

Ocean Alkalinity, Buffering and Biogeochemical Processes

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Key Points:

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

Abstract

Alkalinity, the excess of proton acceptors over donors, plays a major role in ocean chemistry, buffering and 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

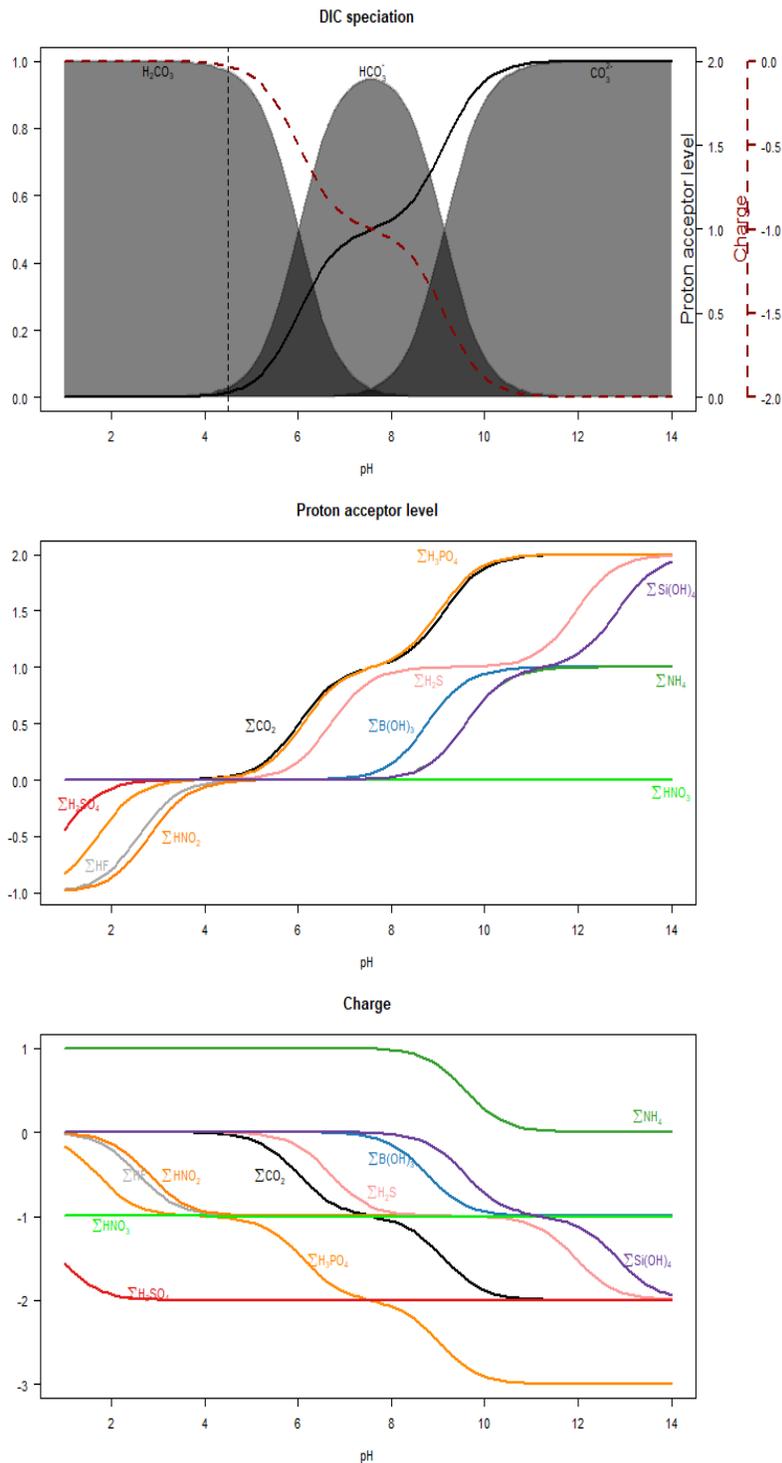
The ocean plays a major role in controlling atmospheric carbon dioxide and storage of anthropogenic carbon (Gruber et al., 2019). For the last decade, ocean uptake of anthropogenic carbon was $2.5 \pm 0.6 \text{ Pg C y}^{-1}$, i.e. about 23 % of annual anthropogenic carbon emissions due to fossil fuels, 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 $160 \pm 20 \text{ Pg C}$ (~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 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 essential 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 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, but 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.

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.



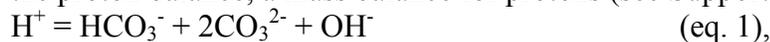
2 Ocean alkalinity

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). Dickson (1992) provides an excellent account 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 and necessary 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. 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.

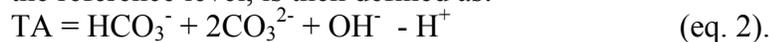
2.1 Titration alkalinity

In 1981 Dickson defined the titration 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 ≥ 4.5) to continue the common practice to match the reference level with the carbonic acid equivalence point of a titration.

