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2 **Ocean Alkalinity, Buffering and Biogeochemical Processes**

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10 **Key Points:**

- 11 • Titration and charge-balance alkalinity differ
- 12 • Ocean buffering is quantified using sensitivity factors
- 13 • The impact of biogeochemical processes on pH depends on environmental conditions
- 14 • Ocean alkalinity budget is balanced when the additional alkalinity input from riverine
15 particulate inorganic carbon and sedimentary sources is included
- 16

Abstract

Alkalinity, the excess of proton acceptors over donors, plays a major role in ocean chemistry, in buffering and in calcium carbonate precipitation and dissolution. Understanding alkalinity dynamics is pivotal to quantify ocean carbon dioxide uptake during times of global change. Here we review ocean alkalinity and its role in ocean buffering as well as the biogeochemical processes governing alkalinity and pH in the ocean. We show that it is important to distinguish between measurable titration alkalinity and charge-balance alkalinity that is used to quantify calcification and carbonate dissolution and needed to understand the impact of biogeochemical processes on components of the carbon dioxide system. A general treatment of ocean buffering and quantification via sensitivity factors is presented and used to link existing buffer and sensitivity factors. The impact of individual biogeochemical processes on ocean alkalinity and pH is discussed and quantified using these sensitivity factors. Processes governing ocean alkalinity on longer time scales such as carbonate compensation, (reversed) silicate weathering and anaerobic mineralization are discussed and used to derive a close-to-balance ocean alkalinity budget for the modern ocean.

Plain Language Summary

The ocean plays a major role in the global carbon cycle and the storage of anthropogenic carbon dioxide. This key function of the ocean is related to the reaction of dissolved carbon dioxide with water to form bicarbonate (and minor quantities of carbonic acid and carbonate). Alkalinity, the excess of bases, governs the efficiency at which this occurs and provides buffering capacity towards acidification. Here we discuss ocean alkalinity, buffering and biogeochemical processes and provide quantitative tools that may help to better understand the role of the ocean in carbon cycling during times of global change.

1 Introduction

The ocean plays a major role in controlling atmospheric carbon dioxide and storage of anthropogenic carbon (Gruber et al., 2019). For the last decade, ocean uptake of anthropogenic carbon was $2.5 \pm 0.6 \text{ Pg C y}^{-1}$, i.e. about 23 % of annual anthropogenic carbon emissions due to fossil fuels, cement production and land-use change (Friedlingstein et al., 2019). The cumulative (1850-2019) total release of anthropogenic carbon was $655 \pm 65 \text{ Pg C}$, of which $160 \pm 20 \text{ Pg C}$ (about 24 %) has accumulated in the ocean (Friedlingstein et al., 2019). This crucial role of the ocean in attenuating the increase in atmospheric carbon dioxide, and thus global warming, is related to the large volume (and surface area) of the ocean and the reaction of dissolved carbon dioxide with water to form carbonic acid, a weak acid that dissociates to protons and the conjugated bases bicarbonate and carbonate which are not directly exchangeable with the atmosphere (Butler, 1982). The redistributions among gaseous and dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions are governed by multiple co-occurring equilibria with the result that approximately 19 out of the 20 molecules of carbon dioxide entering the ocean are converted into bicarbonate and carbonate ions. The total amount of dissolved inorganic carbon (DIC) in the ocean is typically about 200 times that of dissolved carbon dioxide (Zeebe and Wolf-Gladrow, 2001; Middelburg, 2019).

This re-equilibration following the principles of le Chatelier (1884) provides resistance to, but does not entirely eliminate, changes in ocean carbon chemistry. Oceanic uptake of anthropogenic carbon dioxide has caused increases in dissolved carbon dioxide and total inorganic carbon concentrations, and decreases in carbonate ions and ocean pH, i.e. ocean acidification (Gattuso and Hanson, 2011). Ocean acidification has consequences for further ocean carbon dioxide uptake, the precipitation and dissolution of carbonate minerals and for the functioning and survival of marine organisms (Kroeker et al., 2013). It is therefore important that we understand and are able to quantify the buffering, i.e. resistance, of the ocean in the changing world of the Anthropocene. Detailed understanding and quantification of how biogeochemical processes impact pH and marine carbon dioxide equilibria is pivotal to predicting the impact of ocean acidification on marine organisms, carbonate mineral precipitation and dissolution, (seasonal) variability in carbonate system parameters and the resilience of various ecosystem functions (Orr et al., 2018). Understanding is also required to use pH observations to infer the intensity and changes in biogeochemical processes and to evaluate the feasibility of ocean engineering options (Soetaert et al., 2007; Renforth and Henderson, 2017; Gattuso et al., 2018).

Although acid-base equilibria of simple solutions are well understood (Butler, 1964, 1982; Stumm and Morgan, 1981; Morel and Hering, 1993), the carbon dioxide system in seawater remains challenging because of the complexity of multiple equilibria (Zeebe and Wolf-Gladrow, 2001). Alkalinity, the excess of bases (proton acceptors) over acids (proton donors) in a solution (a complete definition is provided in section 2), is not only impacted by acid-base additions, but also by redox reactions and mineral dissolution and precipitation. Oxidation reactions involving oxygen generally consume alkalinity, while anaerobic processes usually produce alkalinity. Dissolution of minerals is often accompanied by alkalinity generation. Alkalinity is a central concept in our treatment of the oceanic carbon dioxide system, because it is measurable, it remains unchanged with pressure and temperature (i.e. it is conservative), it is governed by the net effect of multiple chemical equilibria and often needed to solve the mathematical equilibrium problem (Butler, 1982; Stumm and Morgan, 1981). However, there are multiple interpretations, and even definitions, of alkalinity that are not always used in a consistent way. One of the goals of this review is to clarify inconsistencies or sources of confusion, e.g. the distinction between titration alkalinity (that can be measured) and charge-balance alkalinity (that should be used to interpret biogeochemical processes in nature). Another goal is to discuss approaches to quantify the resistance (buffering) or its inverse, the sensitivity of the ocean carbon dioxide system and pH to change. While many geochemical and oceanographic studies mention ocean buffering there are few where buffer and/or sensitivity factors are being used, except for the well-known Revelle factor expressing the sensitivity of $p\text{CO}_2$ to changes in DIC (Revelle and Suess, 1957; Bolin and Eriksson, 1959; Sundquist et al., 1979; Sarmiento and Gruber, 2006). This is surprising as rigorous treatments of buffering have been published a century ago (Koppel and Spiro, 1914; Van Slyke, 1922).

Following a treatment of ocean alkalinity (section 2) and sensitivity and buffer factors (section 3), we will discuss the impact of biogeochemical processes on pH and $p\text{CO}_2$ (section 4), heterogeneous buffering, including carbonate compensation (section 5) and factors governing ocean alkalinity, including an alkalinity budget of the ocean (section 6). Basic terminology is explained in Box 1. The Supporting Information accompanying this article contains three sections and the R script used to generate figures and results.

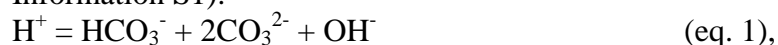
2 Ocean alkalinity

There is a long history from the 18th century observation that seawater is alkaline (Marsigli, 1725) to the modern concept of seawater alkalinity (Dickson, 1981; Zeebe and Wolf-Gladrow, 2001). The term alkalinity was already in use by chemists in the first half of the 19th century (e.g., Donovan, 1839) and utilized since in multiple disciplines, including medicine (Andral, 1850) and oceanography (Dittmar, 1884). Dickson (1992) provides an excellent historical account on the alkalinity concept in seawater and showed that it involved both advances in analytical procedures as well as the development of a chemical model for seawater. Rather than recapitulating the historical context, we believe it is instructive to formally distinguish between titration alkalinity, i.e. total alkalinity, as defined by Dickson (1981) and the charge balance alkalinity needed to quantify buffering and pH changes in natural environments. Observational and experimental studies in the ocean are normally based on titration alkalinity, but theoretical, modelling and geological studies sometimes employ the charge balance approach (e.g., Broecker, 1974; Boudreau, 1996; Turchyn and DePaolo, 2019). The charge balance alkalinity concept is often used in freshwater systems (with high concentrations of dissolved organic matter) and is also known as the excess negative charge (ENC; Soetaert et al., 2007) and linked to the explicit conservative expression of total alkalinity (Zeebe and Wolf-Gladrow, 2001; Wolf-Gladrow et al., 2007). This difference between titration alkalinity (TA) and charge balance alkalinity (CBA) is related to the equations used to solve the chemical equilibrium problem: the TA is based on a proton balance, while CBA is based on a charge balance closure (Supporting Information S1). Depending on the specific problem at hand and definition of the system, TA and CBA may differ or be identical. The lack of distinction between TA and CBA has caused confusion and discussion.

2.1 Titration alkalinity

In 1981 Dickson defined the alkalinity (TA) as follows: “*The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample*”. The definition is stated in gravimetric units to remain independent of the temperature and pressure of the system. Furthermore, Dickson (1981) adopted a pK value of 4.5 as the reference level to distinguish between proton donors (acids with a dissociation constant $pK < 4.5$) and proton acceptors ($pK \geq 4.5$) to continue the common practice to match the reference level with the carbonic acid equivalence point of a titration.

Using this exact definition of alkalinity of Dickson (1981), it is straightforward to calculate the titration alkalinity for any system for which the contributing components are known and characterized in terms of dissociation constants. Figure 1A shows the distribution diagram of acid-base pairs (Bjerrum plot) for the carbonate system in seawater. For the $\text{CO}_2\text{-H}_2\text{O}$ system, at $\text{pH}=4.5$, carbonic acid is by far the dominant species and used as reference. Referenced to this point, we then arrive at the proton balance, a mass balance for protons (see Supporting Information S1):



with proton donors on the left-hand side and proton acceptors on the right-hand side. The carbonate ion is counted twice because it is two protons below the reference level H_2CO_3 . The titration alkalinity, i.e. excess of proton acceptors over donors with respect to carbonic acid, the reference level, is then defined as:

$$\text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (\text{eq. 2}).$$

Other acid-base systems can be included in the alkalinity expression. To this end, all chemical species in the solution have to be classified either as proton donor or acceptor relative to the zero level of protons for each acid-base system (Fig. 1B). Dickson (1981) included fluoride, sulphate, borate, phosphate, silicate, ammonia and hydrogen sulphide to eventually arrive at:

$$\text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{HPO}_4^{2-} + 2\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + \text{NH}_3 + \text{HS}^- + 2\text{S}^{2-} - \text{H}^+ - \text{HF} - \text{HSO}_4^- - \text{H}_3\text{PO}_4 \quad (\text{eq.3}).$$

This proton balance approach towards alkalinity allows an exact definition of alkalinity. Dickson (1981) focused on the quantification of alkalinity in seawater from titration data and therefore did not include the strong acids H_2SO_4 and HNO_3 , nor HNO_2 and $\text{H}_2\text{SiO}_4^{2-}$. However, these can easily be included using the same approach (Soetaert et al., 2007; Wolf-Gladrow et al., 2007) and results in:

$$\text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{HPO}_4^{2-} + 2\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + 2\text{H}_2\text{SiO}_4^{2-} + \text{NH}_3 + \text{HS}^- + 2\text{S}^{2-} - \text{H}^+ - \text{HF} - \text{HSO}_4^- - 2\text{H}_2\text{SO}_4 - \text{H}_3\text{PO}_4 - \text{HNO}_2 - \text{HNO}_3 \quad (\text{eq. 4}),$$

where H_2SO_4 and HNO_3 are zero for the pH values > 0 .

The titration alkalinity definition of Dickson (1981) is fully consistent with the conservation equation for hydrogen ions (TOT_H) of Morel and Hering (1993), which is also based on a proton (mass) balance (Supporting Information S1). Specifically, $\text{TA} = -\text{TOT}_\text{H}$ when the components chosen are the reference level species at pH=4.5.

2.2. Charge balance alkalinity

Electrolyte solutions, including seawater, obey the electroneutrality condition: i.e. the sum of negative and positive charges balances at the macroscale (Boudreau et al., 2004; Wolf-Gladrow et al., 2007; Soetaert et al., 2007). For seawater, we thus have to balance the sum of cation concentrations:

$$\text{Na}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + 2\text{Sr}^{2+} + (\dots) + \text{NH}_4^+ + \text{H}^+ \quad (\text{eq. 5a}),$$

with the sum of anion concentrations:

$$\text{Cl}^- + \text{Br}^- + (\dots) + \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{H}_2\text{PO}_4^- + 2\text{HPO}_4^{2-} + 3\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + 2\text{H}_2\text{SiO}_4^{2-} + \text{HS}^- + 2\text{S}^{2-} + \text{F}^- + \text{HSO}_4^- + 2\text{SO}_4^{2-} + \text{NO}_2^- + \text{NO}_3^- \quad (\text{eq. 5b}),$$

where the ellipses (...) stand for additional ions in solution. In charge conservation equations, ions are multiplied with their charge. This equation can be re-arranged into a part that is conservative and a part that is not and involves species exchanging protons. Accordingly, when ignoring minor conservative species (...), the sum of strong base cations minus the sum of strong acid anions (i.e. excess positive charge of conservative ions):

$$\text{EPC} = \text{Na}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + 2\text{Sr}^{2+} - \text{Cl}^- - \text{Br}^- \quad (\text{eq. 6a})$$

should balance the excess negative charge (ENC) of non-conservative ions that are involved in proton exchange reactions:

$$\text{ENC} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{H}_2\text{PO}_4^- + 2\text{HPO}_4^{2-} + 3\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + 2\text{H}_2\text{SiO}_4^{2-} + \text{HS}^- + 2\text{S}^{2-} + \text{F}^- + \text{HSO}_4^- + 2\text{SO}_4^{2-} + \text{NO}_2^- + \text{NO}_3^- - \text{NH}_4^+ - \text{H}^+ \quad (\text{eq. 6b}).$$

This excess negative charge (Soetaert et al., 2007) is also known as charge balance alkalinity (CBA). Hence, CBA is defined as the sum of non-conservative ions involved in proton exchange reactions that account for the difference between the sum of conservative cations and anions. Charge balance alkalinity (CBA; eq. 6b) and titration alkalinity (TA; eq. 4) are linked via:

$$TA = CBA + \sum NH_3 - \sum NO_3 - \sum NO_2 - \sum PO_4 - 2\sum SO_4 - \sum F \quad (\text{eq. 7}),$$

where $\sum NH_3 = NH_3 + NH_4^+$, $\sum NO_3 = NO_3^- + HNO_3$, $\sum NO_2 = NO_2^- + HNO_2$, $\sum PO_4 = H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$, $\sum SO_4 = H_2SO_4 + HSO_4^- + SO_4^{2-}$ and $\sum F = HF + F^-$ are the total concentrations of ammonia, nitrate, nitrite, phosphate, sulphate and fluoride, respectively. This difference between titration and charge-balance alkalinity is due to the charge of components at the reference pH level of 4.5. At pH 4.5, ammonia is present as ammonium (+1), while nitrate, nitrite, fluoride and phosphate have an overall charge of -1 and sulphate is present as SO_4^{2-} with charge -2 (Fig. 1C). Accordingly, dissolved inorganic carbon does not appear in eq. 7 because it is present as the uncharged carbon dioxide at pH 4.5. In other words, the difference between CBA and TA is caused by components for which the species used as zero proton level are charged (e.g. $H_2PO_4^-$ is the zero-proton level for phosphate, Dickson, 1981).

Wolf-Gladrow et al. (2007) introduced the explicitly conservative expression of total alkalinity (TA_{ec}) that relates the sum of conservative cations and anions (i.e. excess positive charge, eq. 6a) and total concentrations of ammonia, nitrate, nitrite, phosphate, sulphate and fluoride with titration alkalinity (TA):

$$TA_{ec} = Na^+ + 2 Mg^{2+} + 2 Ca^{2+} + K^+ + 2 Sr^{2+} - Cl^- - Br^- + (\dots) + \sum NH_3 - \sum NO_3 - \sum NO_2 - \sum PO_4 - 2\sum SO_4 - \sum F \quad (\text{eq. 8}),$$

or alternatively formulated: $TA_{ec} = EPC + TA - CBA$.

This explicitly conservative form of alkalinity is equivalent to Dickson's expression (as $EPC - CBA = 0$) for titration alkalinity (eq.4), but each single term is conservative to proton exchange and pressure and temperature changes (Wolf-Gladrow et al., 2007). Since charge balance alkalinity is directly related to the difference between conservative cations and anions, it is evident that CBA and thus also TA co-vary with salinity. Alkalinity and salinity are both affected to the same degree by processes that dilute or concentrate seawater, such as precipitation, evaporation and melting or formation of ice.

2.3 Alternative alkalinity and related expressions

The titration and charge balance alkalinity expressions (eq. 4 and 6b) are well defined and traceable to the use of a proton or charge balance (Supporting Information S1), but alternative expressions are often used. There are a number of reasons for this. One, alkalinity and related concepts are used in multiple disciplines (e.g., chemistry, medicine, environmental engineering, ecology, geology, hydrology, limnology, oceanography) with their own specific scientific traditions and terminology. Two, although many species are included in the formal definition of alkalinity in seawater, a few of these dominate by far and most others can be ignored as a first-order approximation. Carbonate alkalinity ($CA = HCO_3^- + 2CO_3^{2-}$) typically accounts for >95% of the total alkalinity in the ocean. Many studies (e.g., Broecker and Peng, 1982) use a simple form of alkalinity including only water and carbonate alkalinity terms (eq. 2). In seawater, a slightly more accurate expression is obtained when borate alkalinity is included as well. Zeebe and Wolf-Gladrow (2001) termed this alkalinity for most practical purposes (PA_{ZW-G}):

$$PA_{ZW-G} = HCO_3^- + 2CO_3^{2-} + B(OH)_4^- + OH^- - H^+ = CA + \text{borate alkalinity} + \text{water alkalinity} \quad (\text{eq. 9}).$$

PA_{ZW-G} is often used interchangeably with TA because it typically represents > 99% of total alkalinity in oxygenated ocean surface waters. In anoxic waters and pore-waters of marine sediments in which metabolites (ammonia, phosphate, sulphide and silicate) have accumulated, some of these are then included in the operational definition of alkalinity for that system (Ben-Yaakov, 1973; Boudreau and Canfield, 1993; Hiscock and Millero, 2006). Finally, a major reason for alternative alkalinity expressions relates to application of the measurable property TA to biogeochemical processes that impact CBA because of electroneutrality constraints.

2.3.1 Use of titration alkalinity as proxy for charge balance alkalinity

Charge balance and titration alkalinity differ by the total amounts of nitrite, nitrate, ammonia, phosphate, sulphate and fluoride (eq. 7; Soetaert et al., 2007; Wolf-Gladrow et al., 2007). Processes such as primary production, organic matter degradation and nitrification involve these components and thus potentially impact alkalinity. Brewer and Goldman (1976) and Goldman and Brewer (1980) documented increases in alkalinity due to nitrate and phosphate uptake and a decrease in alkalinity due to ammonium uptake (see section 4). These alkalinity changes (ΔTA) due to biological consumption or production processes have to be taken into account when using measured TA values for quantification of calcium carbonate precipitation or dissolution. Specifically, Brewer et al. (1975) introduced the potential alkalinity change ($\Delta P.A.$) as a measure of calcite formation/dissolution:

$$\Delta P.A. = \Delta TA + \Delta \sum NO_3 + \Delta \sum PO_4 \quad (\text{eq. 10}).$$

By comparing eq. 10 and 7, it is clear that potential alkalinity change is a proxy for CBA change based on measured nitrate, phosphate and TA. However, only changes in nitrate and phosphate due to biological processes should be considered, not those due to physical mixing (Huang et al., 2015). Similarly, Kanamori and Ikegami (1982) identified the need to include nitrate, phosphate and sulphate when using measured TA for calculating alkalinity changes due to calcium carbonate dynamics. Including nitrate, phosphate and sulphate contributions in Redfield proportions would result in the following expression for potential alkalinity (P.A.):

$$P.A. = TA + a^* \sum NO_3 \quad (\text{eq. 11})$$

where a varies from 1.06 (Chen, 1978), 1.26 (Kanamori and Ikegami, 1982) to 1.36 (Wolf-Gladrow et al., 2007), depending on the Redfield ratios considered.

The Alk^* tracer (Carter et al., 2014) combines the potential alkalinity (eq. 11 with $a=1.26$) with salinity normalization to single out the effect of calcium carbonate dynamics on alkalinity. Similarly, Feely et al. (2002) introduced the TA^* tracer which expresses the change in TA due to calcium carbonate dynamics: $TA^* = 0.5 (TA_s - TA_s^0) + 0.63^*(0.0941 \text{ AOU})$, where TA_s and TA_s^0 are the measured and preformed salinity-normalized TA, respectively, and AOU is the apparent oxygen utilization, introduced to correct for charges generated during organic matter dynamics. Finally, ecologists studying calcification by benthic communities (coral reefs, bivalves) often employ the alkalinity anomaly technique (Kinsey, 1978; Chisholm and Gattuso, 1991; Gazeau et al., 2015) which involves measurement of TA and correcting it with ammonium, nitrate and phosphate for obtaining calcium carbonate dynamics.

