dissolved carbon dioxide:  $[H_2CO_3] = K_H \times fCO_2$ . The fugacity is not exactly the same as the partial pressure, the product of  $CO_2$  mol fraction ( $x'_{CO_2}$ ) times total gas pressure, as presented above (in Eq. 5.8). Because most readers are more familiar with the  $pCO_2$ , than  $fCO_2$ , we will use the former notation, noting that they are different.

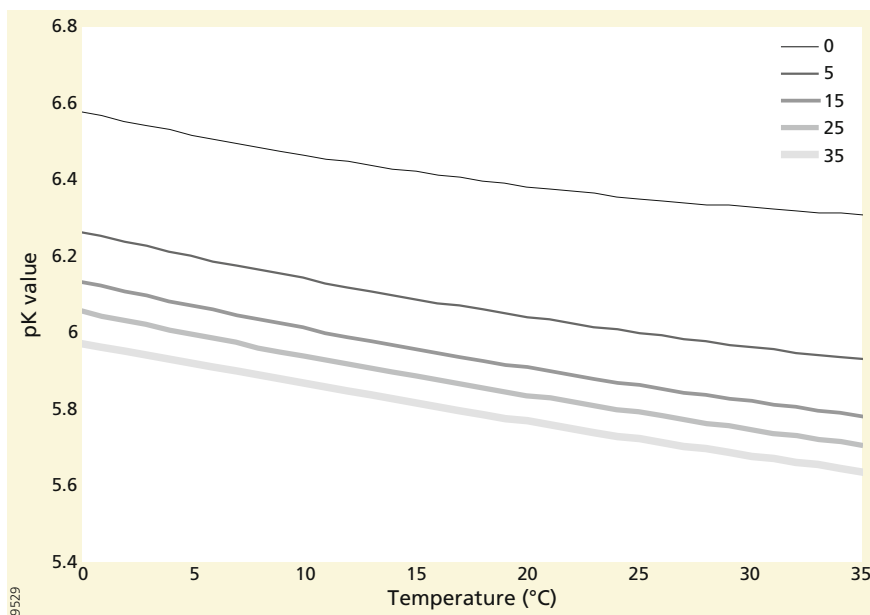
**Table 5.1** Acid-base reaction in seawater and examples of expression of their stoichiometric constants (Dickson et al. 2007). T is absolute temperature (K), S is salinity

Reaction	Equilibrium relations	Stoichiometric constant expression
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-]$	$\ln(K_w) = \frac{-13847.26}{T} + 148.9652 - 23.6521 \ln(T)$ $+ \left( \frac{118.67}{T} - 5.977 + 1.0495 \ln(T) \right) S^{0.5} - 0.01615S$
$\text{CO}_{2(g)} \rightleftharpoons \text{H}_2\text{CO}_3$	$[\text{H}_2\text{CO}_3] = K_H \times p\text{CO}_2$	$\ln(K_H) = 93.4517 \left( \frac{100}{T} \right) - 60.2409 + 23.3585 \ln \left( \frac{T}{100} \right)$ $+ S \left( 0.023517 - 0.023656 \left( \frac{T}{100} \right) + 0.0047036 \left( \frac{T}{100} \right)^2 \right)$
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$	$\ln(K_1) = \frac{-3633.86}{T} + 61.2172 - 9.67770 \ln(T)$ $+ 0.011555S - 0.0001152S^2$
$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$	$\ln(K_2) = \frac{-417.78}{T} - 25.9290 + 3.16967 \ln(T)$ $+ 0.01781S - 0.0001122S^2$
$\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}^+$	$K_B = \frac{[\text{B}(\text{OH})_4^-][\text{H}^+]}{[\text{B}(\text{OH})_3]}$	$\ln(K_B) = \frac{-8966.90 - 2890.53S^{0.5} - 77.942S + 1.728S^{1.5} - 0.0996S^2}{T}$ $+ (148.0248 + 137.1942S^{0.5} + 1.62142S)$ $+ (-24.4344 - 25.085S^{0.5} - 0.2474S) \ln(T) + 0.053105S^{0.5}T$

### 5.3 Analytical Parameters of the CO<sub>2</sub> System

Not all individual species of the CO<sub>2</sub> system (pCO<sub>2</sub>, [H<sub>2</sub>CO<sub>3</sub>], [HCO<sub>3</sub><sup>-</sup>], [CO<sub>3</sub><sup>2-</sup>], [OH<sup>-</sup>] and [H<sup>+</sup>]) can be measured directly in seawater, and there is also no need to because they are interlinked via equilibrium, mass balance and charge conservation equations (Dickson 2011). There are five parameters that can be measured:

- The total concentration of dissolved inorganic carbon, often abbreviated as DIC,  $\sum \text{CO}_2$  or C<sub>T</sub>: **DIC** = [H<sub>2</sub>CO<sub>3</sub>] + [HCO<sub>3</sub><sup>-</sup>] + [CO<sub>3</sub><sup>2-</sup>], is normally measured by acidifying the sample, stripping the evolved gas and measuring the total CO<sub>2</sub> content.
- The partial pressure (fugacity) of carbon dioxide (**pCO<sub>2</sub>**) can be obtained by measuring the gas phase composition in equilibrium with the water and the use of Eq. (5.8: Henry's law).
- The **pH** can be measured directly using electrodes and by colorimetry using an indicator dye (Dickson 2011), which then provides data for the hydrogen concentration. However, there is also a large body of research based on the NIST scale (National Institute of Standards and Technology, formerly known as NBS scale), the total (pH<sub>T</sub>) and the seawater (pH<sub>SWs</sub>) scales. The latter two incorporate association of free protons with bisulphate, or bisulphate and fluoride, respectively, and are linked to the free scale as follows: pH ≈ pH<sub>T</sub> + 0.11 and pH ≈ pH<sub>SWs</sub> + 0.12.
- The carbonate ion concentration (**[CO<sub>3</sub><sup>2-</sup>]**) via measurement of the ultraviolet absorbances of lead carbonate complexes in seawater.



**Fig. 5.2** The dependence of  $pK_1$  on the temperature and salinity of water

(E) The total or titration alkalinity (**TA**), which can be seen as the excess of proton acceptors over donors of a solution and is normally derived from an acidimetric titration. The total alkalinity of a solution is relatively easy to measure, and which has the pleasant characteristic that it behaves conservatively as two waters are mixed or if temperature or pressure changes, similar to DIC. A formal definition and detailed treatment follow below.

Let us revisit the simple CO<sub>2</sub>–H<sub>2</sub>O system from above with five species ([H<sub>2</sub>CO<sub>3</sub>], [HCO<sub>3</sub><sup>-</sup>], [CO<sub>3</sub><sup>2-</sup>], [OH<sup>-</sup>] and [H<sup>+</sup>]). Titration of this system with a strong acid results in a decrease in pH and transformation of carbonate to bicarbonate and bicarbonate to carbonic acid. Each bicarbonate ion can accept one proton, each carbonate ion consumes two protons before it is transformed into carbonic acid, and carbonic acid cannot accept protons. For this system, we can define H<sub>2</sub>CO<sub>3</sub> as our reference (zero level of protons). Similarly, the hydroxide ions in solution will accept one proton, while any proton available just adds to the final proton concentration at the end of a titration. TA was formally defined by Dickson (1981) as the excess of proton acceptors ([HCO<sub>3</sub><sup>-</sup>] + 2 [CO<sub>3</sub><sup>2-</sup>] + [OH<sup>-</sup>]) over proton donors [H<sup>+</sup>] of the initial solution:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (5.11)$$

The reader might have noted that this TA definition has much similarity to the charge balance and proton balance Eqs. (5.9), (5.10a, b) for this simple  $\text{CO}_2\text{-H}_2\text{O}$  system. In fact by re-arranging the charge balance (5.9) we obtain the charge balance alkalinity or excess negative charge (ENC):

$$\text{ENC} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (5.12)$$

and we see that this excess negative charge is equivalent to the titration alkalinity for this system. This excess negative charge introduced by Soetaert et al. (2007) is also known as the explicit conservative equation of total alkalinity (Zeebe and Wolf-Gladrow 2001; Wolf-Gladrow et al. 2007).