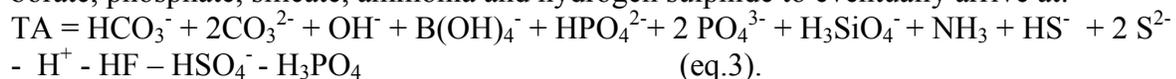
Using this exact definition of alkalinity of Dickson (1981), it is straightforward to calculate the titration alkalinity for any system for which the contributing components are known and characterised in terms of dissociation constants. Figure 1A shows the distribution diagram of acid-base pairs (Bjerrum plot) for the carbonate system in seawater. For the CO₂-H₂O system, at pH=4.5, carbonic acid is by far the dominant species and used as reference. 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 H₂CO₃. The titration alkalinity, i.e. excess of proton acceptors over donors with respect to carbonic acid, the reference level, is then defined as:



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:



This proton condition based approach towards alkalinity allows a unique 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) of Morel and Hering (1993), which is also based on a proton (mass) balance (Supporting Information S1). Specifically, $\text{TA} = -\text{TOT}$ when the components chosen are the reference level species at $\text{pH}=4.5$.

2.2. Charge balance alkalinity

Electrolyte solutions, including seawater, should obey the electroneutrality condition: i.e. the sum of negative and positive charges should balance 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), the term we will use in this review.

Charge balance alkalinity (CBA; eq. 6b) and titration alkalinity (TA; eq. 4) are linked via:

$$\text{TA} = \text{CBA} + \sum\text{NH}_3 - \sum\text{NO}_3 - \sum\text{NO}_2 - \sum\text{PO}_4 - 2\sum\text{SO}_4 - \sum\text{F} \quad (\text{eq. 7}),$$

where $\sum\text{NH}_3 = \text{NH}_3 + \text{NH}_4^+$, $\sum\text{NO}_3 = \text{NO}_3^- + \text{HNO}_3$, $\sum\text{NO}_2 = \text{NO}_2^- + \text{HNO}_2$, $\sum\text{PO}_4 = \text{H}_3\text{PO}_4 + \text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} + \text{PO}_4^{3-}$, $\sum\text{SO}_4 = \text{H}_2\text{SO}_4 + \text{HSO}_4^- + \text{SO}_4^{2-}$ and $\sum\text{F} = \text{HF} + \text{F}^-$ 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):

$$\text{TA}_{\text{ec}} = \text{Na}^+ + 2 \text{Mg}^{2+} + 2 \text{Ca}^{2+} + \text{K}^+ + 2 \text{Sr}^{2+} - \text{Cl}^- - \text{Br}^- + (\dots) \\ + \sum \text{NH}_3 - \sum \text{NO}_3 - \sum \text{NO}_2 - \sum \text{PO}_4 - 2 \sum \text{SO}_4 - \sum \text{F} \quad (\text{eq. 8}),$$

or alternatively formulated: $\text{TA}_{\text{ec}} = \text{EPC} + \text{TA} - \text{CBA}$.

This explicitly conservative form of alkalinity is equivalent to Dickson's expression (as $\text{EPC} - \text{CBA} = 0$) 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 are dependent on salinity. Processes such as precipitation, evaporation and melting or formation of ice impacting salinity thus also affect alkalinity.

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, 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 ($\text{CA} = \text{HCO}_3^- + 2\text{CO}_3^{2-}$) typically accounts for >95% of the total alkalinity in the ocean. Many studies 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 ($\text{PA}_{\text{ZW-G}}$):

$$\text{PA}_{\text{ZW-G}} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{B}(\text{OH})_4^- + \text{OH}^- - \text{H}^+ = \text{CA} + \text{borate alkalinity} + \text{water alkalinity} \\ (\text{eq. 9}).$$

$\text{PA}_{\text{ZW-G}}$ 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). Three, 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. 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: $TA^* = 0.5 (TA_s - TA_s^o) + 0.63 * (0.0941 \text{ AOU})$, where TA_s and TA_s^o 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) 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 a major 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. The composition and thus acid-base properties of dissolved organic compounds depend on whether these compounds are derived from locally produced organic matter or be 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 $\sim 3.7 \pm 2.4$ and $\sim 12.5 \pm 1.8$, 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), and ocean waters (Fong & Dickson, 2019). Organic alkalinity in oceanography is normally calculated by difference: that is, carbonate alkalinity is calculated from two out of three other measurable parameters in the CO₂-H₂O system (pH, DIC or pCO₂), and organic alkalinity is calculated as the difference between TA measured and calculated from the contributions of the inorganic species following eq. 3. Back-titration methods to directly quantify organic alkalinity are used by others (Hernández-Ayon et al., 2007; Muller and Bleie, 2008; Yang et al, 2015). 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 CO₂-H₂O 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 homogenous 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. 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 homogenous reactions in solution and heterogeneous buffering involving interactions with particles (e.g. dissolution or precipitation of carbonate minerals modifying alkalinity). Homogenous 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, but 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.

