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Oceanic Alkalinity and Titration Alkalinity: a novel straightforward approach in keeping with common general chemistry

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Abstract

We present novel exact concepts of Oceanic Alkalinity and Titration Alkalinity that are in keeping with common chemistry.

Oceanic Alkalinity is the small difference of the sum of charges of strong cations and the sum of charges of strong anions in seawater. This difference is compensated by the sum of charges of the weak anions minus the sum of charges of the weak cations.

Titration Alkalinity is operationally defined as "*The Titration Alkalinity of a natural water sample is defined as the concentration of all bases able to accept a hydrogen ion at the equivalence point of the carbonic acid system species.*"

Ideally, acid titration of all weak ions would yield a value of total consumption of added hydrogen ions that then would equate perfectly with the net sum of the charges of the strong ions in Oceanic Alkalinity. Unfortunately, some adjustments are necessary. At the equivalence endpoint of the titration, hydrogen ions are also absorbed by small portions of the strong SO_4^{2-} and F^- anions. Additionally, at the endpoint several phosphate anions are not completely neutralized to the neutral H_3PO_4 state. Due to this non-ideal situation, there is an exact difference between Oceanic Alkalinity and Titration Alkalinity:

$$\mathrm{Alk}_{\mathrm{Oceanic}} = \mathrm{Alk}_{\mathrm{Titration}} + 1.021\,[\mathrm{DIP}] - 0.0003966\,[SO_4^{2-}] - 0.010457\,[F^-]$$

or in terms of salinity:

$$\mathrm{Alk}_{\mathrm{Oceanic}} = \mathrm{Alk}_{\mathrm{Titration}} + 1.021\,[\mathrm{DIP}] - 0.3409\,S$$

where DIP is total phosphate. This allows the derivation of Oceanic Alkalinity, that is the pivotal variable to unravel biogeochemical processes in the oceans.

In addition it is shown that upon decomposition of organic matter, the ensuing increase of Dissolved Inorganic Phosphorus does not affect the value of Alkalinity, this resolving the long time confusion in the literature. Finally, because nowadays the concentration of Dissolved Inorganic Carbon is determined independently by coulometry, there is no need anymore for non-linear curve fitting of the complete acid titration curve. Nowadays it suffices to only fit the second part of the titration curve to determine the second equivalence point, this yielding a more straightforward determination of Titration Alkalinity.

Keywords: Oceanic Alkalinity, Titration Alkalinity, Alkalinity concept, carbon system, phosphate, sulfate, fluoride, pH scale

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1. Introduction

The net emission of CO_2 into the atmosphere due to the burning of fossil fuels and deforestation by mankind has led to an increase of the CO_2 contents of air from 280 μatm in the pre-industrial era (before 1780 AD) to 422 μatm (year 2023) (http://www.esrl.noaa.gov/gmd/ccgg/trends/#mlo_full) and is expected to rise further in coming years and decades. This is the major cause for general warming of the atmosphere, land and oceans (IPCC, 2021). 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 total inorganic carbon (Dissolved Inorganic Carbon, DIC) in the oceans does cause major shifts among the various chemical forms within the DIC pool. Most notably, 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, traditionally there have been four key variables that can be measured directly in a 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). Moreover, nowadays the direct measurement of the concentration of the CO_3^{2-} ion is also feasible (Byrne and Yao, 2008; Guallart et al. 2022). When two of these 4-5 variables are measured, then all others can be calculated from such couple. 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.

In the research field of the oceanic carbon cycle, the Alkalinity concept is quite pivotal. Unfortunately, its definition and its use are not unequivocal, which leads to uncertainty. Middelburg et. al. (2020) extensively review ocean alkalinity, buffering and biogeochemical processes. They write that it is important to distinguish between measurable titration alkalinity and charge balance alkalinity. Presumably this is more or less similar to the approach of the distinction between Titration Alkalinity and Oceanic Alkalinity that we will make here. Moreover, Middelburg et al. (2020) mention that in the preceding literature, the various authors describe quite a wide variety of different definitions of Alkalinity versus its underlying dissolved inorganic ionic constituents of seawater.

The complete historical development of the concept of Alkalinity of seawater has been described by Dickson (1992). During the last 150 years there evolved understanding and definitions of the inorganic chemistry in water solution: aqueous solution chemistry. Some, but by no means all, benchmarks are as follows: Svante Arrhenius (1884, 1887) realized that dissolved salts in water dissociate in both positive and negative ions which earned him the 1903 Nobel Prize in chemistry. Søren Sørensen (1909) and contemporaries had introduced the pH scale and methods for the measurement of pH. The Brønsted–Lowry theory is an acid–base reaction theory which was first developed independently by Johannes Nicolaus Brønsted and Thomas Martin Lowry in 1923. The Debye–Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes. The above and further developments have led to the common general chemistry of aqueous solutions. Unfortunately, during that about 150 years period, various concepts and definitions of Alkalinity in seawater became deviant from the the general chemistry of aqueous solutions; in other words, Alkalinity evolved to become a side street of the main chemistry avenue. The major objective of the present article is to provide definitions and concepts of Alkalinity in seawater in order to bring Alkalinity back into mainstream general chemistry.

There is an extensive array of literature on Alkalinity of seawater. For the purpose of the current article, it was deemed prudent to constrain this article more or less in accordance with four considerations:

A) Major objective is to define and describe Alkalinity in seawater in a straightforward approach in keeping with common chemistry. Over the past more than four decades major improvements were achieved, but accompanied by very specialistic concepts and terminology used exclusively within the relatively small community of ocean inorganic carbon cycle specialists. This quite specialistic jargon of a small expert community has proven difficult to use and explain. Here by adhering to common chemistry the aim is to share this more simple approach with a far wider community of scientists and students. Moreover, with regards to pH the aim is to only utilize the most common free pH scale (pH_{FREE}). This aim is inspired also by the article on "The free proton concentration scale for seawater pH" by Waters and Millero (2013). This is to avoid the two very specialistic pH scales (Total scale pH_{Total}, and SeaWater Scale pH_{SWS}; see Supplementary Material S1). These specialistic pH scales as well as the specialistic concepts of arbitrarily established zero level of protons, and proton donors among the seawater constituents, here are avoided.

B) The focus is on the seawater of the world oceans that is uniform in its relative composition (Table 1) and in general well oxygenated. Seawater conditions of low dissolved oxygen to complete anoxia are beyond the focus, but are briefly mentioned in the Supplementary Material S2. Processes (diagenesis) within marine sediments also are beyond the scope.

C) Currently the reproducibility or precision of the analytical determination of Alkalinity in seawater is in the order of ±1 μmol.kg^{-1}. This reproducibility is about 0.04 % of the ambient values of Alkalinity in the world oceans ranging from ~2250 to ~2450 μmol.kg^{-1} (Figure 1). This implies that any theoretical considerations of minor constituents of seawater that have a less than ~1 μmol.kg^{-1} effect on the value of Alkalinity are now deemed to be less significant and in general can be ignored. Obviously, when perhaps in the future the precision will improve, say tenfold to ±0.1 μmol.kg^{-1}, then at that time a next suite of existing very minor constituents should be taken into account.

