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On the true and the perceived minor interactions of dissolved phosphate and dissolved sulphate and some other constituents with the Alkalinity of oceanic seawater

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Abstract. We have become aware that there is some confusion in the literature on the interactions of dissolved phosphate and dissolved sulphate with the alkalinity of seawater. This paper aims to invite comments and corrections of colleagues towards resolving this confusion and eventually obtaining full agreement among ocean scientists. In the world oceans, the Alkalinity of seawater or Oceanic Alkalinity is defined as the small difference of electric charge between fully dissociated strong cations and the fully dissociated strong anions. As seawater must have an overall neutral electric charge, this small difference of the strong cations and anions must be compensated by a small difference between not fully dissociated weak cations and the weak anions. Oceanic Alkalinity can be determined by acid titration of a seawater sample, this leading to an ensuing value of Titration Alkalinity. In the titration procedure for Titration Alkalinity, both dissolved phosphate and dissolved sulphate play minor roles that can be assessed accurately from measured values of dissolved phosphate and the value of dissolved sulphate on the basis of measured salinity, respectively.

In the past, a perceived role of biological uptake or release of dissolved phosphate has been suggested in the value of Oceanic Alkalinity. To the best of our knowledge, this perceived role is mistaken. Moreover, it has also been reported a perceived role of biological uptake/release of dissolved sulphate from seawater in the value of Oceanic Alkalinity. Latter perceived role in the value of Oceanic Alkalinity is not necessarily wrong, in theoretical principle. However, it deviates from how Alkalinity has traditionally been defined in the literature and how it is used. Moreover, the role of sulphate is not verifiable, because the small amount of biological assimilation of sulphate cannot be discerned from measurement of the very large background concentration value of dissolved sulphate. Consideration of nitrite in Alkalinity has also been suggested and is theoretically not incorrect, but insignificant versus the accuracy of the measurements of Titration Alkalinity. Therefore, it is reasonable to omit and ignore nitrite when considering Alkalinity. Finally, in the classical (1981) expanded equation for Titration Alkalinity, the negative sign of [H_3PO_4] is mistaken and yet another reason that this [H_3PO_4] term best would have been, or from now on should be, omitted from the expanded equation for Titration Alkalinity.

1. The oceanic carbon cycle and CO_2 emissions by mankind

The world oceans comprise some 97% of all the water at the surface of our planet. We focus on the seawater of the world oceans that is very uniform in its composition (Table 1) and in general very well oxygenated. Seawater conditions of low dissolved oxygen to complete anoxia are beyond our focus but will in the end be discussed briefly.Within seawater there exist several chemical forms of dissolved inorganic carbon, that together are known as the total Dissolved Inorganic Carbon (DIC) pool or in the literature also often defined as Total CO_2 (TCO_2 or C_T). The major biological processes depend strongly on DIC and co-determine its concentration. On the one hand, photosynthesis (by single cell microalgae, macroalgae plants as well as coral reef symbionts) utilizes some of the DIC. On the other hand, respiration or (re)mineralization by bacteria and all animals (from zooplankton to whales) replenishes the DIC pool. Moreover, the formation and reverse process dissolution of biogenic calcium carbonate ($CaCO_3$) minerals hard parts in two crystalline forms aragonite and calcite, interact with the DIC pool. Several planktonic algae (for example Emiliania huxleyi) and zooplankton (for example pteropods) as well as shellfish and coral reefs are the producers of such biogenic $CaCO_3$. Within the ocean, DIC is mixed and transported as part of the large-scale and also small-scale water circulation. Last but not least, oceanic surface waters exchange CO_2 with the overlying atmosphere, and this also affects the DIC pool.

Accurate measurements of a suite of dissolved tracers in seawater (Broecker and Peng, 1982) are the foundation for being able to unravel the above processes of the oceanic carbon cycle. For a given seawater sample, these tracers are the salinity (S; Table 1), the DIC and its counterpart the Alkalinity, dissolved oxygen (O_2) and the major nutrients nitrate, phosphate and silicate (or silicic acid). O_2 and the dissolved major nutrients are valuable tracers for photosynthesis/respiration affecting DIC. Unfortunately, for similarly quantifying the formation/dissolution of $CaCO_3$ one cannot detect directly the related changes in the concentration of dissolved calcium (Ca^{2+}), because these changes are not discernible versus the very large background concentration of calcium ion in seawater (Table 1). Nevertheless, the accurate determination of Alkalinity, together with several of the other, above mentioned, tracers, does permit indirect approaches to investigate and quantify the formation/dissolution of $CaCO_3$.

Table 1. The standard mean chemical composition [$mol.kg^{-1}$] of seawater (S=35) after PICES (2007; their Chapter 5, Table 2)

anion	**mol.kg^{-1}**	**cation**	**mol.kg^{-1}**
Cl^-	0.54586	Na^+	0.46906
SO_4^{2-}	0.02824	Mg^{2+}	0.05282
Br^-	0.00084	Ca^{2+}	0.01028
F^-	0.00007	K^+	0.01021
B	0.00042	Sr^{2+}	0.00009

The net emission of CO_2 into the atmosphere due to the burning of fossil fuels by mankind has led to an increase of the CO_2 contents of air from ~ 280 µatm in the pre-industrial era (before ~1780 A.D.) to nowadays ~420 µatm (year 2021) (http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo_full) and continuing to rise in coming years and decades. This is the major cause for general warming of the world atmosphere, land and oceans (IPCC, 2019, 2021). However, some 30-40 % of the emitted extra (fossil fuel) CO_2 has entered the oceans. On the one hand, this may perhaps be seen as beneficial, because otherwise the CO_2 content of the atmosphere and the resulting global warming would have been even higher and of even greater concern. On the other hand, the ensuing general increase of DIC in the oceans does cause major shifts among the various chemical forms within the DIC pool. Most notably, and at first glance perhaps counterintuitive, the concentration of dissolved carbonate ion (CO_3^{2-}) is decreasing. This affects the solubility of biogenic $CaCO_3$, such that it would conceivably become more difficult for marine calcifying organisms to continue to produce their calcareous hard parts. Moreover, old $CaCO_3$ deposits as well as coral reef structures will become prone to enhanced dissolution. This increasing trend of the DIC pool of seawater and the ensuing risks for the marine calcifying biota and their deposits is of major concern and often mentioned to be "the other CO_2 problem".

In order to unravel the various components of the DIC pool, there are four key variables that can be measured directly in a collected sample of seawater. One of these four is Alkalinity, the others are DIC, the partial pressure of CO_2 (pCO_2) and the acidity (i.e., pH). When two of these variables are measured, then all others can be calculated from these. Nowadays in major research programs of the oceanic carbon cycle, it is quite common that the Alkalinity and DIC pair is routinely measured by acid titration and coulometry, respectively.

Yet unfortunately, in the literature there has occasionally evolved quite some apparent confusion on the role of dissolved phosphate for the exact value of Alkalinity in seawater. Moreover, an unusual suggestion was made about the role of biological uptake of dissolved sulphate for the exact value of Alkalinity in seawater (Wolf-Gladrow et al., 2007). This paper intends to describe the apparent confusions, towards eventually reaching a common agreement among ocean scientists of the true roles of dissolved phosphate and sulphate for the exact value of Alkalinity.

Inevitably, the often-described dissolved CO_2 system in seawater must first be defined in the introductory section. Next the concept of Alkalinity is described where we define Oceanic Alkalinity versus its analytical chemical counterpart the Titration Alkalinity. In the following section 1.4. the major applications of Alkalinity are presented. Chapter 2 presents the known, as well as perceived, interactions of dissolved phosphate with Alkalinity. Chapter 3 briefly presents the interactions with Alkalinity of reduced chemical species, that otherwise as mentioned above are somewhat beyond the focus of this paper but presented nevertheless. Chapter 4 presents several conceivable deviations from the general concept of salinity being conservative, and their effects on Alkalinity. Chapter 5 evaluates the concept of an explicit conservative equation for Alkalinity. Finally, we end with Discussion and Conclusions.

1.1. Dissolved Inorganic Carbon and the biological cycle

Marine photosynthesis in the oceans tends, on average, to follow the overall reaction

$$106\ \mathrm{DIC} + 122\ H_2O + 16\ HNO_3 + 1\ H_3PO_4 + \text{solar energy} \rightleftarrows [(CH_2O)_{106}(NH_3)_{16}(H_2PO_4)]_{\text{organic biomass}} + 138\ O_2 \qquad (1)$$

after Redfield et al. (1963). The resulting organic biomass is energetically rich, and hence serves as a food and energy source for bacteria and animals in the reverse reaction (1), that is remineralization or respiration. DIC in seawater occurs in concentrations varying around ~2 mmol. kg^{-1} seawater. It can be measured with an accuracy of about 2 $\mu mol.kg^{-1}$.

DIC really constitutes the summation of four different forms that exist in mutual chemical equilibria, dissolved CO_2, carbonic acid, bicarbonate ion and carbonate ion:

$$DIC = [CO_2]_{aqueous} + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{2}$$

In natural seawater, the bicarbonate ion $[HCO_3^-]$ is dominant, at ~1800 $\mu mol.kg^{-1}$ representing ~90% of the DIC pool, followed by the carbonate ion $[CO_3^{2-}]$ at about 50-150 $\mu mol.kg^{-1}$ representing ~9% and next the $[CO_2]_{aqueous}$ at about 10-20 $\mu mol.kg^{-1}$ representing merely ~1% of the total DIC. Finally, the chemical form $[H_2CO_3]$, that is the undissociated carbonic acid, occurs in very low abundance (~0.02-0.04 $\mu mol.kg^{-1}$) representing ~0.002 % only.

There are three major processes that affect the DIC pool in the oceans, these are (i) photosynthesis/respiration, (ii) biocalcification/dissolution and (iii) air/sea gas exchange of CO_2. Overall photosynthesis removes DIC from seawater (1), and its reverse respiration adds DIC to seawater. Biocalcification removes both Ca^{2+} and DIC from seawater and the reverse dissolution of $CaCO_3$ shells returns Ca^{2+} and DIC to seawater. These biologically-driven changes can be traced by measurements of both DIC and Alkalinity (Sect. 1.2).

For the DIC pool in a given volume of seawater, there are the following equilibrium reactions:

$$CO_{2(g)} \rightleftarrows CO_{2(aq)} \tag{3}$$
$$CO_{2(aq)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(aq)} \tag{4}$$
$$H_2CO_{3(aq)} \rightleftarrows H^+_{(aq)} + HCO^-_{3(aq)} \tag{5}$$
$$HCO^-_{3(aq)} \rightleftarrows H^+_{(aq)} + CO^{2-}_{3(aq)} \tag{6}$$

For each of these reactions there exists a conditional equilibrium constant K' where the ' symbol stands for conditional, that is, that the actual value of K' is a function of the salinity S, temperature T and pressure p (i.e., depth). The carbonic acid ($H_2CO_{3(aq)}$) cannot be analytically distinguished from the dissolved $CO_{2(aq)}$ (Weiss, 1974). In order to simplify the equations of the above carbonate system, it is customary to combine the concentrations of $CO_{2(aq)}$ and $H_2CO_{3(aq)}$ into the hypothetical species $CO^*_{2(aq)}$.

$$CO_{2(aq)} + H_2CO_{3(aq)} \rightleftarrows CO^*_{2(aq)} \tag{7}$$

This is not an approximation but exact, also because when desired, the two terms at left still can be calculated separately by using the relevant conditional equilibrium constant:

$$K' = [CO_{2(aq)}] / [H_2CO_{3(aq)}] \tag{8}$$

The numerical value of K' being around 500, one realizes the difference between $CO_{2(aq)}$ and $CO^*_{2(aq)}$ is only very small, in the order of 0.2 percent. This avoidance of a separate $H_2CO_{3(aq)}$ term yields the following set of simplified equilibrium reactions:

$$CO_{2(g)} \rightleftarrows CO^*_{2(aq)} \tag{9}$$
$$CO^*_{2(aq)} + H_2O_{(l)} \rightleftarrows H^+_{(aq)} + HCO^-_{3(aq)} \tag{10}$$
$$HCO^-_{3(aq)} \rightleftarrows H^+_{(aq)} + CO^{2-}_{3(aq)} \tag{11}$$

The definition of (DIC) is accordingly simplified to become:

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO^*_{2(aq)}] \tag{12}$$

These dissolved substances (often called 'carbonate species') are present in relative concentrations that are described by the *conditional equilibrium constants K'*.

$$K'_0 = [CO_2^*] / fCO_2 \tag{13}$$
$$K'_1 = [H^+] [HCO_3^-] / [CO_2^*] \tag{14}$$
$$K'_2 = [H^+] [CO_3^{2-}] / [HCO_3^-] \tag{15}$$

In Eq. (13), the term fCO_2 represents the fugacity of CO_2 gas in equilibrium with the concentration of dissolved $CO^*_{2(aq)}$ in the seawater. The fugacity approximately corresponds to the idealized *partial pressure* of the gas, with

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a minor correction factor to account for non-ideal behavior of the gas mixture. In Eqs. (14) and (15) there is the proton concentration [H^+]. The proton concentration in a sample is usually reported as the pH:

$$\mathrm{pH} = -\log([\mathrm{H}^+]) \qquad (16)$$

The conditional equilibrium constant K'_w (Eq. 17) directly relates the concentration of H^+ to the concentration of hydroxide ion (OH^-) in seawater.

$$K'_w = [\mathrm{H}^+]\,[\mathrm{OH}^-] \qquad (17)$$

This Eq. (17) shows that in the modern, slightly basic (alkaline) surface ocean of pH=~8, the hydroxide ion is about 100-fold more abundant than free protons (10^{-6} versus 10^{-8} moles per liter, respectively). The values of the conditional equilibrium constants K'_0, K'_1, K'_2 and K'_w are a function of salinity, pressure and temperature (S, p and T). As a consequence of that, when the temperature or pressure of a seawater sample (with given, measured DIC and Alkalinity; for latter see below Sect. 1.2) is changed, shifts will take place in the concentrations of the individual species of dissolved inorganic carbon, and of OH^- and H^+. The relationships between the conditional equilibrium constants and S, p and T have been described in the literature.
The various equilibrium reactions above (Eqs. 13, 14, 15 and 17) do not only observe *mass balance* (Eq. 12), but additionally must respect *charge balance*. The latter charge balance is tracked by the Alkalinity (Sect. 1.2).