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 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 homogenous Revelle factor to allow for changes in alkalinity (e.g. due to calcification/dissolution):

$$R_{tot} = \frac{DIC}{pCO_2} \left(\frac{dpCO_2}{dDIC} \right) = \frac{DIC}{pCO_2} \left[\left(\frac{\partial pCO_2}{\partial DIC} \right)_{TA} + \left(\frac{\partial pCO_2}{\partial TA} \right)_{DIC} \cdot \frac{dTA}{dDIC} \right] \quad (\text{eq. 15}).$$

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)

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

and the normalized first-order sensitivity coefficient is:

$$S_{pH,TA}^{nor} = \frac{\partial pH}{\partial pTA} = -2.3 TA \frac{\partial pH}{\partial TA} \quad (\text{eq. 19}).$$

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

$$\beta_{pH} = \left(\frac{\partial pH}{\partial TA} \right)^{-1} \quad (\text{eq. 20})$$

(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), but Egleston et al. (2010) and Hofmann et al. (2010) presented definitions based on the natural logarithm of proton concentrations and proton concentrations, respectively:

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

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, pH, CO₂, HCO₃⁻, CO₃²⁻, T, S or any property X can thus be described as:

$$dY = \left(\frac{\partial Y}{\partial TA}\right) dTA + \left(\frac{\partial Y}{\partial DIC}\right) dDIC + \left(\frac{\partial Y}{\partial pH}\right) dpH + \left(\frac{\partial Y}{\partial CO_2}\right) dCO_2 + \left(\frac{\partial Y}{\partial HCO_3^-}\right) dHCO_3^- + \left(\frac{\partial Y}{\partial CO_3^{2-}}\right) dCO_3^{2-} + \left(\frac{\partial Y}{\partial T}\right) dT + \left(\frac{\partial Y}{\partial S}\right) dS + \left(\frac{\partial Y}{\partial X}\right) dX \quad (\text{eq. 22})$$

For instance, the dependence of pH, pCO₂ and CO₃²⁻ on carbonate system parameters can be given by:

$$dpH = \left(\frac{\partial pH}{\partial TA}\right) dTA + \left(\frac{\partial pH}{\partial DIC}\right) dDIC + \left(\frac{\partial pH}{\partial pCO_2}\right) dpCO_2 + \left(\frac{\partial pH}{\partial T}\right) dT + \left(\frac{\partial pH}{\partial S}\right) dS + \dots \quad (\text{eq.23})$$

$$dpCO_2 = \left(\frac{\partial pCO_2}{\partial TA}\right) dTA + \left(\frac{\partial pCO_2}{\partial DIC}\right) dDIC + \left(\frac{\partial pCO_2}{\partial pH}\right) dpH + \left(\frac{\partial pCO_2}{\partial T}\right) dT + \left(\frac{\partial pCO_2}{\partial S}\right) dS + \dots \quad (\text{eq. 24})$$

$$dCO_3^{2-} = \left(\frac{\partial CO_3^{2-}}{\partial TA}\right) dTA + \left(\frac{\partial CO_3^{2-}}{\partial DIC}\right) dDIC + \left(\frac{\partial CO_3^{2-}}{\partial pCO_2}\right) dpCO_2 + \left(\frac{\partial CO_3^{2-}}{\partial pH}\right) dpH + \left(\frac{\partial CO_3^{2-}}{\partial T}\right) dT + \left(\frac{\partial CO_3^{2-}}{\partial S}\right) dS + \dots \quad (\text{eq. 25})$$