D) Many excellent studies have been published on the role of the ocean carbon cycle including the Alkalinity. Here our vantage point is from the oceanwide programs where along ocean sections the CO_2 system is determined at many station positions and, in general, at some 24 or more, judiciously chosen sampling depths over the full, say 4-5 km water column depth. In these international hydrographic programs there is much emphasis on precision and accuracy towards optimal internal consistency of the jointly produced overall CO_2 system database. The pioneering Geochemical Ocean Sections (GEOSECS) program in the 1970s (Supplementary Material S3) was followed by several other programs and projects, such as the World Ocean Circulation Experiment (WOCE) in the 1990s, and the Joint Global Ocean Flux Study (JGOFS) with field work in 1989-1998. Nowadays ongoing are the GEOTRACES (www.geotraces.org) and the GO-SHIP programs (www.go-ship.org).

Within seawater there exist several chemical forms of Dissolved Inorganic Carbon, that together are known as the total DIC pool, in the literature also known as Total CO_2 (TCO_2 or C_T). The major biological processes depend strongly on DIC and co-determine its concentration. On one hand, photosynthesis utilizes some of the DIC. On the other hand, respiration or (re)mineralization by bacteria and all animals replenishes the DIC pool. Moreover, the formation and its reverse process dissolution of biogenic calcium carbonate ($CaCO_3$) 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 water circulation. Last but not least, oceanic surface waters exchange CO_2 with the overlying atmosphere, which also affects the DIC pool.

Accurate measurements of a suite of dissolved tracers in seawater is 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), DIC and its counterpart the Alkalinity, dissolved oxygen (O_2) and the 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 generally 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 $CaCO_3$.

2. Dissolved Inorganic Carbon, nitrate, phosphate and the oceanic biological cycle

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

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

after Redfield et al. (1963; see also Supplementary Material S4), where DIP is total dissolved inorganic phosphorus, see eq. 17 below.

DIC in seawater occurs in concentrations varying around 2000-2350 μmol. kg^{-1} seawater (Figure 1; Table 2). DIC can be measured by a coulometric method with accuracy of about 2 μmol.kg^{-1}. Dissolved nitrate and phosphate occur from very low (below detection limit) concentrations in oligotrophic surface waters to more than 40 μmol. kg^{-1} (nitrate) and about 3.3 μmol. kg^{-1} (phosphate) in the oxygen minimum zone (OMZ) of the North Pacific Ocean (Figure 1; Table 2). Overall photosynthesis removes DIC and nitrate and DIP from seawater and its reverse respiration adds it. 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.

DIC is the summation of dissolved CO_2, carbonic acid, bicarbonate ion and carbonate ion (see Box 1). In natural seawater, bicarbonate $[HCO_3^-]$ is dominant, representing ~90% of the DIC pool, followed by carbonate $[CO_3^{2-}]$ representing ~9% and the $[CO_2]_{\text{aqueous}}$ representing merely ~1% of the total DIC. The undissociated carbonic acid $[H_2CO_3]$ occurs in very low abundance (~0.02-0.04 μmol.kg^{-1}) representing ~0.002 % only. The dissolved nitrate in seawater exists in the fully dissociated NO_3^- state. This is true for natural seawater in the $7.6 < pH < 8.1$ range, but also at the low $3 < pH < 4$ after acid titration for determination of Alkalinity (see section 3.1 below). In other words, NO_3^- is always in the NO_3^- state throughout the overall range $3 < pH < 10$ of acidity in consideration. Akin to the four different forms of DIC in Eq. (2), DIP also happens to occur in four different forms (see Box 1).

The various equilibrium reactions in Box 1 do not only observe *mass balance*, but additionally must respect *charge balance*. The latter is tracked by the Alkalinity (see Section 3).

In addition to bio-essential elements C, N and P, all living organism also require sulfur (S), as well as a suite of bio-essential trace elements, notably iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), nickel (Ni) and cobalt (Co) (De Baar et al., 2017b). Fe, Zn, Mn, Cu, Ni, Co occur at extremely low nanomolar (10^{-9} M) to picomolar (10^{-12} M) concentrations in oceanic seawater and are deemed not significant ($<10^{-8}$ M) versus the ~1 µmol.kg^{-1} (10^{-6} M) precision of the acid titration of Alkalinity. Phytoplankton also requires magnesium (Mg) that is the central atom in chlorophylls *a, b,* c_1 *and* c_2 (Fraga and Álvarez-Salgado, 2005). Moreover, major taxa of phytoplankton, notably the diatoms, utilize the dissolved nutrient silicate for biosynthesis of external hard skeleton parts. Finally, major planktonic groups utilize calcium (Ca) for the biosynthesis of external $CaCO_3$ hard parts. Among these additional "biological" elements of interest, S, Mg, Si and Ca affect Alkalinity significantly.

$$\mathrm{DIC} = [\mathrm{CO_2}]_{\mathrm{aqueous}} + [\mathrm{H_2CO_3}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \quad (2)$$

with equilibrium reactions:

$$\mathrm{CO_{2(gaseous)}} \rightleftarrows \mathrm{CO_{2(aqueous)}} \quad (3)$$

$$\mathrm{CO_{2(aqueous)}} + \mathrm{H_2O} \rightleftarrows \mathrm{H_2CO_{3(aqueous)}} \quad (4)$$

$$\mathrm{H_2CO_{3(aqueous)}} \rightleftarrows \mathrm{H^+_{(aqueous)}} + \mathrm{HCO^-_{3(aqueous)}} \quad (5)$$

$$\mathrm{HCO^-_{3(aqueous)}} \rightleftarrows \mathrm{H^+_{(aqueous)}} + \mathrm{CO^{2-}_{3(aqueous)}} \quad (6)$$

governed by conditional equilibrium constant K^* (see Supplementary Material S1).
The concentrations of $\mathrm{CO_{2(aq)}}$ and $\mathrm{H_2CO_{3(aq)}}$ are combined into the hypothetical species $\mathrm{CO^*_{2(aq)}}$ as follows:

$$\mathrm{CO_{2(aqueous)}} + \mathrm{H_2CO_{3(aqueous)}} = \mathrm{CO^*_{2(aqueous)}} \quad (7)$$

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

$$K^* = [\mathrm{CO_{2(aqueous)}}] / [\mathrm{H_2CO_{3(aqueous)}}] \quad (8)$$

The value of K* being around 500, the difference between $\mathrm{CO_{2(aq)}}$ and $\mathrm{CO^*_{2(aq)}}$ is only in the order of 0.2 %. The above eqs. (3) and (4) are replaced by

$$\mathrm{CO_{2(g)}} \rightleftarrows \mathrm{CO^*_{2(aq)}} \quad (9)$$

DIC (see eq. 2) then becomes:

$$\mathrm{DIC} = [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] + [\mathrm{CO^*_{2(aq)}}] \quad (10)$$