1.2. Oceanic Alkalinity, its concept, definition and its measurement by titration

1.2.1. Why bother

The Alkalinity is a variable we can measure directly with great accuracy by acid titration. Therefore, it is a pivotal variable, yet unfortunately its underlying chemistry is complicated. There are two major reasons for defining and measuring Alkalinity. One is for being able to unravel (by combination with, notably, the measured value of DIC) the chemical speciation of the various carbon dioxide species in seawater. Conversely, the in principle arbitrary choice of the endpoint of the titration, is tailored for the second equivalence point of the dissolved carbon dioxide system (DIC) in seawater. The second major reason is that, again by combination with some of the other dissolved tracers, one can indirectly assess the changes of dissolved calcium (Ca^{2+} ion) due to biomineralization/dissolution of calcium carbonate ($CaCO_3$).

Dickson (1992) has in great detail described the development of the Alkalinity concept in marine chemistry. Dickson also mentions the initial confusion about the concept and its measurement, but in more than one century progress was made in parallel to progress in general chemistry. Notably, the chosen name Alkalinity was and still is confusing versus the far more general chemistry principle for any aqueous solution being either alkaline ($pH > 7$) or acidic ($pH < 7$). Otherwise, in 1939 the term Alkalinity was adopted as the standard designation (Dickson, 1992) and commonly used ever since then. Another important notion of its history is that until the early 1990's the titration method served for determination of both Alkalinity and DIC, whereas nowadays DIC is determined separately by coulometry (Johnson et al., 1987). Nowadays Titration Alkalinity still is determined by acid titration.

The values of Oceanic Alkalinity in the world oceans range from ~2250 to ~2450 $\mu mol.kg^{-1}$ (Fig. 1). For the accuracy of the determination of Alkalinity here we assume the reported $\underline{+}1.5$ $\mu mol.kg^{-1}$ in most modern articles. This implies that any theoretical considerations of very minor constituents of seawater that have a less than 1.5 $\mu mol.kg^{-1}$ effect on the value of Alkalinity, are of little or no use. Obviously, when perhaps in the future the accuracy has improved say tenfold to $\underline{+}0.15$ $\mu mol.kg^{-1}$ than a whole next suite of such very minor constituents should be taken into account. Hence our focus is on real values and their real precision and accuracy in the open ocean. Therefore, theoretical considerations of negligible entities are to be ignored. Also, the focus is on well oxygenated oceanic waters.

1.2.2. Overall neutral electric charge of seawater

Briefly, natural seawater comprises strong cations and anions, that is, from bases or acids that at all times are fully dissociated, as well as weak cations and anions that, to some extent, are non-dissociated, in other words, still partly bound with OH or H, respectively. Most importantly, seawater must be electrically neutral, that is, the sum of all positive charged ions must equal the sum of all negative charged ions:

$$\Sigma \text{ charges strong cations} + \Sigma \text{ charges weak cations} = \Sigma \text{ charges strong anions} + \Sigma \text{ charges weak anions} \qquad (18)$$

Re-arrangement yields

$$\Sigma \text{ charges strong cations} - \Sigma \text{ charges strong anions} = \Sigma \text{ charges weak anions} - \Sigma \text{ charges weak cations} \tag{19}$$

after Broecker (1974), Takahashi (1975), Broecker and Peng (1982), Bakker (1998), Sarmiento and Gruber (2006). Strictly spoken and indeed used in the original literature, these charges were expressed in units of micro equivalent charge per kilogram seawater, that is, the µeq.kg^{-1} notation. However, for the sake of (i) more uniform units in chemical oceanography, and because (ii) the righthand side of Eq. (19) is analytically determined by acid titration where the weak anions and weak cations are functioning as weak bases and acids, respectively, it is nowadays agreed to use the µmol.kg^{-1} notation.

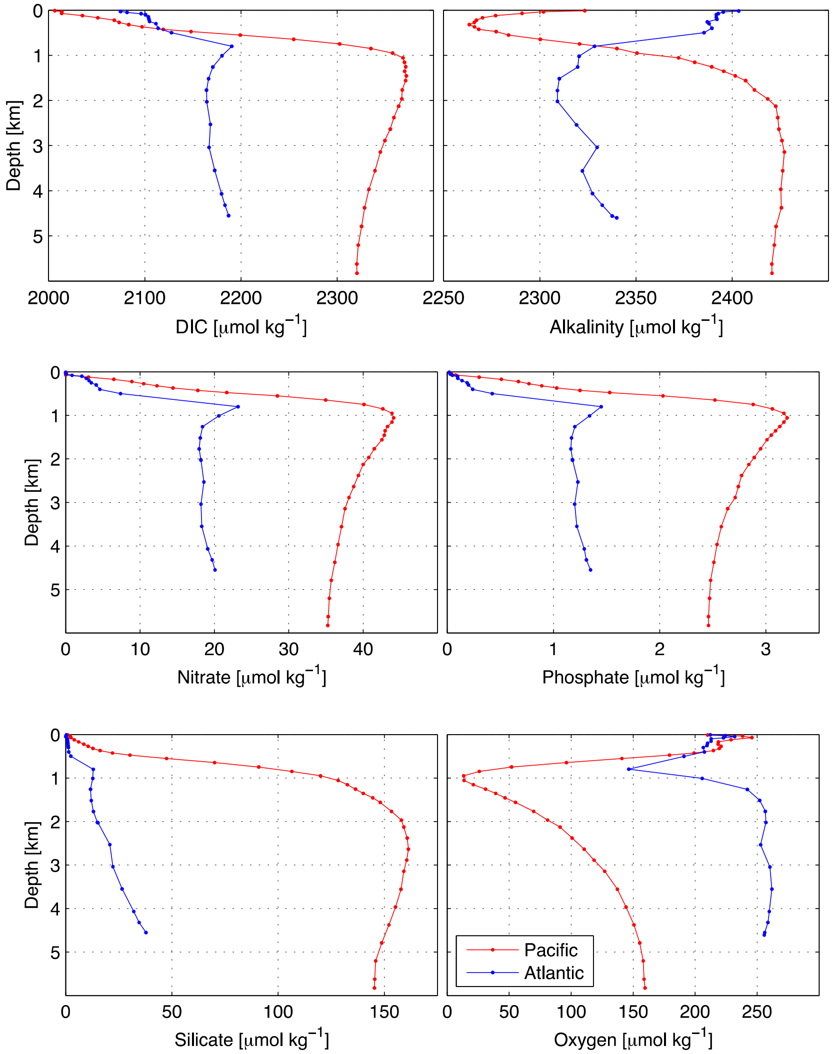

Figure 1. Vertical profiles of the DIC, Alkalinity, nitrate, phosphate, silicate and oxygen for the Northwest Atlantic (blue dots) and the Northeast Pacific Oceans (red dots). Higher DIC in deep Pacific versus deep Atlantic is due to (i) respiration of organic matter plus (ii) dissolution of $CaCO_3$. Higher nitrate and phosphate in deep Pacific versus Atlantic due to respiration, also explaining the opposite lower dissolved oxygen. Data for Bermuda Atlantic Time-Series Station (BATS) of GEOTRACES cruise GA02-64PE321 aboard RV *Pelagia*, station 21 (31045.92'N 64004.95'W at 13 June 2010), after Rijkenberg et al. (2014), is available at www.geotraces.org. Data for North Pacific is from RV *Melville* cruise 318M2004, station 119 (30.000N,159.700W at 4 August 2004), is available in

GLODAPv2 via CCHDO (https:// cchdo.ucsd.edu/cruise/ 318M200406). Figure adapted after De Baar et al. (2017a).

1.2.3. Oceanic Alkalinity

On the left-hand side of Eq. (19) the strong cations are Na^+, Mg^{2+}, Ca^{2+}, K^+ and Sr^{2+} and at salinity S=35 their total charge concentration is 605.0 $mmol.kg^{-1}$ but taking double the double charged ions Mg^{2+}, Ca^{2+} and Sr^{2+}. The strong anions are Cl^-, double charged SO_4^{2-}, Br^-, F^-, and also NO_3^- (for reasons given below) and their total charge is 602.8 $mmol.kg^{-1}$. Overall, the exact definition of Oceanic Alkalinity in natural seawater is thus:

$$\text{Oceanic Alkalinity} = [Na^+] + [K^+] + 2\cdot[Ca^{2+}] + 2\cdot[Mg^{2+}] + [Sr^{2+}] - [Cl^-] - 2\cdot[SO_4^{2-}] - [Br^-] - [F^-] - [NO_3^-] \qquad (20)$$

or in values at salinity S=35 this is given below for a 'typical' value as follows:

$$\text{Oceanic Alkalinity} = 605.0 - 602.8 = 2.2\ mmol.kg^{-1} = 2200\ \mu mol.kg^{-1} \qquad (21)$$

One may now realize that this (typical) value of Oceanic Alkalinity in seawater may vary for three reasons. Firstly, in Eq. (20) the difference is a function of the concentrations of the major ions, in other words, a function of salinity, where at lower or higher salinity than the here given example S=35 the Oceanic Alkalinity will decrease or increase accordingly. Secondly, bio-calcification/dissolution of $CaCO_3$ removes or adds, respectively, Ca^{2+} ion from seawater and hence the value of Oceanic Alkalinity decreases/increases accordingly. Thirdly, photosynthesis/respiration (Eq. 1) implies uptake or release of strong anion nitrate (NO_3^-) and hence Oceanic Alkalinity increases/decreases accordingly. This is a small effect but discernible, hence cannot be ignored in accurate interpretations of Oceanic Alkalinity. The range of concentrations of nitrate in the world oceans is 0 - 45 $\mu mol.kg^{-1}$ going from nitrate-depleted surface waters in oligotrophic central ocean gyres, to ~45 $\mu mol.kg^{-1}$ at the nutrient maximum at ~1000 m depth in the North Pacific Ocean (Fig. 1; Table 2). The corresponding effect on the value of Oceanic Alkalinity ranges from zero to -45 $\mu mol.kg^{-1}$. This is at most some (45/~2200) = ~2 % of Oceanic Alkalinity.

Table 2. Typical concentrations (in $\mu mol.kg^{-1}$) of DIC and major nutrients in surface and deep waters of different oceans; after De Baar et al. (2017a).

Entity	**North Atlantic Ocean**		**Southern Ocean**		**North Pacific Ocean**	
	surface	deep	surface	deep	surface	deep
C DIC	2050	2200	2210-2220	2240-2260	2000	~2350
N Nitrate	<1	25	25-30	30-38	<1	45
Si Silicate	<1	40	35-63	83-129	<1	170
P Phosphate	<0.1	1.2-1.5	1.6-1.9	2.26-2.35	<0.1	2.5-3.3

1.2.4. Measurement by titration

The small difference between charges of the strong ions (Eq. 20) is compensated on the right-hand side of Eq. (19) by the weak anions and weak cations the sum of which can be measured by titration, as follows:

$$\text{Titration Alkalinity} = A_{\text{Titration}} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] - [HSO_4^-] - [HF] \qquad (22)$$

as per equation (4) of Dickson (1981). In words, Dickson (1981) defines Titration Alkalinity as follows:

The total alkalinity of a natural water is 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 $K \leq 10^{-4.5}$ at 25ºC and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample.

Among these the proton $[H^+]$ has a primary link with the CO_2 system via equilibria (14) and (15) and via the water equilibrium (17) also with the $[OH^-]$ ion. The $[B(OH)_4^-]$, $[HSO_4^-]$ and $[HF]$ only have a minor, but significant role.