Although seawater is a much more complex system, because it contains many potential proton acceptors and donors, such as borate, phosphate and silicate species, the same approach can be used. Dickson (1981) formally defined total alkalinity of filtered seawater by the excess of proton acceptors over proton donors with respect to the proton condition at pH 4.5 (Dickson 1981), which then leads to the expression:

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] \\ & + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{NH}_3] + [\text{HS}^-] + 2[\text{S}^{2-}] - [\text{H}^+] - [\text{HF}] - [\text{HSO}_4^-] \\ & - 2[\text{H}_2\text{SO}_4] - [\text{H}_3\text{PO}_4] - [\text{HNO}_2] - [\text{HNO}_3] \end{aligned} \quad (5.13)$$

Following Wolf-Gladrow et al. (2007) and Soetaert et al. (2007), some additional proton acceptors ( $\text{H}_2\text{SiO}_4^{2-}$ ,  $\text{S}^{2-}$ ) and proton donors ( $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) have been added to the original definition of Dickson (1981). Most of these additional terms are close to zero in oxic seawater. Moreover, TA in marine waters is dominated by the carbonate species and simpler relations than (5.13) are often used. The carbonate alkalinity (CA) is defined as the alkalinity contribution of bicarbonate and carbonate species:

$$\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (5.14)$$

and usually accounts for >95% of the alkalinity, with borate contributing another ~3–4%. While the presence of these additional species hardly impacts measurement of TA by titration, it will affect the use of TA in calculations to obtain the sought-after distribution of bicarbonate and carbonate concentrations.

The excess negative charge concept, as introduced earlier (5.12) can also be applied to seawater (Soetaert et al. 2007; Wolf-Gladrow et al. 2007):



$$\begin{aligned} \text{ENC} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] \\ & + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{NO}_3^-] + [\text{NO}_2^-] + [\text{F}^-] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] - [\text{H}^+] - [\text{NH}_4^+]. \end{aligned} \quad (5.15)$$

ENC and TA are related via:

$$\text{TA} = \text{ENC} + \sum \text{NH}_4 - \sum \text{NO}_3 - \sum \text{NO}_2 - \sum \text{PO}_4 - 2 \sum \text{SO}_4 - \sum \text{F} \quad (5.16)$$

where the various  $\sum$ -terms refer to total concentration of the respective acid-base pairs (e.g.  $\sum \text{NH}_4 = [\text{NH}_4^+] + [\text{NH}_3]$ ). This difference between TA and ENC is caused by components for which the species used as zero proton levels are charged. In other words, DIC and  $\sum \text{B}(\text{OH})_3$  do not appear because they are uncharged at their zero proton level. This distinction between TA measured by titration (*sensu* Dickson) and ENC (charge balance alkalinity) is needed to understand the impact of biogeochemical processes on pH or pCO<sub>2</sub>, in particular those involving ion-exchange or nutrient uptake (Zeebe and Wolf-Gladrow 2001; Soetaert et al. 2007; Wolf-Gladrow et al. 2007). For instance, nitrate or ammonium uptake by phytoplankton has a distinct effect on TA (decrease and increase, respectively; Brewer and Goldman 1976; Goldman and Brewer 1980) that cannot be inferred from the Dickson definition of TA (5.13), but is clear from Eqs. 5.15 and 5.16. The concept of potential alkalinity (Brewer et al. 1975) and its derivatives, such as TA\*, are special cases of the ENC concept. The need to correct for nutrient cycling when using the alkalinity anomaly technique to quantify calcification is also made explicit when using Eq. 5.16.

## 5.4 Buffering

Natural waters, in particular seawater, contain multiple weak acids and their conjugate bases. Any addition or removal of an acid or base results in re-adjustment of the equilibrium distribution of acids and conjugated bases, with the consequence that the disturbance is attenuated (the principle of *le Chatelier*). Buffering can involve only dissolved components (homogenous) or also solid phases (heterogeneous). Heterogeneous buffering in the ocean is called ocean carbonate compensation (Box 5.2). Homogenous buffering of waters is most often quantified by the buffering value (B), which is formally defined as the concentration of acid or base to be added to influence pH (Van Slyke 1922; Urbanksy and Schock 2000):

$$\text{B} = \frac{dC_b}{dpH} = - \frac{dC_a}{dpH}, \quad (5.17)$$

**Table 5.2** Buffer capacities expressed in proton concentrations ( $\beta$ ) and pH (B)

Acids	$\beta = -\frac{dT_A}{dH^+}$ (mol kg <sup>-1</sup> )	$B = \frac{dT_A}{dpH}$ (mol kg <sup>-1</sup> )
H <sub>2</sub> O	$-\frac{K_w}{[H^+]^2} - 1$	$\ln(10) \left( \frac{K_w}{[H^+]} + [H^+] \right)$
B(OH) <sub>3</sub>	$-[B]_T \times \frac{K_b}{(K_b + [H^+])^2}$	$\ln(10) [B]_T \times \frac{K_b [H^+]}{(K_b + [H^+])^2}$
H <sub>2</sub> CO <sub>3</sub>	$-[CO_2]_T K_1 \times \frac{K_1 K_2 + 4K_2 [H^+] + [H^+]^2}{(K_1 K_2 + K_1 [H^+] + [H^+]^2)^2}$	$\ln(10) [CO_2]_T K_1 [H^+] \times \frac{K_1 K_2 + 4K_2 [H^+] + [H^+]^2}{(K_1 K_2 + K_1 [H^+] + [H^+]^2)^2}$
H <sub>3</sub> PO <sub>4</sub>	$-\frac{[P]_T K_1 \times}{4K_1 K_2 K_3 [H^+] + K_1 K_2 [H^+]^2 + 4K_2 [H^+]^3 + [H^+]^4 + K_1 K_2^2 K_3 + 9K_2 K_3 [H^+]^2}$	$\frac{\ln(10) [P]_T K_1 [H^+] \times}{4K_1 K_2 K_3 [H^+] + K_1 K_2 [H^+]^2 + 4K_2 [H^+]^3 + [H^+]^4 + K_1 K_2^2 K_3 + 9K_2 K_3 [H^+]^2}$
	$\frac{(K_1 K_2 K_3 + K_1 K_2 [H^+] + K_1 [H^+]^2 + [H^+]^3)^2}{(K_1 K_2 K_3 + K_1 K_2 [H^+] + K_1 [H^+]^2 + [H^+]^3)}$	$\frac{(K_1 K_2 K_3 + K_1 K_2 [H^+] + K_1 [H^+]^2 + [H^+]^3)^2}{(K_1 K_2 K_3 + K_1 K_2 [H^+] + K_1 [H^+]^2 + [H^+]^3)}$

*Notes*

- (1) K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> are the first, second and third equilibrium constant for polyprotic acids
- (2) The total buffer capacity is obtained summing all acid-base systems contributing (Hagens and Middelburg 2016)
- (3) The inverse of B and  $\beta$  are the sensitivity factors

where  $C_b$  and  $C_a$  are the concentration of added base and acid, respectively. The term buffer value as used here is identical to the terms buffer capacity, intensity and index in use by analytical chemists, geochemists and engineers. Buffer values are always positive because solutions resist changes according to the le Chatelier principle; consequently, a minus is needed when considering acid addition. The buffer value is a continuous non-linear function, as it is the inverse of the slope of the titration curve, i.e. a derivative (Stumm and Morgan 1996). The buffering value of seawater is expressed using the total alkalinity:

$$B = \frac{dT_A}{dpH}. \quad (5.18)$$

For notational simplicity, we present buffer value as a derivative, while it is a partial derivative because all other concentrations are kept constant when determining this buffer value by titration (Hagens and Middelburg 2016). Van Slycke's original definition of buffer value was in pH, but in seawater it is instructive to express buffering value in terms of proton concentration ( $\beta$ ):