2.3.2 Organic alkalinity

While oceanographers usually measure TA and introduce empirical corrections to arrive at the CBA needed for quantitative applications (eq. 10, 11), freshwater scientists studying soft natural waters have to use a charge balance of the major conservative ions because of an important contribution of organic acids (Hemond, 1990). Contrary to the inorganic acid-base species discussed before, dissolved organic compounds comprise a complex, heterogeneous group, which poses a challenge on classifying its acid-base properties and quantifying their contribution to TA (Hu, 2020). The composition and thus acid-base properties of dissolved organic compounds depend on whether these compounds are derived from locally produced organic matter or transported from adjacent terrestrial ecosystems (Leenheer and Croue, 2003). Phytoplankton-derived dissolved organic compounds are found to have two distinct proton binding sites with pK values of 4.4-4.9 and 6.1-6.9, respectively (Ko et al., 2016). In contrast, terrestrially-derived organic matter is dominated by humic substances. These comprise a much wider range of proton binding sites, often described by carboxyl and phenolic groups having average pK values of about 3.7 ± 2.4 and about 12.5 ± 1.8 , respectively (Perdue et al., 1984). This wide range in pK values implies that at least part of the dissolved organic compounds, either of autochthonous or allochthonous origin, acts as proton acceptor at pK 4.5, thus contributing to TA despite being absent in eq. 4.

Substantial contributions of organic alkalinity to TA have been found in laboratory incubations (Ko et al., 2016), estuaries (Cai et al., 1998), sediment pore waters (Łukawska-Matuszewska, 2016; Łukawska-Matuszewska et al. 2018), coastal waters receiving high terrestrial inputs, like the Baltic Sea (Kulínski et al., 2014; Hammer et al., 2017) or salt marsh-influenced coastal waters (Song et al., 2020), and ocean waters (Fong & Dickson, 2019). Organic alkalinity is normally assessed by difference: that is, carbonate alkalinity is derived from two out of three other measurable parameters in the $\text{CO}_2\text{-H}_2\text{O}$ system (pH, DIC or pCO_2), and organic alkalinity is calculated as the difference between TA measured and calculated from the contributions of the inorganic species following eq. 3. This method relies on at least one parameter (pH or pCO_2) which value is affected by the presence of organic compounds, and therefore does not allow for an exact value of organic alkalinity. Back-titration methods to directly quantify organic alkalinity are used by others (Cai et al., 1998; Hernández-Ayon et al., 2007; Muller and Bleie, 2008; Yang et al, 2015), showing no clear correlation with organic alkalinity estimated by difference (Song et al, 2020). Alternatively, chemical equilibrium models describing proton binding to humic substances, which are well-known in the freshwater community (Kinniburgh et al., 1999), can be coupled to inorganic carbonate system calculations (Ulfsbo et al., 2015).

2.3.3 Acid neutralizing capacity

Although not often used in oceanography, the term acid neutralizing capacity (ANC), is closely linked to titration alkalinity (TA). The ANC of a solution to the carbonic acid equivalent point of a titration is fully consistent with the Dickson (1981) definition of TA (Weber and Stumm, 1963; Stumm and Morgan, 1981). Other equivalence points are termed p- alkalinity (phenolphthalein endpoint of titration, corresponding to the proton balance of eq. 1.13 in Supporting Information S1) and caustic alkalinity, the reverse of acidity, with the proton balance: $\text{TOT} = \text{OH}^- - \text{H}^+ - 2 \text{H}_2\text{CO}_3 - \text{HCO}_3^-$ (Stumm and Morgan, 1981). Theoretically, one can use any expression for alkalinity to solve the $\text{CO}_2\text{-H}_2\text{O}$ system as long it is properly defined.

Some researchers distinguish between TA and ANC whether water samples are filtered or not, respectively (Asuero and Michalowski, 2011; Michalowski and Asuero, 2012). The chemical model underlying Dickson's TA only includes homogeneous reactions in solution and ignores proton exchange with particles and organisms. This implies that water samples for alkalinity should be filtered before titration because of potential proton exchange with the surface of phytoplankton, bacteria and inorganic particles and the dissolution of suspended particulate inorganic carbon (Kim et al., 2006), and dedicated filtration methods have been developed (Bockman and Dickson, 2014). However, differences between filtered and unfiltered samples are often negligible (open ocean: Chanson and Millero, 2007; coastal systems: Hagens et al., 2015), but might be substantial in experimental systems with high densities of organisms or particles.

Section 3. Buffering and sensitivity factors

Seawater is a solution with multiple weak acids and bases in contact with both the atmosphere and sediments containing minerals that have the potential to react when solution composition or physical conditions change. Seawater is consequently well buffered, i.e. able to resist changes by transferring protons. The response of a chemical equilibrium system to a perturbation follows the principle of le Chatelier. The original statement of Henry Louis le Chatelier (1884) "*Tout système en équilibre chimique stable soumis à l'influence d'une cause extérieure qui tend à faire varier soit sa température, soit sa condensation (pression, concentration, nombre de molécules dans l'unité de volume) dans sa totalité ou seulement dans quelques-unes de ses parties, ne peut éprouver que des modifications intérieures, qui, si elles se produisaient seules, amèneraient un changement de température ou de condensation de signe contraire à celui résultant de la cause extérieure.*" is often re-phrased as: whenever a system in equilibrium is disturbed by changing the conditions, the positions of the equilibria shift in such a way that the effect of the change will be moderated.

In this section, we discuss the sensitivity and resistance of ocean chemistry to changes. It is instructive to distinguish between homogeneous reactions in solution and heterogeneous buffering involving interactions with particles (e.g. dissolution or precipitation of carbonate minerals modifying alkalinity). Homogeneous buffering takes place nearly instantaneously and is most relevant for quantifying and understanding the impact of biogeochemical processes on pH on short (hour-days) timescales (Frankignoulle, 1994; Soetaert et al., 2007; Egleston et al., 2010). Heterogeneous buffering reactions may involve very long time scales (months to millions of years) and will be discussed in section 5.

3.1. Buffer capacity systematics

Although the buffer capacity of seawater and its role in earth system science has been recognized in the first part of the 20th century (Thompson and Bonnar, 1931; Mitchell and Rakestraw, 1933) and mathematical tools to quantify buffer efficiency have been developed a century ago (Koppel and Spiro, 1914; van Slyke, 1922), quantitative treatments of seawater buffering have historically received little attention, except for the homogeneous Revelle factor (Revelle and Suess, 1957) and the acid-base buffer capacity (van Slyke, 1922; Weber and Stumm, 1963). The acid-base buffer value β was originally defined for biological fluids by Koppel and Spiro (1914) but is commonly attributed to van Slyke (1922):

$$\beta = \frac{-dC_a}{dpH} \quad (\text{eq.12})$$

where C_a is the quantity of acid added to a solution. For seawater, TA is substituted for C_a and partial derivatives are used to indicate that other properties are kept constant during the titration:

$$\beta = \frac{\partial TA}{\partial pH} \quad (\text{eq.13})$$

The buffer value β is always positive because every solution resists pH change according to the principle of le Chatelier. It is based on pH rather than proton concentrations because of historical reasons and laboratory procedures.

The Revelle factor (R ; Revelle and Suess, 1957; Bolin and Eriksson, 1959; Sundquist et al., 1979) expresses the sensitivity of pCO_2 to changes in DIC:

$$R = \frac{\partial \ln pCO_2}{\partial \ln DIC} = \frac{DIC}{pCO_2} \left(\frac{\partial pCO_2}{\partial DIC} \right) \quad (\text{eq. 14})$$

where use is made of the property $\partial \ln x = \frac{1}{x} \partial x$. This Revelle factor is limited to homogeneous systems, because the partial derivatives indicate that other variables such as alkalinity are kept constant. Sundquist and Plummer (1981) extended the homogeneous Revelle factor to allow for changes in alkalinity (e.g. due to calcification/dissolution):

$$R_{tot} = \frac{DIC}{pCO_2} \left(\frac{\partial pCO_2}{\partial DIC} \right) = \frac{DIC}{pCO_2} \left[\left(\frac{\partial pCO_2}{\partial DIC} \right)_{TA} + \left(\frac{\partial pCO_2}{\partial TA} \right)_{DIC} \cdot \frac{dTA}{dDIC} \right] \quad (\text{eq. 15}).$$

In seawater, the term $\left(\frac{\partial pCO_2}{\partial TA} \right)_{DIC}$ is negative, while $\frac{dTA}{dDIC}$ varies from zero (no TA change) to 2 when all changes in DIC are due to calcium carbonate dissolution; heterogeneous buffering thus lowers the Revelle factor (i.e. ocean buffering is larger when carbonate minerals are involved).

The Revelle and acid-base buffer factors are just two out of many ways to quantify the response of seawater to changes and some additional (chemical) buffer factors have been proposed (e.g., Frankignoulle, 1994; Frankignoulle et al., 1994; Egleston et al., 2010; Hagens and Middelburg, 2016a; Table 1). However, there are multiple inconsistencies in terminology and their relationships are not clear (Table 1). To clarify matters and link the various buffer capacities and factors in the literature, we present a systematic treatment involving partial derivatives as sensitivities. While the application of Le Chatelier's principle is straightforward for simple systems, it becomes difficult to predict the response of individual reactions when multiple reactions sharing ions are involved (Fishtik et al., 1995) and a sensitivity analysis is then useful. Sensitivities are also known as chemical buffer factors (Frankignoulle, 1994; Soetaert et al., 2007; Egleston et al., 2010). Sensitivities express the rate of change of output quantities (Y) in terms of input quantities (X), i.e. their partial derivatives (Morel et al., 1976; Smith and Missen, 2003). The (first-order) sensitivity coefficient (Smith and Missen, 2003) or interaction capacity (Morel et al., 1976) is defined as:

$$S_{Y,X} = \frac{\partial Y}{\partial X} \quad (\text{eq.16})$$

which can be normalized using logarithms so that the % change in output can be directly linked to % change in input (interaction intensity values (Morel et al., 1976) or normalized first-order sensitivities, (Smith and Missen, 2003)):

$$S_{Y,X}^{nor} = \frac{\partial \ln Y}{\partial \ln X} \quad (\text{eq. 17})$$

In the case of pH during an acid titration of TA, the sensitivity is the inverse of the well-known acid-base buffer capacity (β , eq. 13)

$$S_{pH,TA} = \frac{\partial pH}{\partial TA} = \beta^{-1} \quad (\text{eq. 18}).$$

The use of both sensitivities (=tendency to change), in which the cause of change is in the denominator and the resulting change is in the numerator (e.g., $\frac{\partial pH}{\partial TA}$), and buffering capacities (=resistance to change), which are just the inverse (e.g., $\frac{\partial TA}{\partial pH}$) is one of the reasons for confusion in the literature. Buffer capacity β expresses the ability to resist changes and is normally presented as

$$\beta_{pH} = \left(\frac{\partial pH}{\partial TA} \right)^{-1} \quad (\text{eq. 19})$$

(Stumm and Morgan, 1981; Morel and Hering, 1993; Middelburg, 2019). The Revelle factor (R, eq. 14) is a (normalized) sensitivity factor.

Another cause of inconsistencies among studies relates to the use of pH, $\ln[H^+]$ or $[H^+]$. The original buffer factor β is based on pH (eq. 13, 19), but Egleston et al. (2010) and Hofmann et al. (2010) presented definitions based on the natural logarithm of proton concentrations and proton concentrations, respectively:

$$\beta_{TA} = \left(\frac{\partial \ln H}{\partial TA} \right)^{-1} \quad \text{and} \quad \beta_H = \left(\frac{\partial H}{\partial TA} \right)^{-1} \quad (\text{eq. 20, 21}).$$

While β_{pH} values are always positive, β_H and β_{TA} are negative. Note that these buffer factors have been defined as inverse of sensitivity factors. The interchangeable and inconsistent use of the terms buffer capacity, intensity, and index for β is another cause of confusion. Analytical chemists favour the term buffer capacity, geochemists prefer buffer intensity and engineers use the term buffer index (Urbansky and Schock, 2000). Others distinguish between buffer intensity for the actual value at a certain pH (the differential) and buffer capacity for the integral over a distinct range (Chiriac and Balea, 1997).

Using a first-order sensitivity approach the response in Y due to changes in the drivers TA, DIC, T, S and any other property X can be described as:

$$dY = \left(\frac{\partial Y}{\partial TA} \right) dTA + \left(\frac{\partial Y}{\partial DIC} \right) dDIC + \left(\frac{\partial Y}{\partial T} \right) dT + \left(\frac{\partial Y}{\partial S} \right) dS + \left(\frac{\partial Y}{\partial X} \right) dX \quad (\text{eq. 22})$$

where the partial derivatives imply that the other factors are constant. These and other sensitivities have been used and named in the literature, either in this particular, a normalized or similar form (Table 1). Sometimes a different name is used for the same sensitivity or the same name is used for different sensitivities. For instance, Sarmiento and Gruber (2006) define their alkalinity factor (γ_{TA}) as

$$\gamma_{TA} = \left(\frac{\partial pCO_2}{\partial TA} \right) \frac{TA}{pCO_2} = \left(\frac{\partial \ln pCO_2}{\partial \ln TA} \right) \quad (\text{eq. 23})$$

while Egleston et al. (2010) use the same symbol for a different sensitivity:

$$\gamma_{TA} = \left(\frac{\partial TA}{\partial \ln CO_2} \right) \quad (\text{eq. 24}).$$

Similarly, the Revelle factor (R, eq. 14) is also known as homogeneous buffer factor B_{hom} (Sundquist et al., 1979), β_D (Frankignoulle, 1994) and γ_{DIC} (Sarmiento and Gruber, 2006). Moreover, it relates to DIC/γ_{DIC} using the γ_{DIC} definition of Egleston et al. (2010), which is again different from that of Sarmiento and Gruber (2006). Most of the sensitivities in Table 1 can be explicitly linked (Frankignoulle, 2004; Hagens and Middelburg, 2016a) as documented in Supporting Information S2. *To prevent further confusion and propagation of inconsistencies, we propose to explicitly add the term sensitivity to factors such as the Revelle sensitivity factor and restrict the use of buffer for its inverse, i.e. the resistance to change. Consequently, we discourage the common use of the term buffer or chemical buffer factor for sensitivities.*

3.2 Sensitivity of seawater

Most of the sensitivities presented above depend non-linearly on the solution composition. Figure 2 shows the sensitivities of pH towards changes in CBA and DIC and of $p\text{CO}_2$ towards a change in DIC (Revelle sensitivity factor) as a function of pH for average seawater. The carbonic acid system dominates the buffering capacity of seawater and these sensitivities thus show extrema related to the pK_1 (≈ 5.9) and pK_2 (≈ 9) values of carbonic acid in seawater. The sensitivity $\left(\frac{\partial pH}{\partial CBA}\right)$ shows maxima at pH values of about 4.5 and 7.5. The former is the proton reference level chosen at the well-known inflection point of the alkalinity titration (Dickson, 1981) and the latter is consistent with the minor species theorem that it should be half way between pK_1 and pK_2 (Morel and Hering, 1993; Egleston et al., 2010). These sensitivities show minima close to the pK_1 and pK_2 values of carbonic acid in seawater, consistent with the well-established concept that buffers are most efficient close to their pK value (Butler, 1964; Stumm and Morgan, 1981). At pH values of about 7.5, sensitivity towards addition of dissolved inorganic carbon $\left(\frac{\partial pH}{\partial DIC}\right)$, a weak acid, is similar to that of $\left(\frac{\partial pH}{\partial CBA}\right)$, addition of proton acceptors, but for the sign. However, seawater is more sensitive to CBA than to DIC changes below the pK_1 of the carbonic acid system ($pH \approx 5.9$). Conversely, the sensitivity towards DIC changes is larger than that due to CBA changes at $pH > 7.5$. This can be attributed to the number of protons released (Egleston et al., 2010). The Revelle sensitivity factor is very low at pH values below 6 and above 12, and shows maxima at pH values of about 7.5 and 10 and a minimum around the pK_2 of the carbonic acid system ($pH \approx 9$) because of the prominent role of the carbonate ion in buffering the carbon dioxide added (Gattuso and Hanson, 2011):



These and other seawater sensitivities have many applications, ranging from propagating uncertainties in the carbonic acid system (Orr et al., 2018), attributing changes in $p\text{CO}_2$ to temperature, salinity and other factors (Takahashi et al., 1993; 2014; Sarmiento and Gruber, 2006; Middelburg, 2019), understanding factors governing pH seasonality (Hagens and Middelburg, 2016b) and how these factors will change because of global warming and ocean acidification (Hagens and Middelburg, 2016a). For instance, Richier et al. (2018) showed that the CO_2 sensitivity of phytoplankton correlates with the sensitivity $\left(\frac{\partial pH}{\partial DIC}\right)$ of seawater. This quantification of sensitivities is pivotal to understanding earth system functioning and the magnitude of climate feedbacks during times of global change. For instance, Frankignoulle et al. (1994) showed how the stoichiometry of carbon dioxide release during calcite precipitation would change with increasing atmospheric carbon dioxide levels. Multiple authors have shown that the seasonality of pH and $p\text{CO}_2$ will increase due to elevated sensitivities induced by ocean acidification (Riebesell et al., 2009; Schulz and Riebesell, 2013; Hagens and Middelburg, 2016a; Kwiatkowski and Orr, 2018; Gallego et al., 2019). Seawater sensitivity analysis has also contributed to elucidating interactions among various factors perturbing seawater pH and $p\text{CO}_2$ such as hypoxia (Cai et al., 2011; 2017; Hagens et al., 2015; Hagens and Middelburg, 2016a) and atmospheric deposition (Hagens et al., 2014). Finally, explicit quantification of sensitivities allows estimation of simple projections or retrodictions. For instance, the present-day value for $\left(\frac{\partial pH}{\partial p\text{CO}_2}\right)$ is about -0.0011 (ppmv^{-1} ; Hagens and Middelburg, 2016a). Combining this sensitivity with global annual increases in $p\text{CO}_2$ of 1.1 to 2.1 ppmv yr^{-1} for the periods 1964-1975 and 2005-2014 generates annual ocean pH declines of about 0.0012 to 0.0023 units, similar to that

observed (Dore et al., 2009). Similarly, using the sensitivity $\left(\frac{\partial DIC}{\partial pCO_2}\right)$ of about 0.51 ($\mu M \text{ kg}^{-1} / \text{ppmv}$), one would retrodict that the global ocean surface DIC would have increased by about 1 $\mu M \text{ kg}^{-1} \text{ yr}^{-1}$ from 1994 to 2007, consistent with observations by Gruber et al. (2019).

4. Biogeochemical processes and inorganic carbon dynamics

The marine carbon dioxide system is impacted by many biogeochemical processes: mineral dissolution and precipitation, organic matter production and respiration and transfers of electrons, i.e. redox processes (Soetaert et al., 2007; Wolf-Gladrow et al., 2007; Middelburg, 2019). The impact of biogeochemical processes on pH and pCO_2 is often analysed graphically in the form of TA versus DIC plots with isolines for pH and pCO_2 (Fig. 3). The impact of biogeochemical processes on DIC, TA or any of its constituents can be represented as a vector (Deffeyes, 1965). For instance, calcium carbonate dissolution results in the release of one unit DIC and two units of TA and the resulting vector on Figure 3 shows that it will cause an increase in pH and decrease in pCO_2 . However, for the very same process intensity (vector length and direction), the resulting change in pH and pCO_2 is different because it depends on the initial conditions (i.e. the sensitivity of the system, section 3.2). Changes in pH and pCO_2 are smaller in well buffered water with a high TA: DIC ratio, i.e. low sensitivity (Fig. 3).

Although this graphical approach is instructive, there is a need to quantify these changes to improve our predictive capabilities. Ben-Yaakov (1973) recognized that a given reaction can change the pH of a solution by changing the total charge or by adding (or removing) an acid or base. Soetaert et al. (2007) elaborated this approach and showed that the effect of a single biogeochemical process on pH can be calculated from the product of the net charge exchanged during a biogeochemical process (Δcharge) and the sensitivity factor of seawater $\left(\frac{\partial pH}{\partial CBA}\right)$. Specifically, the instantaneous effect of a single process with intensity I_{process} ($\text{mol m}^{-3} \text{ s}^{-1}$) on pH can be calculated as:

$$dpH = \Delta\text{charge} \cdot \left(\frac{\partial pH}{\partial CBA}\right) \cdot I_{\text{process}} \quad (\text{eq. 26})$$

where Δcharge is the sum of the pH independent ΔCBA (Table 2) and the pH dependent charge (i.e. proton transfer) calculated from reaction stoichiometry and charge of acid-base systems (see Soetaert et al., 2007). Since both the sensitivity of seawater $\left(\frac{\partial pH}{\partial CBA}\right)$ and Δcharge depend on the pH, this equation shows that the effect of a specific biogeochemical process on pH also depends on pH. Hofmann et al. (2010a) and Middelburg (2019) presented similar approaches, but focused on proton rather than charge transfers and used the sensitivity factors $\left(\frac{\partial H}{\partial TA}\right)$ and $\left(\frac{\partial pH}{\partial TA}\right)$, respectively.