Oceanographers are mostly interested in the inorganic carbon system, that is, the terms $[HCO_3^-]$ and $2[CO_3^{2-}]$ in Eq. (22) and hence can be defined the Carbonate Alkalinity by re-arranging as follows:

$$\text{Carbonate Alkalinity} = A_{\text{carbonate}} = [HCO_3^-] + 2[CO_3^{2-}] = A_{\text{Titration}} - [B(OH)_4^-] - [OH^-] + [H^+] + [HSO_4^-] + [HF] \qquad [23]$$

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Focusing only on the dominant $[HCO_3^-]$ and $2[CO_3^{2-}]$ terms one may qualitatively get a feeling for changes due to biological processes. Photosynthesis (Eq. 1) causes a decrease of DIC, due to which in the mass balance equation (12) the $[HCO_3^-]$ decreases but this would cause an excess positive charge in Eq. (22), yet that is compensated by conversion of some of the single charged $[HCO_3^-]$ to double charged $2[CO_3^{2-}]$ such that, overall, the charge balance remains to be equal to the constant Oceanic Alkalinity (here not yet taking into the account the small effect of NO_3^-). The reverse respiration (Eq. 1 in reverse) leads to the opposite, an increase of the $[HCO_3^-]$ term and a decrease of the $2[CO_3^{2-}]$ term. The above Eqs. (22) and (23) are valid, in principle, for well oxygenated conditions in the open oceans.

Dickson (1981) states that in a number of natural samples (notably from anoxic waters) a variety of other systems may make small, but significant, contributions to the Titration Alkalinity. These are phosphate, silicate, hydrogen sulfide and ammonia. This leads to an expanded equation for Titration Alkalinity as follows:

$$\begin{aligned} Alk_{Titration} &= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] \\ &+ [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [HS^-] + 2[S^{2-}] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \end{aligned} \qquad (24)$$

In the above overall expanded Eq. (24) after Dickson (1981), these additional systems phosphate, silicate, hydrogen sulfide and ammonia are given in the second text line. Conversely, one realizes that these latter four systems are not, or virtually not, making a significant contribution to Titration Alkalinity in well oxygenated seawater.

The titration by small additions of 0.1 N HCl into an exact volume of seawater with, for example, an initial pH= ~8.1 is towards the first equivalence point and next the second equivalence point where the solution has arrived at the following proton condition

$$[H^+] = [HCO_3^-] \qquad (25)$$

In practice the titration is continued beyond the second equivalence point for the sake of optimal curve fitting by a computer routine. In fact, the measurement is in millivolt units (mV) of an electrode, and the second equivalence point (mV) is derived from curve fitting by defining the second derivative of mV as function of added volume acid V, that is d^2mV/dV^2. The situation of the most rapid change of mV is the mathematical inflexion point or the chemical equivalence point, as defined by the maximum value of d^2mV/dV^2 along the titration curve. The magnitude of the electrochemical potential across the glass bulb of the electrode is linearly related to the pH according to the Nernst equation (for details, see Supplementary Material S1). In other words, the curve fitting defines the second equivalence point and hence the pH = ~4.5 and not the reverse that an arbitrarily chosen pH = 4.5 is the endpoint. Otherwise, the value pH = ~4.5 obviously would correspond to the equilibrium constant as in Eq. (14) of the dominant reaction (Eq. 10) at the second equivalence point. Presumably by inserting the value of K_1' at given salinity and temperature after Mehrbach (1973) refitted by Dickson and Millero (1987), and for [CO2*] the values of total CO_2 (C_T or DIC) because by its definition at the second equivalence point (almost) all CO_2 species have been converted to [CO2*], one may derive $[H^+]x[HCO_3^-] = \sim10^{-9}$. This together with the above proton condition (25) yields $[H^+] = [HCO_3^-] = \sim10^{-4.5}$ µmol.kg^{-1}. Assuming this reasoning is correct, then the value pH = 4.5 as in the literature (Sverdrup et al., 1942; Dickson, 1981; and others) results from well understood chemistry. In the above is stated "(almost)" for [CO2*] = C_T as obviously some $[HCO_3^-]$ still exists at $\sim10^{-4.5}$ µmol.kg^{-1} such that in fact $[CO_2^*] = C_T - 10^{-4.5}$ µmol.kg^{-1} but C_T being in typical 2 x 10^{-3} molar concentration the $10^{-4.5}$ molar discrepancy represents merely some very small difference. Moreover, and more importantly, because in equation (14) the role of [CO2*] is in a ratio, this small discrepancy (i.e., the minor $10^{-4.5}$ component of 10^{-3}) does not really matter. For example, using $pK_1^* = 5.86$ at S = 35 and T = 25ºC after Figure 1.1.2 of Zeebe and Wolf-Gladrow (2001) and say C_T = 2000 µmol.kg^{-1} then one derives

$$K_1^* \text{ x } [CO_2^*] = 10^{-5.86} \text{ x } 2\ 10^{-3} = 2 \text{ x } 10^{-8.86} \qquad (26)$$

of which the square root is ~1.4 x $10^{-4.43}$ for the concentrations of both $[H^+]$ and $[HCO_3^-]$ at the second equivalence point of the titration. This is more or less the same as the value pH = 4.5 by Dickson (1981) as a result of the strong dominance of the K_1^* in the overall seawater solution. However, strictly speaking, Dickson (1981) did somewhat simplify by stating pH = 4.5 as the endpoint, because the endpoint is defined by the second derivative of the titration curve in combination with Eqs. (25) and (14), such that for any individual seawater sample, the pH value at this 'endpoint' may presumably vary slightly around 4.5 as function of the intrinsic S, T, and composition, of the sample. (The simplification by Dickson (1981) and earlier articles, may, or may not, relate to the fact that initially the end-point was determined by linearization rather than curve fitting of the titration curve.)

Because we are interested in calculating the concentrations of $[HCO_3^-]$ and $[CO_3^{2-}]$ in the original seawater sample, we next use the chemical speciation model software CO2SYS (Lewis and Wallace, 1998) to calculate these species of the CO_2 system. Here one not only enters given (measured) values for two CO_2 system variables, but also values for two major nutrients phosphate and silicate, as well as values for salinity and temperature. The phosphate is for taking into account according to Eq. (24) the titration of minor amounts of $[HPO_4^{2-}] + 2[PO_4^{3-}]$ taking up 1 or 2 protons, respectively, and the strictly theoretical (see below section 2.2.) loss of one proton of the $[H_3PO_4]$, because at the endpoint pH=4.5 of the titration all 3 phosphate species are in the $[H_2PO_4^-]$ state. Otherwise in natural seawater at pH=~8.1 the $[H_3PO_4]$ state is completely negligible, in other words, it does hardly exist (see below section 2.2). The third major nutrient nitrate exists as the strong anion NO_3^- and does not affect Titration Alkalinity but is significant in the Oceanic Alkalinity (Eq. 20). Obviously, the CO2SYS software does not request an input value of dissolved nitrate.

1.3. The major applications of Alkalinity

Here four major groupings of the applications of Alkalinity are given. For each of these groupings, merely one or a few example citations are given. Many more example citations do exist in the literature, but the objective of the current paper is not an exhaustive review of all such applications.

1.3.1. Solubilities of calcium carbonates crystalline states aragonite and calcite

By far the first and most important application of Alkalinity is as input value together with one other CO_2 system variable for the calculation of $[CO_3^{2-}]$ with regards to the calcium carbonate ($CaCO_3$) saturation states of bio-minerals aragonite ($\Omega_{aragonite}$) and calcite ($\Omega_{calcite}$). For aragonite this saturation state is defined as follows:

$$\Omega_{aragonite} = \{[Ca^{2+}]_{sw} \cdot [CO_3^{2-}]_{sw}\} / K^*_{SP\ aragonite} \qquad (27)$$

where $[Ca^{2+}]_{sw}$ and $[CO_3^{2-}]_{sw}$ are the concentrations in ambient seawater and $K^*_{SP\ aragonite}$ is the solubility product of aragonite as function of salinity, temperature and pressure (Takahashi, 1975; Broecker and Peng, 1982; Sarmiento and Gruber, 2006; Jones et al., 2021). The major biotic $CaCO_3$ minerals aragonite and calcite and abiotic $CaCO_3$ mineral ikaite each have such solubility equation, but each with their own solubility product K^*_{SP}. Ikaite is extremely unstable and can only exist in crystalline form at low temperatures and high salinity (Dieckmann et al., 2008 and references cited therein). Major marine pelagic calcifying organisms are the pteropods producing aragonite, and the foraminifera producing calcite. Moreover, benthic coral reefs are largely composed of aragonite. Aragonite is the less stable bio-mineral found in marine calcifiers due to its comparatively higher solubility relative to calcite. As such, aragonite is most vulnerable to dissolution and seawater is undersaturated when $\Omega_{aragonite} < 1$, whereby conditions can become energetically costly and potentially even corrosive for calcifiers (Feely et al., 2004; Orr et al., 2005). For a long time, there was most interest in the preservation versus dissolution of calcite sedimentary deposits (Sverdrup et al., 1942; Takahashi, 1975), where in general the upper oceanic water column is oversaturated, in contrast to deeper, older waters that tend to be undersaturated (Fig. 2). Nowadays, there is the ongoing emission of CO_2 due to burning of fossil fuels, and ensuing decreasing time trend of $[CO_3^{2-}]$ in seawater. This has led to more and more concern about aragonite becoming undersaturated even in the upper water layers, such that coral reefs are at peril, and pelagic pteropods at risk of high energetic costs in producing and maintaining aragonites and potential dissolution of the shells.

1.3.2. Uptake of CO_2 and/or HCO_3^- by biota

Given the three major chemical forms CO_2, HCO_3^- and CO_3^{2-} in seawater, several articles exist for unraveling the uptake of one or another of these three in photosynthesis and/or biocalcification. Here we mention merely two examples.

Neven et al. (2011) applied the isotopic disequilibrium technique to quantify the contributions of either $[CO_2]$ or $[HCO_3^-]$ to the overall DIC uptake by phytoplankton. In this context the concentrations $[CO_2]$ and $[HCO_3^-]$ in the ambient seawater were calculated by CO2SYS software from measurements of DIC and Alkalinity (Van Heuven et al., 2011).

De Baar et al. (2017a) observed a strong correlation of dissolved $[CO_2]$ with the cadmium (Cd) stable isotopic composition of seawater along a transect in the Southern Ocean. By combination of the $[CO_2]$ with Alkalinity (Van Heuven et al., 2011), the concentration $[HCO_3^-]$ was calculated, and the dissolved ratio $[CO_2]/[HCO_3^-]$ was found to also have a strong correlation with the Cd stable isotopic composition. One hypothesis for the underlying mechanism would be a role of Cd in the carbonic anhydrase enzyme function for conversion of bicarbonate ion $[HCO_3^-]$ into CO_2, the latter CO_2 being required by RuBisCO (ribulose-1,5-bisphosphate carboxylase/oxygenase) that only accepts CO_2.

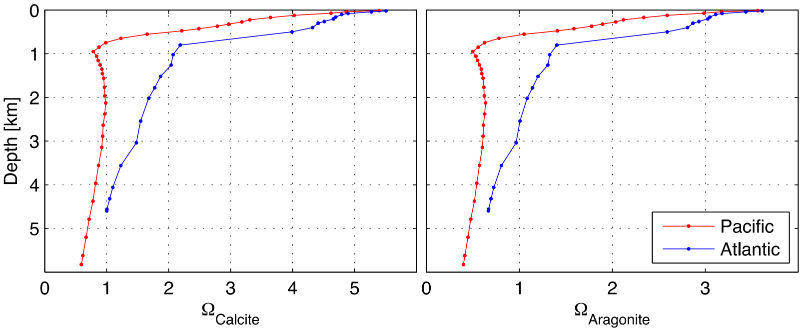

Figure 2. Vertical distributions of $\Omega_{Calcite}$ and $\Omega_{Aragonite}$ (Eq. 27). Northwest Atlantic Ocean (blue connected dots; to 4.5 km depth) versus the Northeast Pacific Ocean (red connected dots; to 5.8 km depth). For station positions and sampling dates see caption of Figure 1.

1.3.3. Unraveling biogenic effects on Oceanic Alkalinity

The changes in DIC (ΔDIC) and Alkalinity (ΔA) result from the main physical and biological processes, such as salinity changes ($\Delta DIC_{salinity}$, $\Delta A_{salinity}$) from freshwater inputs and mixing of different water masses, photosynthesis and respiration ($\Delta C_{organic}$, $\Delta A_{organic}$) and the formation and dissolution of calcium carbonate (ΔDIC_{CaCO3}, ΔA_{CaCO3}). Following Jones et al. (2021), these processes are defined in the following equations:

$$\Delta DIC = \Delta DIC_{salinity} + \Delta DIC_{organic} + \Delta DIC_{CaCO3} \tag{28}$$

$$\Delta A = \Delta A_{salinity} + \Delta A_{organic} + \Delta A_{CaCO3} \tag{29}$$

By salinity normalization (Jones et al., 2021) to, for example, salinity = 35 or better an average salinity value of the region of investigation, the major effect of salinity on Alkalinity is catered for. Next the changes in DIC due to photosynthetic fixation of DIC and production of organic matter ($\Delta DIC_{organic}$) can be determined from changes in salinity-normalized dissolved nitrate (NO_3) and the classical C/N Redfield ratio of 106/16 = 6.6 (Eq. 1). Following Redfield stoichiometry, a decrease in DIC of 1 µmol kg^{-1} due to phytoplankton uptake is accompanied by a decrease of 16/106 = 0.15 µmol kg^{-1} nitrate, which causes a 0.15 µmol kg^{-1} increase in Alkalinity. The $\Delta A_{organic}$ is therefore estimated from $\Delta DIC_{organic}$ by applying 0.15 µmol A kg^{-1} per 1 µmol DIC kg^{-1} removed during photosynthetic production of organic matter. Once the salinity normalized $\Delta A_{organic}$ is entered into the salinity-normalized version of above Eq. (29), the value for salinity-normalized ΔA_{CaCO3} is calculated. Given the double charge of the Ca^{2+} ion the latter salinity-normalized ΔA_{CaCO3} can be divided by the factor 2 in order to arrive at the salinity normalized value of ΔCa^{2+}.