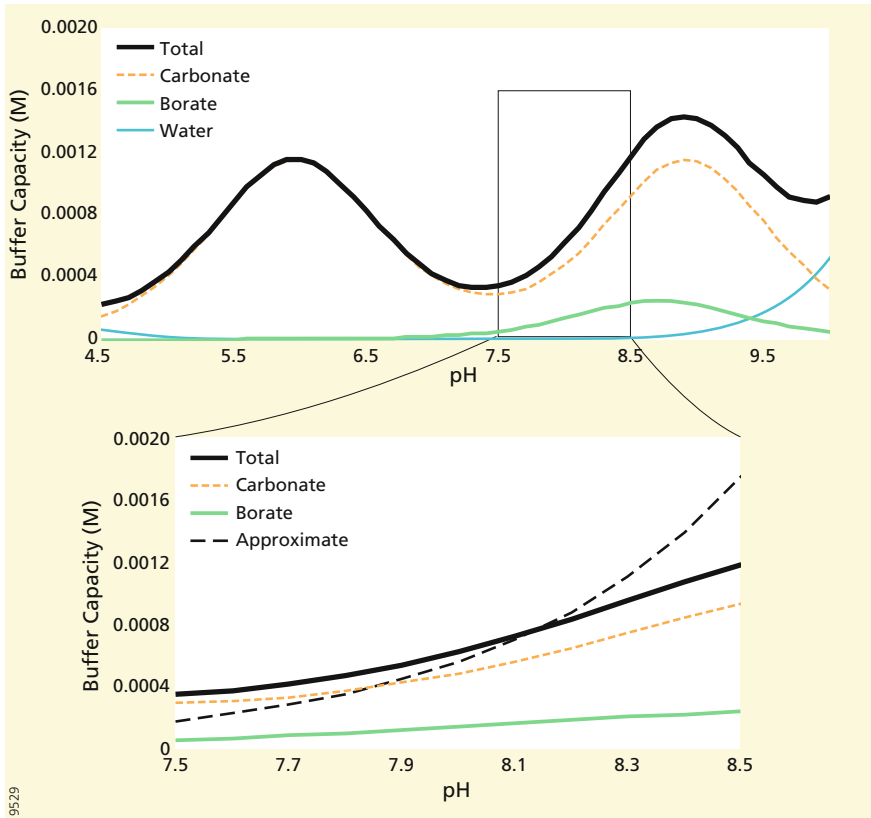
$$\beta = -\frac{dT_A}{dH^+}. \quad (5.19)$$

Buffer values  $B$  and  $\beta$  are linked via  $B = -\ln(10) * H^+ * \beta$ . Table 5.2 gives the relevant equations for  $B$  (in pH) and  $\beta$  (in proton concentrations).

Total alkalinity includes multiple acid-base systems, and the overall buffering value can be obtained by summing the contributions of all the acid-base systems involved (Urbanksy and Schock 2000). The buffer value of seawater is mainly determined by the borate and carbonate contributions, and we therefore limited our calculations to these (and of course the contribution of water). The buffer value of seawater ( $S = 35$ ,  $T = 15$  °C,  $DIC = 2000$   $\mu\text{M}$ ) is a function of pH and has two distinct maxima at pH 6 and 8.9, near the  $pK_1$  and  $pK_2$  of the carbonate system in seawater and a minimum at pH 7.4 (approximately midway between these maxima; Fig. 5.3). Within the pH range of 7.5–8.5 the buffer value increases with pH and can be approximated by the relation:

$$B \cong \ln(10) \frac{K_2 DIC}{H^+}, \quad (5.20)$$

showing that the buffer value of seawater in its normal range primarily depends on the DIC concentration, the pH and  $pK_2$  value. Borate contributes about 15–22% to seawater buffering in this range.



**Fig. 5.3** Buffer capacity of seawater. Top panel: total capacity, carbonate, borate and water contributions. Lower panel: total capacity, carbonate and borate contributions and approximate buffer capacity (see text)

Another useful term related to the buffering is the sensitivity factor defined as the inverse of the buffer value expressed in terms of pH or protons (Soetaert et al. 2007; Egleston et al. 2010; Hagens and Middelburg 2016):

$$\frac{dpH}{dTA} = B^{-1} \quad (5.21)$$

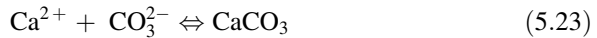
$$-\frac{dH^+}{dTA} = \beta^{-1}. \quad (5.22)$$

These sensitivities and their use will be discussed below.

## 5.5 Carbonate Mineral Equilibria

In the above section, we only considered homogenous buffering, i.e. the re-equilibration among dissolved species. In natural systems, solid phases also contribute to buffering via dissolution and precipitation, and we call this heterogeneous buffering. Carbonate minerals play a dominant role in heterogeneous buffering because of their omnipresence, high solubility and high reactivity.

The precipitation and dissolution of calcium carbonate is represented by the reaction:



for which we can write the equilibrium relation:

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \quad (5.24)$$

where  $K_{sp}$  is the stoichiometric solubility product for calcium carbonate, which is a function of temperature, salinity, pressure and the calcium carbonate mineral. The solubility product is used to calculate the saturation state of seawater ( $\Omega$ ) with respect to the calcium carbonate mineral:

$$\Omega = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{sp}}. \quad (5.25)$$

If  $\Omega = 1$ , then the solution is in equilibrium with that mineral, if  $\Omega > 1$ , then the solution is supersaturated with respect to that mineral and if  $\Omega < 1$ , then the solution is undersaturated with respect to that mineral. Undersaturation and supersaturation promote dissolution and precipitation, respectively.

The two dominant calcium carbonate minerals in the ocean are calcite and aragonite, which differ in crystal structure, mineralogical properties (e.g. density) and solubility (Morse et al. 2007). The thermodynamic solubility products of calcite ( $\text{pK} = 8.48$ ) and aragonite ( $\text{pK} = 8.30$ ) differ by a factor 1.5, while their stoichiometric solubility products at salinity 35 and  $T = 25^\circ\text{C}$  are more than two orders of magnitude higher ( $\text{pK} = 6.36$  and  $6.18$ , respectively). The crystal structure of carbonates has consequences for the incorporation of other ions, with larger cations (e.g.,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) preferably incorporated in the orthorhombic aragonite structure and smaller cations (e.g.,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ) fitting better in the hexagonal calcite structure. Dissolved magnesium concentrations in seawater are rather high ( $>5$  times  $\text{Ca}^{2+}$ ) and Mg incorporation is therefore substantial (up to  $\sim 25\%$  for biogenic carbonates), with large consequences for solubility. The solubility of Mg-calcite with about 2% Mg is lower than that of pure calcite, while calcites with about 12–15% Mg substitution are five times more soluble than aragonite (Arvidson and Morse 2014).

## 5.6 Dissolved Inorganic Carbon Systematics

The conservative properties TA and DIC are often used as master variables to analyse the impact of environmental change on the marine  $\text{CO}_2$  system, because the distribution of the species carbonic acid, bicarbonate and carbonate, and  $\text{pCO}_2$  and pH depend on temperature and salinity. Figure 5.4 shows the temperature dependence of pH,  $\text{pCO}_2$ , bicarbonate and carbonate ion concentrations for seawater (TA = 2300  $\mu\text{M}$ , DIC = 2000  $\mu\text{M}$ ). Increasing temperatures will cause an almost linear decrease in pH with a slope of  $-0.0155 \text{ pH}/^\circ\text{C}$ , while it will cause an exponential increase in  $\text{pCO}_2$  values. Bicarbonate and carbonate ion concentrations will decrease and increase with increasing temperatures (slopes of about  $-0.55$  and  $+0.42 \mu\text{M}/^\circ\text{C}$ , respectively).

There are also distinct dependencies with salinity (Fig. 5.4), but these only include the impact of salinity on stoichiometric equilibrium constants, not the larger effect of salinity on total alkalinity via charge balance. Increasing salinity results in a decline in pH and carbonate ion concentration and an increase in bicarbonate and  $\text{pCO}_2$ .