The three species in eq. (12) are governed by

$$K^*_0 = [\mathrm{CO_2^*}] / f\mathrm{CO_2} \quad (11)$$

$$K^*_1 = [\mathrm{H^+}]\,[\mathrm{HCO_3^-}] / [\mathrm{CO_2^*}] \quad (12)$$

$$K^*_2 = [\mathrm{H^+}]\,[\mathrm{CO_3^{2-}}] / [\mathrm{HCO_3^-}] \quad (13)$$

where $f\mathrm{CO_2}$ represents the fugacity of $\mathrm{CO_2}$ gas in the atmosphere.

$$(\mathrm{DIP}) = [\mathrm{H_3PO_4}] + [\mathrm{H_2PO_4^-}] + [\mathrm{HPO_4^{2-}}] + [\mathrm{PO_4^{3-}}] \quad (14)$$

with equilibrium reactions:

$$\mathrm{H_3PO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{H_2PO_4^-} \quad (15)$$

$$\mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{H^+} + \mathrm{HPO_4^{2-}} \quad (16)$$

$$\mathrm{HPO_4^{2-}} \rightleftharpoons \mathrm{H^+} + \mathrm{PO_4^{3-}} \quad (17)$$

governed by

$$K^*_{1\mathrm{P}} = [\mathrm{H^+}]\,[\mathrm{H_2PO_4^-}] / [\mathrm{H_3PO_4}] \quad (18)$$

$$K^*_{2\mathrm{P}} = [\mathrm{H^+}]\,[\mathrm{HPO_4^{2-}}] / [\mathrm{H_2PO_4^-}] \quad (19)$$

$$K^*_{3\mathrm{P}} = [\mathrm{H^+}]\,[\mathrm{PO_4^{3-}}] / [\mathrm{HPO_4^{2-}}] \quad (20)$$

The proton concentration corresponds to the pH:

$$\mathrm{pH} = -\log([\mathrm{H^+}]) \quad (21)$$

that is governed by the water equilibrium:

$$K^*_{\mathrm{w}} = [\mathrm{H^+}]\,[\mathrm{OH^-}] \quad (22)$$

In the modern, slightly basic (alkaline) surface ocean of pH=~8, the hydroxide ion is about 100-fold more abundant than free hydrogen ions (10^{-6} versus 10^{-8} mol per liter, respectively).

BOX 1. Mass balances, equilibria and K* of the DIC pool and the DIP pool, and pH in the water equilibrium

3. Alkalinity

The Alkalinity is a pivotal variable, yet unfortunately its underlying chemistry is complicated. The major reason for defining and measuring Alkalinity is for being able to unravel (by combination with, notably, the measured value of DIC) the chemical speciation of the various carbonate species in seawater. Thus, one can calculate the concentration of the CO_3^{2-} ion, as well as all other variables of the CO_2 system and, somewhat indirectly, assess the changes of dissolved calcium (Ca^{2+} ion). The combined values of both the CO_3^{2-} ion and the Ca^{2+} ion jointly determine the status of supersaturation or undersaturation of seawater with regards to biogenic calcium carbonate ($CaCO_3$). One of the great successes of this approach is the explanation of the existence, or absence, of calcareous sedimentary deposits on the seafloor of the world oceans (Li et al., 1969). This and three other main applications of Alkalinity are described in Supplementary Material S5.

In 1939 the term Alkalinity was adopted as the standard designation (see Dickson, 1992) and commonly used ever since then. Unfortunately, the chosen name Alkalinity is confusing from a general chemistry point of view versus the principle for any aqueous solution being either alkaline (pH > 7) or acidic (pH < 7). Until the 1990s the potentiometric method served for determination of both Alkalinity and DIC. Nowadays DIC is determined more accurately separately by coulometry (Johnson et al., 1987). Titration Alkalinity still is determined by acid titration indeed. The values of Oceanic Alkalinity in the world oceans range from about 2250 to 2450 $\mu mol.kg^{-1}$ (Figure 1). For the precision of the determination of Alkalinity we assume the reported 1 $\mu mol.kg^{-1}$ in modern literature.

3.1. The titration method of Alkalinity

An example of titration of seawater with a strong acid is shown in Figure 2. Details are given in Supplementary Material S6 (Operational methodologies of Titration Alkalinity). Briefly, an exact volume V_0 [ml] of the seawater sample in a thermostated (e.g., 20°C or 25°C) titration cell is titrated by addition in small increments (e.g., 0.1 ml) of dilute hydrochloric acid with accurately known acid strength N (normality) at about 0.1 M (molarity). Upon each small volume addition of HCl, the pH electrode in the titration cell produces an ensuing measured change in electromotive force (e.m.f. with symbol E) in milliVolt (mV). This mV reading corresponds to the pH of the seawater sample as per the Nernst equation (see Supplementary Material S7). The second equivalence point of the titration is in Figure 2 indicated by the at this point added volume V_2 that is determined by a non-linear least squares fitting routine (see Supplementary Material S6). Thus one derives as follows:

$$\{(V_0 \text{ x Titration Alkalinity})/(V_o + V_2)\} = \{(V_2 \text{ x N})/\ )/(V_o + V_2)\} \qquad (23)$$

after Johansson and Wedborg (1982) and Millero (1993), where V_o is the original volume of the seawater sample in milliliter (ml = 10^{-3} L); Titration Alkalinity [$\mu M = 10^{-6}$ moles per Liter]; V_2 is the total volume [ml] of added dilute acid; and N is the normality of the dilute acid. Notice that the identical denominator terms ($V_o + V_2$) at each side of the equation (25) cancel each other out, i.e. disappear. For example one may envision a seawater sample volume V_0 = 100 ml, total added acid volume V_2 = 2.36 ml, normality N = 0.1 M of the dilute acid. The Eq. (25) upon some rearrangement then yields

$$\text{Titration Alkalinity } [\mu M] = \{2.36 \text{ [ml]} / 100 \text{ [ml]}\} \text{ x } 0.1 \text{ M} = 0.00236 \text{ M} = 2360\ 10^{-6} \text{ M} = 2360\ \mu M$$

Next by relying on (i) the known salinity of the seawater sample, (ii) the (thermostated) temperature, and (iii) the atmospheric pressure of 1 atm, the density of the samples is calculated from the international equation of state for seawater (Millero and Poisson, 1981). This permits conversion of Alkalinity [μM] to Alkalinity [$\mu mol.kg^{-1}$].

Nowadays the DIC is determined independently by coulometry, hence the value V_1 for the term (V_2-V_1) representing DIC is not needed anymore. Here it suffices to only determine the value of V_2 (representing Titration Alkalinity) by non-linear curve fitting of only the second part of the overall titration curve (see further in Supplementary Material S6).

The above summarized illustration of the method for Titration Alkalinity briefly describes the most commonly used method in international ocean science programs, i.e., commonly agreed among all (or almost all) ocean scientists. However, when it comes to ascribing the above described measured value of Titration Alkalinity, to the several underlying inorganic ionic constituents of natural seawater, there are several different approaches and definitions in the literature (Middelburg et al., 2020). Here we focus on two such approaches or definitions or concepts: Oceanic Alkalinity and Titration Alkalinity.