Many of the above 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

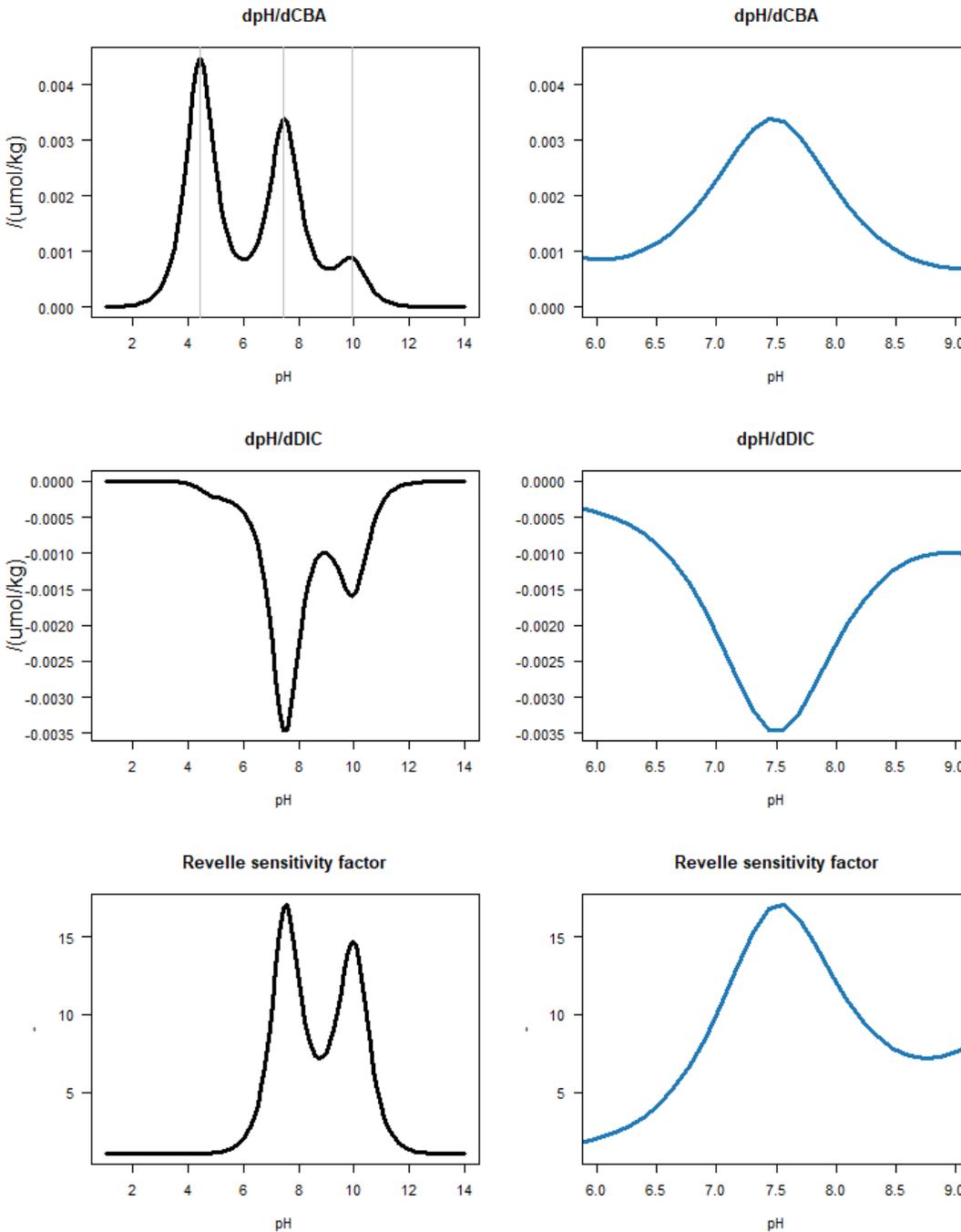
$$\gamma_{TA} = \left(\frac{\partial pCO_2}{\partial TA}\right) \frac{TA}{pCO_2} = \left(\frac{\partial \ln pCO_2}{\partial \ln TA}\right) \quad (\text{eq. 26})$$

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

$$\gamma_{TA} = \left(\frac{\partial TA}{\partial \ln CO_2}\right) \quad (\text{eq. 27}).$$

Similarly, the Revelle factor (R, eq. 14) is also known as homogenous 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.

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.



3.2 Sensitivity of seawater

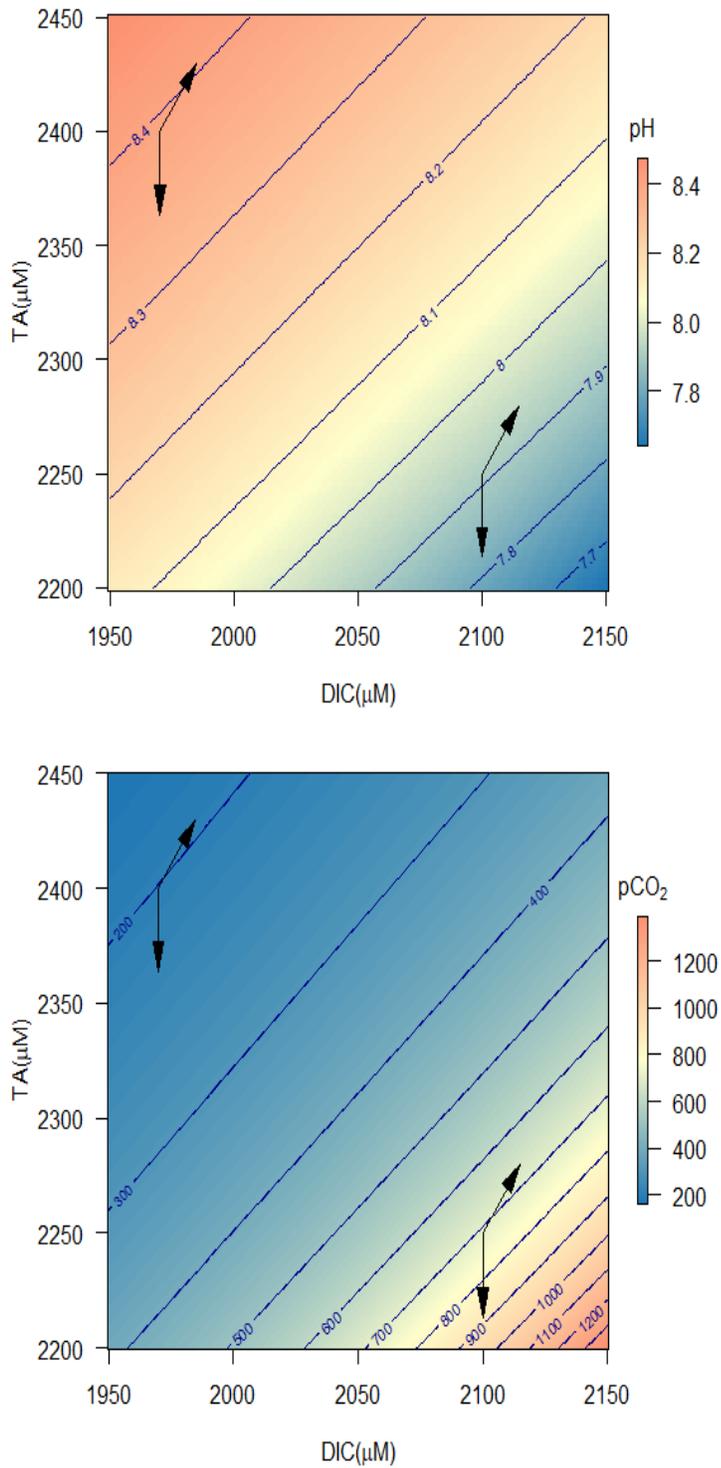
Most of the sensitivities presented above depend non-linearly on the solution composition. Figure 2 shows the sensitivities of pH towards changes in CBA and DIC and of