In summary, by comparison of the calculated salinity-normalized values of $\Delta A_{organic}$ and ΔA_{CaCO3} one can assess the relative importance of these two processes as drivers of changes of the Alkalinity. Moreover, this approach via Alkalinity permits the indirect determination of ΔCa^{2+} in µmol kg^{-1}, a value that is too small to be discernible by direct measurement of the very large background concentration of 10280 µmol kg^{-1} in seawater (Table 1).

1.3.4. Internal consistency of CO_2 system measurements in seawater

Last but not least, Titration Alkalinity is among the four CO_2 system variables that can be measured, the others being the DIC, pH and pCO_2. The overall CO_2 system (Sect. 1.1) is such that when two variables are measured, all other variables can be calculated. Next, when a third (and fourth) variable is also measured, the system is overdetermined and this allows to verify for internal consistency of the 3-4 measurements. For example, when primarily measuring DIC and Titration Alkalinity, one may calculate pH and/or pCO_2 and compare this with the measured value(s) of pH and/or pCO_2. Obviously, the various equilibrium constants (section 1.1), notably their uncertainties, also play a role here (Millero et al., 2006, see also their Table 1). Such verification of internal consistency has a long tradition, for example from the GEOSECS expeditions in the 1972-1978 era (see GEOSECS 1981-1987; Data Report Volumes 1, 3 and 5), to nowadays the GO-SHIP program and efforts (Fong and Dickson, 2019). Over the years, these excellent efforts and ensuing articles have been pivotal for greatly improving the accuracy of our studies of the CO_2 system in seawater (Millero et al., 1993a,b; Lueker et al., 2000; Chen et al., 2015; Patsavas et al., 2015; Salt et al., 2016; Raimondi et al., 2019; among several others).

2. Interactions of phosphate with Alkalinity

2.1. Historic literature

The more complete history of Alkalinity by Dickson (1992) is a most valuable source of information. Here we refrain ourselves to two restrictions, firstly the interactions of phosphate with alkalinity, and secondly, the modern history as off 1965.

2.1.1. Three benchmark articles

Dyrssen (1965) in the final sentence of his benchmark article on the Gran titration of seawater for both DIC and Titration Alkalinity, mentions that [HPO_4^{2-}] does also consume H^+ in a titration with HCl, as follows:
"To a slight extent (< 5 % of HCO_3^-) CO_3^{2-}, $H_2BO_3^-$, HPO_4^{2-} and F^- also consume H^+ in a titration with HCl".
Moreover, Dyrssen and Sillén (1967, their page 115) reckon that 0.0023 mM phosphate (2.3 µmolar) may be neglected (but in anoxic waters may have to be considered).

Edmond (1970) further refined the titration method for Titration Alkalinity and DIC that next was used in the ensuing GEOSECS program (see Supplementary Material S2). Edmond (1970) mentions that (at pH = ~ 8) "the contribution from phosphate, (HPO_4^{2-}) is not normally included in the definition of At (i.e., Titration Alkalinity), but can be significant at the 0.1 % level (10^{-6} mol/kg sea water). The only important contribution from the phosphate (significant at the 0.1 % level) is due to the protonation of HPO_4^{2-} and can be corrected for using the apparent constant, Kp_2' of Kester and Pytkowicz (1967) and the measured phosphate concentration of the sample. However, the accuracy of alkalinity determinations hitherto (year 1970) has been such that nutrient corrections are probably justified in only a formal sense."

2.1.2. Other studies of Alkalinity with or without the interaction with phosphate

Takahashi (1975) mentions that the total Alkalinity, ΣA, of seawater is defined commonly as:
$\Sigma A = (HCO_3^-) + 2(CO_3^{2-}) + (H_2BO_3^-) + (OH^-) - (H^+) = (K^+) + (Na^+) + 2(Ca^{2+}) + 2(Mg^{2+}) - (Cl^-) - 2(SO_4^{2-})$
where the left-hand term is our term Titration Alkalinity (Eqs. 22 and 24) and the righthand term is our term Oceanic Alkalinity (Eq. 20). Here please notice that the major nutrients nitrate and phosphate were at the time still omitted by Takahashi (1975).

Skirrow (1975) using a suite of chemical equations for the formation of organic matter (as per Eq. (1)) shows that uptake of 16 units nitrate yields a +16 units increase of Oceanic Alkalinity, but parallel uptake of 1 unit of phosphate yields a zero change of Oceanic Alkalinity. Nowadays this still is our understanding of the contribution of dissolved nitrate to Oceanic Alkalinity and the zero contribution of phosphate to Oceanic Alkalinity. On the other hand, dissolved nitrate does not affect Titration Alkalinity but dissolved phosphate does play a minor role among all the weak ions in the Eq. (24) of Titration Alkalinity.

Chen (1978) reckoned that for the decomposition of organic matter (as per our above equation 1) the value of Oceanic Alkalinity decreases with 17 units, that is the implicit summation of 16 nitrate and 1 phosphate added to seawater. This perceived effect of phosphate on Oceanic Alkalinity will be discussed further in below Sect. 2.3. (Otherwise, it is noted that the equation (3) of Chen (1978) cannot be reconstructed by us when applying CO2SYS.) Four years later, Chen et al. (1982) had changed their mind. At first, they again concluded that consequently, a decrease of 17 mol kg^{-1} in TA (Oceanic Alkalinity) occurs with the decomposition of one mole of organic matter per kg of seawater; this value 17 representing 16 nitrates plus 1 phosphate. However next, upon more careful evaluation of the proton balances, Chen et al. (1982) eventually concluded more recently that, in theory, the release of H_3PO_4 due to the decomposition of organic matter should have no effect on TA (i.e., Oceanic Alkalinity). Next Chen et al. (1982) defined what we call Titration Alkalinity in their equation (3) that does comprise the term +[HPO_4^{2-}]. Chen et al. (1982) also defined what we call Oceanic Alkalinity in their equation (4) that does comprise the term -(NO_3^-) and not any phosphate term.

Brewer and Goldman (1976) and Goldman and Brewer (1980) did phytoplankton growth experiments assessing the effect on alkalinity (i.e., Oceanic Alkalinity) by the uptake of nitrate, nitrite, ammonia or urea as nitrogen source. This work is the recognized basis for the since then common understanding that uptake of 1 unit of nitrate leads to an increase with 1 unit of Oceanic Alkalinity. Moreover, they also considered competing hypotheses whether or not the uptake of phosphate would affect Oceanic Alkalinity. Goldman and Brewer (1980) concluded that the experimental results were tending to support the notion that uptake of phosphate does

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not affect Oceanic Alkalinity, but mentioned that analytical error, in combination with the narrow range of phosphate concentrations covered, did preclude a completely satisfactory observation.

Broecker and Peng (1982) mention as follows: "When organically bound nitrogen is released during respiration (as per our above Eq. 1), the NO_3^- so produced adds to the anionic charge and reduces the alkalinity (Oceanic Alkalinity) of the deep water. Correspondingly, the removal of the NO_3^- ion to form organic matter increases the alkalinity of surface water. This is clearly quantified in their Table 2-6 where the formation of 4 units of organic matter corresponds to a -4 change of DIC and a -0.6 change of NO_3 and a +0.6 change of Alkalinity. Now multiplying these numbers with a factor (106/4) = 26.5 to arrive at our above Eq. (1) yields a 106 decrease of DIC and 15.9=~16 decrease of dissolved nitrate and 15.9=~16 increase of Oceanic Alkalinity. Broecker and Peng (1982) for teaching objectives used the simplest numerical values, but these agree very well with our Redfield Eq. (1). Most relevant here is that the uptake or release of phosphate is not mentioned at all, therefore does not affect Oceanic Alkalinity.

Some 16 years later, Broecker and Peng (1998) explain (at their page K-52) the for our paper relevant ocean tracer approaches as follows:

"These hypothetical ΣCO_2 amounts (that is: DIC amounts) are based on three measured properties of the water: salinity, phosphate content, and alkalinity (corrected for the nitrate contribution). Salinity is important because the removal of fresh water by evaporation enriches all the ions in sea water (and hence also ΣCO_2) and, of course, the addition of fresh water by precipitation dilutes them. The phosphate content is important because it provides a measure of the changes in ΣCO_2 related to biological cycles. Each mole of phosphorus removed from sea water by photosynthesis is accompanied by about 125 moles of ΣCO_2. Or putting it the other way around, waters rich in dissolved phosphate will have a correspondingly high respiration CO_2 content. The alkalinity is important because it provides a measure of the amount of ΣCO_2 lost to the formation of $CaCO_3$ shells or gained from their dissolution. On the time scale of ocean mixing, only two chemical mechanisms exist to change the alkalinity of sea water, namely, gains or losses of Ca^{++} to $CaCO_3$ and of NO_3^- to organic tissue."

Broecker and Peng (1998) obviously do mention the role of phosphate and yet in the final sentence of this same paragraph clearly state that the alkalinity of seawater (Oceanic Alkalinity) is affected by gains or losses of Ca^{2+} and NO_3^-, where obviously parallel changes or losses of phosphate are omitted, hence gains or losses of phosphate do implicitly not affect Oceanic Alkalinity.

Campbell (1983) describes as follows in his text section 44.3.2.1.:

"The variations of Alkalinity in the oceans are due primarily to differences in salinity. If this was the sole mechanism then alkalinity would be a conservative tracer. However, precipitation and dissolution of $CaCO_3$, as well as removal and regeneration of nitrate, are significant contributors to the non-conservative behavior of alkalinity in the oceans." Obviously in the above cited text of Campbell (1983) there is no mentioning of either phosphate or sulphate affecting Oceanic Alkalinity; see also Chester (1990).

2.2. True Interactions of phosphate species with Titration Alkalinity

2.2.1. Different viewpoints in historical articles

As mentioned by Dickson (1992), there had been some confusion in the 1970s with regards to inclusion of minor constituents of seawater in the equation for Titration Alkalinity. However, it is manifest (see Sect. 2.2.2. below) that at the pH=4.5 second equivalence point of the acid titration, almost all phosphate exists in the $H_2PO_4^-$ state and not (i.e., only negligibly) in the fully protonated H_3PO_4 state.

Gieskes (1974) used the term $3[PO_4^{3-}]$ thus assuming the free $[PO_4^{3-}]$ state of the original seawater sample at natural pH=~8 and the fully protonated H_3PO_4 end state at the second equivalence point of the titration. Peng et al. (1987) apparently were aware of the three different states of phosphate existing at the natural pH~8 before the titration, yet presumably by the coefficients also did assume a fully protonated H_3PO_4 end state:

$$Ap = (H_2PO_4^-) + 2(HPO_4^{2-}) + 3(PO_4^{3-}) \qquad (30)$$

where *Ap* is the phosphate alkalinity. On the other hand, Bradshaw et al. (1981) more correctly incorporated phosphate into the Titration Alkalinity, as follows:

". . the sample alkalinity with regard to the second equivalence point must be adjusted by adding:

$$2[PO_4^{3-}]_0 + [HPO_4^{2-}]_0 - [H_3PO_4]_0 \qquad (31)$$

where the subscript 0 refers to the sample."

This approach of Bradshaw et al. (1981) agrees with the nowadays common agreement on the role of the three different phosphate species in the original (pH = ~8) seawater sample as in the above complete Eq. (24) of

Titration Alkalinity after Dickson (1981). Nevertheless, in the below Sect. 2.2.2. it is demonstrated that the thus far commonly agreed role of $[H_3PO_4]_0$ is mistaken.

2.2.2. The exact chemical speciation of phosphate in the original ocean seawater sample before titration

The concentrations of dissolved phosphate in the world oceans range from 0 µM in oligotrophic surface waters to ~2.5 µM in the North Pacific deep water to ~3.3 µM in the oxygen minimum zone of the North Pacific (Fig. 1; Table 2). This is far less than the chosen value of 10 µM as used by Dickson (1981) in an example assessment of the effect of dissolved phosphate on the value of Titration Alkalinity. Latter example may be more relevant for seasonal eutrophication in some coastal waters. Also, anoxic basins may show higher dissolved phosphate. For example, the anoxic deep waters of the largest anoxic basin, the Black Sea, comprise some 5-7 µM dissolved phosphate (Codispoti et al., 1991; Schijf et al., 1991).