4. Oceanic Alkalinity

4.1. 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, i.e., still partly bound with OH or H, respectively. Most importantly, seawater is electrically neutral, that is, the sum of all charged ions must equal zero:

$$\Sigma\text{charges strong cations} + \Sigma\text{charges weak cations} - \Sigma\text{charges strong anions} - \Sigma\text{charges weak anions} = 0 \quad (24)$$

Re-arrangement yields

$$\Sigma\text{charges strong cations} - \Sigma\text{charges strong anions} = \Sigma\text{charges weak anions} - \Sigma\text{charges weak cations} \quad (25)$$

This approach after Broecker and Peng (1982) is the charge balance approach, that is leading to the concept of Oceanic Alkalinity and presumably is more or less a similar approach as the Charge Balance Alkalinity classification of Middelburg et al. (2020).
In above equation (24) one may fill in actual constituents

$$[Na^+] + [K^+] + 2\cdot[Ca^{2+}] + 2\cdot[Mg^{2+}] + 2.[Sr^{2+}] – [Cl^-] – 2\cdot[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-]$$
$$[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [SiO(OH)_3^-] = 0 \quad (26)$$

Re-arrangement as per above schematized Eq. (25) yields:

$$[Na^+] + [K^+] + 2\cdot[Ca^{2+}] + 2\cdot[Mg^{2+}] + 2.[Sr^{2+}] – [Cl^-] – 2\cdot[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] =$$
$$[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [SiO(OH)_3^-] \quad (27)$$

Strictly spoken and indeed used in the original literature, these charges were expressed in units of micro-equivalent charge per kilogram seawater (μeq.kg^{-1}). However, for the sake of more uniform units in chemical oceanography, and because the righthand side of Eq. (27) is analytically approximated by acid titration where the weak anions and weak cations are functioning as weak bases and acids, respectively, it was agreed to use the μmol.kg^{-1} notation (Broecker, 1974; see Supplementary Material S8).

Ideally, the acid titration of all weak ions at the right hand side of Eq. (27), would yield a value that would then equate perfectly with the sum of the strong ions at the lefthand side. Unfortunately, seawater is not ideal. On the one hand, the hydrogen ions of the added acid also are absorbed somewhat by small portions of the SO_4^{2-} and the F^- anions at the left hand side of Eq. (27). On the other hand, the various phosphate anions at the right hand side of Eq. (27) are at the endpoint of the acid titration not completely neutralized to the neutral H_3PO_4 state.

4.2. The sum of charges of the strong ions in seawater

On the left-hand side of Eq. (27) the strong cations are Na^+, Mg^{2+}, Ca^{2+}, K^+ and Sr^{2+} and given their concentrations at salinity S=35 (Table 1), their total charge concentration is 605.65 mmol.kg^{-1} (taking double the double charged ions Mg^{2+}, Ca^{2+} and Sr^{2+}). The strong anions are Cl^-, SO_4^{2-}, Br^-, F^-, and also NO_3^- (for reasons given below) and their total charge is 603.25 mmol.kg^{-1}. Overall, the definition of Oceanic Alkalinity in natural seawater is thus:

$$\text{Oceanic Alkalinity} = [Na^+] + [K^+] + 2\cdot[Ca^{2+}] + 2\cdot[Mg^{2+}] + 2.[Sr^{2+}] – [Cl^-] – 2\cdot[SO_4^{2-}] – [Br^-] - [F^-] - [NO_3^-] \quad (28)$$

For seawater with S=35 (Table 1) it follows: Oceanic Alkalinity = 605.65 - 603.25 = 2.4 mmol.kg^{-1} = 2400 μmol.kg^{-1}. This value of Oceanic Alkalinity in seawater may vary for three reasons. Firstly, in Eq. (28) 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 S=35 the Oceanic Alkalinity will decrease or increase accordingly. This effect of salinity accounts for in the order of ~90% of the observed variations of Alkalinity in the oceans. 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. This uptake/release of Ca^{2+} ion accounts for in the order of ~10% of the observed variations of Alkalinity in the oceans. 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 μmol.kg^{-1} going from nitrate-depleted surface waters in oligotrophic central ocean gyres, to ~45 μmol.kg^{-1} at the nutrient maximum at about 1000 m depth in the North Pacific Ocean (Figure 1; Table 2). The corresponding effect on the value of Oceanic Alkalinity ranges from zero to -45 μmol.kg^{-1} which is some 2% of Oceanic Alkalinity at most.

4.3. The sum of charges of the weak anions and weak cations in natural seawater

Natural seawater in the oceans has a typical pH in the order of 8.0-8.1 in the surface layer. During intense phytoplankton blooms the pH of surface seawater may temporarily increase to values up to pH = 9. Usually after some days or weeks, such phytoplankton blooms tends to collapse, upon which the pH of surface waters decreases again to the values in the 8.0-8.1 range. In contrast, in deeper waters due to overall net decomposition of organic debris, the pH can be lower to even pH = 7.6 in the around 1000 m depth range of the Oxygen Minimum Zone (OMZ) in the North Pacific Ocean. Under these natural conditions 7.6 < pH < 8.0-8.1 < 9.0 the small difference between charges of the strong ions is compensated on the right-hand side of Eq. (27) by the charges of the weak anions and weak cations, the sum of which is as follows:

$$\text{Sum weak ions} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [SiO(OH)_3^-] \quad (29)$$

where taken double are the double charged CO_3^{2-} and HPO_4^{2-} anions, and taken threefold the PO_4^{3-} anion. The $[HCO_3^-]$ and $2[CO_3^{2-}]$ terms are dominant. According to the water equilibrium (BOX 1), the $[OH^-]$ is dominant versus $[H^+]$, such that at typical pH=8 the 10^{-8} molar = 10^{-2} μmol.kg^{-1} charge of the hydrogen ion H^+ is negligible versus the ~1.0 to ~1.5 μmol.kg^{-1} reproducibility of Alkalinity and can be ignored. Due to net photosynthesis/respiration and the production/dissolution of biogenic opaline (SiO_2) frustules of diatom algae, all of the terms in Eq. (29) are directly variable, except the $[B(OH)_4^-]$ term that, at most, is indirectly affected by biological processes. The uptake/release of weak ion entities DIC and DIP, as well $[SiO(OH)_3^-]$, does NOT affect Oceanic Alkalinity (for DIP see Supplementary Material S13), but does lead to the above mentioned changes and shifts among the weak ions in Eq. (29).

5. Titration Alkalinity

In section 3.1. an experimental/operational definition is given of Titration Alkalinity including the accompanying Figure 2 and the Supplementary Material S6. When it comes to ascribing a measured value of Titration Alkalinity (Eq. 23) to the several underlying inorganic ionic constituents of natural seawater, there are different approaches and definitions in the literature. These various descriptions of Titration Alkalinity in the literature do not necessarily agree with one another, or for that matter with our chosen approach and description of Titration Alkalinity.