Figure 4 shows the impact of denitrification with Redfield organic matter (R2 in Table 2) on the Δcharge and pH. The process involves the production of DIC, $\sum NH_3$ and $\sum PO_4$, and the consumption of $\sum NO_3$. Denitrification does not impact charge balance alkalinity ($\Delta CBA = 0$). At $pH < 4$, nitrate is charged negatively, ammonium positively while DIC and $\sum PO_4$ are present as uncharged carbonic and phosphoric acids, the Δcharge of the reaction is about +0.95. At $pH > 10$, nitrate is still charged negatively, while carbonate and phosphate ions dominate the DIC and $\sum PO_4$ with the consequence that the Δcharge of the reaction is about -1.08 (Fig. 4). At a pH of about 7 the Δcharge is zero because the positive charge due to nitrate consumption and ammonium production is compensated by the production of bicarbonate, the major species in the

DIC pool at this pH, with contributions from carbonate, dihydrogenphosphate and hydrogenphosphate. The overall effect of denitrification on pH is obtained by multiplying the Δcharge and sensitivity at a specific pH value (eq. 26; Fig. 4). Consequently, the pH increases at pH values below about 7 ($\Delta\text{charge} > 0$), while it decreases pH at higher pH because the production of bicarbonate, carbonate and phosphate ions outcompetes the consumption of nitrate and production of ammonium ($\Delta\text{charge} < 0$). Thus, Δcharge defines the direction of the pH change (i.e. increase or decrease), while the sensitivity determines the magnitude of the response.

Soetaert et al (2007) presented a full list of processes and how they impact pH over the full pH range, here we focus on aerobic and anaerobic mineralization, primary production and calcium carbonate production and dissolution (Table 2). Figure 5 shows that the overall impact of a biogeochemical process on pH is a highly non-linear function with multiple processes crossing the zero-pH-change line, implying that the direction (sign of Δcharge) and magnitude (sensitivity times Δcharge) of pH change depend on the initial conditions. For instance, calcium carbonate dissolution always increases the pH but the response depends on the sensitivity factor, i.e. on the initial conditions, consistent with the graphical approaches presented above (Fig. 3). Aerobic respiration (R1) and methanogenesis (R6) increase pH at pH < 5.2 and 5.6, respectively (Soetaert et al., 2007), because the production of ammonium is not compensated by sufficient production of anions (bicarbonate and phosphate anions). At higher pH, aerobic respiration and methanogenesis decrease pH because of bicarbonate, carbonate and phosphate ion production (Fig. 5). Aerobic respiration accompanied by nitrification (oxidation of ammonium to nitrate, R 7) always results in a pH decrease (Fig. 5) because there is no positive charge produced (Soetaert et al., 2007). Similarly, primary production based on nitrate always results in pH increase, while regenerated production based on ammonium results in pH decrease at low pH (ammonium uptake is compensated by proton release for electroneutrality; Soetaert et al., 2007; Wolf-Gladrow et al., 2007). Sulphate reduction (R5) causes a stronger pH increase at low pH values because of sulphate ion consumption and switches to proton production (pH decrease) at a higher pH value. In other words, the impact of sulphate reduction in sediments on pH depends on the initial conditions: i.e. whether the sediment has experienced extensive denitrification and metal-oxide reduction before initiation of sulphate reductions (Boudreau and Canfield, 1993; Soetaert et al, 2007; Meister, 2013).

5. Heterogeneous buffering

While homogeneous buffering due to equilibria in solution is nearly instantaneous and can be quantified using seawater sensitivities discussed in section 3, heterogeneous buffering mechanisms involving particles occur over multiple time scales (Archer et al., 1998; Sarmiento and Gruber, 2006; Boudreau et al., 2018). For instance, proton sorption to surfaces occurs almost instantaneously, while mineral dissolution and precipitation are kinetically controlled (Lasaga, 1998). Moreover, homogeneous buffering is spatially rather uniform in the ocean because of the limited range and relative uniform distribution of salinity, dissolved inorganic carbon and alkalinity. Heterogeneous buffering involves particles suspended in the water column, sediments deposited at the seafloor and benthic and pelagic calcifying organisms. Calcification is dominated by pelagic organisms in the open ocean, while benthic organisms dominate in the coastal domain (Milliman, 1993; Morse and Mackenzie, 1990; Morse et al., 2007). Sediments dominate heterogeneous buffering because of the large size of this reservoir: i.e. there are orders of magnitude more particles at the seafloor than suspended in the water column.

Particles suspended in the water column and deposited on the seafloor may contribute to buffering of seawater via dissolution, precipitation and mineral surface reactions. Sorption of protons to surfaces increases alkalinity (Table 2). Reactions at the surfaces of organic, biogenic carbonate and detrital silicate particles contribute to instantaneous buffering; alkalinity titrations of unfiltered samples containing phytoplankton and bacteria have shown that particulate matter surfaces neutralize some of the protons added (Kim et al., 2006). However, this heterogeneous buffer capacity is very limited for typical marine suspended matter concentrations. The role of surface reactions in buffering pore-water chemistry is largely unknown although Jahnke and Jahnke (2004) identified the need to consider mineral surface reactions to properly understand sediment pH dynamics.

Dissolution, precipitation and transformation reactions of sedimentary silicates and biogenic carbonates govern heterogeneous buffering in the ocean. Heterogeneous buffering in the ocean is dominated by carbonate compensation (Pytkowicz, 1967; Berner, 2004; Ridgwell and Zeebe, 2005) and we will focus on this as well (section 5.2), realizing that processes involving silicate minerals, such as reverse weathering and submarine weathering contribute as well, in particular on very long times scales (section 5.1; Sillen, 1967; Mackenzie and Garrels, 1966; Wallmann et al., 2008; Isson and Planavsky, 2018).

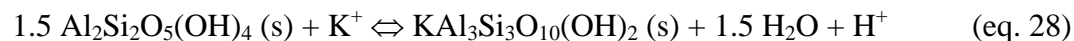
5.1 Silicate reactions

The impact of seawater-rock interactions on alkalinity is often quantified via a charge balance of major cations on the one hand and chloride, sulphate and alkalinity on the other hand (Antonelli et al., 2017; Turchyn and dePaolo, 2019):

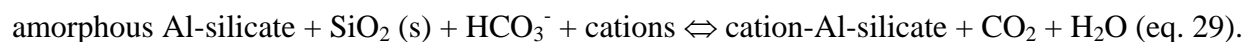
$$\text{Na}^+ + \text{K}^+ + 2 \text{Mg}^{2+} + 2 \text{Ca}^{2+} = \text{Cl}^- + 2 \text{SO}_4^{2-} + \text{alkalinity} \quad (\text{eq.27}),$$

where exchanges between the univalent and divalent cations or between magnesium and calcium are considered of less importance for the balance. High-temperature hydrothermal vents result in the removal of Ca^{2+} and SO_4^{2-} via anhydrite precipitation and of Mg^{2+} via hydroxy-silicate formation (Antonelli et al., 2017). The latter process generates acidity that enhances release of Ca^{2+} from basalt so that charge remains balanced. Most of the calcium released is eventually precipitated as calcium carbonate in the oceanic crust. Overall, submarine weathering results in carbon dioxide consumption and bicarbonate and calcium release (Staudigel et al., 1989; Caldeira, 1995; Berner, 2004).

Reverse weathering refers to the consumption of alkalinity and generation of protons during marine authigenic clay formation. Weathering on the continents results in the formation of cation-depleted clay minerals which after transport and deposition at the seafloor react with major elements in seawater. Reverse weathering can be written in multiple forms: e.g. kaolinite to mica transformation (Sillen, 1967),



or cation-poor amorphous Al-silicate to clay (Mackenzie and Garrels, 1966),



The latter reaction involves the transformation of bicarbonate to carbon dioxide via reaction with cation-depleted, acidic Al-silicates. Reverse weathering can be written in multiple forms, but

they all lower marine pH and alkalinity, and increase carbon dioxide concentrations (Isson and Planavsky, 2018).

Another submarine weathering process is induced by organic matter degradation in anoxic sediments. This degradation results in the release of carbon dioxide and dissolved organic matter (fulvic and humic acids) and these may cause dissolution of primary silicate minerals and generate high alkalinity levels (Wallmann et al., 2008). Marine weathering contributes to carbon dioxide consumption and alkalinity release and thus counteracts reverse weathering processes. Although seafloor weathering and in particular reverse weathering processes may have played a prominent role during past periods with warm, silica-rich ocean waters (e.g. Precambrian), these heterogeneous buffering reactions involving silicates are considered of less importance for the present ocean than those involving carbonate minerals (Pytkowicz, 1967; Berner, 2004; Isson and Planavsky, 2018; see section 6).

5.2 Carbonate compensation dynamics

Carbonate compensation refers to the reactions between carbonate minerals and seawater and it is instructive to distinguish between chemical and biological carbonate compensation. Chemical compensation focuses on the dissolution or preservation of carbonates at the seafloor, while biological compensation centres on the role of precipitation and its dependence on solution chemistry (Boudreau et al. 2018).

Surface oceans waters are supersaturated with respect to most carbonate minerals (Morse and Mackenzie, 1990). Supersaturation must be reduced to undersaturation, at least in the local microenvironment, before carbonate minerals will dissolve and contribute to buffering (but for surface reactions). Carbonate particles settling to the ocean floor will experience pressure increases and temperature decreases that increase solubility of carbonate minerals (Morse and Mackenzie, 1990; Millero, 2007). Moreover, subsurface ocean waters are usually richer in carbon dioxide and lower in carbonate ions because of organic matter degradation (Sarmiento and Gruber, 2006). As a consequence, seawater becomes undersaturated with respect to carbonate minerals at a certain depth and below this saturation depth mineral dissolution rates increase with depth (Ridgwell and Zeebe, 2005). At the carbonate compensation depth, the flux of carbonate particles downwards is exactly balanced by the rate of carbonate dissolution (at the seafloor) with the consequence that no carbonate minerals accumulate at steady state (Boudreau et al., 2010a). The lysocline refers to the depth range between the carbonate saturation and compensation depths (Boudreau et al., 2018). Ocean buffering dynamics is reflected in changes in the depth distribution of the saturation and compensation depths (Sigman et al., 1998; Ridgwell and Zeebe, 2005; Boudreau et al., 2010b). During periods of ocean acidification, saturation and carbonate compensation depths will shallow, causing increases in carbonate mineral dissolution and alkalinity release, counteracting the acidification. Conversely, during ocean alkalization, saturation and compensation depths will deepen, with the result that carbonate dissolution and alkalinity release diminish (Sigman et al., 1998; Ridgwell and Zeebe, 2005; Boudreau et al., 2018).

Almost all marine carbonate minerals are of biological origin: e.g. coccoliths, pteropods and foraminifera in the open ocean and corals and mollusks in the coastal domain (Morse and Mackenzie, 1990; Milliman, 1993). Calcifying organisms consume alkalinity and any change in their activity due to alteration in environmental conditions (e.g. temperature, ocean acidification) or food web structure (e.g. food resources, predators or viruses) consequently impacts their role

in ocean buffering. This role of calcifiers in carbonate compensation has impact on buffering at multiple timescales (Caldeira and Rampino, 1993; Boudreau et al., 2018). Lower calcification rates because of ocean acidification (Gazeau et al., 2007; Kroeker et al., 2013) or global warming (Hoegh-Guldberg et al., 2007) directly impact alkalinity removal and thus represent a rapidly operating negative feedback mechanism, that will be detectable within decades (Schlunegger et al., 2019). Less calcification in the surface layer also implies less export of biogenic calcite and thus less calcite dissolution in the subsurface. Boudreau et al. (2010a, 2018) provided an equation to approximate carbonate compensation depth (z_{CCD}):.

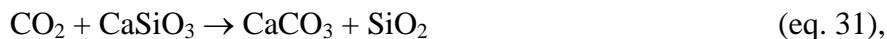
$$z_{CCD} \approx z_{ref} \ln \left(\frac{F_{car}[Ca^{2+}]}{K_{sp}A\beta_{mt}} + \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \right) \quad (\text{eq. 30})$$

where F_{car} is the export flux of calcium carbonate, A is the surface area of the seafloor, β_{mt} is the mass transfer of solutes across the diffusive boundary layer at the seafloor, K_{sp} is the temperature, salinity and pressure dependent stoichiometric solubility product, $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of dissolved calcium and carbonate ions and z_{ref} is a scaling parameter. Lower calcification and export of calcium carbonate F_{car} will thus lead to a shallowing of the carbonate compensation depth on shorter time scales (years), but would cause additional deepening on longer timescales (10^4 years), because of alkalinity accumulation during periods of lower calcification (Boudreau et al., 2018). This additional deepening due to biological carbonate compensation is an alternative to CO_2 -enhanced continental weathering (Ridgwell, 2007; Zeebe et al., 2009) for $CaCO_3$ overshooting in the geological record (Luo et al., 2016).

6 Processes governing alkalinity in the ocean

The distribution of alkalinity often co-varies with salinity. This is logical because oceanographic processes impacting salinity by freshwater addition (such as precipitation, river and groundwater discharge and ice melting) or removal (e.g. evaporation and ice formation) also impact alkalinity. These processes are most intense in surface waters that are exposed to the atmosphere, cryosphere and riverine inputs. It is for this reason that alkalinity can be predicted quite well in ocean surface water using salinity and temperature (Millero et al., 1998; Lee et al., 2006). Alkalinity is often normalized to salinity to infer the other processes affecting alkalinity such as calcite production and dissolution (Feely et al., 2004; Sarmiento and Gruber, 2006; Carter et al., 2014). However, salinity normalization might induce biases, because of regional differences in salinity-alkalinity relationships (Friis et al., 2003; Jiang et al., 2014).

Whole ocean alkalinity is largely governed by the balance between ions generated by weathering and removal of ions via the formation of calcium carbonate. Continental weathering on land generates cations that are charge balanced by alkalinity (Mackenzie and Garrels, 1966; Berner and Berner, 2012; Turchyn and DePaolo, 2019). Rivers and groundwater deliver cations and alkalinity to the ocean where calcifiers produce skeletons and remove alkalinity. On million-year timescales this is usually represented by the Urey-Ebelman reaction (Urey, 1952; Berner, 2004):



which illustrates the net transfer of carbon from the atmosphere to the sedimentary record. Accordingly, over geological timescales one would expect that riverine delivery of alkalinity to the ocean is balanced by burial of carbonate in marine sediments (Fig. 6A).

Estimates of riverine alkalinity delivery range from 26 to 36 Tmol y^{-1} (Supporting Information S3, Table 3) and have been derived either from river DIC export or global estimates

of CO₂ consumption by chemical weathering of silicate and carbonate rocks (Berner et al., 1983; Meybeck, 1987; Ludwig et al., 1996; 1998; Gaillardet et al., 1999; Suchet et al., 2003; Hartmann et al., 2014; Li et al., 2017). River biogeochemists normally assume that bicarbonate equals the alkalinity and dissolved inorganic carbon (Suchet et al., 2003; Raymond and Hamilton, 2018). Consequently, global estimates of DIC delivery to the ocean can be used as a proxy for alkalinity transfer from weathering to the ocean. Carbonate burial estimates range from 18 to 34 Tmol C y⁻¹ (Supporting Information S3), with clear consensus about carbonate burial in the deep sea of 11-12 Tmol C y⁻¹, while ocean margin contributions vary from 6 to 23 Tmol C y⁻¹ (Morse and Mackenzie, 1990; Milliman, 1993; Wollast, 1994; Milliman and Droxler, 1996; Iglesias-Rodrigues et al., 2002; Smith, 2013; Smith and Mackenzie, 2016; O'Mare and Dunne, 2019). Calcium carbonate formation involves the consumption of two moles of alkalinity per mole of carbon (Table 2), indicating an imbalance between alkalinity inputs from chemical weathering (26-36 Tmol y⁻¹) and alkalinity outputs by carbonate burial (54-62 Tmol y⁻¹), the latter based on carbonate (carbon) burial equal to 27-31 Tmol C y⁻¹ (Fig. 6 and Supporting Information S3). This imbalance has been identified before based on Ca and HCO₃⁻ budgets of the ocean (Berner and Berner, 2012).

This imbalance of 18 to 36 Tmol y⁻¹ can be explained in three ways. One, the present-day ocean may not be at steady-state regarding alkalinity (Milliman, 1993). The inventory of alkalinity in the ocean is about 3.15 10¹⁸ mol, based on a total ocean volume of 1.34 10¹⁸ m³ and a mean ocean alkalinity of about 2.35 mol m⁻³ (Sarmiento and Gruber, 2006). Accordingly, the residence time of alkalinity is about 88-121 ky with respect to a riverine input of 26-36 Tmol y⁻¹. Consequently, the modern ocean alkalinity budget may still be recovering from last glacial sea level drop and related shifts in carbonate burial/exposure on continental shelves. Two, carbonate burial in ocean margin sediments may be lower than consensus values (16-20 Tmol C y⁻¹: Milliman and Droxler, 1996; Iglesias-Rodrigues et al., 2002; Smith, 2013; Smith and Mackenzie, 2015; O'Mare and Dunne, 2019). Morse and Mackenzie (1990; their Fig. 5.1) reported a long-term carbonate burial of about 6 Tmol C y⁻¹ in ocean margin sediments. Total alkalinity removal by carbonate burial would then be about 34 Tmol y⁻¹ (2*(6+11)) and result in a balanced budget. van der Ploeg et al. (2019) reported an alkalinity removal via Cenozoic marginal carbonate burial of 14.3 Tmol y⁻¹ by balancing riverine and anaerobic mineralization inputs with marginal and deep-sea carbonate burial. However, there is consensus that modern carbonate burial in ocean margins is about 16-20 Tmol C y⁻¹ (Supporting Information S3), hence an alkalinity removal of 32-40 Tmol y⁻¹. Three, this simple depiction of riverine alkalinity balancing calcium carbonate burial in marine sediment (Fig. 6A) requires revision because of additional alkalinity inputs from land (e.g., riverine particulate inorganic carbon and groundwater alkalinity) or from marine sediments (Fig. 6B).

Rivers deliver elements to the ocean not only in dissolved form, but also in particulate form (Martin and Meybeck, 1979). If riverine particulate carbonates are unreactive they will eventually be buried in marine sediments and are then implicitly included in the marine carbonate burial term. Similarly, if riverine particulate carbonates are reactive and dissolve, they represent an alkalinity source and should be added to the input. Irrespective of their fate, transfer of particulate inorganic carbon from rivers to the ocean would reduce the imbalance. There are very few data on the global particulate inorganic carbon input to the ocean. On the basis of a very small dataset, Meybeck (1987) reported a PIC flux of 14.2 Tmol C y⁻¹ and this is still used in global carbon assessments (Li et al., 2017). This PIC flux implies an additional alkalinity source of 28.4 Tmol y⁻¹. This is not only of similar magnitude as the alkalinity delivered in

dissolved form, but it would also close the modern ocean alkalinity budget (Table 3). This large, so far overlooked, alkalinity input to the ocean is however poorly constrained. Using the global sediment delivery estimate (19 Pg y^{-1} ; range $11\text{--}27 \text{ Pg y}^{-1}$) of Beusen et al. (2005) and the average of PIC content of US rivers (0.47 wt\% C) from Canfield (1997), a lower riverine PIC delivery is estimated ($7.4 \text{ Tmol C y}^{-1}$, range $4.3\text{--}10.6 \text{ Tmol C y}^{-1}$). However, this would still correspond to an alkalinity flux of almost 15 Tmol y^{-1} . This difference is primarily due to difference in PIC content of suspended particles (0.9 wt\% for Meybeck (1982) versus 0.47 wt\% in US river data base (Canfield, 1997)). The average of these two uncertain numbers is used for the alkalinity budget (Fig. 6B, Table 3).

Part of the freshwater return flow to the ocean occurs via groundwater discharge rather than via rivers (Slomp and van Cappellen, 2005) and this is an additional alkalinity input. Zhou et al. (2019) reported a global freshwater submarine discharge flux of $489 \text{ km}^3 \text{ y}^{-1}$, which corresponds to about 1.3% of the global river discharge and is significantly lower than the 5% adopted by Slomp and van Cappellen (2005). Combining these fractions with assumptions about the alkalinity of groundwater (one to three times that of river water, Zhang & Planavasky, 2019), we estimate a global fresh groundwater alkalinity input of about 1 Tmol y^{-1} , range $0.4\text{--}4.7 \text{ Tmol y}^{-1}$; Supporting Information S3).

Besides these additional alkalinity inputs from riverine PIC and submarine groundwater discharge, there is also alkalinity production and consumption in marine sediments due to anaerobic degradation of organic matter, organic matter burial and reactions involving silicates (Berner et al. 1970; Ben-Yaakov, 1973; Boudreau and Canfield, 1993; Soetaert et al., 2007; Wallmann et al., 2008; Hu and Cai, 2011). Although we understand the impact of individual processes on TA quite well (see sections 4 and 5), the overall effect of these processes on ocean TA is more difficult to assess because of the tight coupling between alkalinity generating and consuming processes within a sediment column. For instance, dissimilatory sulphate reduction and sulphate reduction coupled to anaerobic methane oxidation generate TA (Table 2), but most of the sulphide and ammonium generated during these processes are re-oxidized, resulting in alkalinity consumption (Table 2). Consequently, net overall impact of sedimentary sulphate reduction on ocean alkalinity is limited to the small fraction of reduced sulphur that is eventually buried (Wallmann et al., 2008; Hu and Cai, 2011; Krumins et al., 2013; Gustafsson et al., 2019). Moreover, alkalinity released from the sediment in the form of reduced substances (e.g. ammonium, sulphide) that are subsequently oxidized (e.g. nitrification, sulphide oxidation) in the water column does not contribute to the whole ocean alkalinity balance either (Hu and Cai, 2011).