The acidic properties of phosphate are as follows. In water solutions, phosphoric acid is mostly dissociated into some combination of its three anions, except at very low pH. The equilibrium equations are:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad (32)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad (33)$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad (34)$$

Following DOE (1994) and PICES (2007), the conditional equilibrium constants in seawater at S=35 and T=25°C are

$$K_{1P} = [H^+]\,[H_2PO_4^-]\,/\,[H_3PO_4] \quad \ln(K_{1P}/k^o) = -3.71 \quad (K_{1P}/k_{o)} = 0.0245 \qquad (35)$$

$$K_{2P} = [H^+]\,[HPO_4^{2-}]\,/\,[H_2PO_4^-] \quad \ln(K_{2P}/k^o) = -13.727 \quad (K_{2P}/k^o) = 1.0926\ 10^{-6} \qquad (36)$$

$$K_{3P} = [H^+]\,[PO_4^{3-}]\,/\,[HPO_4^{2-}] \quad \ln(K_{3P}/k^o) = -20.24 \quad (K_{3P}/k^o) = 1.6214\ 10^{-9} \qquad (37)$$

An example of the speciation of phosphate in natural surface seawater is shown in Table 3, after De Baar and Gerringa (2008). When now taking this speciation at pH = 8.07 as the starting point of the titration for Alkalinity that reaches the second equivalence point of the carbonate system at pH = 4.5 we can rely on the above Titration Alkalinity Eq. (24) to quantify the role of phosphate in the case of its total concentration at 1.52 µmol.kg^{-1}. At the endpoint at pH = 4.5 (virtually) all phosphate is converted into the $H_2PO_4^-$ state. Therefore the 2.2 % $H_2PO_4^-$ at the initial pH=8.07 is not changed and does not contribute to the value of Titration Alkalinity. Indeed, the initial $H_2PO_4^-$ state is not part of the Titration Alkalinity Eq. (24). The dominant HPO_4^{2-} species at the initial pH=8.07 has been converted to $H_2PO_4^-$ at pH 4.5 and hence has consumed 1.46 µmol.kg^{-1} protons. The minor PO_4^{3-} species at initial pH=8.07 has been converted to $H_2PO_4^-$ and hence has consumed (2 x 0.0243) = 0.0486 µmol.kg^{-1} protons. Finally, the undissociated H_3PO_4 species at initial pH = 8.07 is listed as such in the Titration Alkalinity Eq. (24) but at 1.61 10^{-8} µmol.kg^{-1} (Table 3) has an orders of magnitude lower concentration in the original seawater at pH=~8.1 and hence is irrelevant (see also Figure 1.2.12 of Zeebe and Wolf-Gladrow, 2001). Thus, for normal seawater in the world oceans, the H_3PO_4 term in the Titration Alkalinity Eq. (24) is merely theoretical and practically at best leading to confusion for some readers.

Another cause of confusion is the negative sign for the $[H_3PO_4]$ term in Eq. (24). Perhaps this was presumably intended to have the meaning that every $[H_3PO_4]$ of the initial seawater sample at pH=8.07 would give off one proton to end up in the dominant $[H_2PO_4^-]$ state at the pH=~4.5 endpoint of the titration. This is not the case. When in the above example assuming that indeed all the initial HPO_4^{2-} species as well as all the initial PO_4^{3-} species have at pH=4.5 endpoint been converted to the dominant $[H_2PO_4^-]$ state, then, also including the original amount of $[H_2PO_4^-]$, a safe approximation is that $[H_2PO_4^-] = 1.52\ 10^{-6}$ mol.kg^{-1} at the pH=4.5 endpoint.

Upon next entering this value and $[H^+] = 10^{-4.5}$ mol.kg^{-1} into Eq. (35) one may derive as follows:

$[H_3PO_4] = [10^{-4.5}]\ [1.52\ 10^{-6}]\ /\ [0.0245] = [3.1623\ 10^{-5}]\ [1.52\ 10^{-6}]\ /\ [0.0245] = 1.962\ 10^{-3}$ µmol kg^{-1}

By this, admittedly simplified, approximation, the $[H_3PO_4] = 1.962\ 10^{-3}$ µmol.kg^{-1} at the pH=4.5 endpoint. On the one hand, this concentration is negligible compared to the total phosphate = 1.52 µmol.kg^{-1} thus implying that the above assumption that all phosphate is $[H_2PO_4^-] = 1.52$ µmol.kg^{-1} is in essence correct. In other words, at the endpoint pH=4.5 the dominant $[H_2PO_4^-]$ represents 99.87 %, the remaining $[H_3PO_4] = 1.962\ 10^{-3}$ µmol.kg^{-1} indeed is negligible. On the other hand, the concentration $[H_3PO_4] = 1.962\ 10^{-3}$ µmol.kg^{-1} is more than five orders of magnitude higher at pH=4.5 than the original $[H_3PO_4] = 1.61\ 10^{-8}$ µmol.kg^{-1} at pH=8.07 in the original natural seawater. In other words, the negative sign of $[H_3PO_4]$ in the Eq. (24) is mistaken and yet another reason that this $[H_3PO_4]$ term best would have been, or should be, omitted from Eq. (24).

Table 3. Example of the chemical speciation of dissolved phosphate in surface seawater after De Baar and Gerringa (2008). Relevant are the summation values for phosphate linked with zero, one, two or three protons. The chemical equilibrium model used for the speciation calculations was Mineql+ version 4.6.1 (Secher and McAvoy, 2007) with constants of the seawater CO_2 system after Mehrbach et al. (1973). The composition of the model seawater was obtained from 50 m depth at station 107 (18 February 2008) from expedition ANT XXIV-3 (2008) with RV *Polarstern* in the Atlantic sector of Southern Ocean (Van Heuven et al., 2011; Neven et al., 2011). The salinity and concentrations of nitrate, phosphate, silicate used are concentrations as measured during the expedition. The measured values of Alkalinity and DIC (Van Heuven et al., 2011) were used with CO2SYS to calculate the pCO_2 = 360 µatm and pH = 8.07 values. Latter pH value was used as input variable in Mineql+.

MgH_2PO4^+	0.00941 µmol.kg^{-1}			
H_2PO4^-	0.0241 µmol.kg^{-1}			
Summation:		**$H_2PO_4^-$**	**0.0335 µmol.kg^{-1}**	**2.2 %**
$MgHPO_4$	0.625 µmol.kg^{-1}			
$NaHPO_4^-$	0.393 µmol.kg^{-1}			
$KHPO_4^-$	0.00534 µmol.kg^{-1}			
HPO_4^{2-}	0.439 µmol.kg^{-1}			
Summation:		**HPO_4^{2-}**	**1.46 µmol.kg^{-1}**	**96.2 %**
$CaPO_4^-$	0.0224 µmol.kg^{-1}			
$MgPO_4^-$	0.00185 µmol.kg^{-1}			
PO_4^{3-}	0.0000703 µmol.kg^{-1}			
Summation:		**PO_4^{3-}**	**0.0243 µmol.kg^{-1}**	**1.6 %**
H_3PO_4	1.61 10^{-8} µmol.kg^{-1}			
Summation:		**H_3PO_4**	**1.61 10^{-8} µmol.kg^{-1}**	**1.06 10^{-6} %**
GRAND TOTAL			1.52 µmol.kg^{-1}	100 %

Adding all up for this example calculation, the concentration of 1.52 µmol.kg^{-1} phosphate in a seawater sample contributes {1.46 + 0.0486 + (0.0001985 - 1.61 10^{-8})} = 1.509 µmol.kg^{-1} to the value of Titration Alkalinity. This is in the same order of magnitude of the ~1.5 µmol.kg^{-1} precision of modern determinations of Titration Alkalinity. At most for the maximum dissolved phosphate at ~3.3 µmol.kg^{-1} in the North Pacific oxygen minimum zone (Fig. 1), the contribution of the combined phosphate species is about twice the precision of Titration Alkalinity. During GEOSECS (1972-1978; see Supplementary Material S2) the precision of Titration Alkalinity was reported to be 0.1%, that is ~2.3 µmol.kg^{-1} such that for almost all samples of all three major oceans, the effect of phosphate in the 0 to ~3.3 µmol.kg^{-1} range was at most near the precision of GEOSECS at its time.

2.2.3. Overall effects of photosynthesis/respiration on Titration Alkalinity

Following Eq. (1), photosynthesis uses 106 units DIC, 16 units nitrate and 1 unit phosphate from seawater. The uptake of 16 units nitrate causes an increase of 16 units Oceanic Alkalinity. This new higher value of Oceanic Alkalinity must be equaled by the Titration Alkalinity. This and the large loss of 106 DIC units yields a reshuffle among the weak ions of Titration Alkalinity. Let us begin to take into account only the Carbonate Alkalinity

$$\text{Carbonate Alkalinity} = A_{\text{carbonate}} = [HCO_3^-] + 2[CO_3^{2-}] \qquad (23)$$

Most importantly a significant amount of the single charged $[HCO_3^-]$ is converted to the double charged $[CO_3^{2-}]$ in order to not only maintain, but also increase with 16 units, the total negative charge. This is mostly to overcome that the total dissolved inorganic carbon DIC has decreased with 106 units. The couple $[HCO_3^-]$ and $[CO_3^{2-}]$ jointly being the very dominant pH buffer of natural seawater, one may in a qualitative description assume that all the remaining minor ions in the complete Eq. (24) of Titration Alkalinity simply follow the pH value dictated by the carbonate system pH buffer. This includes an adjustment of phosphate speciation, also because the total dissolved phosphate has decreased with one unit. The exact determination of all these changes can be done by a computer chemical speciation program, for example MINEQL, or the CO2SYS algorithms that are tailored for the key variables of the CO_2 system in seawater. For the reverse respiration/mineralization (reverse of Eq. 1), all the above applies in opposite direction.

Please notice all the above is expressed in units yet to be defined. For example, for realistic photosynthesis in a surface water during one day, some 100-fold to 10-fold lower number would apply in units of µmol.kg^{-1}

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seawater. In other words, a daily decrease in ambient seawater of 1.06 μmol.kg^{-1} DIC is accompanied by a decrease of 0.16 μmol.kg^{-1} nitrate and a decrease of 0.01 μmol.kg^{-1} phosphate.

In summary, there is common agreement that photosynthesis/respiration does on the one hand via uptake/release of nitrate affects Oceanic Alkalinity. On the other hand, via uptake/release of DIC there is a major reshuffle among the suite of ions in Titration Alkalinity. Finally, the uptake/release of phosphate yields a relatively much smaller effect in the re-arrangement of the suite of ions in Titration Alkalinity.

2.3. Perceived interactions of dissolved phosphate with Oceanic Alkalinity

This sub-chapter is one of two pivotal sections – the other pivotal section is Sect. 4.1.2. on the assimilation of sulphate by biota. Briefly there are in the literature two competing (Popper, 1963) or actually opposing, hypotheses on whether or not the concentration of dissolved phosphate, and its changes due to biological uptake or release (Eq. 1), does affect the value of Oceanic Alkalinity, as follows:

- Hypothesis 1 is that dissolved phosphate does not affect Oceanic Alkalinity. This hypothesis is supported by the authors and as such already part of the current texts.
- Hypothesis 2 is that dissolved phosphate does affect Oceanic Alkalinity. This hypothesis is presented below.

Wolf-Gladrow et al. (2007) in their sub-section 5.4. stated that uptake/release of phosphate causes a corresponding change of Oceanic Alkalinity, as follows:
"Uptake of 1 mole of phosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}) by algae in accordance with the nutrient-H$^+$ -compensation principle increases alkalinity by 1 mole per mole P."
Presumably this statement is inspired by the article of Chen (1978) given the introductory sentence of a subsequent sub-section 5.7. of Wolf-Gladrow et al. (2007), as follows:
"Following Chen (1978) we will now express the change of alkalinity as a function of the amount of $CaCO_3$ precipitation, ΔCa (mol), and amount of particulate organic matter produced (measured in units of POP = Particulate Organic Phosphorus, mol P, or PON = Particulate Organic Nitrogen, mol N)."
Indeed Chen (1978) had argued, as described in our above Sect. 2.1.2., that for the reverse process of decomposition, the release of phosphate changes Oceanic Alkalinity with 1 μmol.kg^{-1} for each 1 μmol.kg^{-1} phosphate. This together with the commonly agreed change of Oceanic Alkalinity with 16 μmol.kg^{-1} for every 16 μmol.kg^{-1} nitrate would then lead to an overall change of Oceanic Alkalinity with 17 μmol.kg^{-1} for the decomposition of 106 moles organic matter (as per Eq. 1). However, Wolf-Gladrow et al. (2007) presumably have overlooked the subsequent article by Chen et al. (1982) that rejects, thus effectively retracts, the previous suggestion that uptake/release of phosphate does affect Oceanic Alkalinity of Chen et al. (1978). This most relevant part of the Chen et al. (1982) article is described in the above Sect. 2.1.2.

3. On Alkalinity interactions with reduced chemical species

3.1. Chemical thermodynamic equilibrium and deviations thereof

In well oxygenated seawater, the reduced hydrogen sulfide, ammonia and nitrite should not exist according to the laws of chemical thermodynamics. However as result of biological processes, sulfide or ammonia or nitrite can be introduced in the ambient seawater and may exist as short-lived intermediates. When avoiding exposure of a seawater sample to the high O_2 atmosphere, and doing rapid determinations quickly after sampling, these reduced forms may be found, occasionally in the samples from the biological active upper euphotic zone, and usually in the oxygen minimum zone. The more intense such minimum zone is, for example in the Northeast Pacific Ocean (Fig. 1), the more one might expect to find one or more of such reduced constituents.