pCO₂ 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 the pK₁ (≈5.9) and pK₂ (≈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 pK₁ and pK₂ (Morel and Hering, 1993; Egleston et al., 2010). These sensitivities show minima close to the pK₁ and pK₂ 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 pK₁ of the carbonic acid system (pH≈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 pK₂ of the carbonic acid system (pH≈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 pCO₂ 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 CO₂ 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 pCO₂ 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 pCO₂ such as hypoxia (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 $\left(\frac{\partial pH}{\partial pCO_2}\right)$ is about -0.0011 (ppmv⁻¹; Hagens and Middelburg, 2016a). Combining this sensitivity with global annual increases in pCO₂ 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 (μM kg⁻¹/ ppmv), one would retrodict that the global ocean surface DIC would have increased by about 1 μM kg⁻¹ yr⁻¹ from 1994 to 2007, consistent with observations by Gruber et al. (2019).

Figure 3. TA versus DIC plots (i.e. Deffeyes diagrams) showing the equilibrium pH at free scale (A) and $p\text{CO}_2$ 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 $p\text{CO}_2$ for the same amount of calcite dissolved or acid added (same vector) differs because of differences in sensitivity (buffering).



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 pCO₂ is often analysed graphically in the form of TA versus DIC plots with isolines for pH and pCO₂ (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 pCO₂. However, for the very same process intensity (vector length and direction), the resulting change in pH and pCO₂ is different because it depends on the initial conditions (i.e. the sensitivity of the system, section 3.2). Changes in pH and pCO₂ 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 biogeochemical process (Δcharge) and the sensitivity factor of seawater $\left(\frac{\partial\text{pH}}{\partial\text{CBA}}\right)$. Specifically, the instantaneous effect of a single process with intensity I_{process} (mol m⁻³ t⁻¹) on pH can be calculated as:

$$dpH = \Delta\text{charge} \cdot \left(\frac{\partial\text{pH}}{\partial\text{CBA}}\right) \cdot I_{\text{process}} \quad (\text{eq. 29})$$

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 $\left(\frac{\partial\text{pH}}{\partial\text{CBA}}\right)$ and Δcharge depend on the pH, this equation shows that the effect of a specific biogeochemical process on pH also depends on pH.

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, $\sum\text{NH}_3$ and $\sum\text{PO}_4$ and the consumption of $\sum\text{NO}_3$. Denitrification does not impact charge balance alkalinity ($\Delta\text{CBA} = 0$). At pH < 4, nitrate is charged negatively, ammonium positively while DIC and $\sum\text{PO}_4$ are present as uncharged carbonic and phosphoric acids, the Δcharge of the reaction is $\sim +0.95$. At pH > 10, nitrate is still charged negatively, while carbonate and phosphate ions dominate the DIC and $\sum\text{PO}_4$ with the consequence that the Δcharge of the reaction is ~ -1.08 (Fig. 4). At a pH of ~ 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. 29; Fig. 4). Consequently, the pH increases at pH values below ~ 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.

Figure 4 The response in pH due to denitrification as a function of pH. (A) The sensitivity dpH/dC_{BA} of seawater, (B) The change in charge due to denitrification, $\Delta Charge$, (C) The resulting change in pH.