In the context of the global ocean alkalinity balance, anaerobic alkalinity production can conceptually be considered as an anion charge transfer process, as discussed in section 4 (Ben-Yaakov, 1973; Hu and Cai, 2011). During denitrification (reduction of nitrate to dinitrogen gas), the charge of nitrate is transferred to bicarbonate and thus increases alkalinity. Similarly, the reduced sulphur buried in marine sediments initially entered the ocean as a sulphate ion; this implies a charge transfer to bicarbonate. In contrast, solid phase oxidants such as iron and manganese oxides enter the ocean uncharged and leave the ocean in an uncharged solid form (e.g. FeS_2), with no impact on global ocean alkalinity. Accordingly, it is only the charge transfer from land-derived nitrate and sulphate to bicarbonate produced by anaerobic respiration that matters for the whole ocean alkalinity balance (Hu and Cai, 2011).

Net alkalinity production due to denitrification/anammox is thus about 1.5 Tmol y^{-1} (Hu and Cai, 2011) based on a river nitrate input of 21 Tg N y^{-1} (Seitzinger et al., 2006). The net

alkalinity production due to sulphate reduction is derived from the burial of sulphur in marine sediments because most of the sulphate produced is re-oxidized (Jorgensen, 1977, 1982). Estimates of sulphur burial are based on organic carbon burial and vary from 1.2 (Berner, 1982) to 3.4 Tmol S y⁻¹ (Supporting Information S3), implying a potential alkalinity source of 2.4 to 6.9 Tmol y⁻¹ to the ocean. These are upper estimates because part of the net alkalinity generated within sediments results in authigenic carbonate formation and does not contribute to ocean alkalinity. Accordingly, the total contribution of anaerobic biogeochemical processes to the ocean alkalinity balance varies between 3.9 and 8.4 Tmol y⁻¹.

Primary production based on new nitrogen (e.g. nitrate) is an alkalinity source, while aerobic respiration accompanied by nitrification represent an alkalinity sink (Table 2). If all organic matter produced were respired there would be no impact on alkalinity, but a small part of the organic matter produced in the photic zone is eventually buried in marine sediments. Based on organic carbon burial estimates of Berner (1982) and Burdige (2007) we estimate a net alkalinity production of 3 Tmol y⁻¹ (see Supporting Information S3).

Quantifying the contribution of sediment silicate reactions to ocean alkalinity is also complicated by multiple alkalinity production and consumption processes: reverse weathering in surface sediments, marine weathering at depth, in particular in the methanogenic zone (Wallmann et al., 2008) and ocean crust weathering (Staudigel et al., 1989; Caldeira, 1995; Berner, 2004). Moreover, the alkalinity generated at depth by mineral weathering result in authigenic carbonate formation. Although alteration of oceanic crust is likely on the order of 2 Tmol y⁻¹, most bicarbonate generated is precipitated as calcite and does not contribute to ocean alkalinity. Reverse weathering is a sink of alkalinity (e.g. equations 28 and 29) on the order of about 0.5-1.5 Tmol y⁻¹ (Isson and Planavsky, 2018), but varies locally depending on the supply of materials (Michalopoulos and Aller, 1995, 2004 Rahman et al., 2016). Wallmann et al. (2008) reported high rates of submarine weathering of 3.3 to 13.3 Tmol y⁻¹. Their estimate is based on the assumption that all carbon dioxide produced during methanogenesis is converted to bicarbonate and that one third is removed by authigenic carbonate formation and two-third is released as alkalinity to the ocean. These numbers are likely too high given that these are based on global methane production rates of 5 Tmol C y⁻¹ (Reeburgh et al., 1993) and 20 Tmol C y⁻¹ (Hinrichs and Boetius, 2002). More recent estimates for marine methane formation are 2.8 Tmol y⁻¹ (Egger et al., 2018) and 0.3 to 2.1 Tmol C y⁻¹ (Wallmann et al., 2012). This would lower submarine weathering alkalinity input to 2-3 Tmol y⁻¹ (Supporting Information S3).

Figure 6A and Table 3 clearly show that the ocean alkalinity budget based on the balance between riverine alkalinity inputs and carbonate burial at the ocean floor is imbalanced by about 27 Tmol y⁻¹ and provides only part of the story. Additional alkalinity from riverine PIC delivery (about 21 Tmol y⁻¹), anaerobic mineralization (about 6.2 Tmol y⁻¹) provides the majority of the alkalinity to balance the budget with minor additional inputs from submarine groundwater discharge (about 1 Tmol y⁻¹), organic matter burial (about 3 Tmol y⁻¹) and silicate interactions (about 1 Tmol y⁻¹: submarine weathering minus reversed weathering).

7. Conclusions

Alkalinity is a central concept in ocean buffering and it is of the utmost importance to understand and quantify its role in carbon dioxide uptake, carbonate mineral formation and ocean buffering during times of global change. In section 2 we have shown that it is instructive to distinguish between measurable titration alkalinity (TA) that is based on a proton balance and

charge-balance alkalinity (CBA). This distinction is needed to understand and quantify the impact of biogeochemical processes such as calcification or primary production on alkalinity.

Although much progress has been made in accurate and reproducible measurements of titration alkalinity, quantification of ocean buffering through the use of buffer or sensitivity factors is underexplored, except for the Revelle sensitivity factor (Sundquist et al., 1979) and the acid-base buffer capacity (Weber and Stumm, 1963). This is unfortunate because such a sensitivity analysis is critical to attribute changes in $p\text{CO}_2$ and/or pH to physical (temperature, salinity) and chemical/biological changes (alkalinity, dissolved inorganic carbon). In section 3 we have provided a systematic treatment of these sensitivity factors and identified and resolved inconsistent terminology. Together with the availability of public domain packages such as *seacarb* (Gattuso et al., 2019) and *AquaEnv* (Hofmann et al., 2010b) that facilitate their calculation, this provides researchers with the tools to understand and predict changes in ocean chemistry. This can be retrodiction of past or prediction of future pH changes due to ocean acidification, or prediction of future pH, $p\text{CO}_2$ or carbonate saturation values upon alkalinity manipulation during geo-engineering (Renforth and Henderson, 2017).

While these sensitivity factors provide a powerful approach to deal with equilibrium reactions, they are less useful when buffering is provided by interactions with slowly reacting solids or by changes in biological processes (e.g. calcification). These heterogeneous buffering reactions are dominated by calcium carbonate formation and dissolution, and normally discussed in terms of ocean carbonate compensation dynamics (Boudreau et al., 2018). Traditionally the focus has been on the role of carbonate mineral dissolution in the water column and sediments, i.e. chemical dissolution, which provides long-term buffering (Archer et al., 1998; 2009; Sigman et al., 1998; Ridgwell and Zeebe, 2005). However, ocean acidification or warming also impact calcification (e.g. coral bleaching). This biological carbonate compensation mechanism has implications on the short-term (months) for the carbonate compensation depth and on the longer term (kyr) for alkalinity accumulation in the ocean (Boudreau et al., 2018). Homogeneous buffering, chemical and biological carbonate compensation and weathering feedbacks together govern the long-term fate of anthropogenic carbon dioxide (Archer et al., 1998; 2009; Boudreau et al., 2010a). The very same processes have also been involved in the recovery of ocean chemistry to carbon perturbations in the past (Ridgwell and Zeebe, 2005; Boudreau et al., 2018).

Ocean alkalinity is controlled by multiple processes operating over multiple time scales complicating the elucidation of the present-day budget (Table 3) as well as reconstructions of alkalinity, carbon and pH of the past ocean. Nevertheless, some studies (Tyrell and Zeebe, 2004; Caves et al., 2016; Boudreau et al., 2019; Zeebe and Tyrell, 2019;) have reported alkalinity reconstructions for the last 50-60 million years indicating relatively minor fluctuations: e.g. between 1.5 and 3 mM. The Urey-Ebelmen concept implies that riverine alkalinity delivery should be balanced by carbonate burial in the ocean on geological timescales (Fig. 6A). The imbalance of the present-day ocean alkalinity budget between riverine DIC input and marine carbonate burial cannot be resolved by including alkalinity delivery by submarine groundwater or within ocean alkalinity production by anaerobic mineralization or submarine weathering. However, the alkalinity budget can readily be balanced by including alkalinity input to the ocean through riverine particulate inorganic carbon delivery (Table 3, Fig. 6B). The global riverine flux of PIC is poorly known but reasonable estimates (7.5 to 15 Tmol C y^{-1} ; corresponding to an alkalinity flux of 15-30 Tmol y^{-1}) indicate that it is similarly sized as the global riverine DIC flux (26-36 Tmol y^{-1}). This not only urges detailed research to better constrain this flux, but also

implies a reconsideration of past and present ocean alkalinity budgets that ignore physical weathering products delivered to the ocean.

Box 1. Terminology

- *Acid*: substance donating a proton
- *Base*: substance accepting a proton
- *Conjugated acids/bases*: substances that only differ by one proton
- *strong acid*: acid that donates all protons in natural water
- *weak acid*: acid that partly dissociates to conjugate base and proton in water
- *pH*: $-\log_{10}$ of proton concentration (H^+)
- *pK*: $-\log_{10}$ of equilibrium constant (K)
- *Bjerrum plot*: graph showing the distribution of acids and their conjugated bases as a function of pH
- *alkalinity*: the excess of proton acceptors (over proton donors) in a solution
- *titration alkalinity (TA)*: measurable alkalinity based on a proton balance
- *charge balance alkalinity (CBA)*: alkalinity based on excess of proton exchanging anions over cations, also known as excess negative charge (ENC)
- *buffer*: solution with a mixture of weak acids and conjugated bases that resist changes by transferring protons
- *homogeneous buffer*: solution resisting drastic changes by re-arrangement of protons in solution phase only
- *heterogeneous buffer*: a buffer system comprising both a solution and particles
- *buffer capacity*: ability of a solution to resist changes, also known as buffer index or intensity.
- *sensitivity factor*: change in output due to change in input, also known as chemical buffer factor, and the inverse of buffer capacity
- *carbonate compensation*: response of carbonate production and dissolution processes in the ocean upon changes
- *proton balance*: mass balance of protons
- *proton acceptor level*: the number of protons that can be accepted for an acid-base system at a specific pH, the reverse is known as the proton level
- *reference level species*: the major species of an acid-base system present at the reference level (e.g. pH=4.5)
- *Revelle factor*: a sensitivity factor expressing the change in carbon dioxide to the change in dissolved inorganic carbon

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953 **Author contributions**

954 JJM designed research and wrote the manuscript with contributions from KS and MH, in
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956 5.

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References

- Andral, M. (1850) Researches on the Acidity and Alkalinity of Certain Liquids of the Human Body, in the State of Health and Disease. *Edinb Med Surg J.* 73(182):124–132.
- Antonelli, M., Pester, N.J., Brown, S.T. & DePaolo, D.J. (2017) Effect of paleoseawater composition on hydrothermal exchange in midocean ridges. *Proc. Natl. Acad. Sci. U.S.A.* 114: 12413–12418.
- Archer, D., Kheshgi, H. & Maier-Reimer E. (1998) Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃, *Global Biogeochem. Cycles*, 12, 259– 276.
- Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K., Matsumoto, K., Munhoven, G., Montenegro, A., & Tokos K. (2009), Atmospheric lifetime of fossil fuel carbon dioxide, *Ann. Rev. Earth Planet. Sci.*, 37, 117– 134, doi:[10.1146/annurev.earth.031208.100206](https://doi.org/10.1146/annurev.earth.031208.100206).
- Asuero, A.G. & Michałowski T. (2011) Comprehensive formulation of titration curves referred to complex acid–base systems and its analytical implications. *Crit. Rev. Anal. Chem.* 41, 151–187. doi: 10.1080/10408347.2011.559440.
- Ben-Yaakov, S., (1973), pH buffering of pore water of recent anoxic marine sediments, *Limnology and Oceanography*, 18, doi: 10.4319/lo.1973.18.1.0086.
- Berner, R. A., Scott, M. R. & Thomlinson C. (1970), Carbonate alkalinity in the pore waters of anoxic marine sediments, *Limnol. Oceanogr.*, 15, 544– 549, doi:[10.4319/lo.1970.15.4.0544](https://doi.org/10.4319/lo.1970.15.4.0544).
- Berner, R. A. (1982), Burial of organic carbon and pyrite sulfur in the modern ocean; its geochemical and environmental significance, *Am. J. Sci.*, 282, 451– 473, doi:[10.2475/ajs.282.4.451](https://doi.org/10.2475/ajs.282.4.451).
- Berner R.A. (2004) *The phanerozoic carbon cycle: CO₂ and O₂*. Oxford University Press, Oxford
- Berner, E. K., & Berner, R. A. (2012). *Global environment: Water, air, and geochemical cycles*. Princeton, N.J: Princeton University Press.
- Berner, R.A., Lasaga, A.C., & Garrels, R.M. (1983) Carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Science* 283, 641-683; doi:10.2475/ajs.283.7.641.
- Beusen, A. H. W., Dekkers, A. L. M., Bouwman, A. F., Ludwig, W., & Harrison, J. (2005), Estimation of global river transport of sediments and associated particulate C, N, and P, *Global Biogeochem. Cycles*, 19, GB4S05, doi:[10.1029/2005GB002453](https://doi.org/10.1029/2005GB002453).
- Bockman, E.E., & Dickson, A.G. (2014) A seawater filtration method suitable for total dissolved inorganic carbon and pH analyses. *Limnol Oceanogr-Meth* 12: 191–195. DOI: [10.4319/lom.2014.12.191](https://doi.org/10.4319/lom.2014.12.191)
- Bolin, B., & Eriksson, E., (1959) Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion. In *The Atmosphere and the Sea in Motion* pp. 130–141.

- 997 Boudreau, B. P., & Canfield, D. E. (1993) A comparison of closed and open-system models for
 998 porewater pH and calcite-saturation state, *Geochim. Cosmochim. Ac.*, 57, 317–334,
 999 1993.
- 1000 Boudreau B. P., Meysman, F.J.R., & Middelburg, J.J., (2004) Multicomponent Ionic Diffusion in
 1001 Porewaters: Coulombic Effects revisited. *Earth Plan. Sci. Lett.* 222, 653–666.
- 1002 Boudreau, B. P., Middelburg, J. J., Hoffmann, A. F., & F. J. R. Meysman (2010a), Ongoing
 1003 transients in carbonate compensation, *Global Biogeochem. Cycles*, 24, GB4010,
 1004 doi:[10.1029/2009GB003654](https://doi.org/10.1029/2009GB003654).
- 1005 Boudreau, B. P., Middelburg, J. J., & F. J. R. Meysman (2010b), Carbonate compensation
 1006 dynamics, *Geophys. Res. Lett.*, 37, L03603, doi:[10.1029/2009GL041847](https://doi.org/10.1029/2009GL041847).
- 1007 Boudreau, B.P., Middelburg J.J. & Y. Luo (2018) The role of calcification in carbonate
 1008 compensation. *Nature Geosciences* 11, 894–900 (2018)
- 1009 Boudreau, B.P., Middelburg, J.J., Sluijs, A. & van der Ploeg R. (2019) Secular Variations in the
 1010 Carbonate Chemistry of the Oceans over the Cenozoic. *Earth Planet Science Letters* 512:
 1011 194–206.
- 1012 Brewer, P. G., Wong, G. T. F., Bacon, M. P., & Spencer, D. W. (1975), An oceanic calcium
 1013 problem?, *Earth Planet. Sci. Lett.*, 26(1), 81– 87.
- 1014 Brewer, P. G., & Goldman J. C. (1976), Alkalinity changes generated by phytoplankton growth,
 1015 *Limnol. Oceanogr.*, 21(1), 108– 117.
- 1016 Broecker, W.S. (1974) *Chemical Oceanography*. Harcourt Brace Jovanovich.
- 1017 Broecker, W.S. & T.H. Peng (1982) *Tracers in the Sea*. Lamont-Doherty Geological
 1018 Observatory.
- 1019 Burdige, D. J., (2007), Preservation of organic matter in marine sediments: Controls,
 1020 mechanisms, and an imbalance in sediment organic carbon budgets? *Chem. Rev.*, 107,
 1021 467– 485, doi:[10.1021/cr050347q](https://doi.org/10.1021/cr050347q).
- 1022 Butler, J.N. (1964) *Solubility and pH Calculations*. Reading Mass: Addison-Wesley Publishing
 1023 Company Inc.
- 1024 Butler, J. N. (1982). *Carbon Dioxide Equilibria and Their Applications*. Reading, Mass.:
 1025 Addison-Wesley.
- 1026 Cai, W. J., Wang, Y. C., & Hodson, R. E. (1998), Acid-base properties of dissolved organic
 1027 matter in the estuarine waters of Georgia, USA, *Geochim. Cosmochim. Acta*, 62(3), 473–
 1028 483, doi:[10.1016/s0016-7037\(97\)00363-3](https://doi.org/10.1016/s0016-7037(97)00363-3).
- 1029 Cai, W.-J., Hu, X., Huang, W.-J., Murrell, M. C., Lehrter, J. C., Lohrenz, S. E., Chou, W.-C.,
 1030 Zhai, W., Hollibaugh, J. T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M., &
 1031 Gong G.-C. (2011). Acidification of subsurface coastal waters enhanced by
 1032 eutrophication. *Nat. Geosci.* 4, 766–770.
- 1033 Cai, W.-J., Huang, W.-J., Luther, G. W., Pierrot, D., Li, M., Testa, J., ... Kemp, W. M. (2017).
 1034 Redox reactions and weak buffering capacity lead to acidification in the Chesapeake Bay.
 1035 *Nature Communications*, 8(1), 369. <https://doi.org/10.1038/s41467-017-00417-7>

- 1036 Caldeira, K (1995) Long-term control of atmospheric carbon dioxide; low-temperature seafloor
1037 alteration or terrestrial silicate-rock weathering? *Am J Sci* 295:1077-1114;
1038 doi:10.2475/ajs.295.9.1077
- 1039 Caldeira, K., & Rampino, M.R. (1993) Aftermath of the end-Cretaceous mass extinction:
1040 possible biogeochemical stabilization of the carbon cycle and climate.
1041 *Paleoceanography*, 8 515-525, [10.1029/93PA01163](https://doi.org/10.1029/93PA01163)
- 1042 Canfield, D.E., (1997) The geochemistry of river particulates from the continental USA: Major
1043 elements. *Geochim. Cosmochim. Acta* 61, 3349-3365.
- 1044 Carter, B. R., Toggweiler, J. R., Key, R. M. & Sarmiento, J. L. (2014), Processes determining the
1045 marine alkalinity and calcium carbonate saturation state distributions, *Biogeosciences*, 11,
1046 7349– 7362, doi:[10.5194/bg-11-7349-2014](https://doi.org/10.5194/bg-11-7349-2014).
- 1047 Caves, J.K., Jost, A.B., Lau, K.V., & Maher K. (2016) Cenozoic carbon cycle imbalances and a
1048 variable weathering feedback *Earth Planet. Sci. Lett.*, 450, 152-163,
1049 [10.1016/j.epsl.2016.06.035](https://doi.org/10.1016/j.epsl.2016.06.035)
- 1050 Chanson, M., & Millero, F. J., (2007), Effect of filtration on the total alkalinity of open-ocean
1051 seawater, *Limnol. Oceanogr. Methods*, 5, doi:10.4319/lom.2007.5.293.
- 1052 Chen, C.T. (1978): Decomposition of calcium carbonate and organic carbon in the deep oceans.
1053 *Science*, 201, 735–736.
- 1054 Chiriac, V., & Balea, G., (1997). Buffer index and buffer capacity for a simple buffer solution. *J.*
1055 *Chem. Educ.* 74, 937-939.
- 1056 Chisholm, J.R.M., & Gattuso, J.P., (1991) Validation of the alkalinity anomaly technique for
1057 investigating calcification of photosynthesis in coral reef communities. *Limnology and*
1058 *Oceanography* 36,1232–1239. doi: 10.4319/lo.1991.36.6.1232.
- 1059 Deffeyes, K. S. (1965), Carbonate equilibria: A graphic and algebraic approach. *Limnology and*
1060 *Oceanography*, 10, 412-426.
- 1061 Dickson, A. G. (1981), An exact definition of total alkalinity and a procedure for the estimation
1062 of alkalinity and total inorganic carbon from titration data, *Deep Sea Res. Part A*, 28,
1063 609– 623, doi:[10.1016/0198-0149\(81\)90121-7](https://doi.org/10.1016/0198-0149(81)90121-7).
- 1064 Dickson, A. G. (1992), The development of the alkalinity concept in marine chemistry, *Mar.*
1065 *Chem.*, 40, 49– 63.
- 1066 Dittmar, W. (1884), Report on researches into the composition of ocean water, collected by
1067 H.M.S. Challenger, during the years 1873-1876. In: J. Murray (Editor), Report on the
1068 Scientific Results of the Voyage of H.M.S. Challenger, during the years 1873-1876.
1069 Physics and Chemistry, Vol. 1. H.M.S.O., London, pp. 1-251.
- 1070 Donovan, M. (1839) *A treatise on chemistry*. Longman, UK.
- 1071 Dore, J. E., Lukas, R., Sadler, D. W., Church, M. J., & Karl D. M. (2009), Physical and
1072 biogeochemical modulation of ocean acidification in the central North Pacific, *Proc.*
1073 *Natl. Acad. Sci. U.S.A.*, 106(30), 12,235– 12,240, doi:[10.1073/pnas.0906044106](https://doi.org/10.1073/pnas.0906044106).
- 1074 Egger, M., Riedinger, N., Mogollón, J.M., Jørgensen, B.B. (2018) Global diffusive fluxes of
1075 methane in marine sediments. *Nat. Geosci.*, 11, 421-425