However, when a collected seawater sample is stored some time and then being analyzed by Titration Alkalinity, there is a risk that the reduced constituents which originally were present and also quickly analyzed, have in fact become oxidized due to exposure to atmospheric oxygen in the shipboard laboratory. If so, then the insertion of the independently (quickly stabilized) measured value(s) of sulfide, ammonia, nitrite in the complete Eq. (24) of Titration Alkalinity would yield a false result. One way to avoid such discrepancy is by collecting the seawater sample in a sub-sample bottle without any air headspace, akin to collecting samples for dissolved oxygen, and next store the sample and titrate the sample all under an oxygen free atmosphere.

For truly anoxic seawater basins, for example the deeper waters of the Black Sea, the concentrations of sulfide and ammonia are much higher and would be more significant in the Titration Alkalinity Eq. (24).

3.2. From conditions of oxygen-replete to low oxygen to suboxic and anoxic conditions

Within the oxygen replete to low oxygen regions, dissolved oxygen is always detectable. In deep, poorly ventilated basins (e.g., Cariaco Trench, Black Sea) suboxic and anoxic conditions exist. Within suboxic zones neither dissolved oxygen nor dissolved sulfide is detectable (Schijf et al., 1991). Anoxic conditions are devoid of oxygen and comprise detectable sulfide.

3.2.1. Nitrite versus Nitrate

It has been suggested that dissolved nitrite may also contribute to Titration Alkalinity (Wolf-Gladrow et al., 2007). Therefore, at least in theory, nitrite would become part of the overall Eq. (24) of Titration Alkalinity.

At the pH=~8.0 of natural surface seawater both nitrate and nitrite are fully dissociated strong anions. Shipboard analyses of dissolved nitrate by spectrophotometry in one channel of an autoanalyzer may also comprise a small amount of the dissolved nitrite. The ensuing overall nitrate as next inserted in the Oceanic Alkalinity Eq. (20) in fact is the sum of nitrate plus occasional trace amount nitrite. Moreover, nitrite in a subsample can be determined independently after the method of Strickland and Parsons (1968).

At the pH=4.5 endpoint of the alkalinity titration, a small portion of the dissolved nitrite (NO_2^-) has absorbed a proton and thus formed HNO_2. Presumably the equilibrium is defined as follows:

$$K = 10^{-3.3} = [NO_2^-]\,[H^+] \,/\, [HNO_2] \qquad (38)$$

Then at pH = 4.5 hence $[H+] = 10^{-4.5}$ one derives $[NO_2^-]/[HNO_2] = 10^{1.2} = 16$
Thus, at pH = 4.5 the percentage $[HNO_2]$ is merely 6 %, the remaining 94% remains to be the fully dissociated $[NO_2^-]$ anion. This appears to be in fair agreement with the nitrite Bjerrum plot of Wolf-Gladrow et al. (2007).

The occasional nitrite concentrations in the surface ocean typically are in the 0 - 0.3 µmol kg^{-1} range. At upper limit 0.3 µmol kg^{-1} the 6% HNO_2 after titration to pH = 4.5 would be merely 0.018 µmol kg^{-1}. The corresponding proton consumption is well below the precision ±1.5 µmol kg^{-1} of the Titration Alkalinity. Therefore, nitrite does not significantly affect the value of Titration Alkalinity.

This being stated, in the suboxic zone in the ~50-100 m depth range of the Black Sea, the nitrite is also very low, except at their one station 10 (27 June 1988) that shows two maxima of ~0.5 and ~0.7 µmol kg^{-1} (Codispoti et al. (1991). Here the contribution of nitrite to Titration Alkalinity would be higher in the order of 0.03 to 0.04 µmol kg^{-1} but still below the precision of the Alkalinity A_T ±1.5 µmol kg^{-1}. Moreover, all the above assumes that between sampling and the titration for alkalinity, none of the nitrite has meanwhile become oxidized to nitrate.

3.2.2. Contribution of sulfide to Titration Alkalinity

For truly anoxic seawater basins, for example the deeper waters of the Black Sea, the concentrations of sulfide are detectable ($H_2S > 0$) and can in fact be very high and would be more significant in the Titration Alkalinity equation. In the Black Sea, the concentration of sulfide steadily increases with depth to values more than 400 µmol.kg^{-1} at ~2100 m depth (Luther, 1991). Investigations of Alkalinity in the Black Sea in 1988 (Goyet et al., 1991), 2001 (Hiscock and Millero, 2006) and 2010-2011 (Kondratiev et al., 2017) provide further insights in the interactions of Alkalinity with the dissolved nutrients and sulfide.

3.2.3. Contributions of ammonia to Titration Alkalinity

For ammonia the relative abundance of the two forms NH_4^+ and NH_3 is prescribed by the equilibrium constant pK=9.3 (Dickson, 1981). In natural seawater at typical pH = ~8 almost all the ammonia exists in the NH_4^+ state, but a small (about 5 %) portion in the NH_3 state. Upon acid titration, each NH_3 combines with a proton such that all ammonia is in the NH_4^+ state at the end point pH = 4.5 of the titration. The very small number of protons absorbed in this conversion of NH_3 to NH_4^+ does contribute to the total Titration Alkalinity. For example, at an overall ammonia concentration of 1 µmol.kg^{-1}, the contribution of proton assimilation by NH_3 to overall Alkalinity would be about 0.05 µmol.kg^{-1}. This is negligible versus the about 1.5 µmol.kg^{-1} analytical error of Titration Alkalinity. In a very extreme oxygen minimum zone, the overall ammonia concentration may be as high as about 10 µmol.kg^{-1} (Bristow et al., 2016). Here the contribution of proton assimilation by NH_3 to overall Alkalinity would be about 0.5 µmol.kg^{-1} that still is less than the analytical error of Titration Alkalinity. Within the anoxic deep water column of the Black Sea, the dissolved ammonia steadily increases with depth to about 40 µmol.kg^{-1} at 350m depth (Codispoti et al., 2011) and ultimately more than 90 µmol.kg^{-1} at the greatest depth of about 2000m (Friederich et al., 1990). Obviously in these extreme anoxic conditions, ammonia does play a more significant role in the determination of Titration Alkalinity.

3.2.4. Contributions of silicate to Titration Alkalinity

The dissolved silicate system does not belong to the redox affected constituents of this Chapter 3, nevertheless here briefly mentioned for sake of completeness. In natural seawater at typical pH = ~8 almost all exists in the neutral $Si(OH)_4$ state, but a very small concentration in the $SiO(OH)_3^-$ state. Upon acid titration the latter small amount is completely converted to the $Si(OH)_4$ state at the end point pH = 4.5 of the titration. The small amount of protons absorbed in this conversion of $SiO(OH)_3^-$ to $Si(OH)_4$ contributes to the total Titration Alkalinity. The concentration range of total silicate is from <1 µmol.kg^{-1} in oligotrophic seawater to about 170 µmol.kg^{-1} in intermediate depth waters of the North Pacific Ocean (Table 2). In natural ocean water, the $SiO(OH)_3^-$ state amounts to about 1% of the total dissolved silicate (De Baar and Gerringa, 2008). Thus at 1 µmol.kg^{-1} total dissolved silicate, the 1% $SiO(OH)_3^-$ state would at the pH=4.5 end of the alkalinity titration have consumed about 0.01 µmol.kg^{-1} protons. This is negligible compared to the ~ 1.5 µmol.kg^{-1} accuracy of Titration Alkalinity. Similarly, at the upper total silicate concentration of 170 µmol.kg^{-1} the effect would be about 1.7 µmol.kg^{-1} that is just about in the range of accuracy of Titration Alkalinity. It is commonly agreed that when using CO2SYS to calculate all chemical forms of the DIC pool, one would be able to accurately take into account the silicate system by entering the total dissolved silicate concentration as measured independently in the seawater sample.

4. The concept of conservative components of salinity and deviations thereof

The general concept of the conservative components of salinity (Table 1) is a cornerstone in oceanography. Yet upon looking in detail, several deviations are conceivable, some of which are discussed below.

4.1. Interactions of dissolved sulphate with Alkalinity

Dissolved sulphate is a strong anion in natural seawater (pH=~8) but absorbs some protons at the pH=4.5 endpoint of Titration Alkalinity. The strong anion [SO_4^{2-}] exists as one of the conservative components of the salinity of seawater (Table 1), such that for total dissolved sulphate:

$$[SO_4^{2-}] + [HSO_4^-] = 0.02824 \text{ mol.kg}^{-1} \qquad (39)$$

For the equilibrium

$$[HSO_4^-] = [H^+] + [SO_4^{2-}] \qquad (40)$$

the equilibrium constant is

$$K_S = [H^+]_F\,[SO_4^{2-}]\,/\,[HSO_4^-] \qquad (41)$$

where the hydrogen ion concentration is expressed on the “free” scale. At S=35 and T=25ºC the handbooks (DOE 1994; PICES, 2007) give the value

$$\ln (K_S/k°) = -2.30 \text{ such that } (K_S/k°) = 0.1003.$$

At the pH=~8 of natural surface seawater and [SO_4^{2-}] = 0.02824 mol.kg^{-1} one derives from Eq. (41) that

$$[HSO_4^-] = \{[10^{-8}]\,[0.02824]\}/\,(0.1003) = 0.282\ 10^{-8} \text{ mol.kg}^{-1} = 2.82\ 10^{-3}\ \mu\text{mol.kg}^{-1}$$

This 0.282 10^{-8} mol.kg^{-1} is negligible such that at natural pH=~8 in principle all sulphate is indeed [SO_4^{2-}] = 0.02824 mol.kg^{-1}. Moreover, the very low 2.82 10^{-3} µmol.kg^{-1} is well below the accuracy of 1.5 µmol.kg^{-1} of Alkalinity and hence in natural seawater the sulphate is to be treated as a fully dissociated strong anion, and as such part of the Eq. (20) of Oceanic Alkalinity.

This being stated, the situation is different for Titration Alkalinity at the pH=4.5 endpoint of the titration. Here one similarly derives from the above Eq. (41) that with [H^+] = $10^{-4.5}$ = 3.2 10^{-5} one obtains

$$[HSO_4^-] = \{[3.2\ 10^{-5}]\,[0.02824]\}/\,(0.1003) = 0.90\ 10^{-5} \text{ mol.kg}^{-1} = 90\ \mu\text{mol.kg}^{-1}$$

This is well above the accuracy of Titration Alkalinity. In other words, a small (~0.3 %) portion of the sulphate has absorbed some protons and this is accounted for by the term [HSO_4^-] in the overall Eq. (24) of Titration Alkalinity. In summary, all chemical oceanographers fully agree that sulphate is a strong anion in natural seawater (pH=~8) but has absorbed some protons at pH=4.5.

4.1.1. Perceived effect on Oceanic Alkalinity due to the assimilation of sulphate by biota

The famous Redfield Eq. (1) comprises merely three bio-essential nutrient elements, namely C, N and P. Among these the oceanic distributions of dissolved nitrate and phosphate do directly and completely reflect this biological uptake and release. For carbon, this is more complicated (see Sect. 1). Moreover, the major group of diatom algae utilizes dissolved Si, such that the oceanic distribution of dissolved Si is also nutrient-type, ranging from zero in oligotrophic surface waters to high values in deep ocean waters and in the Southern Ocean.

These stoichiometric relationships of C/N/P/Si are based on the oceanic distributions of dissolved constituents in seawater. An alternative or complementary approach would be to collect samples of marine plankton and determine the C/N/P/Si composition of this plankton. However, this plankton composition is known to exhibit a very wide variability of C/N/P/Si stoichiometry, not only because of the wide variability of different plankton species each having their own evolutionary history of the C/N/P/Si stoichiometry, but also because latter stoichiometry of each species also varies as function of growth conditions, notably the irradiance (Finkel et al., 2006). Collecting and analyzing hundreds or thousands of plankton samples will inevitably yield a wide range of C/N/P/Si stoichiometry, hence upon averaging, a very wide standard deviation of such average value. In contrast, the dissolved constituents DIC, nitrate, phosphate (and silicate), have due to processes of oceanic mixing serving as an averaging tool, already arrived at mutual stoichiometry (Eq. 1) that is very accurate with very low standard deviations.

For the assimilation of sulphate into plankton cells, the resulting elemental sulfur content of marine plankton also shows a wide variability (Finkel et al., 2006). This and the similar variability of the phosphorus content together yield a wide variability of the elemental S:P ratio in plankton (Finkel et al., 2006).

In addition to these major bio-essential chemical elements C, N and P, there are six bio-essential trace metal elements Fe, Mn, Zn, Co, Cu, Ni and at least one trace element Cd that is utilized by some biota (De Baar et al., 2017b). None of these six bio-essential trace elements and element Cd is deemed to affect the value of Oceanic Alkalinity. This being stated, the oceanic distributions of dissolved Zn and Cd closely reflect the distributions of nutrient-type elements Si and P, respectively (Middag et al., 2018, 2019). For dissolved Cu and Ni, the relationships with major nutrients are less rigorous, likely due to other processes being at play as well. Finally for the dissolved Fe and Mn, while pivotal bio-essential trace elements, there are several processes that interfere with simple relations of dissolved Fe or Mn with dissolved major nutrients nitrate, phosphate, silicate.