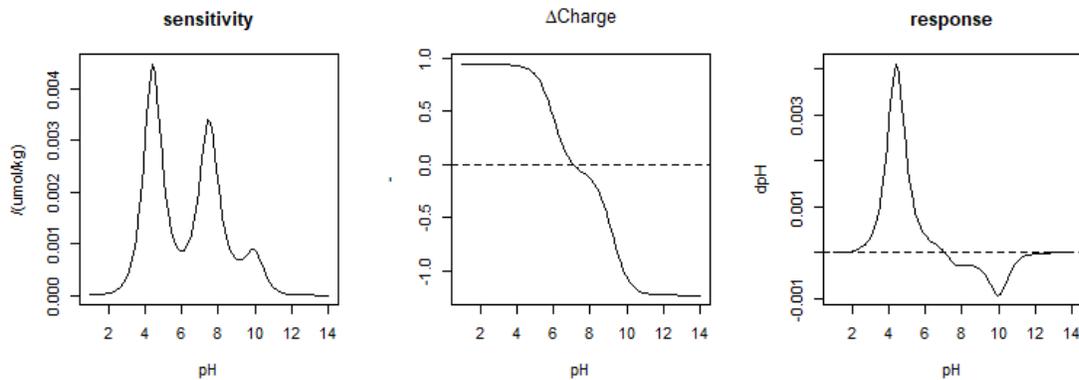
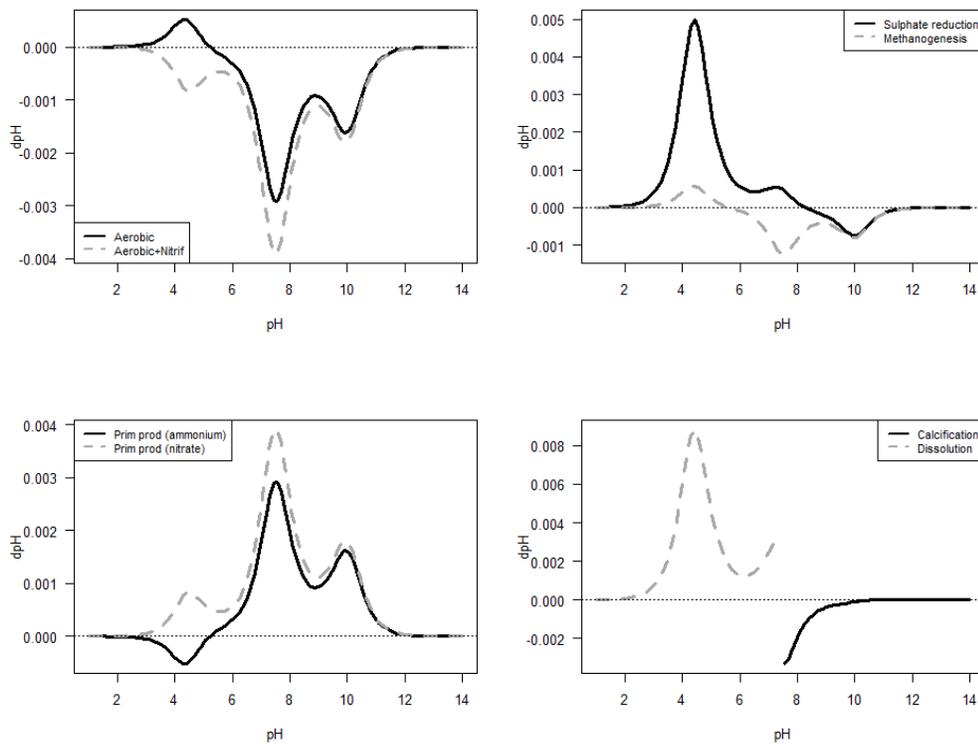


Figure 5 The impact of biogeochemical processes on pH. (A) The change in pH for aerobic mineralization with and without nitrification. (B) The change in pH due to sulphate reduction and methanogenesis. (C) The change in pH due to primary production based on ammonium or nitrate. (D) The change in pH due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



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 $\text{pH} < \sim 5.2$ 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). Sulfate reduction (R5) causes a stronger pH increase at low pH values because of sulfate 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). 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).

5. Heterogeneous buffering

While homogenous 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.

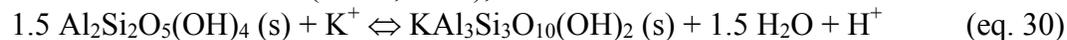
Particles suspended in the water column and deposited on the seafloor may contribute to buffering of seawater via dissolution, precipitation and mineral surface reactions. Sorption of protons to surfaces increases alkalinity (Table 2). Reactions at the surfaces of organic, biogenic carbonate and detrital 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.

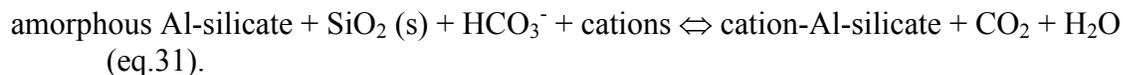
Dissolution, precipitation and transformation reactions of sedimentary silicates and biogenic carbonates govern heterogeneous buffering in the ocean. Heterogeneous buffering in the ocean is dominated by carbonate compensation (Pytkowicz, 1967; Berner, 2004; Ridgwell and Zeebe, 2005) and we will focus 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

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).