We adopt an operational definition after Millero (1995) and Fraga and Álvarez-Salgado (2005) as follows: "*The Titration Alkalinity of a natural water sample is defined as the concentration of all bases able to accept a hydrogen ion at the equivalence point of the carbonic acid system species.*"

On the one hand, for every individual seawater sample, the titration yields an individual second equivalence point with its corresponding pH value. On the other hand, this second equivalence point of the titration is strongly dominated by the conditional stability constant K'_1 as given in eq. (12) in BOX 1.

As a result, the actual mV reading and corresponding pH value in the second equivalence point would for every individual seawater sample vary only slightly from that expected on basis of the conditional stability constant. Below are given three "typical" examples for pH in the second equivalence point: (i) the nominal pH=4.5 after Dickson (1981), Millero (1995) and several others; (ii) the pH=4.4 after Fraga and Álvarez-Salgado (2005) for their simplified overall titration equation

$$[H^+] \sim [HCO_3^-] + 2x[CO_3^{2-}] \quad (30)$$

and finally (iii) the equivalence point of a titration determination at a pH_{SWS} of ~4.25 (hydrogen ion activity, a_H = ~$10^{-4.4}$) also after Fraga and Álvarez-Salgado (2005). Here pH_{SWS} stands for the seawater scale (see Supplementary Material S1). It should be noted that the nominal pH=4.5 was at first defined in context of combined assumptions of a zero proton condition related to an arbitrarily defined distinction between proton donors and proton acceptors (Dickson (1981), in other words not necessarily as the equivalence point (Dickson, 1981). However, in subsequent articles by other scientists, very often the pH=4.5 was reportedly deemed to be the equivalence point.

5.1. The major constituents with respect to Alkalinity determination by titration

The Bjerrum plot (Figure 3) of the major constituents with respect to Titration Alkalinity provides a visual representation of the changes that take place in a seawater sample due to the titration. With decreasing pH, the concentrations of the CO_3^{2-} ion and of the HCO_3^- ion steadily decrease in favor of CO_2^*, such that at the nominal pH=4.5 equivalence point of the titration in essence all exists as non-charged $[CO_2^*]$. The concentration of the

$B(OH)_4^-$ ion at pH=~8 has at the nominal pH=~4.5 endpoint been completely converted to the non-charged $B(OH)_3$. Similarly, the OH^- ion in natural seawater at pH=~8 has disappeared at the nominal pH=~4.5 endpoint. Throughout the titration pathway the addition of hydrogen ions (also named protons) is equivalent to the charges of the weak ions in the original seawater sample. Therefore, a first approximate definition of Titration Alkalinity is as follows:

$$Alk_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \qquad (31)$$

as per equation (4) of Takahashi (1975); but see also Millero (1995; their Eq. 8); Fraga and Álvarez-Salgado (2005; their Eq. 1). As a matter of fact, the complete equation (4) of Takahashi (1975) reads:

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] = [K^+] + [Na^+] + 2\cdot[Ca^{2+}] + 2\cdot[Mg^{2+}] + [Sr^{2+}] - [Cl^-] - 2\cdot[SO_4^{2-}] \qquad (32)$$

such that the approximate definition of Titration Alkalinity (at lefthand side) equals the charge balance of the above described Oceanic Alkalinity (at right hand side). It is worthwhile noting that also the above right hand term in Eq. (32) is an approximate definition, because the small negative contributions of $[Br^-]$ and $[F^-]$ and $[NO_3^-]$ of Oceanic Alkalinity (Eq. 28) had been ignored. For $[NO_3^-]$ such contribution was realized only one year later due to the work of Brewer and Goldman (1976). Nevertheless, the above approximate Eqs. (31 and 32) are a valid first approach good for some 1% precision.

Sarmiento and Gruber (2006) defined their equation (8.2.8.; see their page 323) as follows

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] + \text{minor bases} \qquad (33)$$

that is operationally defined by the titration with H^+ of all weak bases present in the solution. Alternatively, their equation is defined (their 8.2.9.; see their page 323)

$$Alk = [Na^+] + [K^+] + 2\cdot[Mg^{2+}] + 2\cdot[Ca^{2+}] + \text{minor cations}$$
$$- [Cl^-] - 2\cdot[SO_4^{2-}] - [Br^-] - [NO_3^-] - \text{minor anions} \qquad (34)$$

that can be viewed as the charge balance of all strong acids and bases unaffected by this titration. This Eq. (34) derives from the same approach as the above defined Oceanic Alkalinity (Eq. 28). The contributions of minor constituents were deemed usually below one percent (Sarmiento and Gruber, 2006; see their page 323).

The above definitions (Eqs. 31, 32, 33, 34) of Titration Alkalinity are approximate because some minor constituents that contribute to Titration Alkalinity have not yet been included. In Figure 3 the horizontal dotted line at the 10^{-6} mol.kg^{-1} = 1 μmol.kg^{-1} concentration more or less represents the reproducibility of the determination of Alkalinity. Any concentrations of dissolved ions that are less than ~1 μmol.kg^{-1} are deemed non-significant. It should be noted that at the nominal pH=~4.5 endpoint, the HSO_4^- ion is well above this 1 μmol.kg^{-1} bottom line.

5.2. The minor constituents with respect to Titration Alkalinity

Some minor constituents are described below in sequence from more to less effect on Titration Alkalinity.

5.2.1. Assimilation of added hydrogen ions by a minor portion of dissolved sulfate

Dissolved sulfate is a strong anion in natural seawater of pH=~8 but still absorbs some protons at the nominal pH=4.5 endpoint of Titration Alkalinity. The SO_4^{2-} exists as one of the conservative components of the salinity of seawater (Table 1), such that for total dissolved sulfate: $[SO_4^{2-}] + [HSO_4^-] = 0.02824$ mol.kg^{-1}.
For the equilibrium

$$[HSO_4^-] = [H^+] + [SO_4^{2-}] \qquad (35)$$

the (conditional) equilibrium constant is

$$(K^*_S) = [H^+]\,[SO_4^{2-}] / [HSO_4^-] \qquad (36)$$

Here the hydrogen ion concentration $[H^+]_{FREE}$ is expressed on the free scale pH_{FREE} after DOE (1994) and PICES (2007) (see also Supplementary Material S1). At S=35 and T=25°C the constant is:
$\ln (K^*_S)_{FREE} = -2.30$ such that $(K^*_S)_{FREE} = 0.1003$.
At the pH=8 of natural surface seawater and $[SO_4^{2-}] = 0.02824$ mol.kg^{-1} (Table 1) one derives from Eq. (36) that $[HSO_4^-] = \{[10^{-8}]\,[0.02824]\}/\,(0.1003) = 0.282\ 10^{-8}$ mol.kg^{-1} = $2.82\ 10^{-3}$ μmol.kg^{-1}.
This $2.82\ 10^{-3}$ μmol.kg^{-1} is negligible versus the precision of Alkalinity such that at natural pH=8 virtually all sulfate is indeed $[SO_4^{2-}] = 0.02824$ mol.kg^{-1} Hence in natural seawater the sulfate is to be treated as a fully dissociated strong anion, and as such part of the Eq. (28) of Oceanic Alkalinity.