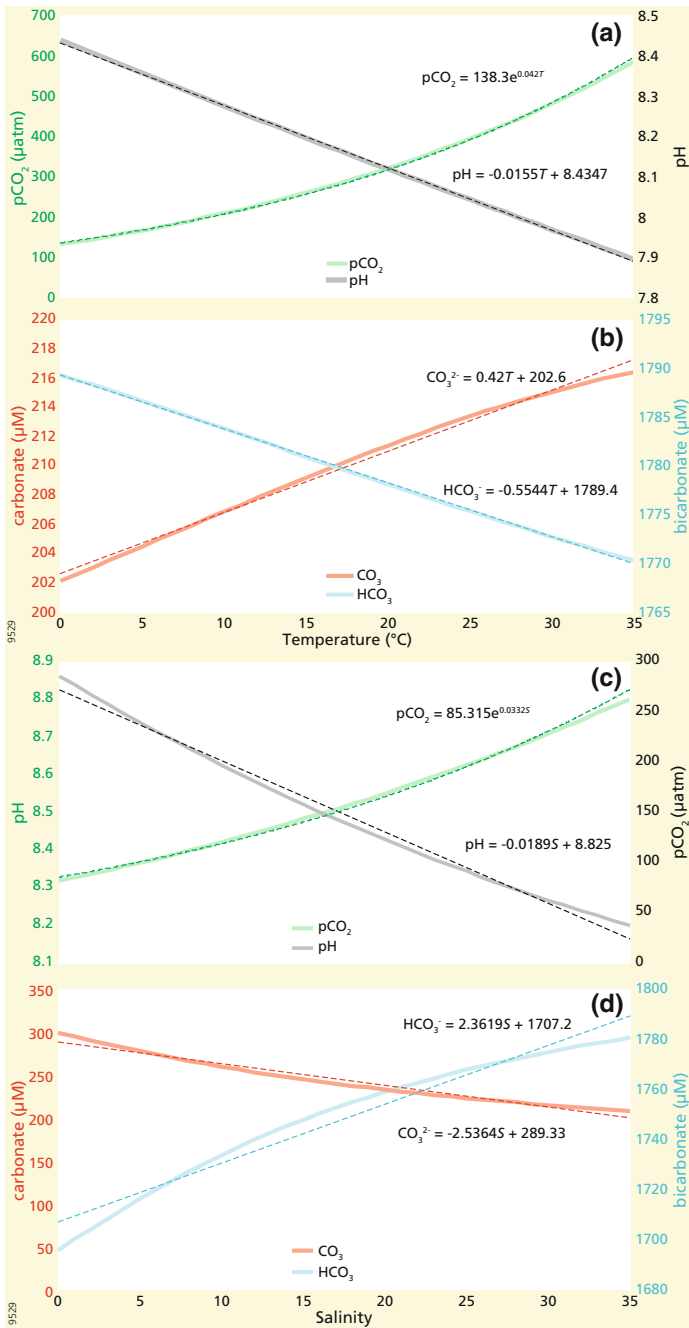
Relations among TA, DIC,  $\text{pCO}_2$  and pH are often presented graphically in the form of TA versus DIC plots with isolines for pH or  $\text{pCO}_2$  (Fig. 5.5) for seawater ( $T = 15$ ,  $S = 35$ ). The addition or removal of TA or DIC or any of its constituents on such a plot is a vector property (Deffeyes 1965). For instance,  $\text{CO}_2$  addition will increase DIC concentration, but not affect TA and thus result in a horizontal vector pointing to the right;  $\text{pCO}_2$  of the water will increase and the pH will decline. Addition of protons will decrease TA, but not impact DIC; the downward heading vertical vector indicates that pH will decline and  $\text{pCO}_2$  will increase. The addition of  $\text{HCO}_3^-$  will impact both DIC and TA by one unit; the vector will have a slope of one and both pH and  $\text{pCO}_2$  will slightly increase. The addition of  $\text{CO}_3^{2-}$  will increase DIC by one unit and TA by two units, and the resulting vector indicates a lowering in  $\text{pCO}_2$  and increase in pH.

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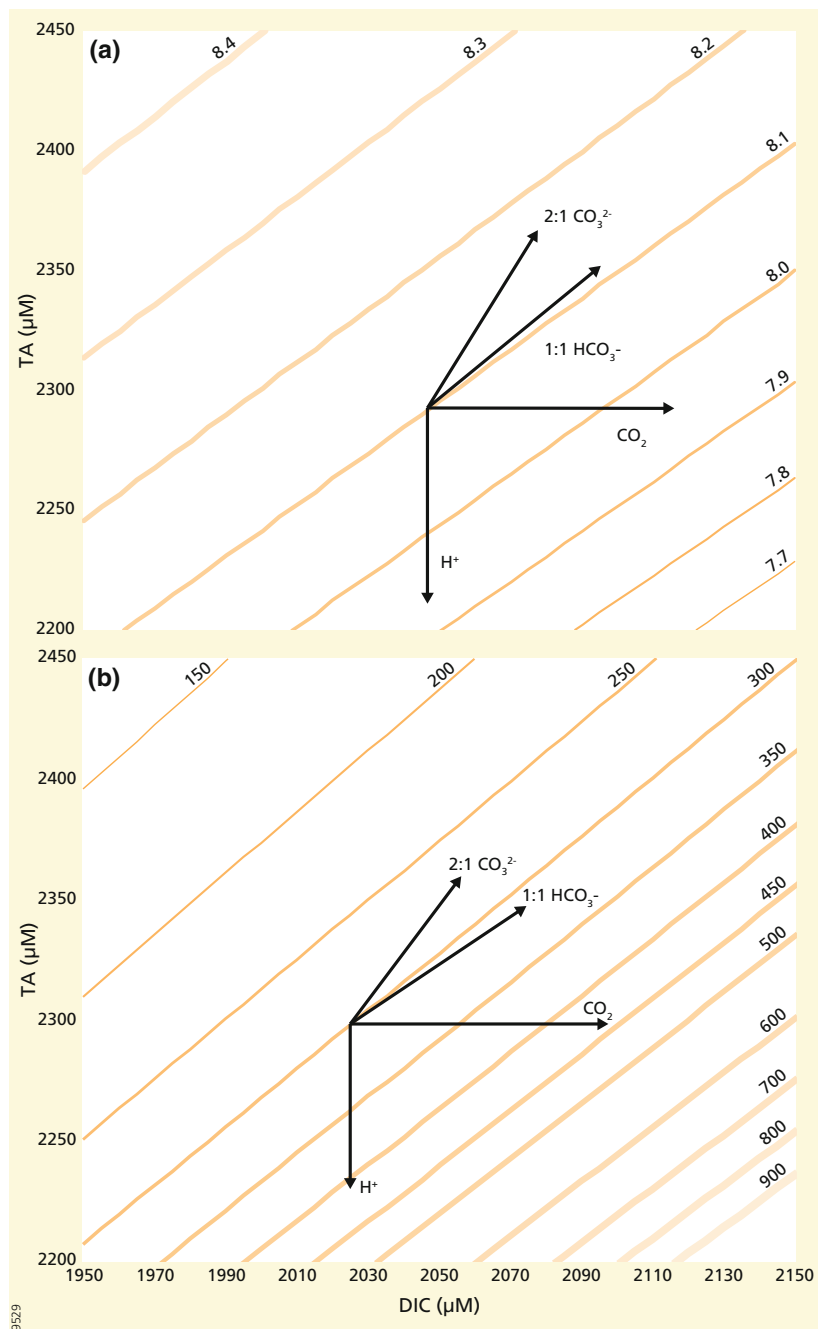
## 5.7 The Impact of Biogeochemical Processes

Most biological and physical exchange processes occur on longer time scales than the chemical equilibrium reactions, and any addition or removal of a compound due to biology and physics thus causes re-equilibrations following the le Chatelier principle; i.e. buffering occurs. The impact of biogeochemical processes on the dissolved inorganic carbon system can be analysed (graphically or numerically) using their impact on DIC and TA.

*Gas exchange.* Invasion of  $\text{CO}_2$  from the atmosphere into seawater causes an increase in DIC, but does not change TA, with the consequence that  $\text{pCO}_2$  increases and pH declines. The reverse process, an efflux of  $\text{CO}_2$  from seawater to the atmosphere, results in  $\text{pCO}_2$  decline and pH increase (Fig. 5.6). These  $\text{CO}_2$  exchange processes may be initiated either by changing atmospheric mixing ratios of  $\text{CO}_2$  or by cooling or warming of seawater.

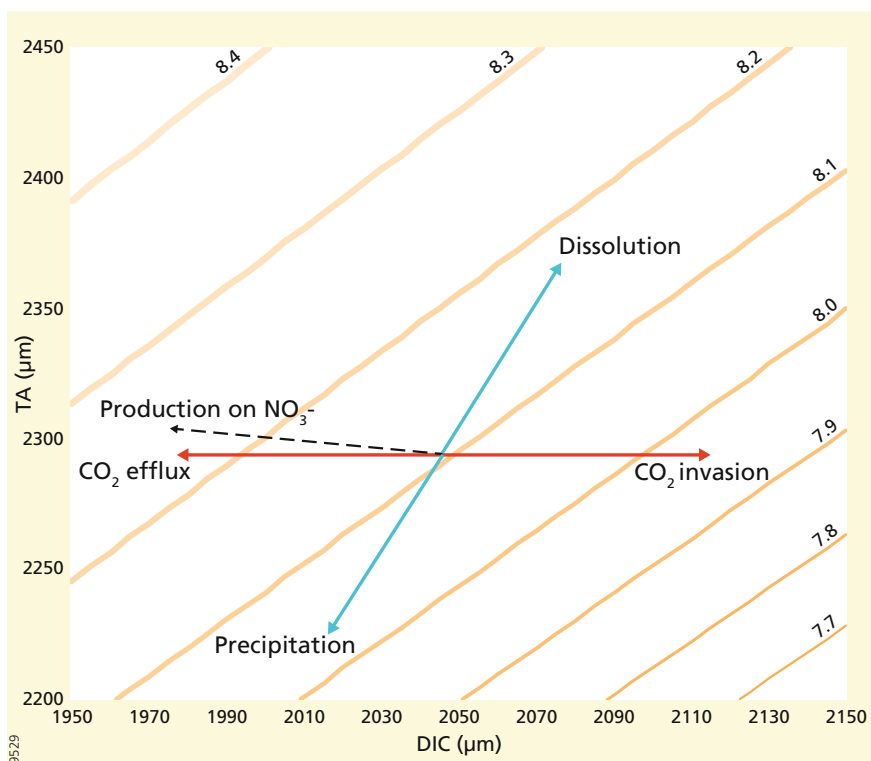


**Fig. 5.4** **a** Dependence of seawater  $p\text{CO}_2$  and pH on temperature; **b** Dependence of carbonate and bicarbonate ions on temperature; **c** Dependence of seawater  $p\text{CO}_2$  and pH on salinity; **d** Dependence of seawater carbonate and bicarbonate ions on salinity. Dashed lines are regression equations