Submarine weathering involves the reactions of ocean crust with seawater which results in carbon dioxide consumption and bicarbonate and calcium release, followed by calcium carbonate precipitation (Staudigel et al., 1989; Caldeira, 1995; Berner, 2004). 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 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 explicit equation for the carbonate compensation depth (z_{CCD}):

$$z_{CCD} \approx z_{ref} \ln \left(\frac{F_{car}[Ca^{2+}]}{K_{sp}A\beta_{mt}} + \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \right) \quad (\text{eq. 32})$$

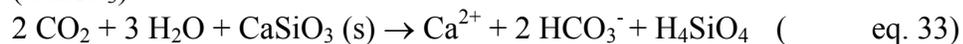
where F_{car} is the export flux of calcium carbonate, A is the surface area of the seafloor, β_{mt} is the mass transfer of solutes across the diffusive boundary layer at the seafloor, K_{sp} is the temperature, salinity and pressure dependent stoichiometric solubility product, $[Ca^{2+}]$ and $[CO_3^{2-}]$ 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).

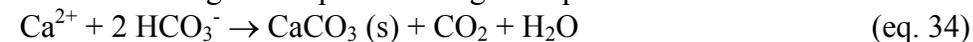
6 Processes governing alkalinity in the ocean

The most important factor governing alkalinity of the total ocean and the distribution of alkalinity in ocean surface waters is salinity. This is logical because (charge balance) alkalinity is determined by the difference between the sum of cations and anions (section 2.2). Consequently, 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) have a major effect on 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). This salinity control on alkalinity is also the main reason for interocean differences in alkalinity. 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 governed by the balance between ions generated by weathering and removal of ions via salt formation (and a small loss to the atmosphere). 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 reactions (Urey, 1952; Berner, 2004). It starts with the weathering of a generalized calcium silicate (CaSiO_3):



followed by transfer of cations, anions (including alkalinity) and dissolved silica via rivers to the ocean where organisms produce biogenic opal and calcium carbonate:



Combination of reactions 34-36 eventually leads to the overall Urey-Ebelman reaction (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 26.6 to 36.3 Tmol y^{-1} (Supporting Information S3, Table 3) and have been derived either from river DIC export or global estimates of CO_2 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

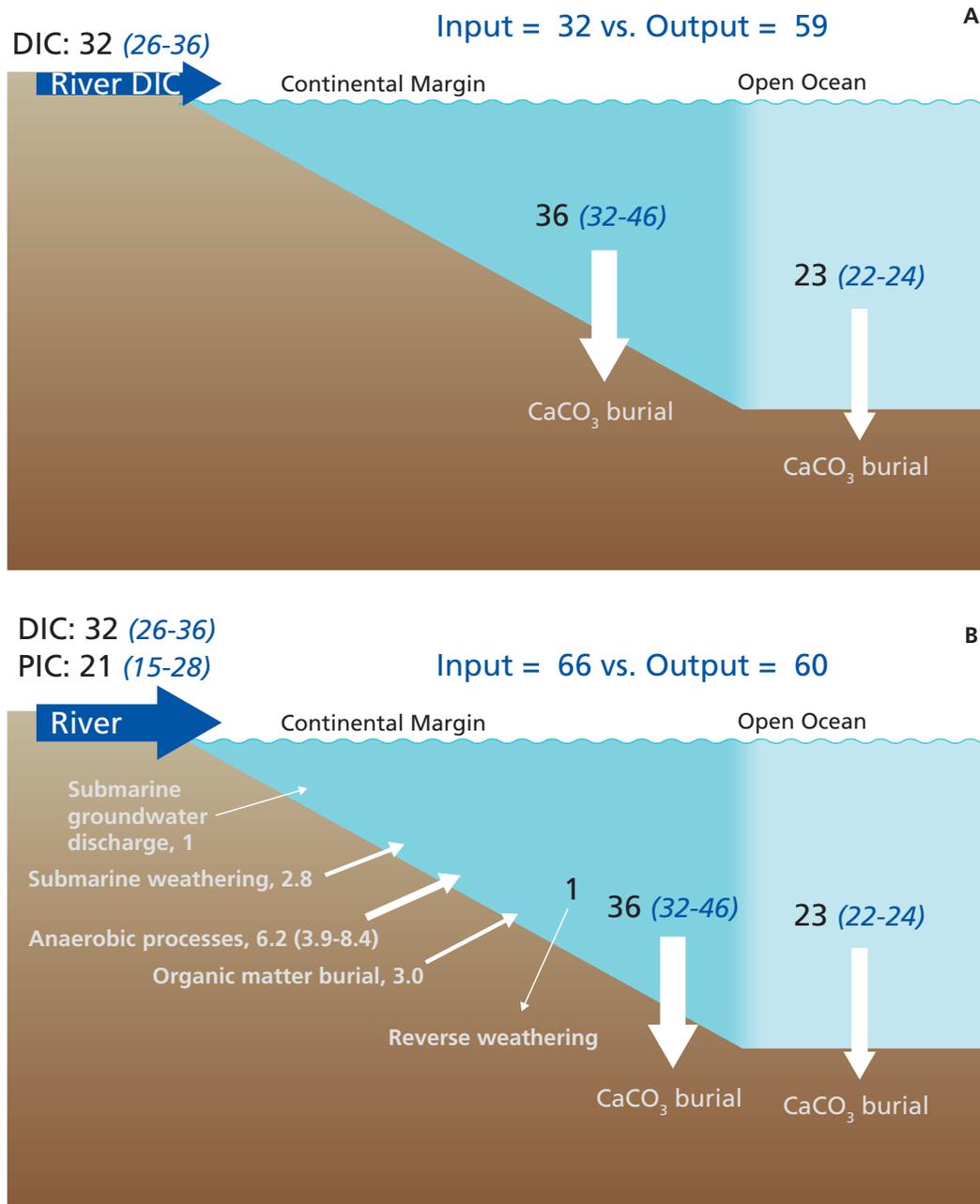
alkalinity and dissolved inorganic carbon (Suchet et al., 2003; Raymond and Hamilton, 2018). Consequently, global estimates of DIC delivery to the ocean can be used as a proxy for alkalinity transfer from weathering to the ocean. Carbonate burial estimates range from 18 to 34 Tmol C y⁻¹ (Supporting Information S3), with clear consensus about carbonate burial in the deep sea of 11 Tmol C y⁻¹, while ocean margin contributions vary from 6 to 23 Tmol C y⁻¹, with the most recent numbers between 16 and 20 Tmol C y⁻¹ (Morse and Mackenzie, 1990; Milliman, 1993; Wollast, 1994; Milliman and Droxler, 1996; Iglesias-Rodriguez et al., 2002; Smith, 2013; Smith and Mackenzie, 2016; O'Mare and Dunne, 2019). Calcium carbonate formation involves the consumption of two units of alkalinity (eq. 35), indicating an imbalance between alkalinity inputs from weathering (26-36 Tmol y⁻¹) and outputs by carbonate burial in the ocean (27-31 Tmol C y⁻¹; hence 54-62 Tmol y⁻¹, using consensus based marginal carbonate burial numbers of 16-20 Tmol C y⁻¹ (Fig. 6A). This imbalance has been identified before based on Ca and HCO₃⁻ budgets of the ocean (Bernier and Bernier, 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 kyr with respect to a riverine input of 26- 36 Tmol C 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-Rodriguez 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 a 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). 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 the 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 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 11-27 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