- 1076 Egleston, E. S., Sabine, C. L., & Morel, F. M. M. (2010). Revelle revisited: Buffer factors that
 1077 quantify the response of ocean chemistry to changes in DIC and alkalinity. *Global*
 1078 *Biogeochemical Cycles*, 24, GB1002. <https://doi.org/10.1029/2008GB003407>
- 1079 Feely, R. A., et al., (2002) In situ calcium carbonate dissolution in the Pacific Ocean, *Global*
 1080 *Biogeochem. Cycles*, 16(4), 1144, doi:[10.1029/2002GB001866](https://doi.org/10.1029/2002GB001866).
- 1081 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., & Millero, F. J.,
 1082 (2004), Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans, *Science*, 305,
 1083 362– 366, doi:[10.1126/science.1097329](https://doi.org/10.1126/science.1097329).
- 1084 Fishtik, I., Nagypál, I., & Gutman, I. (1995). Sensitivity analysis of multiple chemical equilibria:
 1085 Sensitivity coefficients and response equilibria. *The Journal of Chemical Physics*,
 1086 103(17), 7545-7555.
- 1087 Frankignoulle, M. (1994), A complete set of buffer factors for acid/base CO₂ system in seawater,
 1088 *J. Mar. Syst.*, 5(2), 111– 118, doi:[10.1016/0924-7963\(94\)90026-4](https://doi.org/10.1016/0924-7963(94)90026-4).
- 1089 Frankignoulle, M., Canon, C. & Gattuso J.P. (1994), Marine calcification as a source of carbon
 1090 dioxide: Positive feedback of increasing atmospheric CO₂, *Limnol. Oceanogr.*, 39, 458–
 1091 462, doi:[10.4319/lo.1994.39.2.0458](https://doi.org/10.4319/lo.1994.39.2.0458).
- 1092 Friedlingstein, P., Jones, M. W., O'Sullivan, M., Andrew, R. M., Hauck, J., Peters, G. P., Peters,
 1093 W., Pongratz, J., Sitch, S., Le Quéré, C., Bakker, D. C. E., Canadell, J. G., Ciais, P.,
 1094 Jackson, R. B., Anthoni, P., Barbero, L., Bastos, A., Bastrikov, V., Becker, M., Bopp, L.,
 1095 Buitenhuis, E., Chandra, N., Chevallier, F., Chini, L. P., Currie, K. I., Feely, R. A.,
 1096 Gehlen, M., Gilfillan, D., Gkritzalis, T., Goll, D. S., Gruber, N., Gutekunst, S., Harris, I.,
 1097 Haverd, V., Houghton, R. A., Hurtt, G., Ilyina, T., Jain, A. K., Joetzjer, E., Kaplan, J. O.,
 1098 Kato, E., Klein Goldewijk, K., Korsbakken, J. I., Landschützer, P., Lauvset, S. K.,
 1099 Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Marland, G., McGuire, P. C.,
 1100 Melton, J. R., Metzl, N., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Neill, C.,
 1101 Omar, A. M., Ono, T., Peregón, A., Pierrot, D., Poulter, B., Rehder, G., Resplandy, L.,
 1102 Robertson, E., Rödenbeck, C., Séférian, R., Schwinger, J., Smith, N., Tans, P. P., Tian,
 1103 H., Tilbrook, B., Tubiello, F. N., van der Werf, G. R., Wiltshire, A. J., Zaehle, S. (2019)
 1104 Global Carbon Budget 2019, *Earth Syst. Sci. Data*, 11, 1783-1838.
- 1105 Friis, K., Körtzinger, A., & Wallace, D. W. R., (2003), The salinity normalization of marine
 1106 inorganic carbon chemistry data, *Geophys. Res. Lett.*, 30(2), 1085,
 1107 doi:[10.1029/2002GL015898](https://doi.org/10.1029/2002GL015898).
- 1108 Fong, M.B. & Dickson, A.G. (2019) Insight from GO-SHIP hydrography data into the
 1109 thermodynamic consistency of CO₂ system measurements in seawater. *Marine*
 1110 *Chemistry*, 211, 52-63. doi.org/10.1016/j.marchem.2019.03.006
- 1111 Gaillardet, J., Dupré, B., Louvat, P., & Allègre, C. J. (1999), Global silicate weathering and CO₂
 1112 consumption rates deduced from the chemistry of large rivers, *Chem. Geol.*, 159, 3– 30,
 1113 doi:[10.1016/S0009-2541\(99\)00031-5](https://doi.org/10.1016/S0009-2541(99)00031-5).
- 1114 Gallego, M. A., Timmermann, A., Friedrich, T., & Zeebe, R. E. (2018) Drivers of future seasonal
 1115 cycle changes in oceanic pCO₂, *Biogeosciences*, 15, 5315–5327,
 1116 <https://doi.org/10.5194/bg-15-5315-2018>.

- 1117 Gattuso, J.-P., & Hansson, L. (2011), Ocean acidification: Background and history, in *Ocean*
 1118 *Acidification*, edited by J.-P. Gattuso and L. Hansson, Chap. 1, p. 1– 20, Oxford Univ.
 1119 Press, Oxford.
- 1120 Gattuso, J. P., Epitalon, J.M., Lavigne, H., & Orr, J.C., (2019). seacarb: Seawater Carbonate
 1121 Chemistry R package version 3.2.12. <https://CRAN.R-project.org/package=seacarb>
- 1122 Gattuso J-P, Magnan A.K., Bopp, L., Cheung, W.W.L., Duarte, C.M., Hinkel, J., Mcleod, E.,
 1123 Micheli, F., Oschlies, A., Williamson, P., Billé, R., Chalastani, V.I., Gates, R.D., Irisson,
 1124 J-O, Middelburg, J.J., Pörtner, H-O, & Rau, G.H., (2018) Ocean Solutions to Address
 1125 Climate Change and Its Effects on Marine Ecosystems. *Front. Mar. Sci.* 5:337.
 1126 doi:10.3389/fmars.2018.00337
- 1127 Gazeau, F., Quiblier, C., Jansen, J. M., Gattuso, J.-P., Middelburg, J. J., & Heip, C. H. R. (2007),
 1128 Impact of elevated CO₂ on shellfish calcification, *Geophys. Res. Lett.*, 34, L07603,
 1129 doi:[10.1029/2006GL028554](https://doi.org/10.1029/2006GL028554).
- 1130 Gazeau, F., Urbini, L., Cox, T.E., Alliouane, S., Gattuso, J.-P. (2015) Comparison of the
 1131 alkalinity and calcium anomaly techniques to estimate rates of net calcification. *Mar Ecol*
 1132 *Prog Ser* 527:1–12
- 1133 Goldman, J. C., & Brewer, P.G., (1980) Effect of nitrogen source and growth rate on
 1134 phytoplankton-mediated changes in alkalinity, *Limnology and Oceanography*, 25: 352-
 1135 357.
- 1136 Gruber, N., Clement, D., Carter, B. R., Feely, R. A., van Heuven, S., Hoppema, M., Ishii, M.,
 1137 Key, R. M., Kozyr, A., Lauvset, S. K., Lo Monaco, C., Mathis, J. T., Murata, A., Olsen,
 1138 A., Perez, F. F., Sabine, C. L., Tanhua, T., & Wanninkhof, R. (2019). The oceanic sink
 1139 for anthropogenic CO₂ from 1994 to 2007. *Science*, 363(6432), 1193– 1199.
 1140 <https://doi.org/10.1126/SCIENCE.AAU5153>
- 1141 Gustafsson, E., Hagens, M., Sun, X., Reed, D. C., Humborg, C., Slomp, C. P., & Gustafsson, B.
 1142 G. (2019) Sedimentary alkalinity generation and long-term alkalinity development in the
 1143 Baltic Sea, *Biogeosciences*, 16, 437–456, <https://doi.org/10.5194/bg-16-437-2019>.
- 1144 Hagens, M., Hunter, K. A., Liss, P. S., & Middelburg, J. J. (2014) Biogeochemical context
 1145 impacts seawater pH changes resulting from atmospheric sulfur and nitrogen deposition,
 1146 *Geophys. Res. Lett.*, 41, 935–941, <https://doi.org/10.1002/2013GL058796>.
- 1147 Hagens, M., Slomp, C. P., Meysman, F. J. R., Seitaj, D., Harlay, J., Borges, A. V., &
 1148 Middelburg, J. J. (2015): Biogeochemical processes and buffering capacity concurrently
 1149 affect acidification in a seasonally hypoxic coastal marine basin, *Biogeosciences*, 12,
 1150 1561–1583, <https://doi.org/10.5194/bg-12-1561-2015>.
- 1151 Hagens, M., & Middelburg J. J. (2016a), Generalised expressions for the response of pH to
 1152 changes in ocean chemistry, *Geochim. Cosmochim. Acta*, 187, 334– 349,
 1153 doi:[10.1016/j.gca.2016.04.012](https://doi.org/10.1016/j.gca.2016.04.012).
- 1154 Hagens, M., & Middelburg, J. J. (2016b), Attributing seasonal pH variability in surface ocean
 1155 waters to governing factors, *Geophys. Res. Lett.*, 43, 12,528– 12,537,
 1156 doi:[10.1002/2016GL071719](https://doi.org/10.1002/2016GL071719).

- 1157 Hammer, K., Schneider, B., Kuliński, K., & Schulz-Bull, D. (2017): Acid-base properties of
1158 Baltic Sea dissolved organic matter, *J. Marine Syst.*, 173, 114–121, 2017.
- 1159 Hartmann, J., Moosdorf, N., Lauerwald, R., Hinderer, M., & West, A. J. (2014). Global chemical
1160 weathering and associated P-release—The role of lithology, temperature and soil
1161 properties. *Chem Geol*, 363: 145–163
- 1162 Hedges J.I., Baldock, J.A., Gélina, Y., Lee, C., Peterson, M.L., & Wakeham, S.G., (2002) The
1163 biochemical and elemental compositions of marine plankton: A NMR perspective.
1164 *Marine Chem.* 78: 47-63.
- 1165 Hemond, H.F., (1990) Acid neutralizing capacity, alkalinity, and acid-base status of natural
1166 waters containing organic acids *Environmental Science & Technology* 24 (10), 1486-
1167 1489 DOI: 10.1021/es00080a005
- 1168 Hernandez-Ayon, J., Zirino, A., Dickson, A., Camiro-Vargas, T., & Valenzuela, E., (2007)
1169 Estimating the contribution of organic bases from microalgae to the titration alkalinity in
1170 coastal seawaters. *Limnol. Oceanogr.: Methods* 5: 225– 232.
1171 doi:[10.4319/lom.2007.5.225](https://doi.org/10.4319/lom.2007.5.225)
- 1172 Hinrichs, K.H. & Boetius A. (2002) The anaerobic oxidation of methane: new insights in
1173 microbial ecology and biogeochemistry in: *G. Wefer, D. Billett, D. Hebbeln, B.B.*
1174 *Jorgensen, M. Schlüter, T.V. Weering (Eds.), Ocean Margin Systems*, Springer, pp. 457-
1175 477
- 1176 Hiscock, W. T., & Millero, F. J., (2006), Alkalinity of the anoxic waters in the western Black
1177 Sea, *Deep Sea Res., Part II*, 53(17–19), 1787– 1801.
- 1178 Hoegh-Guldberg, O., et al. (2007), Coral reefs under rapid climate change and ocean
1179 acidification, *Science*, 318, 1737– 1742, doi:[10.1126/science.1152509](https://doi.org/10.1126/science.1152509).
- 1180 Hofmann, A. F., Middelburg, J. J., Soetaert, K., Wolf-Gladrow, D.A., & Meysman, F.J.R.,
1181 (2010a) Proton cycling, buffering, and reaction stoichiometry in natural waters. *Mar.*
1182 *Chem.* 121: 246–255.
- 1183 Hofmann, A. F., Soetaert K., Middelburg J. J. & Meysman F. J. R. (2010b) AquaEnv: an aquatic
1184 acid–base modelling environment in R. *Aquat. Geochem.* 16, 507–546.
- 1185 Hu, X. & Cai, W.-J. (2011) An assessment of ocean margin anaerobic processes on oceanic
1186 alkalinity budget, *Global Biogeochem. Cy.*, 25, GB3003,
1187 <https://doi.org/10.1029/2010GB003859>, 2011.
- 1188 Hu, X. (2020) Effect of Organic Alkalinity on Seawater Buffer Capacity: A Numerical
1189 Exploration. *Aquat Geochem*, <https://doi.org/10.1007/s10498-020-09375-x>
- 1190 Huang, W.-J., Cai, W.-J., Wang, Y., Hu, X., Chen, B., Lohrenz, S. E., Chakraborty, S., He, R.,
1191 Brandes, J., & Hopkinson, C. S. (2015). The response of inorganic carbon distributions
1192 and dynamics to upwelling-favorable winds on the northern Gulf of Mexico during
1193 summer. *Continental Shelf Research*, 111, 211– 222.
- 1194 Humphreys, M. P., Daniels, C. J., Wolf-Gladrow, D. A., Tyrrell, T., & Achterberg, E. P. (2018)
1195 On the influence of marine biogeochemical processes over CO₂ exchange between the
1196 atmosphere and ocean, *Mar. Chem.*, 199, 1–11,
1197 <https://doi.org/10.1016/j.marchem.2017.12.006>, 2018.

- 1198 Iglesias-Rodriguez, M. D., Armstrong, R., Feely, R., Hood, R., Kleypas, J., Sabine, C., &
 1199 Sarmiento, J. (2002), Progress made in study of ocean's calcium carbonate budget, *EOS*
 1200 *Trans. AGU*, 83(34), 365, doi:[10.1029/2002EO000267](https://doi.org/10.1029/2002EO000267).
- 1201 Isson, T.T., & Planavsky, N.J., (2018) Reverse weathering as a long-term stabilizer of marine
 1202 pH and planetary climate. *Nature* 560:471–475.
- 1203 Jahnke, R.A. & Jahnke, D.B., (2004) Calcium carbonate dissolution in deep sea sediments:
 1204 reconciling microelectrode, pore water and benthic flux chamber results *Geochim.*
 1205 *Cosmochim. Acta*, 68, 47-59
- 1206 Jiang, Z., Tyrrell, T., Hydes, D. J., Dai, M., & Hartman, S. E. (2014). Variability of alkalinity
 1207 and the alkalinity-salinity relationship in the tropical and subtropical surface ocean.
 1208 *Global Biogeochem. Cycles*, 28, 729–742. doi:10.1002/2013GB004678.
- 1209 Jørgensen, B. B. (1977) Sulphur cycle of a coastal marine sediment (Limfjorden, Denmark),
 1210 *Limnol. Oceanogr.*, 22, 814–832.
- 1211 Jørgensen, B. B. (1982) Mineralization of organic matter in the sea bed – the role of sulphate
 1212 reduction, *Nature*, 296, 643–645.
- 1213 Kanamori, S., & Ikegami, H. (1982), Calcium-alkalinity relationship in the North Pacific, *J.*
 1214 *Oceanogr.*, 38, 57– 62.
- 1215 Kim, H.-C., Lee, K. & Choi, W., (2006) Contribution of phytoplankton and bacterial cells to the
 1216 measured alkalinity of seawater. *Limnol. Oceanogr.* 51: 331– 338.
 1217 doi:[10.4319/lo.2006.51.1.0331](https://doi.org/10.4319/lo.2006.51.1.0331)
- 1218 Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., Avena,
 1219 M.J. (1999) Ion binding to natural organic matter: competition, heterogeneity,
 1220 stoichiometry and thermodynamic consistency *Colloid. Surf. Physicochem. Eng. Asp.*,
 1221 151 (1–2), 147-166
- 1222 Kinsey, D. W., (1978) Alkalinity changes and coral reef calcification, *Limnology and*
 1223 *Oceanography*, 23, doi: 10.4319/lo.1978.23.5.0989.
- 1224 Ko, Y. H., Lee, K. , Eom, K. H. & Han, I. (2016), Organic alkalinity produced by phytoplankton
 1225 and its effect on the computation of ocean carbon parameters. *Limnol. Oceanogr.*, 61:
 1226 1462-1471. doi:[10.1002/lno.10309](https://doi.org/10.1002/lno.10309)
- 1227 Koppel, M. & Spiro, K., (1914) Über die Wirkung von Moderatoren (Puffern) bei der
 1228 Verschiebung des Säure-Basengleichgewichtes in biologischen Flüssigkeiten *Biochem.*
 1229 *Ztschr.*, 65, pp. 409-439
- 1230 Kwiatkowski L., & Orr, J. C., (2018) Diverging seasonal extremes for ocean acidification during
 1231 the twenty-first century, *Nature Climate Change*, 10.1038/s41558-017-0054-0, **8**, 2, 141-
 1232 145
- 1233 Kroeker, K.J., Kordas, R.C., Crim, R., Hendriks, I.E., Ramajo, L., Singh, F.S., Duarte, C.M., &
 1234 Gattuso, J.P. (2013) Impacts of ocean acidification on marine organisms: quantifying
 1235 sensitivities and interaction with warming. *Glob Change Biol* 19:1884–1896
- 1236 Krumins, V., Gehlen, M., Arndt, S., Van Cappellen, P., & Regnier, P. (2013) Dissolved
 1237 inorganic carbon and alkalinity fluxes from coastal marine sediments: model estimates

- 1238 for different shelf environments and sensitivity to global change, *Biogeosciences*, 10,
1239 371–398, <https://doi.org/10.5194/bg-10-371-2013>,
- 1240 Kuliński, K., Schneider, B., Hammer, K., Machulik, U., & D. Schulz-Bull (2014) The influence
1241 of dissolved organic matter on the acid–base system of the Baltic Sea. *J. Mar. Syst.* 132:
1242 106– 115. doi:[10.1016/j.jmarsys.2014.01.011](https://doi.org/10.1016/j.jmarsys.2014.01.011)
- 1243 Lasaga, A. C. (1998). *Kinetic Theory in the Earth Sciences*. Princeton Series in Geochemistry.
1244 x+811 pp. Princeton, Chichester: Princeton .
- 1245 Łukawska-Matuszewska, K. (2016) Contribution of non-carbonate inorganic and organic
1246 alkalinity to total measured alkalinity in pore waters in marine sediments (Gulf of
1247 Gdansk, S-E Baltic Sea), *Mar. Chem.*, 186, 211–220,
1248 <https://doi.org/10.1016/j.marchem.2016.10.002>.
- 1249 Łukawska-Matuszewska, K., Grzybowski, W., Szewczun, A., & Tarasiewicz, P. (2018)
1250 Constituents of organic alkalinity in pore water of marine sediments, *Mar. Chem.*, 200,
1251 22–32, <https://doi.org/10.1016/j.marchem.2018.01.012>.
- 1252 Le Chatelier H. (1884) – Sur un énoncé général des lois des équilibres chimiques, *C.R. Hebd.*
1253 *Seances Acad. Sci.*, 99, pp. 786-789
- 1254 Lee, K., Tong, L. T., Millero, F. J., Sabine, C. L., Dickson, A. G., Goyet, C., Park, G.-H.,
1255 Wanninkhof, R., Feely, R. A., & Key R. M. (2006), Global relationships of total
1256 alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys.*
1257 *Res. Lett.*, 33, L19605, doi:[10.1029/2006GL027207](https://doi.org/10.1029/2006GL027207).
- 1258 Leenheer, J.A., & Croué, J-P (2003) Characterizing Aquatic Dissolved Organic Matter
1259 *Environmental Science & Technology* 2003 37 (1), 18A-26A DOI: 10.1021/es032333c
- 1260 Li, M., Peng, C., Wang, M., Xue, W., Zhang, K., Wang, K., Shi, G., & Zhu, Q. (2017). The
1261 carbon flux of global rivers: A re-evaluation of amount and spatial patterns. *Ecological*
1262 *Indicators*, 80(September), 40– 51. <https://doi.org/10.1016/j.ecolind.2017.04.049>
- 1263 Li, Y.H., Takahashi, T. & Broecker, W.S. (1969) Degree of saturation of CaCO₃ in the oceans.
1264 *J. Geophys. Res* 74, 5507-5525.
- 1265 Ludwig W, Suchet P.A., & Probst, J.L. (1996). River discharges of carbon to the world's oceans:
1266 Determining local inputs of alkalinity and of dissolved and particulate organic carbon. *Cr*
1267 *Acad Sci Ii A*. 323, 1007–1014.
- 1268 Ludwig W, Suchet P, Munhoven G, Probst J-L (1998) Atmospheric CO₂ consumption by
1269 continental erosion: Present-day controls and implications for the last glacial maximum.
1270 *Glob Planet Change* 16, 107–120. doi: 10.1016/S0921-8181(98)00016-2
- 1271 Luo, Y., Boudreau, B.P., Dickens, G.R., Sluijs, A., & Middelburg, J.J. (2016) An alternative
1272 model for CaCO₃ over-shooting during the PETM - Biological carbonate compensation.
1273 *Earth and Planetary Science Letters* 453: 223-233.
- 1274 Mackenzie, F.T., & Garrels, R.M., (1966) Chemical mass balance between rivers and oceans *Am*
1275 *J Sci* 264, 507-525; doi:10.2475/ajs.264.7.507.