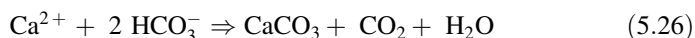
**Fig. 5.5** TA-DIC plot with pH contours (a) and  $\text{pCO}_2$  ( $\mu\text{atm}$ ) contours (b). Vectors are given for addition of protons, carbon dioxide, bicarbonate and carbonate





**Fig. 5.6** Vector diagram on TA-DIC plot showing pH changes due CO<sub>2</sub> invasion and effluxes, carbonate mineral dissolution and precipitation, and primary production using nitrate as nitrogen source

*Carbonate minerals.* Precipitation of calcium carbonate via the reaction:

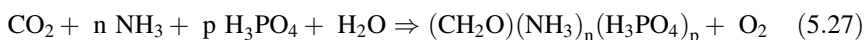


removes one unit DIC from solution ( $-2 \text{HCO}_3^- + \text{CO}_2$ ) and two units of TA ( $-2 \text{HCO}_3^-$ ), with the result that  $\text{pCO}_2$  increases and pH declines. Dissolution of calcium carbonates results in the release of one unit DIC and two units TA and thus a decline in  $\text{pCO}_2$  and pH increase (Fig. 5.6).

The above examples directly involved one of the species of the dissolved inorganic carbon system, but many important biological processes do not directly involve any of these (e.g., oxidation-reduction reactions, such as nitrification or sulphide oxidation) or also involve other compounds besides the inorganic carbon species (e.g., primary production and organic matter degradation), and these do impact pH,  $\text{pCO}_2$  and other parameters. To include these additional processes, we have to return to the relation between Excess Negative Charge (ENC) and Titration Alkalinity (TA).

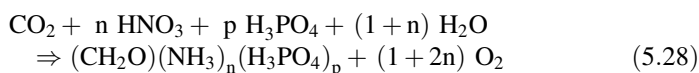
Primary production involves the fixation of inorganic carbon and the assimilation of nitrogen and phosphorus to produce Redfield organic matter (see Chap. 6). Nitrogen assimilated in the form of either nitrate or ammonium has consequences for alkalinity because of the principle of nutrient-proton compensation mechanism (Brewer and Goldman 1976; Soetaert et al. 2007; Wolf-Gladrow et al. 2007). The rationale is as follows. Uptake of a nutrient in ionic form requires either uptake/release of a proton or hydroxide ion if internal compensation (e.g.  $\text{NH}_4^+$  with  $\text{PO}_4^{3-}$ ) is not occurring, otherwise the organism would be charged. Ammonium uptake results in a decrease in alkalinity because either a proton is released or an additional hydroxide ion is assimilated for charge compensation. By analogy, nitrate uptake increases alkalinity because either a proton is consumed or a hydroxide ion is released to maintain electroneutrality.

Accordingly, primary production based on ammonium can be represented as:



where  $n$  and  $p$  are the stoichiometric ratios (16/106 and 1/106 for Redfield ratios, respectively). This reaction lowers TA by  $n-p$ , i.e. 15/106 equivalents and DIC by one unit.

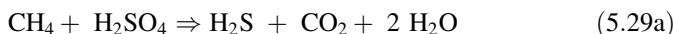
Similarly, primary production based on nitrate, i.e.,



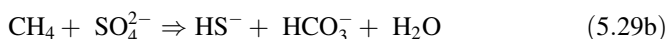
increases TA with  $n+p$ , i.e. 17/106 equivalents and DIC by one unit (based on Redfield).

Note that these reactions have been presented in the form of  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  for convenience, but could have been written also in terms of bicarbonate, ammonium, phosphate and nitrate ions. Because of the electroneutrality condition and rapid equilibration, it does not matter which species is actually taken up. For instance, when  $\text{CO}_2$  is taken up during photosynthesis, buffering will replenish  $\text{CO}_2$  from the large bicarbonate pool, thereby consuming protons, i.e. increasing the pH. Alternatively, when bicarbonate is assimilated, electroneutrality maintenance would imply uptake of a proton or release of a hydroxide ion, the result being an increase in pH.

As another example, consider the anaerobic oxidation of methane coupled to sulphate reduction. We can write this equation either as



or



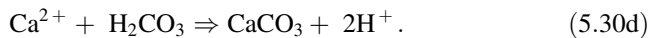
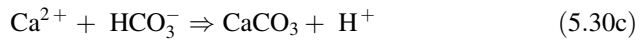
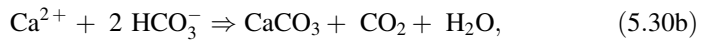
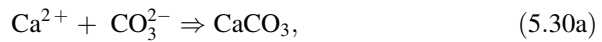
**Table 5.3** Biogeochemical processes and changes in excess negative charge and total alkalinity (Soetaert et al. 2007)

Process	Reaction	$\Delta\text{ENC}$	$\Delta\text{TA}$
Aerobic mineralization	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2 \Leftrightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$	0	$n-p$
Denitrification	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.8 \text{HNO}_3 \Leftrightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.4 \text{N}_2 + 1.4 \text{H}_2\text{O}$	0	$0.8 + n - p$
Mn-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{MnO}_2 + 4\text{H}^+ \Leftrightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 2 \text{Mn}^{2+} + 3\text{H}_2\text{O}$	4	$n-p + 4$
Fe-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{Fe}_2\text{O}_3 + 8\text{H}^+ \Leftrightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 4 \text{Fe}^{2+} + 5\text{H}_2\text{O}$	8	$n-p + 8$
Sulfate reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.5 \text{H}_2\text{SO}_4 \Leftrightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{H}_2\text{S} + \text{H}_2\text{O}$	0	$n-p + 1$
Fermentation	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p \Leftrightarrow 0.5 \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{CH}_4 + \text{H}_2\text{O}$	0	$n-p$
Anaerobic oxidation of methane	$\text{CH}_4 + \text{H}_2\text{SO}_4 \Leftrightarrow \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O}$	0	2
Calcite precipitation	$\text{Ca}^{2+} + \text{CO}_3^{2-} \Leftrightarrow \text{CaCO}_3$	-2	-2
Primary production (nitrate)	$\text{CO}_2 + n \text{HNO}_3 + p \text{H}_3\text{PO}_4 + (1 + n) \text{H}_2\text{O} \Leftrightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + (1 + 2n) \text{O}_2$	0	$p + n$
Primary production (ammonium)	$\text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \Leftrightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2$	0	$p-n$

$n = \text{N/C}$  ratio of organic matter and  $p = \text{P/C}$  ratio of organic matter

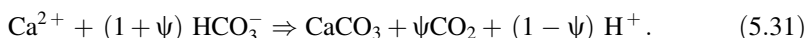
Irrespective of the way formulated TA increases by two units and DIC by one unit. Soetaert et al. (2007) have worked out in detail the impact of biogeochemical processes on changes in ENC and TA (Table 5.3) and the related pH change. These pH changes are dependent on the actual pH of the system.