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)).

Figure 6 Alkalinity balance of the ocean (Fluxes are in Tmol y^{-1}). (A) Alkalinity balance considering river input of DIC and calcium carbonate burial. (B) Alkalinity inputs and output to the ocean considering additional sources and sinks based on 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 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 $1.4 \text{ Tmol C y}^{-1}$, range 0.4-4.7 Tmol C 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 sulfate reduction and sulfate 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 sulfate reduction on ocean alkalinity is limited to that the small fraction of reduced sulfur 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, sulfide) 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, in which the charge from land-derived nitrate and sulfate is transferred to bicarbonate produced by anaerobic respiration (Ben-Yaakov, 1973; Hu and Cai, 2011). 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). 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 sulfate reduction is derived from the burial of sulfur in marine sediments because most of the sulfate produced is re-oxidized (Jorgensen, 1977, 1982). Estimates of sulfur burial are based on organic carbon burial and vary from 1.2 (Berner, 1982) to $3.4 \text{ Tmol S y}^{-1}$ (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 2-4 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 30 and 31) 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 28 Tmol y⁻¹ and provides only part of the story. Additional alkalinity from riverine PIC delivery (about 15 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 (1.4 Tmol y⁻¹), organic matter burial (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) that is most useful when considering 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, but 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 pCO₂ 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). Homogenous 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., 2010). 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) and as well as reconstructions of alkalinity, carbon and pH of the past ocean. Nevertheless, some studies (Tyrell and Zeebe, 2004; Caves et al., 2013; 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 mineralisation 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 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 that products of physical weathering contribute to ocean alkalinity. This has multiple implications not only for the buffering capacity of the modern ocean and how it is impacted by humans, but also for the use of carbonate compensation depth reconstructions as a proxy for past carbon dynamics.

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
- *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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Author contributions

JJM designed research and wrote the manuscript with contributions from KS and MH, in particular for sections 2, 3 and 4. KS and MH performed the calculations presented in Figures 1-5.

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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} | Homogenous 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) |

Table 2 Biogeochemical processes and their impact on charge balance alkalinity (ΔCBA) and 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) Sulfate reduction | $(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.5 \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{H}_2\text{S} + \text{H}_2\text{O}$ | 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 |

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

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

| Alkalinity sources/sinks | Riverine DIC and carbonate burial balance | Complete Alkalinity balance |
|---------------------------------|--|------------------------------------|
| Riverine DIC | 31.5 | 31.5 |
| Riverine PIC | | 21.6 |
| Submarine groundwater | | 1.5 |
| Submarine silicate | | 2.8 |
| Sulfur burial | | 4.7 |
| Denitrification | | 1.5 |
| Organic matter burial | | 3 |
| Total Sources | 31.5 | 66.5 |
| Open ocean carbonate burial | 23 | 23 |
| Ocean margin carbonate burial | 36 | 36 |
| Reverse weathering | | 1 |
| Total sinks | 59 | 60 |
| Imbalance | 27.5 | -6.5 |