- 1276 Marsigli, L.F.c. (1725) *Histoire Physique de la Mer*, Ouvrage Enrichi de figures dessinees
 1277 d'apres le Naturel, Seconde partie. De Son Eau, Aus depens de la Compagnie,
 1278 Amsterdam, pp. 18-43
- 1279 Martin J.M., & Meybeck, M., (1979) Elemental mass-balance of material carried by major world
 1280 rivers. *Mar Chem* 7(3):173–206
- 1281 Meister P. (2013) Two opposing effects of sulfate reduction on carbonate precipitation in normal
 1282 marine, hypersaline, and alkaline environments *Geology*, 41, p. 499–502,
 1283 doi:10.1130/G34185.1
- 1284 Meybeck, M. (1982). Carbon, nitrogen, and phosphorus transport by world rivers. *American*
 1285 *Journal of Science*. <https://doi.org/10.2475/ajs.282.4.401>, 282(4), 401– 450.
- 1286 Meybeck, M. (1987). Global chemical weathering of surficial rocks estimated from river
 1287 dissolved loads. *American Journal of Science*, 287(5), 401– 428.
 1288 <https://doi.org/10.2475/ajs.287.5.401>
- 1289 Michałowski, T., & Asuero, A. G. (2012) New Approaches in Modeling Carbonate Alkalinity
 1290 and Total Alkalinity. *Critical Reviews in Analytical Chemistry* 42, 220-244.
- 1291 Michalopoulos, P., & Aller, R. C., (1995), Rapid clay mineral formation in Amazon delta
 1292 sediments: Reverse weathering and oceanic elemental cycles, *Science*, 270, 614– 617.
- 1293 Michalopoulos, P., & Aller, R. C., (2004), Early diagenesis of biogenic silica in the Amazon
 1294 delta: Alteration, authigenic clay formation, and storage, *Geochim. Cosmochim. Acta*, 68,
 1295 1061– 1085.
- 1296 Middelburg, J.J., (2019) *Marine Carbon Biogeochemistry*. A primer for Earth System scientists.
 1297 Springer Verlag.
- 1298 Millero F.J. (2007) The marine inorganic carbon cycle. *Chem. Rev.* 107: 308-341.
- 1299 Millero, F. J., Lee, K. & Roche, M., (1998), Distribution of alkalinity in the surface waters of the
 1300 major oceans, *Mar. Chem.*, 60(1–2), 111– 130.
- 1301 Milliman, J. D., (1993), Production and accumulation of calcium carbonate in the ocean: Budget
 1302 of a nonsteady state, *Global Biogeochem. Cycles*, 7, 927– 957, doi:[10.1029/93GB02524](https://doi.org/10.1029/93GB02524).
- 1303 Milliman, J. D., & Droxler, A. W., (1996), Neritic and pelagic carbonate sedimentation in the
 1304 marine environment: Ignorance is not bliss, *Geol. Rundsch.*, 85, 496– 504,
 1305 doi:[10.1007/BF02369004](https://doi.org/10.1007/BF02369004).
- 1306 Mitchell, P.H. and N.W. Rakestraw (1933) Buffer capacity of sea water *Biol. Bull. mar. biol.*
 1307 *Lab.*, Woods Hole, 65, 435-451
- 1308 Morel, F. M. M., & Hering, J. G., (1993), *Principles and Applications of Aquatic Chemistry*,
 1309 John Wiley, Hoboken, N. J.
- 1310 Morel, F., McDuff, R. E., & Morgan, J. J., (1976) Theory of Interaction Intensities, Buffer
 1311 Capacities, and pH Stability in Aqueous Systems, with Application to the pH of Seawater
 1312 and a Heterogeneous Model Ocean System. *Mar. Chem.*, 4(1): 1–28.
- 1313 Morse J.W., & Mackenzie, F.T. (1990) *Geochemistry of sedimentary carbonates*. Elsevier,
 1314 Amsterdam

- 1315 Morse, J. W., Arvidson, R. S., & Lüttge, A. , (2007), Calcium carbonate formation and
1316 dissolution, *Chem. Rev.*, 107, 342– 381, doi:[10.1021/cr050358j](https://doi.org/10.1021/cr050358j).
- 1317 Muller, F. L., & Bleie, B., (2008). Estimating the organic acid contribution to coastal seawater
1318 alkalinity by potentiometric titrations in a closed cell. *Anal. Chim. Acta* 619: 183– 191.
1319 doi:[10.1016/j.aca.2008.05.018](https://doi.org/10.1016/j.aca.2008.05.018)
- 1320 Omta, A. W., Goodwin, P. & Follows, M. J., (2010), Multiple regimes of air-sea carbon
1321 partitioning identified from constant-alkalinity buffer factors, *Global Biogeochem.*
1322 *Cycles*, 24, GB3008, doi:[10.1029/2009GB003726](https://doi.org/10.1029/2009GB003726).
- 1323 O'Mara, N., & Dunne, J.P. (2019) Hot Spots of Carbon and Alkalinity Cycling in the Coastal
1324 Oceans. *Scientific Reports*, 9(1), 4434, 2019
- 1325 Orr, J. C., Epitalon, J.-M., Dickson, A. G., & Gattuso, J.-P. (2018). Routine uncertainty
1326 propagation for the marine carbon dioxide system. *Mar. Chem.* 207, 84–107. doi:
1327 [10.1016/j.marchem.2018.10.006](https://doi.org/10.1016/j.marchem.2018.10.006)
- 1328 Perdue, E.M., Reuter, J.H., & Parrish, R.S. (1984) A statistical model of proton binding by
1329 humus *Geochimica Cosmochimica Acta*. 48: 1257-1263. DOI: [10.1016/0016-](https://doi.org/10.1016/0016-7037(84)90060-7)
1330 [7037\(84\)90060-7](https://doi.org/10.1016/0016-7037(84)90060-7)
- 1331 Pytkowicz, R.M., (1967) Carbonate cycle and the buffer mechanism of recent oceans. *Geochim*
1332 *Cosmochim Acta* 31(1):63–73
- 1333 Rahman, S., Aller, R. C., & Cochran, J. K. (2016), Cosmogenic ³²Si as a tracer of biogenic silica
1334 burial and diagenesis: Major deltaic sinks in the silica cycle, *Geophys. Res. Lett.*, 43,
1335 7124– 7132, doi:[10.1002/2016GL069929](https://doi.org/10.1002/2016GL069929).
- 1336 Raymond, P. A. & Hamilton, S. K. (2018), Anthropogenic influences on riverine fluxes of
1337 dissolved inorganic carbon to the oceans. *Limnol. Oceanogr.*, 3: 143-155.
1338 doi:[10.1002/lol2.10069](https://doi.org/10.1002/lol2.10069)
- 1339 Reeburgh, W. S., Whalen S. C. & Alperin, M. J. (1993). The role of methylotrophy in the global
1340 methane budget. pp. 1-14. In J. C. Murrell and D. P. Kelly (eds.) *Microbial Growth on C-*
1341 *I Compounds*, Intercept, Andover, UK.
- 1342 Renforth, P., & Henderson, G. (2017) Assessing ocean alkalinity for carbon sequestration, *Rev.*
1343 *Geophys.*, 55, 636– 674, doi:[10.1002/2016RG000533](https://doi.org/10.1002/2016RG000533).
- 1344 Revelle, R., & Suess, H. E. (1957), Carbon dioxide exchange between atmosphere and ocean and
1345 the question of an increase of atmospheric CO₂ during the past decades, *Tellus*, 9, 18– 27.
- 1346 Richier, S., Achterberg, E.P., Humphreys, M.P., et al. (2018) Geographical CO₂ sensitivity of
1347 phytoplankton correlates with ocean buffer capacity. *Glob Change Biol.* 24, 4438– 4452.
1348 <https://doi.org/10.1111/gcb.14324>
- 1349 Ridgwell, A. (2007), Interpreting transient carbonate compensation depth changes by marine
1350 sediment core modeling, *Paleoceanography*, 22, PA4102, doi:[10.1029/2006PA001372](https://doi.org/10.1029/2006PA001372).
- 1351 Ridgwell, A., & Zeebe, R. (2005), The role of the global carbonate cycle in the regulation and
1352 evolution of the Earth system, *Earth Planet. Sci. Lett.*, 234, 299– 315,

- 1353 Riebesell, U., Körtzinger, A., & Oschlies, A. (2009), Sensitivities of marine carbon fluxes to
 1354 ocean change, *Proc. Natl. Acad. Sci. U.S.A.*, 106(49), 20,602– 20,609,
 1355 doi:[10.1073/pnas.0813291106](https://doi.org/10.1073/pnas.0813291106).
- 1356 Sarmiento, J. L., & Gruber, N. (2006), *Ocean Biogeochemical Dynamics*, 528 pp., Princeton
 1357 Univ. Press, Princeton, N. J.
- 1358 Schlunegger, S., Rodgers K.B., Sarmiento J.L., Frolicher, T.L., Dunne, J.P., Ishii, M., & Slater,
 1359 R. (2019) Emergence of anthropogenic signals in the ocean carbon cycle. *Nat. Clim.*
 1360 *Change* 9, 719-725. Doi: 10.1038/s41558-019-0553-2.
- 1361 Schulz, K.G. & Riebesell, U. (2013) Diurnal changes in seawater carbonate chemistry speciation
 1362 at increasing atmospheric carbon dioxide *Mar Biol* 160: 1889.
 1363 <https://doi.org/10.1007/s00227-012-1965-y>
- 1364 Seitzinger, S., Harrison, J. A., Bohlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B.,
 1365 Tobias, C., & Dreht G. V. (2006), Denitrification across landscapes and waterscapes: A
 1366 synthesis, *Ecol. Appl.*, 16, 2064– 2090, doi:[10.1890/1051-](https://doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2)
 1367 [0761\(2006\)016\[2064:DALAWA\]2.0.CO;2](https://doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2).
- 1368 Sigman, D. M., McCorkle, D. C., & Martin, W. R. (1998), The calcite lysocline as a constraint
 1369 on glacial/interglacial low-latitude production changes, *Global Biogeochem. Cycles*, 12(
 1370 3), 409– 427, doi:[10.1029/98GB01184](https://doi.org/10.1029/98GB01184).
- 1371 Sillén L.G. (1967) The ocean as a chemical system, *Science*, 156, 1189-1197
- 1372 Slomp, C. P., & Van Cappellen, P. (2004). Nutrient inputs to the coastal ocean through
 1373 submarine groundwater discharge: Controls and potential impact. *Journal of Hydrology*,
 1374 295(1-4), 64– 86. <https://doi.org/10.1016/j.jhydrol.2004.02.018>
- 1375 Smith W.R. & Missen, R. W., (2003) Sensitivity analysis in ChE education: Part 1. Introduction
 1376 and application to explicit models *Chemical Engineering Education* 37(3):222-227
- 1377 Smith, S.V. (2013) *Parsing the oceanic calcium carbonate cycle: a net atmospheric carbon*
 1378 *dioxide source, or a sink?* L&O e-Books. Association for the Sciences of Limnology and
 1379 Oceanography (ASLO) Waco, TX. doi: [10.4319/svsmith.2013.978-0-9845591-2-1](https://doi.org/10.4319/svsmith.2013.978-0-9845591-2-1)
- 1380 Smith, S.V. & Mackenzie, F.T. (2016) The Role of CaCO₃ Reactions in the Contemporary
 1381 Oceanic CO₂ Cycle *Aquat Geochem* 22: 153. <https://doi.org/10.1007/s10498-015-9282-y>
- 1382 Soetaert, K., Hofmann, A. F., Middelburg, J. J., Meysman, F. J. R., & Greenwood, J. (2007), The
 1383 effect of biogeochemical processes on pH, *Mar. Chem.*, 105, 30– 51,
 1384 doi:[10.1016/j.marchem.2006.12.012](https://doi.org/10.1016/j.marchem.2006.12.012).
- 1385 Song, S. Wang, Z. A., Gonneea, M. E., Kroeger, K. D., Chu, S.N., Li, D. & Liang H. (2020) An
 1386 important biogeochemical link between organic and inorganic carbon cycling: Effects of
 1387 organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt
 1388 marshes, *Geochim. Cosmochim. Acta*, 275, 123-139.
- 1389 Staudigel, H., Hart, S. R., Schmincke, H.-U., & Smith, B. M. (1989), Cretaceous ocean crust at
 1390 DSDP Sites 417 and 418: Carbon uptake from weathering versus loss by magmatic
 1391 outgassing, *Geochim. Cosmochim. Acta*, 53, 3091– 3094.

- 1392 Stumm, W. & Morgan, J.W., (1981). Aquatic Chemistry, Chemical Equilibria and Rates in
1393 Natural Waters, 2nd ed. John Wiley & Sons, Inc., New York.
- 1394 Suchet, A., Probst, J. L., & Ludwig, W. (2003) Worldwide distribution of continental rock
1395 lithology: Implications for the atmospheric/soil CO₂ uptake by continental weathering
1396 and alkalinity river transport to the oceans, *Global Biogeochem. Cy.*, 17, 1038–1051.
- 1397 Sundquist E.T., Plummer, L.N., & Wigley T.M.I., (1979) Carbon dioxide in the ocean surface:
1398 the homogeneous buffer factor. *Science* 204:1203–1205
- 1399 Sundquist, E.T. & Plummer, L.N., (1981) Carbon Dioxide in the Ocean Surface Layer: Some
1400 Modelling Considerations. In *SCOPE 16 Carbon Cycle Modelling*, edited by B. Bolin,
1401 John Wiley & Sons, 259-270 pp.
- 1402 Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., & Sutherland, S. C. (1993),
1403 Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A
1404 comparative study, *Global Biogeochem. Cycles*, 7(4), 843– 878,
1405 doi:[10.1029/93GB02263](https://doi.org/10.1029/93GB02263).
- 1406 Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., Ho, C., Newberger, T.,
1407 Sweeney, C., & Munro, D. R., (2014), Climatological distributions of pH, pCO₂, total
1408 CO₂, alkalinity, and CaCO₃ saturation in the global surface ocean, and temporal changes
1409 at selected locations, *Mar. Chem.*, 164, 95– 125, doi:[10.1016/j.marchem.2014.06.004](https://doi.org/10.1016/j.marchem.2014.06.004).
- 1410 Thompson T.G. & Bonnar R.U., (1931) The buffer capacity of seawater *Ind. Eng. Chem., Anal.*
1411 *Ed.*, 3, 393-395
- 1412 Turchyn A.V. & DePaolo, D.J., (2019) Seawater chemistry through Phanerozoic Time. *Annual*
1413 *Review of Earth and Planetary Sciences* 47, 197-224
- 1414 Tyrrell, T. & Zeebe, R.E. (2004) History of carbonate ion concentration over the last 100 million
1415 years *Geochim. Cosmochim. Acta*, 68, 3521-3530
- 1416 Ulfssbo, A., Kuliński, K., Anderson, L. G., & Turner, D. R.: Modelling organic alkalinity in the
1417 Baltic Sea using a Humic-Pitzer approach, *Mar. Chem.*, 168, 18–26,
1418 <https://doi.org/10.1016/j.marchem.2014.10.013>, 2015.
- 1419 Urbansky E.T. & Schock, M.R. (2000) Understanding, deriving, and computing buffer capacity.
1420 *J. Chemical Education* 77: 1640-1644.
- 1421 Urey, H.C., (1952) On the early chemical history of the earth and the origin of life. *Proc Natl*
1422 *Acad Sci* 38:352–363
- 1423 van der Ploeg, R., Boudreau, B.P., Middelburg, J. J., & Sluijs, A. (2019) Cenozoic carbonate
1424 burial along continental margins. *Geology* doi: <https://doi.org/10.1130/G46418.1>
- 1425 van Slyke, D.D. (1922) On the measurement of buffer values and on the relationship of buffer
1426 value to the dissociation constant of the buffer and the concentration and reaction of the
1427 buffer solution. *J. Biol. Chem.* 52, 525–570.
- 1428 Wallmann, K., Aloisi, G., Haeckel, M., Tishchenko, P., Pavlova, G., Greinert, J., Kutterolf, S., &
1429 Eisenhauer, A. (2008) Silicate weathering in anoxic marine sediments, *Geochim.*
1430 *Cosmochim. Ac.*, 72, 2895–2918, <https://doi.org/10.1016/j.gca.2008.03.026>.

- Wallmann, K., Pinero, E., Burwicz, E., Haeckel, M., Hensen, C., Dale, A., & Ruepke, L. (2012). The global inventory of methane hydrate in marine sediments: A theoretical approach. *Energies*, 5(12), 2449– 2498. <https://doi.org/10.3390/en5072449>
- Weber, W., & Stumm, W., (1963) Mechanism of hydrogen ion buffering in natural waters *J. Amer. Waterworks Assn.*, 55, 1553-1578
- Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Kortzinger, A., & Dickson A. G. (2007) Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, *Mar. Chem.*, 106, 287– 300, doi:[10.1016/j.marchem.2007.01.006](https://doi.org/10.1016/j.marchem.2007.01.006).
- Wollast, R. (1994) The relative importance of biomineralization and dissolution of CaCO₃ in the global carbon cycle. In: *Past and Present Biomineralization Processes. Consideration about the carbonate cycle*, F. Doumenge (ed.), N° Special **13**, *Bull. Institut Océanog. Monaco*, 11–35.
- Yang, B., Byrne, R. H., & Lindemuth, M. (2015). Contributions of organic alkalinity to total alkalinity in coastal waters: A spectrophotometric approach. *Mar. Chem.* 176: 199– 207. doi:[10.1016/j.marchem.2015.09.008](https://doi.org/10.1016/j.marchem.2015.09.008)
- Zeebe, R. E., & Wolf-Gladrow, D. (2001), *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*, Elsevier Oceanography Series, 360 pp., Elsevier Science B.V.
- Zeebe, R.E., Zachos, J.C. & Dickens, G.R., (2009). Carbon dioxide forcing alone insufficient to explain Palaeocene–Eocene Thermal Maximum warming. *Nat. Geosci.* 2, 576–580.
- Zeebe R.W., & Tyrrell, T. (2019) History of carbonate ion concentration over the last 100 million years II: Revised calculations and new data, *Geochimica et Cosmochimica Acta*, 257, 373-392
- Zhang, S. & Planavsky, N.J. (2019) Revisiting groundwater carbon fluxes to the ocean with implications for the carbon cycle. *Geology*, 48, [/doi.org/10.1130/G46408.1](https://doi.org/10.1130/G46408.1)
- Zhou, Y. Q., Sawyer, A. H., David, C. H., & Famiglietti, J. S. (2019). Fresh submarine groundwater discharge to the near-global coast. *Geophysical Research Letters*, 46, 5855–5863. <https://doi.org/10.1029/2019GL082749>

Table 1. Overview of sensitivities of the ocean carbon system ($\frac{\partial response}{\partial driver}$) and their relations to buffering quantities in the literature. Based on the Hagens & Middelburg (2016a) approach, Supporting Information S2 explicitly links the various sensitivities.