One or several of the major elements constituting the salinity of seawater (Table 1), may also be involved in biological uptake/release. However, the very high background concentration of such major element would prevent to discern any such biological effect in its total concentration in seawater. Notably, when one would take the hypothesized elemental composition ratio S:P of phytoplankton as the given value S:P = 2.4 after Wolf-Gladrow et al. (2007), then for all oceanic waters the range of changes of the concentration of dissolved sulphate would be 2.4-fold the range of the concentrations of dissolved phosphate. Latter range of dissolved phosphate values being in between 0 and 3.3. μmol.kg^{-1} (Table 2) would imply a parallel range of biology-driven dissolved sulphate concentration changes in between 0 and (2.4 x 3.3) = 7.9 μmol.kg^{-1}.

This approach is problematic for the following reasons. Firstly, the wide variability of elemental sulfur content of marine plankton and the similar variability of their phosphorus content, together yield a wide variability of the elemental S:P ratio in plankton (Finkel et al., 2006). Secondly, the assumed S:P = 2.4 value of Wolf-Gladrow et al. (2007) is well above the range $0.060 < (S{:}P) < 1.689$ of the geometric mean values reported by Finkel et al. (2006; their Table 1) for various plankton species at various irradiance levels. Moreover, for each geometric mean value, Finkel et al. (2006) report standard deviations ranging from 1.2% to 46.8%. Thirdly, the background concentration of total dissolved sulphate as function of the salinity S is 0.02924 S/35 mol.kg^{-1}. For standard salinity S=35 this amounts to 29240 μmol.kg^{-1} total dissolved sulphate in seawater. Therefore, the mentioned hypothesized biology-driven sulphate concentration changes would amount to a range from 0 to 0.027 % of the total dissolved sulphate in seawater. To the best of our knowledge, there currently is not available a method of measurement of total dissolved sulphate in seawater with a precision that is adequate to detect with a precision better than this 0.027 %. In other words, the hypothesized biology-driven sulphate concentration changes are not verifiable because undetectable. Therefore, any hypothesized change of the absolute value of Oceanic Alkalinity due to biological uptake/release of dissolved sulphate cannot be assessed.

In other words, the key role of dissolved nitrate in Oceanic Alkalinity, as well as the minor role of dissolved phosphate in Titration Alkalinity, can be discerned from the measured values of the concentrations of dissolved nitrate and phosphate, respectively. In contrast, the hypothesized role of biology-driven changes of dissolved sulphate in Oceanic Alkalinity cannot be discerned.

Last but not least, throughout the existing literature the Oceanic Alkalinity has always been defined without taking into account this more recently suggested (Wolf-Gladrow et al., 2007) effect of biological uptake/release of sulphate. Thus, when one is assuming such effect on Oceanic Alkalinity as per one or another assumed S/P elemental uptake ratio, one must use an adjusted notation, for example Alkalinity$_{\text{biological-sulphate-adjusted}}$ in order to make a clear distinction with the thus far common definition of Oceanic Alkalinity in the existing literature.

4.2. Would magnesium or strontium assimilation into phytoplankton affect Oceanic Alkalinity?

The key molecule chlorophyll *a* for photosynthesis by all plants comprises the element Mg as its central atom. Marine plants, notably single cell marine algae, assimilate Mg from ambient seawater, and upon decomposition of the plant material, the Mg is dissolved again in seawater. Each molecule of chlorophyll *a* comprises one Mg atom. Jakobsen and Markager (2016) mention a wide range of carbon to chlorophyll *a* ratio values (C:Chl *a*; weight:weight) from 6 to 333 in the (until 2016) existing literature. For their own suite of 7578 plankton samples of coastal seawater, Jakobsen and Markager (2016) report C:Chl *a* values ranging from 15 to 96. Here assuming an overall range from 6 to 333, and given the molar mass of 893.509 $g \cdot mol^{-1}$ of chlorophyll *a* and the atomic mass 12 of element C, and 1 atom Mg per molecule chlorophyll *a*, one derives that the Mg:C elemental ratio ranges from 0.04 10^{-3} to 2.2 10^{-3} in marine plankton. Combination with the Redfield Eq. (1) yields an Mg:P ratio of uptake or release ranging from 4.2 10^{-3} to 233 10^{-3} by marine phytoplankton. Given the oceanic concentration range of dissolved phosphate from 0 to 3.3 $\mu mol.kg^{-1}$, the corresponding biological removal or addition of dissolved Mg to seawater would be in the 0 to 0.770 $\mu mol.kg^{-1}$ seawater range. The highest value for uptake/release of 0.770 $\mu mol.kg^{-1}$ seawater is below the commonly reported accuracy of Alkalinity of ±1.5 $\mu mol.kg^{-1}$. In other words, even the maximum assumed effect of biological uptake/release of Mg is negligible with regards to Oceanic Alkalinity. Moreover, such biological assimilation of Mg is not verifiable. The corresponding maximum decrease/increase of dissolved Mg in ambient seawater at 0.77 10^{-6} $mol.kg^{-1}$ is not discernible versus the very high background Mg concentration of 0.053 $mol.kg^{-1}$ in seawater. In summary, akin to the above case for assimilation of sulphate, any effect on Oceanic Alkalinity is insignificant.

The skeletons of the protozoan Acantharea are made of celestine, commonly known as celestite, a mineral consisting of strontium sulphate ($SrSO_4$). Formation/dissolution of celestite would in theory cause a minor decrease/increase of salinity (Table 1), but presumably without a conceivable effect on Alkalinity because the electric charges of Sr^{2+} and SO_4^{2-} would compensate one another, this apart from the likelihood that the separate effect of either Sr^{2+} or SO_4^{2-} would likely be well below the accuracy of Alkalinity. However, other processes are known to also affect the Sr content of seawater.

4.3. External sources and sinks for the major constituents of seawater

Seawater of the world ocean basins forms external sources and sinks of all chemical elements. For the water itself and the dissolved major elements comprising the salinity (Table 1), there are (i) major supplies by rivers into the oceans, as well as (ii) various low temperature exchanges with sediment deposits, as well as (iii) high temperature exchanges at hydrothermal vents. When these external sources and sinks are significant relative to the mixing time within one ocean and/or the interoceanic mixing time between major oceans, then regional deviations do occur from the original concept of uniform proportions of the major elements comprising salinity, and as a result, regional deviations of Oceanic Alkalinity. For example, the high temperature (~350 °C) seawater emanating from hydrothermal vents at the 21° N East Pacific Rise was found to be completely depleted of Mg, but enriched in Ca (Von Damm et al., 1985). In general, the rate of Mg removal at these hydrothermal systems appears to be more or less compensated by the riverine supply of Mg into the oceans (Chester, 1990). For Ca the riverine supply is deemed to be much higher than the hydrothermal supply. Anyway, these external sources and sinks, as well as the biological processes within the oceans, do give rise to regional deviations from the uniformity concept of salinity, and as a result, deviations of Oceanic Alkalinity.

Recently, Lebrato et al. (2020) reported an excellent community effort on the basis of measured modern seawater Mg:Ca and Sr:Ca ratio values in more than 1,100 samples from 79 research cruises worldwide. This excellent article describes the regional deviations, where indeed riverine supply and hydrothermalism do play a major role, next to ocean biological processes. The interactions with Alkalinity are also discussed and shown very nicely for Ca, Mg and Sr, respectively, in their intriguing Figure 3A.

The original first order approach describing Oceanic Alkalinity as a function of mostly salinity explaining some ~90% of its variations, and formation/dissolution of $CaCO_3$ accounting for some ~10% of its variations, and nitrate uptake/release in photosynthesis/respiration accounting for some ~1% of variations, was and remains to be a cornerstone in ocean science. This being stated, one must be aware of the other processes that, when looking more closely, may lead to regional deviations interfering with the original first order approach.

5. The explicit conservative expression of Alkalinity

5.1. On the usefulness and validity of the explicit conservative expression of Alkalinity

The perceived interactions of the uptake by biota of both phosphate (Sect. 2.3.1.) and sulphate (Sect. 4.1.1.) with Oceanic Alkalinity both are part of an article by Wolf-Gladrow et al. (2007) introducing the concept of the explicit conservative expression of Alkalinity. This overall concept does not necessarily affect the perceived roles of assimilation of phosphate and sulphate, but here it is hoped that by looking at this explicit conservative expression, we would be able to shed some light on these issues of the perceived interactions of the uptake by biota of both phosphate and sulphate with Oceanic Alkalinity.

Wolf-Gladrow et al. (2007) have combined the Oceanic Alkalinity equation representing the strong cations and strong anions,

$$\text{Oceanic Alkalinity} = [Na^+] + [K^+] + 2{\cdot}[Ca^{2+}] + 2{\cdot}[Mg^{2+}] + [Sr^{2+}] – [Cl^-] – 2[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] \quad (20)$$

with the Titration Alkalinity equation of the weak cations and weak anions,

$$\begin{aligned} Alk_{Titration} = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] \\ & + [HS^-] + 2[S^{2-}] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (24) \end{aligned}$$

This equation (24) is exactly as the original equation given by Dickson (1981). For this Titration Alkalinity equation, the version of Wolf Gladrow et al. (2007) is their equation (28) here given number (42) as follows:

$$\begin{aligned} Alk_{Titration} = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] \\ & + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - [HNO_2] \quad (42) \end{aligned}$$

This Eq. (42) deviates from the above Eq. (24) by on the one hand addition of the term - $[HNO_2]$ and on the other hand omission of the term + $2[S^{2-}]$ and notation $[H_3SiO_4^-]$ instead of notation $[SiO(OH)_3^-]$. This latter difference of notation is deemed trivial and further ignored. The additional term - $[HNO_2]$ is, as explained in Sect. 3.2.1., deemed to be insignificant.

Some authors also have added a handful of extra terms the so-called ellipses, that stand for additional minor acid or base species that are either unidentified or present in such small amounts that they can be safely neglected. We have left out such ellipses as they are taken to be meaningless and merely adding confusion. Otherwise, it is realized that long time there has been some awareness of the caveat of conceivable interferences by organic molecules (see below Sect. 6.2.), this perhaps having been the rationale for these ellipses.

The combination of Oceanic Alkalinity Eq. (20) with their version of Titration Alkalinity, yields what Wolf-Gladrow et al (2007) call the explicit conservative expression for total alkalinity, their equation (31) here shown as Eq. (43) as follows

$$\begin{aligned} & [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] +2[Sr^{2+}] + [NH_4^+] + [H^+] – [Cl^-] – 2[SO_4^{2-}] – [Br^-] - [NO_3^-] - [NO_2^-]- [HCO_3^-] - 2[CO_3^{2-}] - \\ & [B(OH)_4^-] - [OH^-] - [HS^-] - [H_3SiO_4^-] - [HSO_4^-] - [F^-] - [H2PO_4^-] - 2[HPO_4^{2-}] - [3PO_4^{3-}] = 0 \quad (43) \end{aligned}$$

Firstly, it is not understood what would be the added value of this explicit conservative equation for Total Alkalinity, because the set of complementary concepts of Oceanic Alkalinity and Titration Alkalinity and their actual Eqs. (20 and 24) are perfectly crystal clear and very useful. Moreover, quite paradoxically in this explicit conservative equation the actual major subject, the Alkalinity, has dropped out. This is akin to an article by Andersen (1837). Secondly, there is again omission of the term + $2[S^{2-}]$ from the original equation of Dickson (1981) that here is our Eq. (24). Thirdly, there is omission of the term - $[HNO_2]$ that was part of their equation (28) as above Eq. (42). Finally, there is addition of the term -$[NO_2^-]$.

When we did ourselves combine the equations (20) and (24), the following equation was obtained:

$$\begin{aligned} & [Na^+] + [K^+] + 2\,[Ca^{2+}] + 2\,[Mg^{2+}] + [Sr^{2+}] – [Cl^-] – 2\,[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] - [HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-] \\ & - [HPO_4^{2-}] - 2{\cdot}[PO_4^{3-}] - [SiO(OH)_3^-] - [HS^-] - 2[S^{2-}] - [NH_3] + [H^+] + [HSO_4^-] + [HF] + [H_3PO_4] = 0 \quad (44) \end{aligned}$$

However, when we now look into what Wolf-Gladrow et al (2007) call the explicit conservative expression for total alkalinity, their above copied equation (31) here Eq. (43), we find differences as follows:

This work Eq. (44)	Wolf-Gladrow et al. (2007), here Eq. (43)
- $[NH_3]$	+ $[NH_4^+]$
	- $[NO_2^-]$
- $[HPO_4^{2-}]$	- $2[HPO_4^{2-}]$
- $2{\cdot}[PO_4^{3-}]$	- $3[PO_4^{3-}]$
+ $[H_3PO_4]$	
	- $[H_2PO_4^-]$

Next Wolf-Gladrow et al. (2007) stated that they are able to add terms to both sides of their explicit conservative equation until Dickson's expression for total alkalinity appears on the right-hand side of the equation and produces the left-hand side as their equation (32). To reproduce this using their equations (31) and (28), here Eqs. (42) and (43), respectively, then the following equation is the initial result:

$$\begin{gathered}[Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] – [Cl^-] – 2[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] \\ - [NO_2^-] + [HF] + [NH_4^+] + [NH_3] + [H_3PO_4] - [H_2PO_4^-] - [HPO_4^{2-}] - [PO_4^{3-}] = \\ [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] \\ − [H^+] − [HSO_4^-] − [HF] − [H_3PO_4] - [HNO_2] \qquad (45)\end{gathered}$$

Firstly, what now appears on the left-hand side deviates from our Eq. (20) truly representing the strong cations and strong anions. All the terms after the nitrate term are the deviations, thus the whole suite as follows

$$- [NO_2^-] + [HF] + [NH_4^+] + [NH_3] + [H_3PO_4] - [H_2PO_4^-] - [HPO_4^{2-}] - [PO_4^{3-}]$$

appears but in fact should not be there (except but merely theoretical, for the - $[NO_2^-]$ term as explained below)

Please notice their equation (32) actually comprises also the statements given below their (32) on totals phosphate, ammonia, sulphate, fluoride. This is different from our understanding.