This being stated, the situation is different at the nominal pH=4.5 endpoint of the titration. A significant concentration of the HSO_4^- ion has evolved that is the product of some assimilation of the added hydrogen ions (Figure 3). Here similarly like above one obtains:

For pH=4.5 $[HSO_4^-] = \{[3.16228\ 10^{-5}]\,[0.02824]\}/\,(0.1003) = 0.89\ 10^{-5}$ mol.kg^{-1} = 8.9 μmol.kg^{-1}

For pH=4.4 $[HSO_4^-] = \{[3.98107\ 10^{-5}]\ [0.02824]\}/\ (0.1003) = 1.12\ 10^{-5}\ mol.kg^{-1} = 11.2\ \mu mol.kg^{-1}$

For pH=4.25 $[HSO_4^-] = \{[5.62341\ 10^{-5}]\ [0.02824]\}/\ (0.1003) = 1.58\ 10^{-5}\ mol.kg^{-1} = 15.8\ \mu mol.kg^{-1}$

This is well above the 1 $\mu mol.kg^{-1}$ precision of Titration Alkalinity. A small portion ($8.9\ 10^{-6}/\ 0.02824$) = ~0.000319 (0.03%) of the sulfate has absorbed protons. For the other example endpoint values of pH=4.4 or pH=4.25, the factor would be ($11.2\ 10^{-6}/\ 0.02824$) = 0.000397 (i.e., 0.04%) or ($15.8\ 10^{-6}/\ 0.02824$) = 0.00056 (i.e., 0.06%). This factor then serves as the coefficient in the equation for Titration Alkalinity. For the pH=4.4 example, the provisional equation for Titration Alkalinity representing the states of the constituents of the seawater sample prior to the titration, then reads as follows:

$$\text{Titration Alkalinity} = A_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + 0.000397\ [SO_4^{2-}] \quad (37)$$

In summary, sulfate is a strong anion in natural seawater (pH=8) but some 0.03 to 0.06 % has absorbed protons at the equivalence point of the titration of a given seawater sample.

5.2.2. Assimilation of added hydrogen ions by fluoride

For the equilibrium reaction

$$HF \rightleftarrows H^+ + F^- \quad (38)$$

the conditional equilibrium constant is

$$K_F^* = \{[H^+][F^-]\}/[HF] \quad (39)$$

where

$$\ln (K^*_F) = (1590.2/T) - 12.641 + 1.525\ I^{1/2} + \ln (1 - 0.001005\ S) \quad (40)$$

with T in Kelvin, ionic strength I = (19.924 S)/(1000-1.005S) and S is salinity (DOE, 1994, PICES, 2007; see also Zeebe and Wolf-Gladrow, 2001). For standard salinity S=35 and T=298.15K, it is obtained $\ln (K^*_F) = -6.04676672$ such that $(K^*_F) = 0.00236572$ as defined on the free pH_{FREE} scale. At the pH=8 of natural seawater, the [HF] state is negligible:

$[HF]= \{[H^+][F^-]\}/\ K_F^* = \{[10^{-8}][70\ 10^{-6}]\}/\ 0.00236572 = 22589.3005\ 10^{-14} = 0.226\ 10^{-8}\ \mu mol.kg^{-1}$

For the endpoint of the titration, the three example pH values yield:

At pH=4.5: $\{[3.16228\ 10^{-5}][70\ 10^{-6}]\}/\ 0.00236572 = 0.581\ 10^{-6}\ mol.kg^{-1}$

At pH=4.4: $\{[3.98107\ 10^{-5}][70\ 10^{-6}]\}/\ 0.00236572 = 0.732\ 10^{-6}\ mol.kg^{-1}$

At pH=4.25: $\{[5.62341\ 10^{-5}][70\ 10^{-6}]\}/\ 0.00236572 = 1.034\ 10^{-6}\ mol.kg^{-1}$

The Bjerrum plot (Figure 4) shows that at the typical pH=8 of natural surface seawater, all fluoride is in the F^- state, with an overall concentration of 70 $\mu mol.kg^{-1}$. At the pH=4.4 example of the titration end point, the HF state has increased to 0.73 $\mu mol.kg^{-1}$. This implies the absorption in the order of some 0.73 $\mu mol.kg^{-1}$ of the added hydrogen ions. This is a (0.73/70) = 0.0105 portion (1%) of the total fluoride. For the example pH=4.4 endpoint, the provisional equation for Titration Alkalinity representing the states of the constituents of the seawater sample prior to the titration, then reads as follows:

$$A_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + 0.0003966\ [SO_4^{2-}] + 0.010457\ [F^-] \quad (41)$$

5.2.3. Interconversions of conditional stability constants K* for the free pH_{FREE} scale versus the total pH_T scale.

One major objective of this article is to bring the treatment of Alkalinity in keeping with common general chemistry. Therefore with regards to pH the aim is to utilize the free pH scale (pH_{FREE}). This aim is inspired also by the article on "The free proton concentration scale for seawater pH" (Waters and Millero, 2013; see also Waters et al., 2014). The aim is to avoid the two other very specialistic pH scales (Total scale pH_T, and SeaWater Scale pH_{SWS}; see Supplementary Material S1) that are used exclusively within the relatively small community of ocean inorganic carbon cycle specialists. Moreover the NBS scale pH_{NBS} (see Supplementary Material S1) is also avoided.

From the extensive literature on the oceanic inorganic carbon cycle it is well understood why and how these very specialistic total scale pH_T, and SeaWater Scale pH_{SWS} have evolved during the past several decades.

For the free pH scale here we use the symbol pH_{FREE} in order to avoid confusion with the subscript F for fluoride. (e.g. here K^*_F is the conditional stability constant of fluoride).

Fortunately for both the sulfate system (5.2.1) and the fluoride system (5.2.2.) we were able to use available definitions of their conditional stability constants versus the pH_{FREE} scale. This being stated, for the case of fluoride, there is the opportunity to below also assess findings by comparison with literature results versus the Total pH_T scale. Moreover and more importantly, for the silicate system (5.2.4.) and phosphate system (5.2.5.) the literature only offers conditional stability constants K* on the Total pH_T scale, to the best of our knowledge. These are to be converted to the free pH_{FREE} scale.

The conditional stability constant of sulfate $(K^*)_{FREE}$ defined on the pH_{FREE} scale can be converted to the $(K^*S)_T$ on the Total pH_T scale by the following general relationship:

$$\ln (K^*)_{FREE} = \ln (K^*)_T - \ln \{1 + S_T/(K^*_S)\} \tag{42}$$

adjusted after Zeebe and Wolf-Gladrow (2001, their page 260, section A.6), where S_T is the total dissolved sulfate and K^*_S is the conditional stability constant of sulfate (Eq. 36). At standard salinity S=35, $S_T = [SO_4^{2-}] = 0.02824$ $mol.kg^{-1}$ and $(K^*_S) = 0.1003$ such that one obtains the general equation:

$$\ln (K^*)_{FREE} = \ln (K^*)_T - 0.2480744 \tag{43}$$

This is a general equation in that it is also applicable to other dissolved substances, here notably for fluoride (5.2.2.2), silicate (5.3.2.) and phosphate (5.3.4.).