Driver	Response	Sensitivity factor	Symbol	Name	Reference
TA	pH	$\left(\frac{\partial pH}{\partial TA}\right)$	$-\Phi_H$ β_{pH}^{-1}	Chemical buffer factor Inverse of Buffer capacity	Frankignoulle (1994) Van Slyke (1922)
	lnH	$\left(\frac{\partial \ln H}{\partial TA}\right)$	β_{TA}^{-1}		Egleston et al. (2010)
	H	$\left(\frac{\partial H}{\partial TA}\right)$	$-\beta_H^{-1}$	Negative inverse of Proton concentration buffer factor	Hofmann et al. (2010)
	pCO ₂	$\left(\frac{\partial pCO_2}{\partial TA}\right)$	$-\Pi_H$	Buffer factor	Frankignoulle (1994)
	lnpCO ₂	$\left(\frac{\partial pCO_2}{\partial TA}\right) \frac{TA}{pCO_2}$ or $\left(\frac{\partial \ln pCO_2}{\partial \ln TA}\right)$	γ_{TA}	Alkalinity factor	Sarmiento & Gruber (2006)
	lnCO ₂	$\left(\frac{\partial \ln CO_2}{\partial TA}\right)$	γ_{TA}^{-1}		Egleston et al. (2010)
	CO ₂	$\frac{1}{K_0} \left(\frac{\partial CO_2}{\partial TA}\right)$	$-\Pi_H$		Frankignoulle (1994)
	lnCO ₃ ²⁻	$\left(\frac{\partial \ln CO_3^{2-}}{\partial TA}\right)$	ω_{TA}^{-1}		Egleston et al. (2010)
DIC	pH	$\left(\frac{\partial pH}{\partial DIC}\right)$	Φ $\beta_{CO_2}^{-1}$		Frankignoulle (1994) Weber and Stumm, 1963
	lnH	$\left(\frac{\partial \ln H}{\partial DIC}\right)$	β_{DIC}^{-1}		Egleston et al. (2010)
	pCO ₂	$\left(\frac{\partial pCO_2}{\partial DIC}\right)$	Π_D		Frankignoulle (1994)
	lnpCO ₂	$\left(\frac{\partial pCO_2}{\partial DIC}\right) \frac{DIC}{pCO_2}$ or	R B_{hom}	Homogeneous buffer factor or Revelle factor	Bolin and Eriksson (1959) Sundquist et al. (1979)

		$\left(\frac{\partial \ln pCO_2}{\partial \ln DIC}\right)$	β_D γ_{DIC}		Frankignoulle (1994) Sarmiento & Gruber (2006)
	$\ln CO_2$	$\left(\frac{\partial \ln CO_2}{\partial DIC}\right)$	γ_{DIC}^{-1}		Egleston et al. (2010)
	TA	$\left(\frac{\partial TA}{\partial DIC}\right)$	Q	Isocapnic quotient	Humphreys et al. (2018)
	$\ln CO_3^{2-}$	$\left(\frac{\partial \ln CO_3^{2-}}{\partial DIC}\right)$	ω_{DIC}^{-1}		Egleston et al. (2010)
pCO_2	pH	$\left(\frac{\partial pH}{\partial pCO_2}\right)$	Φ_D		Frankignoulle (1994)
	$\ln H$	$\left(\frac{\partial \ln H}{\partial \ln pCO_2}\right)$	H^{-1}		Omta et al. (2010)
	$\ln CO_3^{2-}$	$\left(\frac{\partial CO_3^{2-}}{\partial pCO_2}\right) \frac{pCO_2}{CO_3^{2-}}$ or $\left(\frac{\partial \ln CO_3^{2-}}{\partial \ln pCO_2}\right)$	β_C^{-1} O^{-1}		Frankignoulle (1994) Omta et al. (2010)

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1475 **Table 2** Biogeochemical processes and their impact on charge balance alkalinity (ΔCBA) and
 1476 titration alkalinity (ΔTA) (after Soetaert et al., 2007).

Process	Reaction	ΔCBA	ΔTA
(R1) Aerobic mineralization	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$	0	n-p
(R2) Denitrification	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.8 \text{HNO}_3 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.4 \text{N}_2 + 1.4 \text{H}_2\text{O}$	0	0.8+n-p
(R3) Mn-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 2 \text{Mn}^{2+} + 3\text{H}_2\text{O}$	4	n-p+4
(R4) Fe-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{Fe}_2\text{O}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 4 \text{Fe}^{2+} + 5\text{H}_2\text{O}$	8	n-p+8
(R5) Sulphate reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.5 \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{H}_2\text{S} + \text{H}_2\text{O}$	0	n-p+1
(R6) Methanogenesis	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p \rightarrow 0.5 \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{CH}_4 + \text{H}_2\text{O}$	0	n-p
(R7) Nitrification	$\text{NH}_3 + 2 \text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$	0	-2
(R8) Annamox	$\text{NH}_3 + \text{HNO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$	0	0
(R9) Aerobic oxidation of methane	$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	0	0
(R10) Anaerobic oxidation of methane	$\text{CH}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O}$	0	2
(R11) Calcite precipitation	$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$	-2	-2
(R12) Primary production (nitrate)	$\text{CO}_2 + n \text{HNO}_3 + p \text{H}_3\text{PO}_4 + (1+n) \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + (1+2n) \text{O}_2$	0	p+n
(R13) Primary production (ammonium)	$\text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2$	0	p-n
(R14) CO_2 emission to air	$\text{CO}_2 \rightarrow \text{CO}_{2(\text{g})}$	0	0
(R15) Proton sorption	$\text{H}^+ \rightarrow \text{H}^+\text{-surface}$	1	1
(R15) Ammonium sorption	$\text{NH}_4^+ \rightarrow \text{NH}_4^+\text{-surface}$	1	0

1477 n = N/C ratio of organic matter and p = P/C ratio of organic matter

1478 **Table 3** Global alkalinity balance of the ocean (Tmol y^{-1}). Supporting Information S3 provides a
 1479 detailed documentation for the various terms, including the range.

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Alkalinity sources/sinks	Riverine DIC and carbonate burial balance	Complete Alkalinity balance
Riverine DIC	32	32
Riverine PIC		21
Submarine groundwater		1
Submarine silicate		2.8
Sulphur burial		4.7
Denitrification		1.5
Organic matter burial		3
Total Sources	32	66
Open ocean carbonate burial	23	23
Ocean margin carbonate burial	36	36
Reverse weathering		1
Total sinks	59	60
Imbalance	27	-6

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Figure captions.

Figure 1. Speciation, proton acceptor levels and charge as a function of pH. (A) Bjerrum plot showing the distribution of carbonic acid, bicarbonate and carbonate as a function of pH and the corresponding proton acceptor level (solid black line) and charge (red dashed line); (B) The proton acceptor level for selected acid-base pairs; (C) The charge for selected acid-base pairs. Details of the calculations are presented in the supporting information.

Figure 2 The sensitivities dpH/dCBA (A), dpH/dDIC (B), and the Revelle sensitivity factor (C) as function of pH. Left column over the entire pH range; right column focuses on the changes from pH 6 to 9. Vertical grey lines indicate maxima/minima. Details of the calculations are presented in the supporting information.

Figure 3. TA versus DIC plots (i.e. Deffeyes diagrams) showing the equilibrium pH at free scale (A) and pCO_2 in μatm (B) as contours. Both graphs show vectors for the addition of protons (vertically downward) and dissolution of calcium carbonate (slope 2:1). Notice that the resulting change in pH and pCO_2 for the same amount of calcite dissolved or acid added (same vector) differs because of differences in sensitivity (buffering). For instance, the ΔpH and ΔpCO_2 for proton additions are -0.074 and +136 μatm , respectively, at low buffering (high DIC/TA ratio), and -0.037 and +20.9 μatm at high buffering (low DIC/TA ratio). Similarly, for the calcite dissolution vector, the ΔpH values are 0.022 and 0.013 and the ΔpCO_2 values are -33.9 and -5.9 μatm for low and high buffering, respectively.

Figure 4 The response in pH due to denitrification as a function of pH. (A) The sensitivity factor dpH/dCBA of seawater, (B) The change in charge due to denitrification, (C) The resulting change in pH as calculated by eq. 26. Details of the calculations are presented in the supporting information.

Figure 5 The impact of biogeochemical processes on pH. (A) The change in pH for aerobic mineralization with and without nitrification. (B) The change in pH due to sulphate reduction and methanogenesis. (C) The change in pH due to primary production based on ammonium or nitrate. (D) The change in pH due to calcification and calcium carbonate dissolution. Note the break at the pH corresponding to calcium carbonate equilibrium (modified from Soetaert et al., 2007). Details of the calculations are presented in the supporting information.

Figure 6 Alkalinity balance of the ocean (Fluxes are in Tmol y^{-1}). (A) Traditional alkalinity balance considering river input of DIC and calcium carbonate burial. (B) Revised oceanic alkalinity balance considering additional sources and sinks based on Table 3.

Figure 1.

DIC speciation

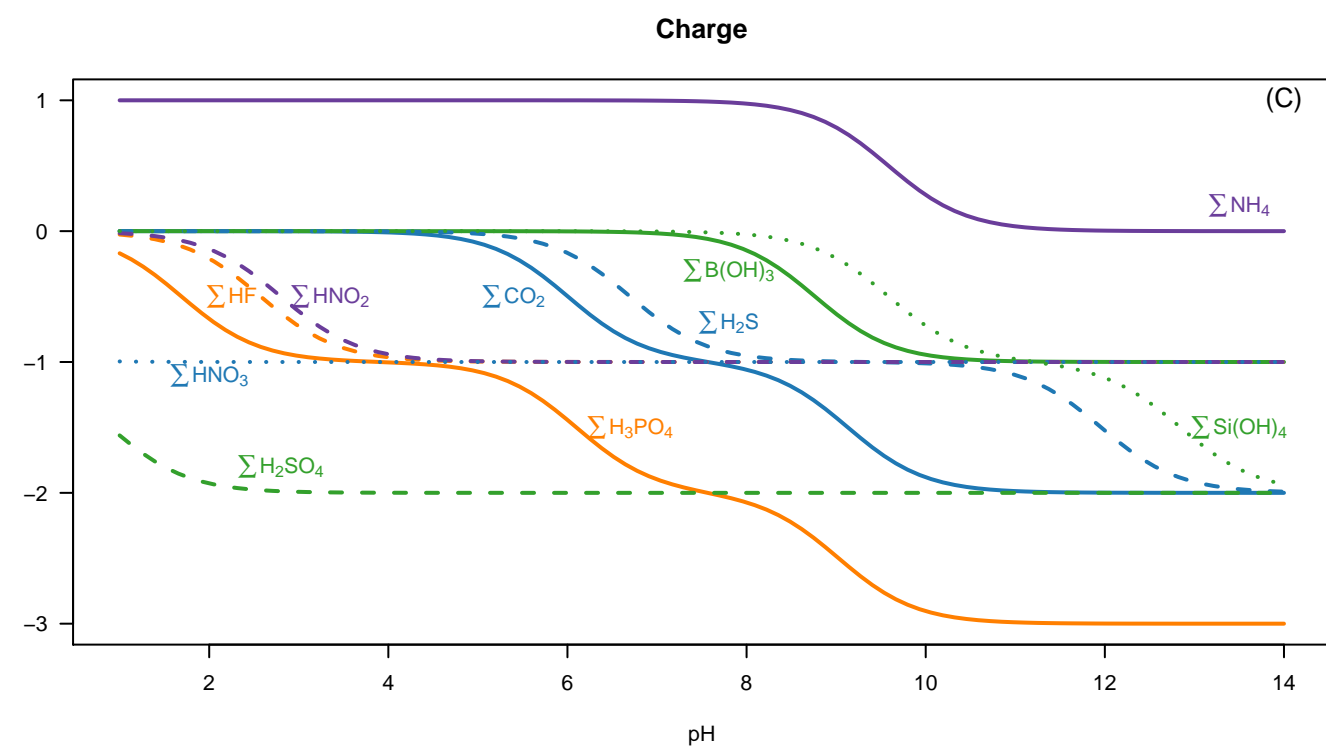
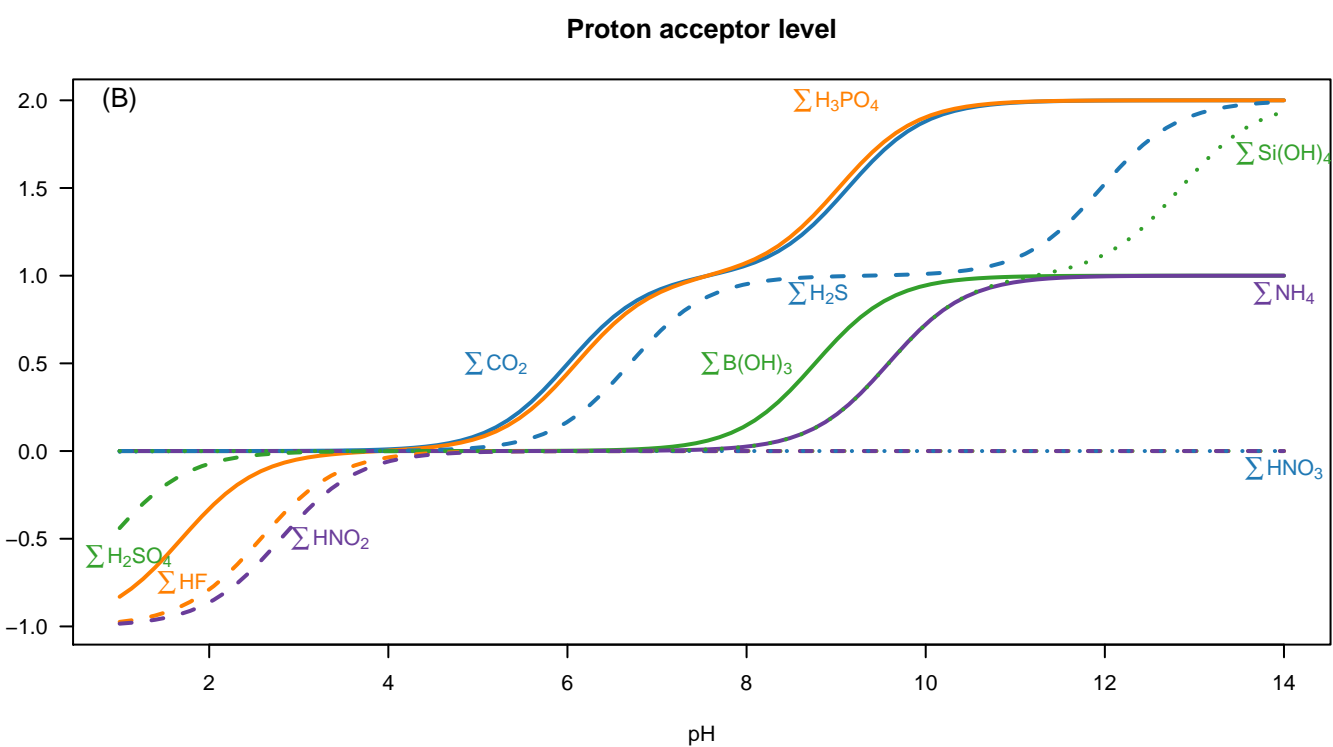
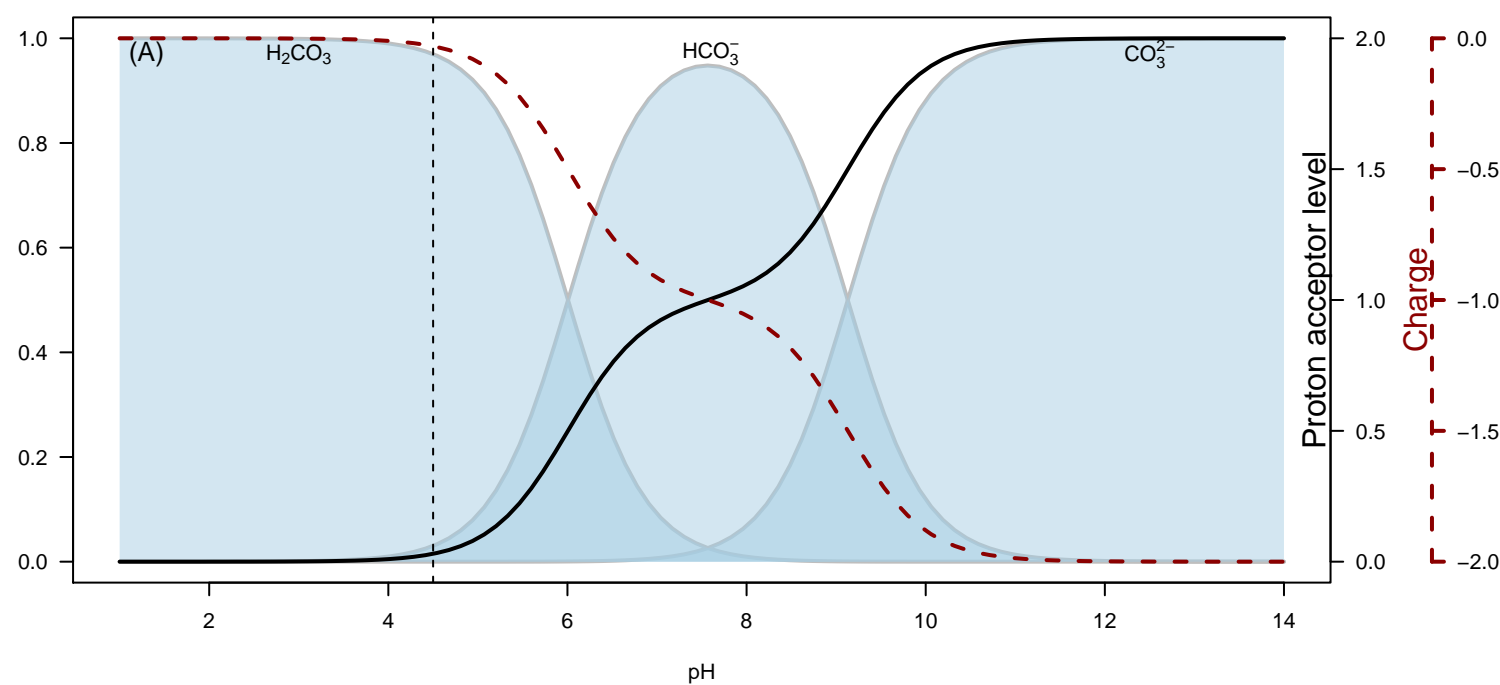
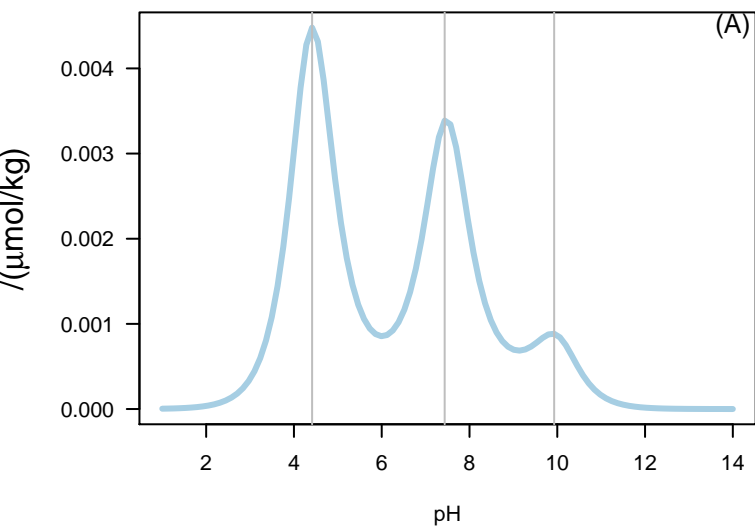
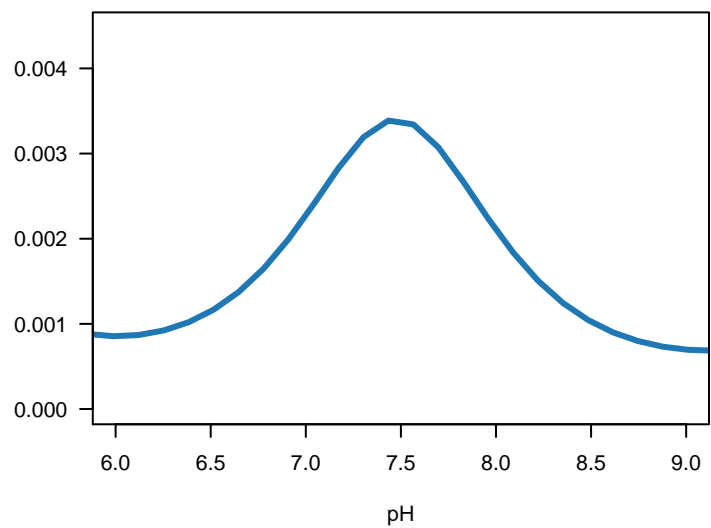


Figure 2.