Thus, formulating their equation (32) is not only by firstly adding terms to both sides of the equation until the Dickson expression for total alkalinity appears on the right-hand side, but also by secondly substituting terms by totals phosphate, ammonia, sulphate, fluoride as defined below their equation (32). When for the latter substitutions one now does the reverse, and in their equation (32) replaces the totals by their individual components as defined in the text below their (32), then the following complete version of their equation (32) appears as the following equation

$$\begin{gathered}[Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] – [Cl^-] – 2[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] + [HF] - [H_3PO4] \\ - [H_2PO_4^-] - [HPO_4^{2-}] - [PO_4^{3-}] + [NH_4^+] + [NH_3] + 2[HSO_4^-] - [NO_2^-] - [HNO_2] = TA_{ec} \qquad (46)\end{gathered}$$

Now compare this with our equation

$$\text{Oceanic Alkalinity} = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [Sr^{2+}] – [Cl^-] – 2[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] \qquad (20)$$

and inevitably one must conclude that all the following extra terms have been added by Wolf-Gladrow et al. (2007):

$$+ [HF] - [H_3PO4] - [H_2PO_4^-] - [HPO_4^{2-}] - [PO_4^{3-}] + [NH_4^+] + [NH_3] + 2[HSO_4^-] - [NO_2^-] - [HNO_2]$$

This is incomprehensible (except but merely theoretical, for the added nitrite terms as explained below). Otherwise also notice that in the left-hand part of this Eq. (46) there is the term - $[H_3PO_4]$ with a negative sign as opposed to the positive sign of the term + $[H_3PO_4]$ in the left-hand part of Eq. (45).

With regards to the discrepancies for phosphate in Eq. (46), these may, or may not, relate to the coefficients of the phosphate species in their equation (31), here Eq. (43). When realizing that at the pH = 4.5 endpoint of the alkalinity titration, that in essence all (> 0.999867 % as per above Sect. 2.2.2.) phosphate then exists in the $[H_2PO_4^-]$ state, the coefficients in their (31) seem to be quantified versus an endpoint $[H_3PO_4]$ state. These deviating coefficients may, or may not, explain the various discrepancies. This apart from the noted negative versus positive signs of the terms $[H_3PO_4]$ in Eqs. (46) and (45), respectively.

Quite uniquely Wolf-Gladrow et al. (2007) introduced consideration of nitrite with regards to Alkalinity. As explained in Sect. 3.2.1., the routine measurements of dissolved nitrate do include any trace amount of dissolved nitrite. Moreover, the nitrite is shown to be irrelevant versus the accuracy of the Alkalinity measurements. Therefore, the additional terms - $[NO_2^-]$ - $[HNO_2]$ in Eq. (46) are theoretically not incorrect, but otherwise irrelevant and only leading to further confusion. Finally, for the other deviating extra terms + [HF] as well as + $[NH_4^+]$ and + $[NH_3]$ in Eq. (46) we have no clue.

Wolf-Gladrow et al. (2007) do not provide any indication on the actual concentration values, let alone the relative importance of such values, of the various variables. For example, it is well known that the concentrations of the $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$ are highly significant for the value of Titration Alkalinity, whereas the various species of phosphate are all together hardly significant (Sect. 2.2.2). This is even more true for nitrite.

The concept of Alkalinity in seawater does together with other dissolved entities DIC, nitrate, phosphate, silicate belong to the domain of dissolved Tracers in the Sea (Broecker and Peng, 1982). Within this seawater domain an overall neutral electric charge of seawater does exist and is to be obeyed in the mathematic equations among these dissolved tracers in the sea (see Sect. 1.2.). This is verifiable on the basis of the actually measured dissolved variables in seawater. In contrast, the article by Wolf-Gladrow et al. (2007) largely focused on the biomass domain with an assumed requirement of overall neutral electric charge balance of the plankton biomass.

The latter various neutral charge balance reasonings for marine plankton are not necessarily valid, and also not necessarily all verifiable.

5.2. Application in another article

More recently, a theoretical study (Humphreys et al., 2018) comprises in its Table 1 a coefficient **q** with regards to Alkalinity A_q for autotrophic production with a listed value +0.21, as well coefficient q with regards to Alkalinity A_q for remineralisation of -0.21. These are listed together with parallel factors -1 and +1, respectively, for C**q**, the latter representing Dissolved Inorganic Carbon (DIC). With regards to Alkalinity A_q these factors +0.21 and -0.21 are mistaken. Given the canonical Redfield ratio C:N:P = 106:16:1 and the assumed (after Wolf-Gladrow et al., 2007) theoretical effect of S uptake, the value 0.21 obviously is based on the simple calculation 21.8/106 = 0.2057 = ~0.21 where the value 21.8 stands for the confusing if not mistaken concept that Oceanic Alkalinity is affected by planktonic uptake of nitrate+phosphate+sulphate with a factor (16+1+4.8) = 21.8 after Wolf-Gladrow et al. (2007). Firstly, the uptake of phosphate does not affect Oceanic Alkalinity (see above Sect. 2.3.) and hence is mistaken by Humphreys et al. (2018). Secondly, the assumed effect of sulphate uptake on Oceanic Alkalinity deviates from the definition of Alkalinity in all the literature thus far, and would require a tailored re-definition, i.e., $\text{Alkalinity}_{\text{biological-sulphate-adjusted}}$ (see Sect. 4.1.1.) in order to make a clear distinction with the thus far common definition of Alkalinity in the existing literature as well as the future literature in years to come. Finally, the correct factor for effect on Oceanic Alkalinity due to uptake by plankton into organic biomass is 16/106=0.15 in accordance with only the uptake of nitrate as per the Redfield stoichiometry (1), where NO_3^- is a strong anion.

6. Discussion

6.1. General laws versus variability and the contributions of scientific progress

Unraveling the biogeochemistry of the world oceans is literally a "*mer a boire*". One major objective is to extract general laws of biogeochemistry from the real measurements of dissolved substances in the world oceans (Fig. 1). However, there is always natural variability that interferes with this in itself laudable objective. Notably the famous equation of Redfield, Ketchum and Richards (our Eq. 1) describes averages and hence must be seen as a canonical equation. As a result of more, and more accurate, measurements of many seagoing expeditions, newer versions of this Eq. (1) with different numerical values for the stoichiometric coefficients have been published in the literature. Similar developments also took place for Alkalinity.

The stoichiometric constants (i.e., 106, 16, 1, -138) in Eq. (1), were at the time largely based on concentrations measured mostly in the North Atlantic region. Since then, variations in ocean distributions of, for example, nitrate and phosphate, and the causes thereof have been discussed on the basis of then available larger more worldwide datasets (Fanning, 1992; De Baar et al., 1997). Significant adjusted values of the stoichiometric constants have been derived and advocated (e.g., Anderson and Sarmiento, 1994), as reviewed by Sarmiento and Gruber (2006) and others. However, for the key questions of the current paper this is not at all an issue.

Quite fortunately, the processes of physical mixing in the ocean interior tend to lead to what can be seen as factual averaging of concentration values. The remarkable uniformity of the salinity of seawater is the prime or most extreme example of this 'averaging-by-mixing' effect. This is for the conservative constituents of salinity. For the non-conservative DIC, Alkalinity, major nutrients and many other biogeochemical tracers this 'averaging-by-mixing' still is very helpful. As a result, an ocean section of some 50 hydrographic stations with some 24 sampling depths in the water column from North to South in a major ocean does yield a dataset that is deemed to be highly representative for all waters in the same ocean that were not really sampled (for example Campbell, 1983; Middag et al., 2018, 2019). Therefore, GEOSECS (see Supplementary Material S2) and nowadays GEOTRACES (www.geotraces.org) and GO-SHIP (Sloyan et al. 2019) do provide highly representative cross-sections of biogeochemical tracers in the world oceans.

6.2. Caveats of Alkalinity

One major, if not the major, rationale for defining Oceanic Alkalinity and measurements of Titration Alkalinity, is that by combination with one other measurable variable (DIC or pCO_2 or pH) of the oceanic carbon cycle, one is able to derive the concentrations of the key constituents [CO2*], $[HCO_3^-]$ and $[CO_3^{2-}]$ of the DIC pool in seawater. Akin to many other concepts in science, there are caveats with the concept of Alkalinity.

One caveat is that regional deviations do occur from the original concept of uniform proportions of the major elements comprising salinity. As a result, regional deviations will occur of Oceanic Alkalinity (see Sect. 4.4.). To the best of our knowledge, thus far there have been no studies of the CO_2 system that also have taken into account such regional deviations from the concept of uniform proportions of the major elements comprising salinity. Notably for assessments of internal consistency of 3-4 measured CO_2 system variables (DIC, Titration Alkalinity, pCO_2, pH) this would perhaps resolve some apparent inconsistencies. However this would require additional and very accurate measurements of for example the elemental ratio values Mg:Ca and Sr:Ca after Lebrato et al. (2020). Apart from the huge additional effort, this would also bring additional variables into assessments of internal consistency, such that by additional error propagation, the overall uncertainty of an assessment would not necessarily improve.

Another caveat is that in the acid titration procedure for determination of Titration Alkalinity, there would occur interferences due to dissolved organic moieties acting as proton acceptors (see Supplementary Material S3). This has been reported and discussed for natural seawater samples (Hernández-Ayon et al., 2007; Kim and Lee, 2009; Yang et al., 2015; Ko et al., 2016; Kerr et al., 2021; among others). Recently, Sharp and Byrne (2021) reported a hitherto undescribed excess alkalinity component in Certified Reference Materials (CRMs) for oceanic CO_2 measurements. This component appears to persist despite filtration and ultraviolet treatment of CRMs, suggesting some dissolved organic proton acceptors may not be fully oxidized by the level of UV light applied to CRMs. These CRMs with verified values of Alkalinity and DIC have been produced for the last three decades and have been used routinely in international ocean programs for measurements of Alkalinity and DIC. As such, these CRMs have greatly improved the accuracy and precision of the latter measurements and the ensuing world ocean datasets of DIC and Alkalinity (Lauvset et al., 2021). Unfortunately, these recent findings of excess Alkalinity in the CRMs appear to be a caveat. Matters are complicated also because different batches of CRMs tend to show different values of such excess Alkalinity. Finally, historically there have been previous suggestions of interferences. Nowadays these are deemed to be merely of historical interest. Nevertheless, one example of such historical suggestion is described in Supplementary Material C.

Given these caveats, one conceivable option would be to avoid routine measurement of Titration Alkalinity and instead routinely measure another CO_2 system variable. Notably, an analysis of four recent GO-SHIP repeat hydrography datasets of measured pH and measured Titration Alkalinity is of great interest (Fong and Dickson, 2019). As a matter of fact, the ongoing GO-SHIP program requires for bottle cast samples the measurement of any two of the three variables DIC, Titration Alkalinity, and pH (https://www.go-ship.org/DatReq.html). Whereas accurate determination of DIC by coulometry is deemed to be beyond doubt or dispute, presumably nowadays pH is very promising as a suitable alternative for Titration Alkalinity.

7. Conclusions

Currently, the perceived role of biological uptake or release of dissolved phosphate in the value of Oceanic Alkalinity is often mistaken, which may be due to two articles with great influence in the biogeochemistry community.

The perceived role of biological uptake/release of dissolved sulphate from seawater in the value of Oceanic Alkalinity is not necessarily wrong, in principle, but deviates from how Alkalinity has always been defined in the literature.

The perceived role of biological uptake/release of dissolved sulphate from seawater is not verifiable because it cannot be discerned from measurement of the relatively very large background dissolved concentration value of sulphate.

The inclusion of nitrite in considerations of Alkalinity is strictly theoretically not incorrect, but insignificant versus the accuracy of Alkalinity and hence useless, moreover merely contributing confusion. This also holds for some other very minor species.

Definitions of Oceanic Alkalinity and Titration Alkalinity should only include those relevant major and minor constituents of seawater that are significant with respect to the state-of-the-art precision of Titration Alkalinity. Trace constituents that do not significantly contribute to Alkalinity should be ignored.

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