In the open oceans the salinity generally varies within a narrow range of 34 < Salinity < 36. Correspondingly in eq. (42) the concentration of total sulfate $S_T = [SO_4^{2-}]$ would be slightly lower or higher than at the standard salinity S=35. For applications to real seawater samples this needs to be taken into account, yielding slight adjustments of the value 0.2480744 in eq. (43).

Verification is done by combining the general interconversion (eq. 42) between K^*_{FREE} and K^*_T with the case of fluoride (5.2.2.) where one obtains $-6.04676672 + 0.2480744 = -5.79869232 = -5.7986 = \ln (K^*)_T$. This is in perfect agreement with the check value $\{(\ln K^*_F)_T\} = -5.7986$ by Zeebe and Wolf-Gladrow (2001, page 261).

5.2.4. Assimilation of added hydrogen ions by silicate

At typical pH=8 almost all silicon exists in the neutral H_4SiO_4 state, but a very small portion is in the $H_3SiO_4^-$ state (Figure 4). At the endpoint at pH=4.5 of the titration this small portion is completely converted to the fully protonated H_4SiO_4 state. In other words, the small portion $H_3SiO_4^-$ that existed in the untreated natural seawater, has at the end of the titration consumed the same amount of the added protons, i.e., does contribute to the value of Titration Alkalinity. For the equilibrium

$$H_4SiO_4 = H^+ + H_3SiO_4^- \tag{44}$$

with

$$K^*_{Si} = \{[H^+][H_3SiO_4^-]\}/[H_4SiO_4] \tag{45}$$

the $\ln(K^*_{Si})_{FREE} = \ln (K^*_{Si})_T - 0.2480744 = -21.61 - 0.2481 = -21.858$ after Eq. (42) where $\ln (K^*)_T = -21.61$ after DOE (1994), (PICES 2007), see also Zeebe and Wolf-Gladrow (2001). As the result $(K^*_{Si})_{FREE} = 3.21484\ 10^{-10}$ (as compared to: $\{K^*_{Si})_T\}_{Total\ scale} = 4.12\ 10^{-10}$).

Thus at 1 $\mu mol.kg^{-1}$ total dissolved silicate in natural seawater at pH=8 the $[H_3SiO_4^-] = 0.032$ $\mu mol.kg^{-1}$ that is 3.2% of the total silicate. For the overall concentration range 0-170 $\mu mol.kg^{-1}$ (Table 2, Figure 1) the contribution to Titration Alkalinity ranges from 0 to (170 x 0.032) = 5.4 $\mu mol.kg^{-1}$. (When alternatively using the total pH_T scale this contribution would range from 0 to (170 x 0.041) = 7.0 $\mu mol.kg^{-1}$). In summary the contribution of silicate should be included in the provisional equation:

$$A_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [H_3SiO_4^-] - [H^+] + 0.0003966\ [SO_4^{2-}] + 0.010457\ [F^-] \tag{46}$$

5.2.5. Interactions of Dissolved Inorganic Phosphorus with Titration Alkalinity

The concentrations of Dissolved Inorganic Phosphorus (DIP, phosphate) in the world oceans range from 0 in oligotrophic surface waters to DIP = ~2.5 μM in the North Pacific deep water to DIP = ~3.3 μM in the oxygen minimum zone of the North Pacific (Figure 1; Table 2). 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 (Figure 4). The equilibrium equations (15, 16, 17) were given in BOX 1, with the conditional equilibrium constants (18, 19, 20). The conditional equilibrium constants K* in seawater at S=35 and T=25°C are obtained on the pH_{FREE} scale, as derived with Eq. (43) from the K* values on the total pH_T scale (DOE, 1994; PICES, 2007) as follows :

$$\{\ln ((K^*_{1P})_{FREE}\} = \{\ln (K^*_{1P})_T\} - \ln (1 + S_T/Ks) = -3.71 - 0.2480744 = -3.958 \tag{47}$$

$$\{\ln ((K^*_{2P})_{FREE}\} = \{\ln (K^*_{2P})_T\} - \ln (1 + S_T/Ks) = -13.727 - 0.2480744 = -13.975$$

$\{\ln ((K^*_{3P})_{FREE}\} = \{\ln (K^*_{3P})_T\} - \ln (1 + S_T/K_s) = -20.24 - 0.2480744 = -20.488$

such that

$(K^*_{1P})_{FREE} = 0.0190998 \quad = 0.0191$
$(K^*_{2P})_{FREE} = 0.852513\ 10^{-6} \quad = 0.8525\ 10^{-6}$
$(K^*_{3P})_{FREE} = 1.26515\ 10^{-9} \quad = 1.2652\ 10^{-9}$ (all factor 0.78 lower than $\{(K^*)_T\}$)

An example of the speciation of DIP in a sample of natural surface seawater with 1.52 μmol.kg^{-1} total Dissolved Inorganic Phosphorus is shown in Table 3, using computations in MINEQL software of De Baar and Gerringa (2008). It is worthwhile noting that the calculated four different species of phosphate agree well with their representation at the pH=8 condition in the Bjerrum plot (Figure 4). Table 3 also provides the relative abundances of the four different species of phosphate at this pH=8.0 condition. The relative abundances are the basis for the case of the concentrations of each of the four species at DIP = 1.00 μmol.kg^{-1} as listed in Table 4a for the pH=8 condition.

In the same Table 4a this is compared with the concentrations of the four species at the endpoint (second equivalence point) of the titration at the nominal pH=4.5, pH=4.4 and pH=4.25 conditions. As expected, given the more than 3000-fold to 5000-fold increase of the ambient hydrogen ion concentration (Table 4a), the $H_2PO_4^-$ species has increased some 43.9-fold to 44.2-fold to 44.6-fold for the example endpoint pH values of 4.5, 4.4 and 4.25, respectively. Similarly, the relative increase of the fully protonated H_3PO_4 species is even more pronounced at some 124.6-fold to 158.1-fold to 225.6-fold for these example endpoint pH values of 4.5, 4.4 and 4.25, respectively.

Here it is noted that at all three examples of endpoint conditions, the phosphate is by no means fully protonated to the H_3PO_4 state. In fact, there still are significant concentrations of the three charged species, the now dominant $H_2PO_4^-$ species and the now relatively minor HPO_4^{2-} and PO_4^{3-} species. This is also obvious in Figure 4. These concentrations can be converted to the actual charges of these three ionic species (Table 4b), where the double charge of HPO_4^{2-} and the triple charge of PO_4^{3-} are taken into account. At $pH_{Total} = 8.07$ the sum of charges is -1.99 μmol.kg^{-1} in fair agreement with -2.149 at pH_{SWS}=8.0 of Fraga and Álvarez-Salgado (2005; their Table 1). (The difference may partly relate to the use of different scales pH_T and pH_{SWS}).