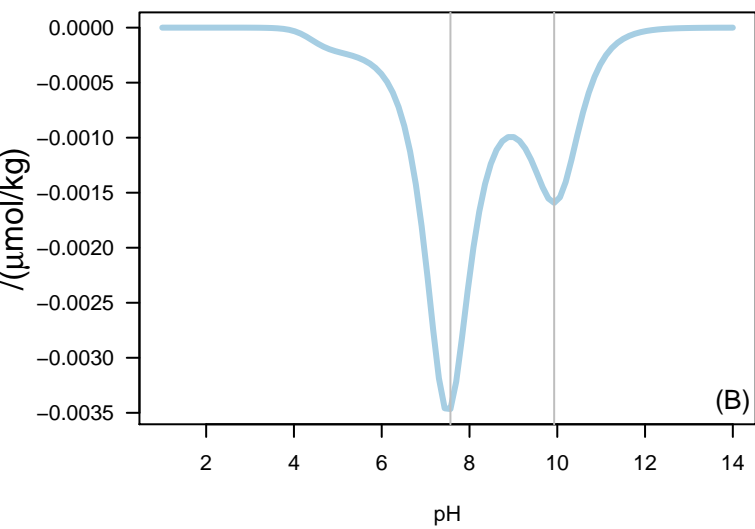
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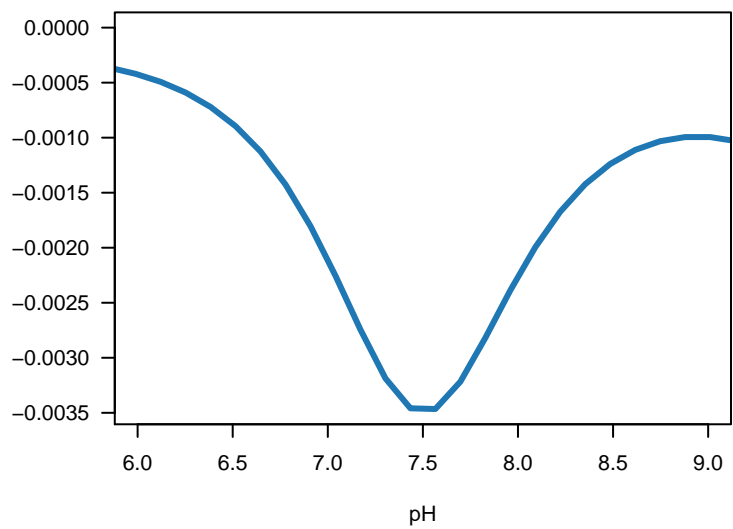
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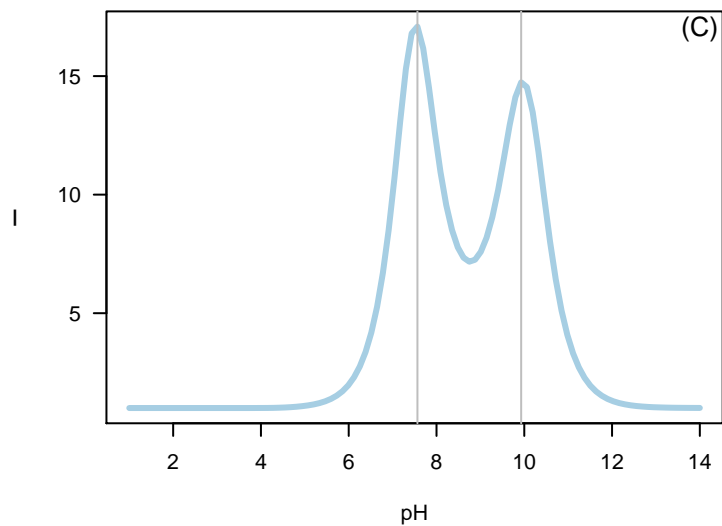
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dpH/dDIC



Revelle sensitivity factor



Revelle sensitivity factor

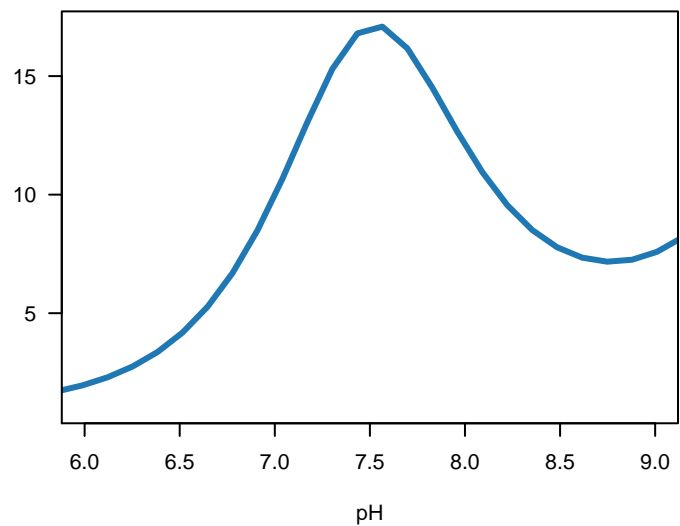


Figure 3.

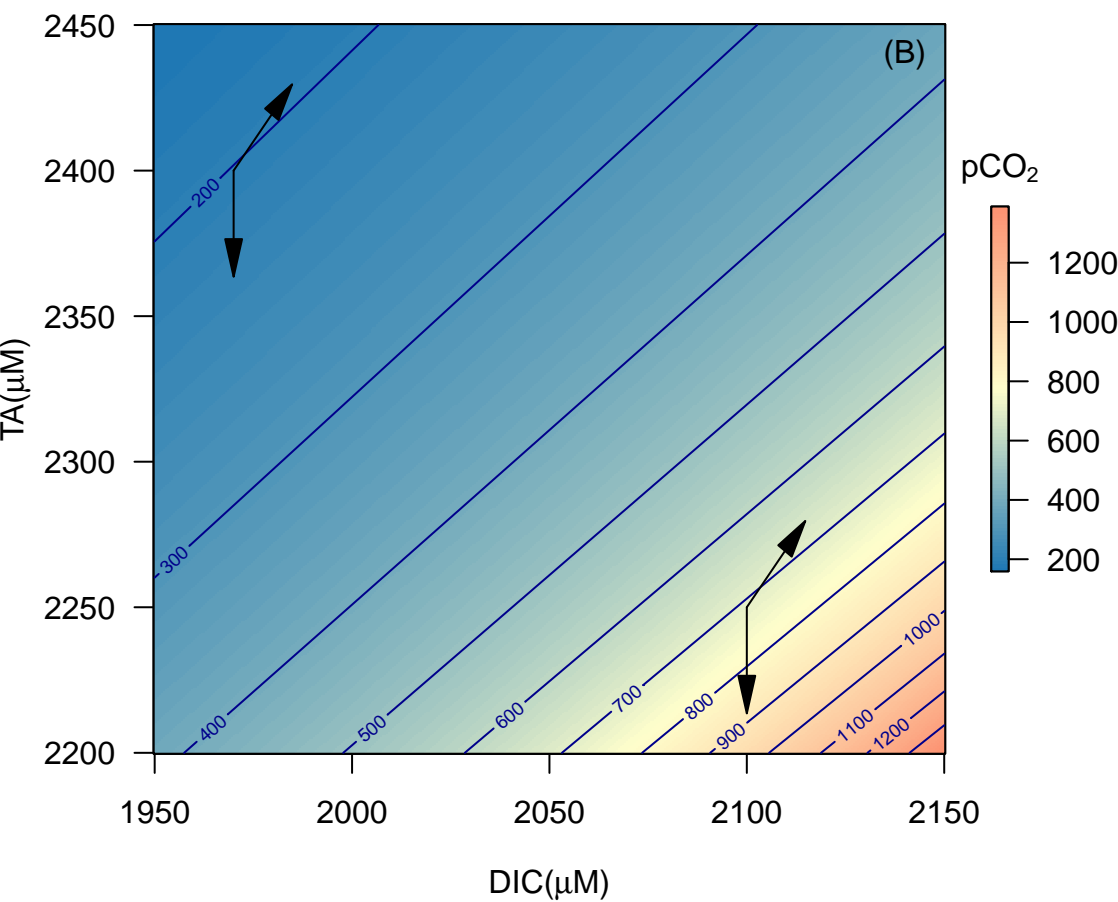
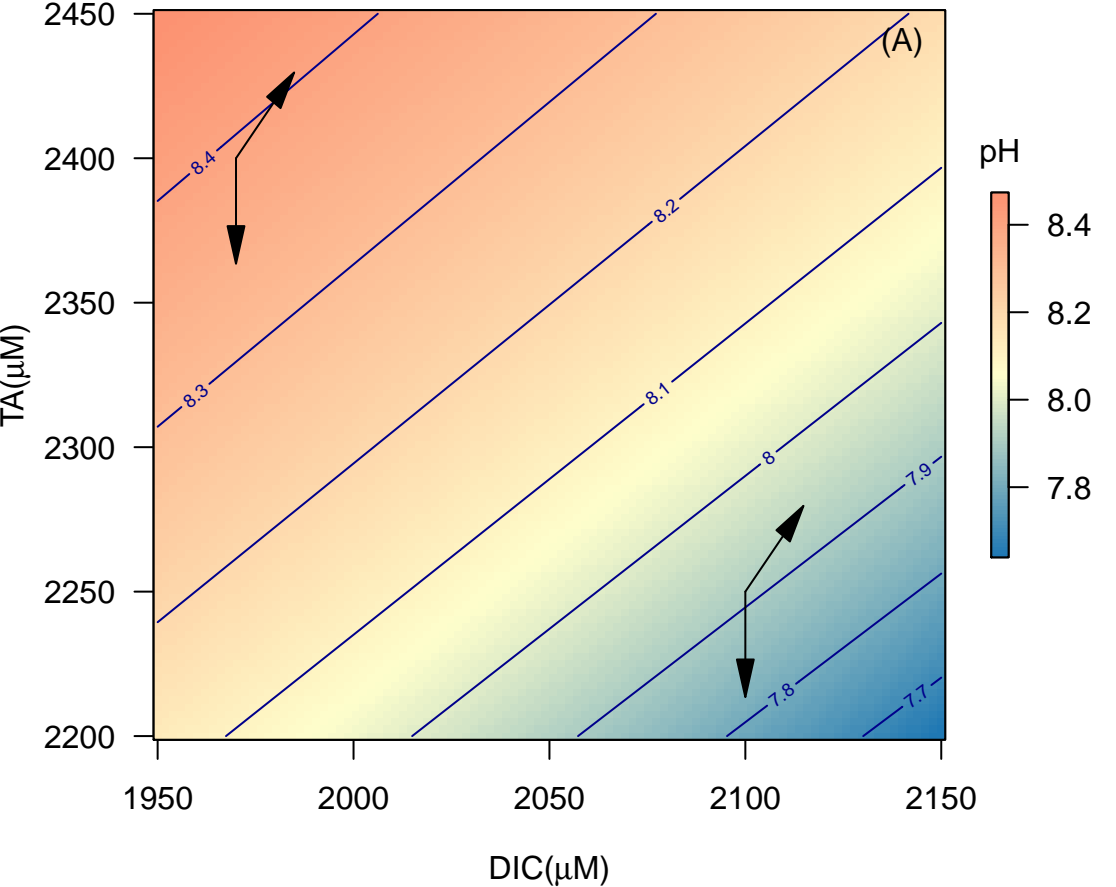


Figure 4.

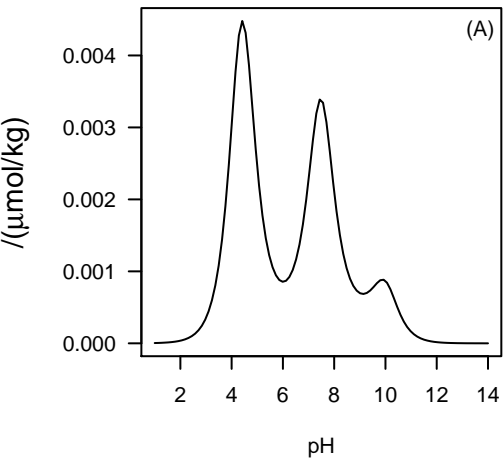
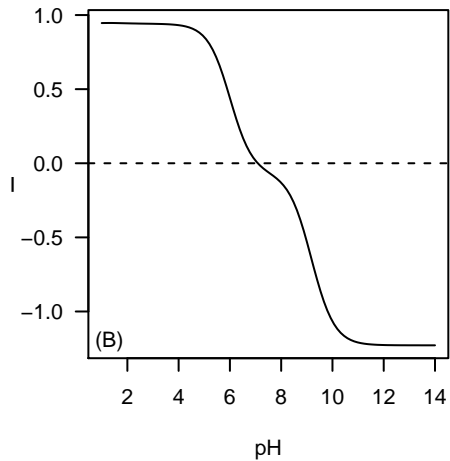
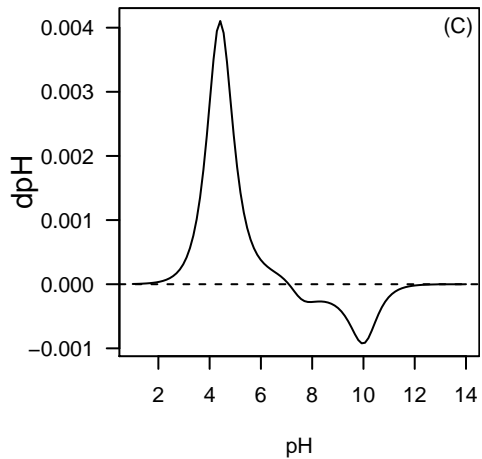
sensitivity **Δcharge** **response**

Figure 5.

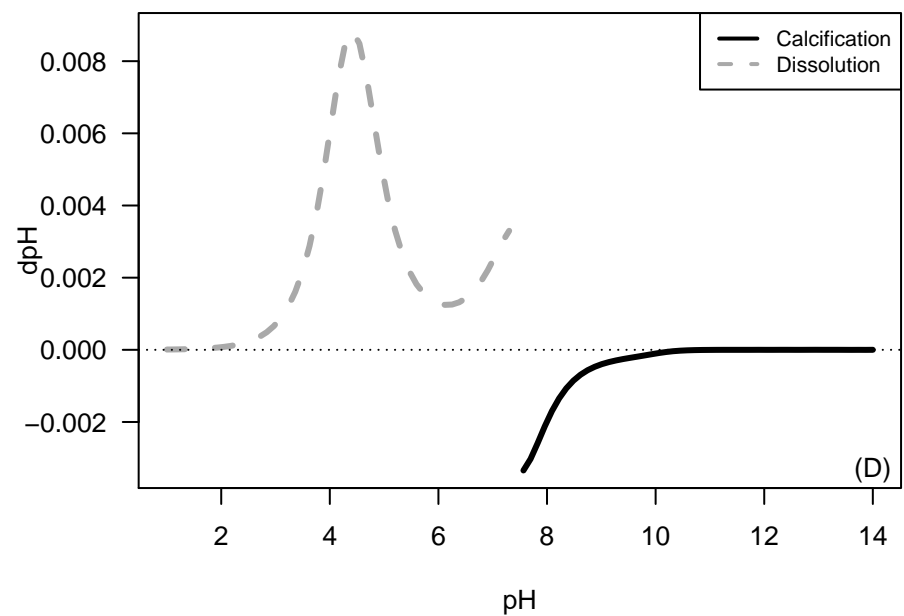
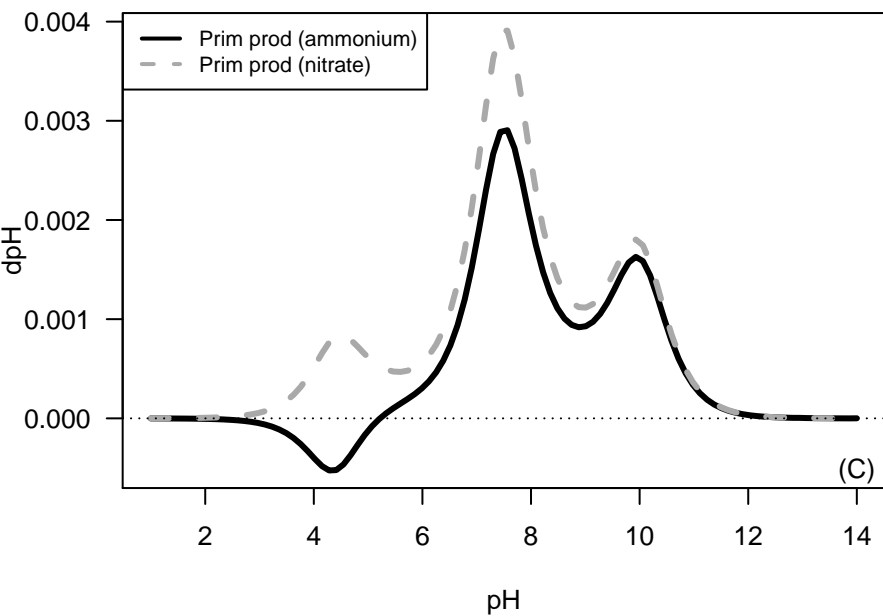
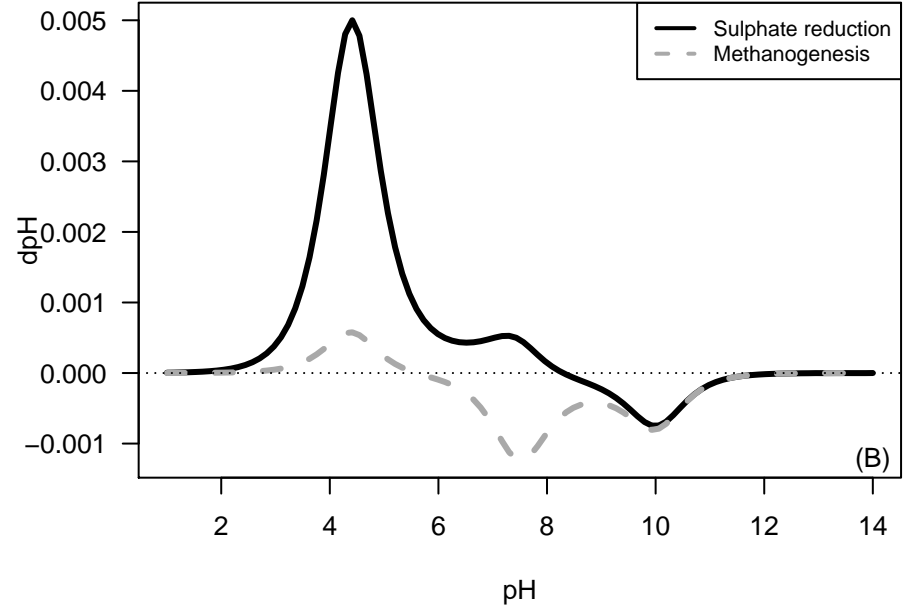
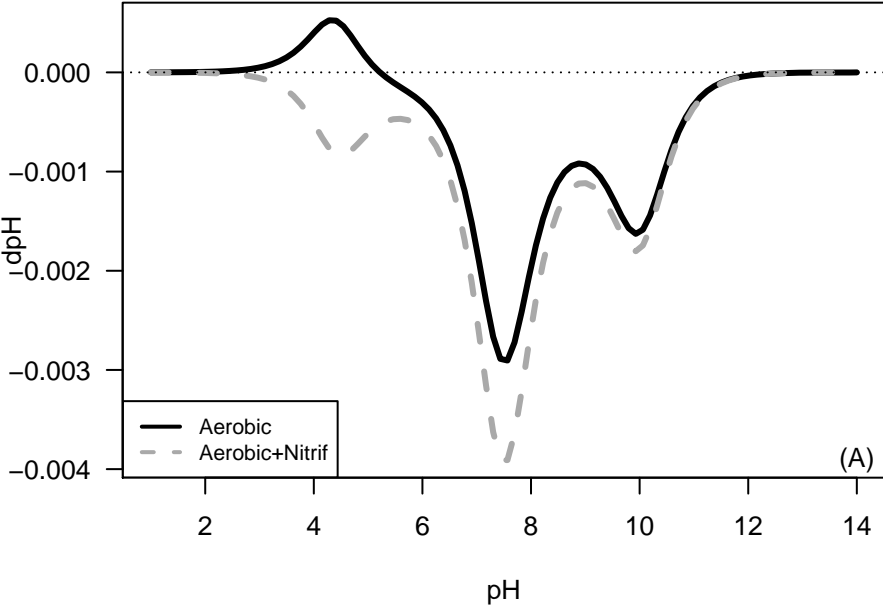
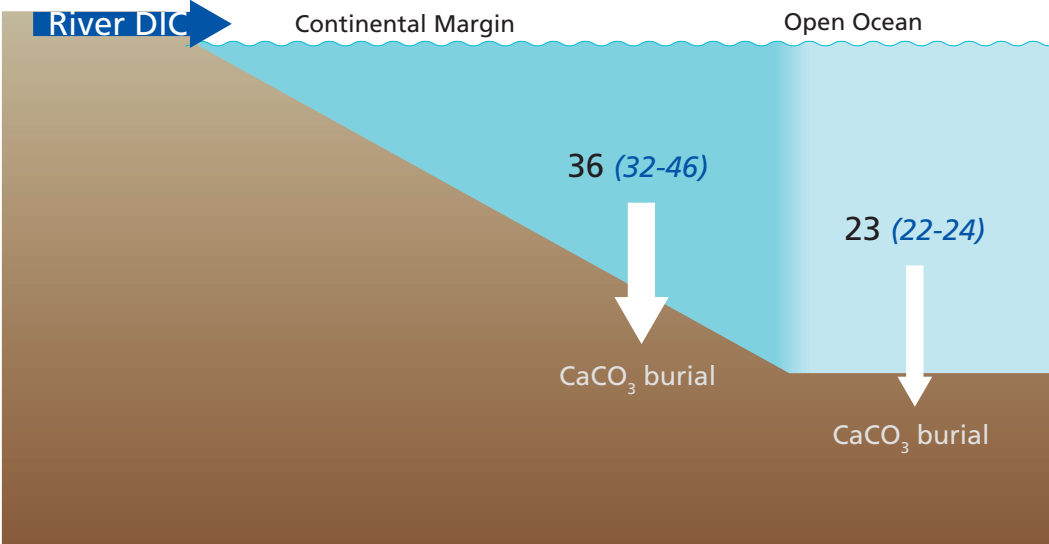


Figure 6.

A

Input = 32 vs. Output = 59

DIC: 32 (26-36)



B

Input = 66 vs. Output = 60

DIC: 32 (26-36)

PIC: 21 (15-28)