To illustrate the latter, we return to the precipitation of calcium carbonate. The precipitation of calcium carbonate can be presented as:



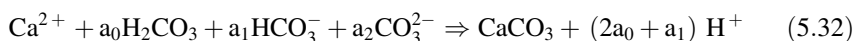
While all these reactions are correct in terms of mass balance and stoichiometry: i.e. two units TA and one unit DIC are consumed for precipitation of one mole  $\text{CaCO}_3$ , the second one indicates production of  $\text{CO}_2$  and the last two imply production of protons. This non-uniqueness is the result of re-equilibration reactions, and these have to be taken into account when presenting calcium carbonate precipitation or

dissolution in a single equation. Evidently, at pH values  $>pK_2$ , the carbonate ion is the most important species (Fig. 5.1) and reaction (5.30a) will be the dominant reaction. This is the equation most often used in laboratory studies performed at high pH and no protons or carbon dioxide are net generated. Most field studies employ reaction scheme (5.30b) and have shown that calcium carbonate precipitation represents a source of carbon dioxide, but not one mole carbon dioxide for one mole of calcium carbonate because of buffering. Frankignoulle et al. (1994) presented the factor  $\psi$  which expresses the amount of carbon dioxide generated per unit calcium carbonate precipitated:



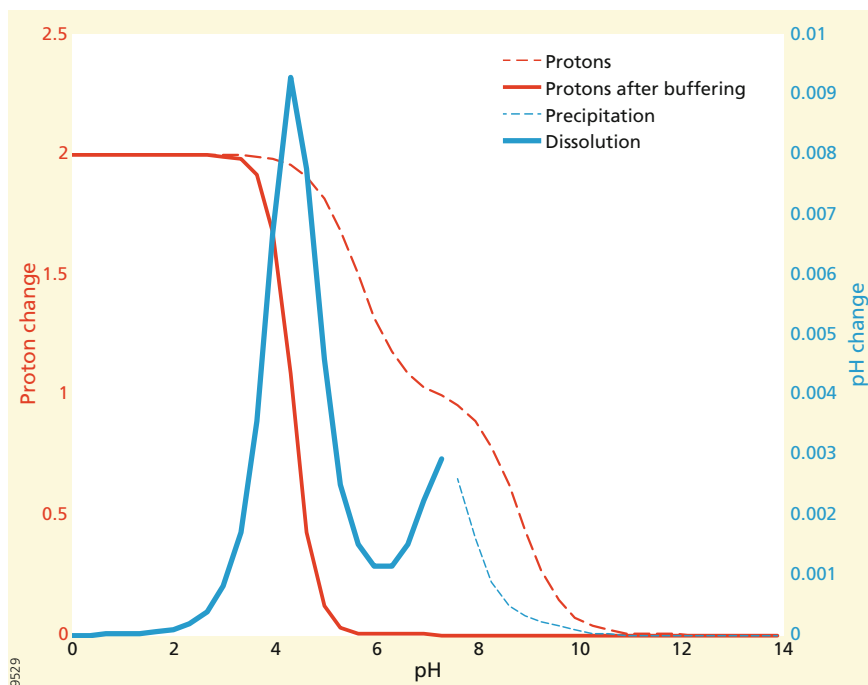
The factor  $\psi$  basically merges reactions (5.30b, c) above and can be calculated analytically and has a value of 0.6–0.7 for most marine waters. The result that  $p\text{CO}_2$  increases and pH declines is consistent with the vector analysis presented above (Fig. 5.5).

An alternative generic treatment has been presented by Hofman et al. (2010).



where  $\alpha_0 = \text{H}_2\text{CO}_3/\text{DIC}$ ,  $\alpha_1 = \text{HCO}_3^-/\text{DIC}$ ,  $\alpha_2 = \text{CO}_3^{2-}/\text{DIC}$  and  $\alpha_0 + \alpha_1 + \alpha_2 = 1$ . The number of protons released by calcite precipitation is given by  $2\alpha_0 + \alpha_1$ , i.e. two times the carbonic acid + bicarbonate contribution to the DIC pool and varies from 2 at low pH to zero at high pH values (Fig. 5.7, red dashed line). However, the protons generated during calcite precipitation will be buffered, and the actual increase in proton concentration is given by  $-\frac{2\alpha_0 + \alpha_1}{\beta}$  (Hofman et al. 2010; red solid line) where  $\beta$  is the buffer value in terms of protons introduced earlier (Eq. 5.22). The released protons will decrease the pH of the solution (blue dashed line). A similar analysis can be made for calcite dissolution: two protons are consumed during calcite dissolution at low pH, the net proton change is less because of buffering and the pH increase shows a non-linear response with two maxima (blue solid line).

Using the information in Table 5.3 and the approach of Soetaert et al. (2007), it is possible to calculate the impact of any process on pH and how it varies with pH. The pH dependence is the product of the change in negative charge (i.e. number of protons involved) and the sensitivity factor (Eq. 5.21). Figure 5.8 shows the pH dependence of the sensitivity factor with distinct maxima at pH 4.3, 7.3 and 9.9. Aerobic mineralization releases carbon dioxide, ammonium and phosphate. Carbon dioxide production decreases the pH for  $\text{pH} > \sim 5$  (Fig. 5.9), in particular at pH 9.9 and 7.3 because of poor buffering, but pH increases for  $\text{pH} < \sim 5$  because of ammonium release. The release of carbon dioxide does not impact the negative charge (or proton balance) at low pH because all inorganic carbon is already present as carbon dioxide. Denitrification lowers pH for  $\text{pH} > \sim 7$ , while it increases pH for  $\text{pH} < \sim 7$  because of nitrate consumption and ammonium release, both impacting

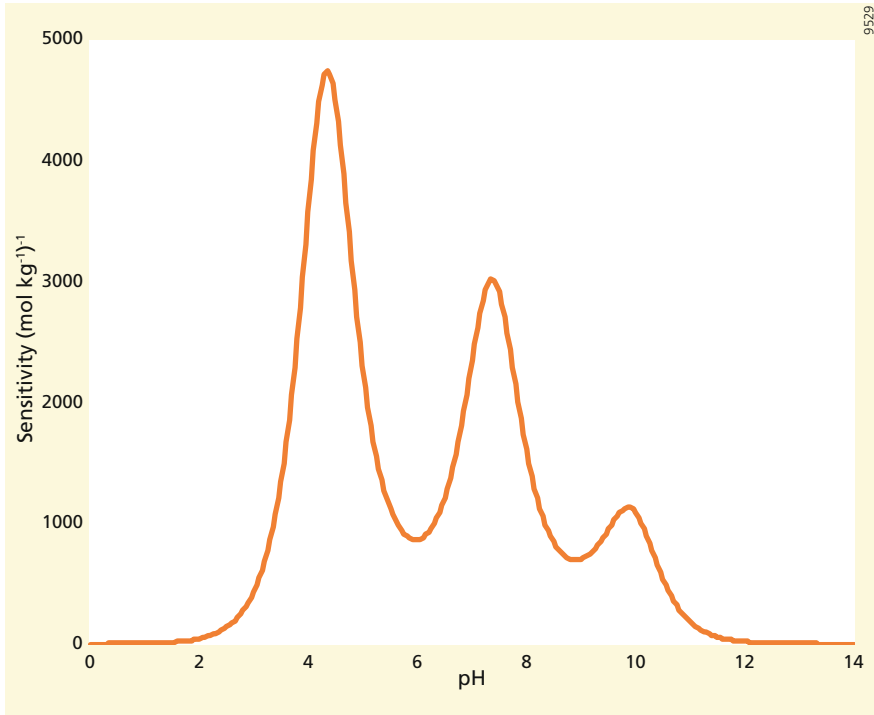


**Fig. 5.7** Calcium carbonate precipitation/dissolution, proton and pH changes as function of pH. The number of proton generated per mole calcite formed/dissolved before buffering (red dashed line) and after buffering (red solid line). The decline in pH for precipitation of one  $\mu\text{mole}$  of calcite (dashed blue line) and increase in pH for dissolution of one  $\mu\text{mole}$  calcite (solid blue line). There is a break at the pH where calcite starts to dissolve or precipitate

the negative excess charge and TA (Eq. 5.16), in particular at pH 4.3 because of the high sensitivity factor (Fig. 5.8). Manganese and iron oxide reduction always increase pH with the relative pH increase primarily depending on the sensitivity factor (Fig. 5.9).

### Box 5.1: Ocean acidification

Atmospheric carbon dioxide concentrations steadily increased during the last century because of the use of carbon-based energy resources, changes in land use, and lime production. Part of this additional carbon dioxide remains in the atmosphere, i.e. an airborne fraction of about 45%, and is the main driver of global warming. The other part ends up in the ocean or terrestrial biosphere. The ocean uptake of anthropogenic carbon accounts for 25–30%, but this service to humankind comes at a price: acid-base equilibria in the ocean have shifted. DIC and bicarbonate concentrations increased (carbonation), while carbonate ions and pH declined (ocean acidification). Ocean acidification, or

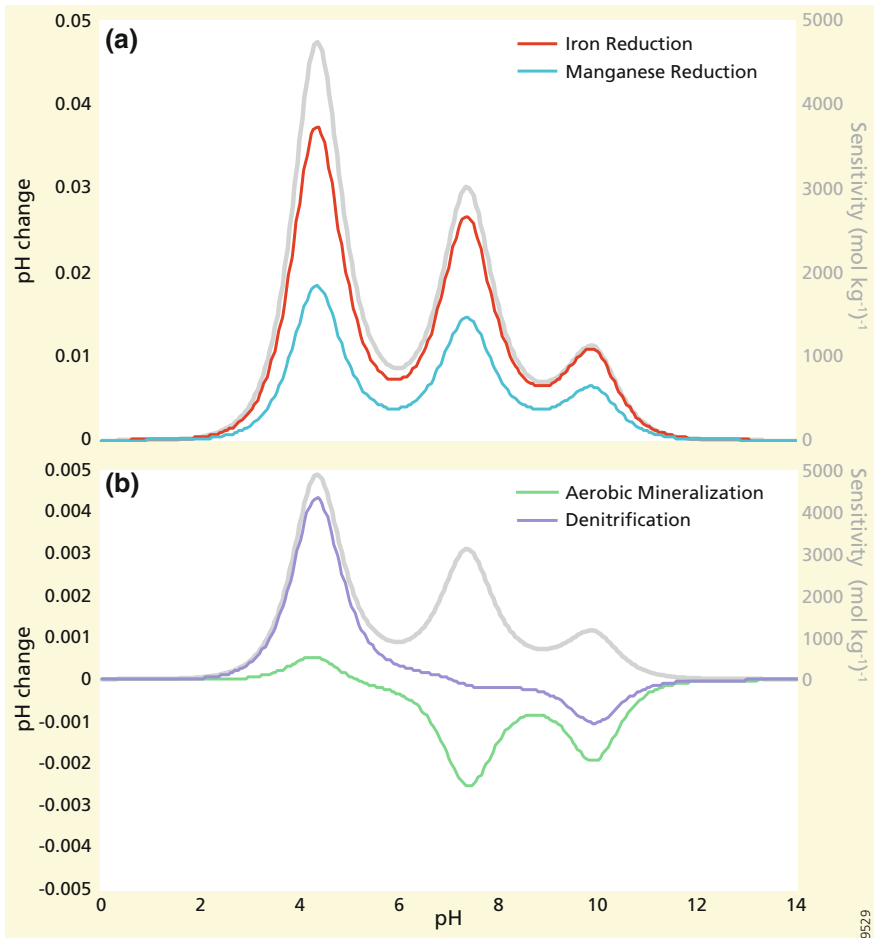


**Fig. 5.8** The sensitivity factor  $(\text{mol kg}^{-1})^{-1}$  as a function of the pH

the “other  $\text{CO}_2$  problem”, has consequences for the chemistry, biology and geology of the ocean.

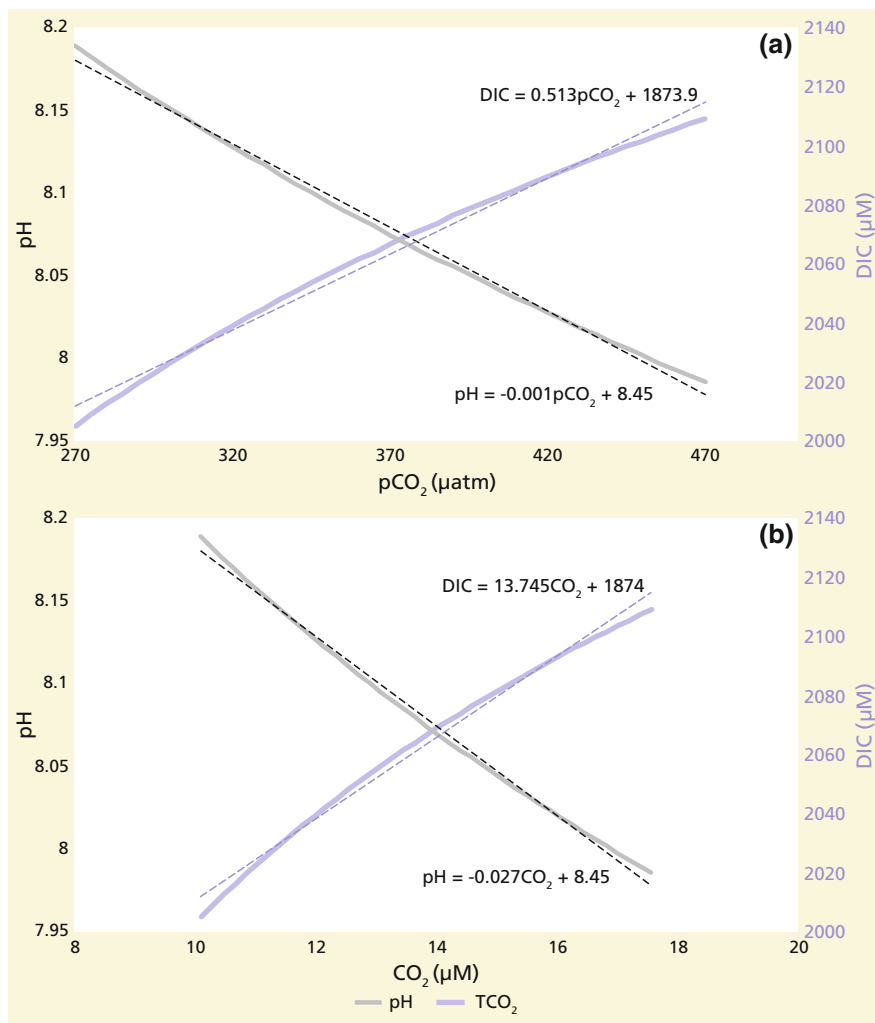
Figure 5.10 shows the dependence of pH and DIC on atmospheric  $\text{pCO}_2$  for a constant alkalinity ocean ( $2300 \mu\text{M}$ ,  $T = 15$ ,  $S = 35$ ). Dissolved inorganic carbon concentrations increase almost linear with a slope of  $0.513 \mu\text{M}/\mu\text{atm pCO}_2$  (or  $13.745 \mu\text{M}/\mu\text{M dissolved CO}_2$ ), while pH declines almost linearly with a slope of  $-0.0011 \text{pH}/\mu\text{atm pCO}_2$  (or  $-0.027 \text{pH}/\mu\text{M dissolved CO}_2$ ). These thermodynamic predictions for declining pH and increasing DIC are fully consistent with observations in the ocean. These dependences of  $\text{CO}_2$  and pH have received much attention and have been treated more formally using differential calculus (Sarmiento and Gruber 2006; Hagens and Middelburg 2016). The changes in pH can be split into multiple parts:

$$dpH = \left(\frac{\partial pH}{\partial T}\right)dT + \left(\frac{\partial pH}{\partial S}\right)dS + \left(\frac{\partial pH}{\partial TA}\right)dTA + \left(\frac{\partial pH}{\partial DIC}\right)dDIC + \dots \quad (5.33)$$



**Fig. 5.9** **a** pH change due to iron-oxide and manganese oxide reduction as function of pH; **b** pH change due to aerobic mineralization and denitrification as a function of pH. The sensitivity factor (Fig. 5.8) is shown as reference (grey)

where  $\left(\frac{\partial pH}{\partial x}\right)$  are partial derivatives, implying that these are, in principle, only valid if the other variables are kept constant, and they can be considered as a measure of the sensitivity of pH to a change in the respective environmental variable. For instance, the first partial derivative,  $\left(\frac{\partial pH}{\partial T}\right)$  has a value of  $\sim -0.014$  per degree (Hagens and Middelburg 2016), close to slope in Fig. 5.10 ( $-0.015$  per degree). The third one,  $\left(\frac{\partial pH}{\partial TA}\right)$ , is the sensitivity factor (Eq. 5.21) shown in Fig. 5.8.



**Fig. 5.10** pH and DIC dependence on  $\text{pCO}_2$  ( $\mu\text{atm}$ ) (a) and dissolved  $\text{CO}_2$  ( $\mu\text{M}$ ) (b). Regression lines are shown as dashed lines

Ocean acidification will lead to a decrease in buffer value (Fig. 5.3), and this is one of the reasons why the ocean is projected to take up less anthropogenic carbon in the future (besides changes in ocean physics and biology). Consequently, the ocean carbon dioxide system will be more sensitive to changes, and diurnal and seasonal changes in pH are projected to increase. Moreover, shifting chemical equilibria will have consequences for sound attenuation in the ocean.



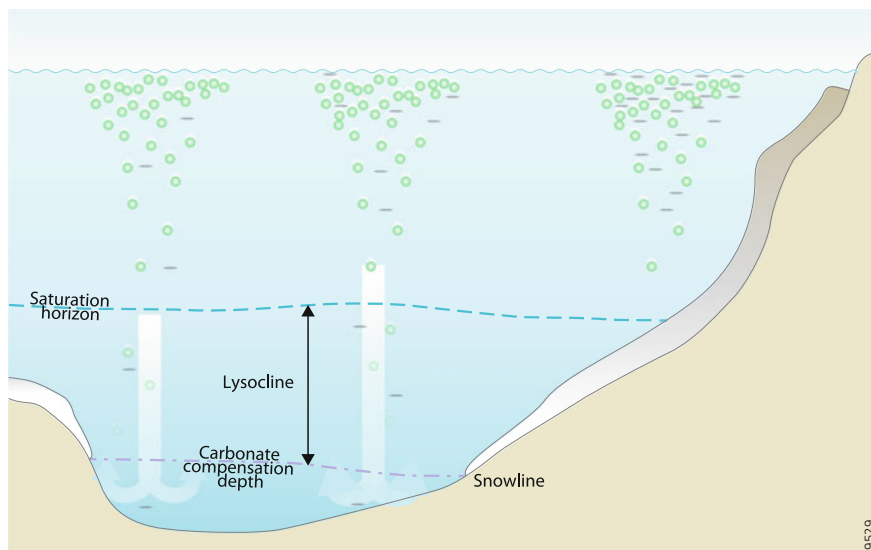
Many organisms, autotrophs as well as heterotrophs, will be impacted by either the decline in pH and carbonate ions or the increase in dissolved inorganic carbon. The latter, carbonation, might stimulate primary producers, which are carbon limited at the moment. Most calcifying organisms are likely going to suffer from the decrease in carbonate ion availability, but calcification is under biological control and sometimes completed inside the organism, such that these responses are rather complex (Kroeker et al. 2013).

### **Box 5.2: Carbonate compensation dynamics**

Buffering in the ocean not only occurs homogeneously by re-arrangement of acids and conjugated bases, but also heterogeneously by re-adjustment of the balance between precipitation and dissolution of carbonate minerals. While homogenous buffering is fast (instantaneous equilibria), heterogeneous buffering has a larger capacity because of the large stock of carbonate minerals stored in marine sediments. This heterogeneous buffering is called carbonate compensation and biology plays a major role.

Carbonate minerals are predominantly formed biologically in the modern ocean, but there are a few exceptions, such as the formation of ooids in tropical systems and authigenic calcite and dolomite formation in sediments. However, even in these cases, biology plays indirectly a major role by governing the chemical composition of the fluids they formed in (e.g. carbonate formation induced by alkalinity production resulting from anaerobic oxidation of methane). Biological carbonate formation takes place in the water column by autotrophs (e.g., coccoliths) and heterotrophs (pteropods and foraminifera) and in the benthos by various organisms, autotrophs (e.g. coralline algae) and heterotrophs (e.g., corals, crustaceans, and molluscs). Biogenic carbonates can be aragonite, calcite or high-Mg calcites and combinations thereof.

Following death of calcifiers in benthic systems, the biogenic carbonate can either dissolve or accumulate at the seafloor and be buried. Carbonate produced in the surface layer of the open ocean can dissolve in the water column while particles settle, dissolve at the seafloor, or accumulate in sediments. Accumulation of biogenic carbonate is a prominent feature of ocean sediments; some sediments consists almost entirely of biogenic carbonate debris. Dissolution of carbonate is primarily driven by undersaturation, and organisms contribute to dissolution in a number of ways. One, many biogenic minerals have organic layers and microbial degradation of these layers exposes new surfaces to undersaturated solutions. Two, boring organisms (sponges, fungi) weaken the structure and texture of biogenic carbonate and consequently accelerate dissolution. Three, the metabolic activity of organisms has consequences for the saturation state of solution, e.g. carbon dioxide



**Fig. 5.11** Carbonate compensation concept. Biogenic  $\text{CaCO}_3$  tests are produced in the photic zone of the oceans (green circles). Upon death, those tests escaping dissolution near the surface, settle along with clays materials. Above the saturation horizon, waters are supersaturated and  $\text{CaCO}_3$  tests are largely preserved. Below the saturation, waters are undersaturated because of increasing solubility with depth and the release of  $\text{CO}_2$  from organic matter decay and  $\text{CaCO}_3$  will dissolve. Dissolution occurs primarily at the sediment surface as the sinking velocity of debris is rapid (broad white arrows). At the carbonate compensation depth, the rate of dissolution exactly matches rate of supply of  $\text{CaCO}_3$  from above. At steady state this carbonate compensation depth is similar to the snowline; the first depth where carbonate poor sediments occur. The lysocline is the depth interval between the saturation and carbonate compensation depth (from Boudreau et al. 2018)

release during respiration and generation of strong acids during re-oxidation reactions (nitrification, sulphur oxidation) lowers the saturation state. The latter processes are important in coastal sediments that receive high organic carbon inputs and that are bioturbated or vegetated.

There are two carbonate compensation mechanisms operating in the ocean: chemical and biological compensation (Boudreau et al. 2018). Chemical compensation focuses on the dissolution or preservation of carbonate minerals at the ocean floor and implicitly assumes that net carbonate production remains constant. Carbonate particles settling in the ocean interior start to dissolve when water becomes thermodynamically undersaturated at depth  $z_{\text{sat}}$ . This carbonate saturation depth can be estimated from:

$$z_{\text{sat}} = z_{\text{ref}} \ln \left( \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}} \right) \quad (5.34)$$

where  $K_{sp}$  is the temperature, salinity and pressure depending stoichiometric solubility product,  $[Ca^{2+}]$  and  $[CO_3^{2-}]$  are the concentration of dissolved calcium and carbonate ions and  $z_{ref}$  is a scaling parameter (Boudreau et al. 2010). This undersaturation is partly due to increasing pressure and declining temperature (thermodynamics) and partly the consequence of a decrease in carbonate ion because of respiration of particulate organic matter (the biological pump). Below  $z_{sat}$  dissolution rates increase systematically with depth, and at a certain depth the dissolution rate balances the settling flux of carbonate (Fig. 5.11). This carbonate compensation depth ( $z_{CCD}$ ) is governed by the following equation (Boudreau et al. 2010):

$$z_{CCD} \approx z_{ref} \ln \left( \frac{F_{car} [Ca^{2+}]}{K_{sp} A \beta_{mt}} + \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}} \right) \quad (5.35)$$

where  $F_{car}$  is the export flux of carbonate,  $A$  is the surface area of the seafloor and  $\beta_{mt}$  is the mass transfer of solutes across the diffusive boundary layer at the seafloor. The carbonate compensation depth ( $z_{CCD}$ ) is always larger than the saturation horizon ( $z_{sat}$ ) because of the first term with only positive parameters. The carbonate compensation depth is equal to the snowline, the depth at which carbonate disappear from sediments, under steady-state conditions. During periods of ocean acidification, bottom-waters will eventually obtain lower carbonate ions concentrations, and the saturation and carbonate compensation depths rise and dissolution of carbonate at the seafloor increases until a new balance between dissolution and export flux of carbonate has been reached. Conversely, during periods of alkalinisation, bottom water will eventually get higher carbonate ion concentrations (by advection), carbonate mineral dissolution decreases, resulting in a deepening of saturation and compensation depth till a new balance has been reached. This carbonate compensation mechanisms operates on a time scale of 100–10,000 years.

This chemical compensation mechanism is based on the assumption that ocean acidification has no impact on calcification and the export of calcium carbonate. However, many experiments have shown that calcification rates, and thus export of calcium carbonate from the surface ocean declines with saturation state of surface water. A decline in carbonate export ( $F_{car}$ ) would lead to shallowing of the carbonate compensation depth on the very short time scale (<1 yr), but would cause additional deepening on the longer term (>10<sup>4</sup> yr) because calcification is an alkalinity sink. With less removal of carbonate ions in the surface waters, deep water will eventually become richer in carbonate and more carbonate minerals will survive dissolution at the seafloor (Boudreau et al. 2018).

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