Next at the endpoint of the titration, defined at either pH=4.5 or pH=4.4 or pH=4.25, the summation of these charges shows that there still remains a negative charge of about -1.026 μmol.kg^{-1} and -1.021 μmol.kg^{-1} and -1.00 μmol.kg^{-1}, respectively. The latter -1.00 value is in good agreement with -1.016 for pH_{SWS}=4.25 by Fraga and Álvarez-Salgado (2005; their Table 1). This implies that this small portion of the negative charges of the original seawater sample has not been titrated, hence not taken into account in the total amount of absorbed added hydrogen ions. Thus, for the overall titration with a typical Titration Alkalinity value in the order of 2250 μmol.kg^{-1} to 2400 μmol.kg^{-1} and DIP = 1.00 μmol.kg^{-1}, there is a mismatch in the order of -1.026 μmol.kg^{-1} to -1.00 μmol.kg^{-1} for the negative charged ions, with the charge balance of the original seawater sample at pH=~8.

These cases, at example value pH=8.07 for the original untreated natural seawater sample, and for the endpoint after titration, at example values 4.5 or 4.4 or 4.25 merely are examples indeed. In practice for each natural seawater sample that has been titrated, one derives the actual pH value before the titration, and the endpoint pH of the titration from the mV readings converted via the Nernst equation to pH (Figure 2).

Because of the dominance of the carbonate system, the pH value of the endpoint for any titrated seawater sample will tend to be very close to 4.4 or 4.25. Here we take the value pH=4.4 (Table 4). For DIP = 1.0 μmol.kg^{-1} the sum of charges is 1.99 μmol.kg^{-1} at the pH=8.07 and 1.02 μmol.kg^{-1} at the pH=4.4 example endpoint. The difference (1.99-1.02)= 0.97 μmol.kg^{-1} is due to assimilation of hydrogen ion. Latter value serves as the coefficient of DIP in the complete Titration Alkalinity equation as follows:

$$\begin{aligned}Alk_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] - [H^+] \\ + 0.97\,[DIP] + 0.0003966\,[SO_4^{2-}] + 0.010457\,[F^-] \qquad (48)\end{aligned}$$

where the DIP must be entered from its independent measurement. Eq. (48) is suitable for well oxygenated seawater of the open ocean. The terms $[SO_4^{2-}]$ and $[F^-]$ can be substituted by salinity (S) on basis of Table 1, as follows in units of μmol.kg^{-1}:

$[SO_4^{2-}] = (28240/35).S$ and $[F^-] = (70/35).S$, yielding: $\{0.0003966 \times (28240/35)\ S\} + \{0.010457 \times (70/35)\ S\} = (0.32 + 0.020914)\ S = 0.3409\ S$ such that:

$$Alk_{Titration} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] - [H^+] + 0.97\,[DIP] + 0.3409\,S \qquad (49)$$

As mentioned, for each seawater sample the exact values of the coefficients would need to be calculated from (i) the exact value of the initial pH of the untreated natural seawater sample, and (ii) the exact pH of the endpoint of each titration. The coefficients thus derived for every individual sample would only slightly deviate from the given coefficients in Eq. (49) for the pH=8.07 and pH=4.4 values. Nevertheless, in an intense phytoplankton bloom the pH value can be higher up to even some pH = 9. On the other hand, in very old deep waters of for example the intense Oxygen Minimum Zone (OMZ) at the around ~1000 m depth in the Pacific Ocean (Figure 1), the cumulative effect of mineralization of organic debris may lead to values as low as pH = 7.6 (thin dotted line in Figure 4, after Lauvset et al., 2020). In other words, the exact pH value of the initial untreated seawater sample must also be taken into account for calculating the exact value of the total charge of DIP (Eq. 14)(Table 4b).

On the other hand, the coefficients of sulfate and fluoride are not significantly affected by the value of the initial pH of the untreated seawater sample. Here a significance level of 10^{-8} mol.kg^{-1} = 10^{-2} μmol.kg^{-1} is deemed appropriate, this being 100-fold lower than the ±1 μmol.kg^{-1} precision of the titration of alkalinity.

Overall, this quite straightforward set of a handful of accurate definitions is deemed to be suitable for incorporation as the corresponding algorithms in the computer software of the acid titration, as well as in the software of a chemical speciation model that quantifies all CO_2 system variables on the basis of the input variables, akin to CO2Sys (Lewis and Wallace, 1998; see also Pierrot et al., 2006; Van Heuven et al., 2011b). Briefly, with external determined input values of salinity and DIP and total dissolved silicate, the pH values at begin of untreated seawater sample and at the endpoint after titration do result and from these the coefficients of [DIP] and $[SO_4^{2-}]$ and $[F^-]$ in above Eq. (49) for the given seawater sample. In practice, these coefficients would in general have a very similar value as in the above example (49).

5.2.6. Alternative computations of the DIP system with K* values defined versus the total pH$_T$ scale

DOE (1994), PICES (2007) and Zeebe and Wolf-Gladrow (2001) defined K^*_{1P}, K^*_{2P} and K^*_{3P} on the total pH$_T$ scale. In the Supplementary Material S10, the ensuing alternative results of Tables 4a and 4b are shown. The values for the Summation Total charge (μmol.kg^{-1}) at the endpoint pH examples (4.5, 4.4 and 4.25) are 1.032 μmol.kg^{-1} and 1.016 μmol.kg^{-1} and 1.019 μmol.kg^{-1}, respectively. These values hardly deviate from -1.026 μmol.kg^{-1} and -1.021 μmol.kg^{-1} and -1.00 μmol.kg^{-1}, respectively as given above versus the pH$_{FREE}$ scale. Notably, when rounded to two decimals, for the pH=4.4 example endpoint the charge difference versus the initial pH=8 condition is the same at (1.99-1.016) = 0.97 μmol.kg^{-1}. In summary, the preferred approach versus the pH$_{FREE}$ scale yields results for DIP that agree well with the findings versus the pH$_T$ scale.

6. The difference between Oceanic Alkalinity and Titration Alkalinity

It is concluded that at least two definitions of Alkalinity exist. Oceanic Alkalinity (Eq. 28) is based on charge balance considerations. The complementary acid-base considerations lead to Titration Alkalinity, that is, the amount of added hydrogen ions absorbed by the weak ions in seawater. However, during the titration, small portions of sulfate and fluoride in Oceanic Alkalinity have assimilated some of the added hydrogen ions. In contrast, from the charged phosphate anions at pH=8 not all are completely titrated when at the endpoint such that some charged phosphate anions remain. Fortunately, the resulting small (~1%) difference between the values of Oceanic Alkalinity and Titration Alkalinity, can for each individual titration (Figure 2) of each individual seawater sample be accurately calculated following the findings in Section 5.2.

For phosphate, the pH value at the endpoint of the titration, in combination with the independently measured concentration of DIP, yields with Eqs. 18, 19 and 20 the exact concentrations of the four different phosphate species (Table 4a), and the exact sum of the charges of these four species (Table 4b). The final sum of charges at the endpoint (examples pH=4.5 or pH=4.4 or pH=4.25) represents the contribution to the difference between Oceanic Alkalinity and Titration Alkalinity. For the given example (Table 4b), for the nominal pH=4.5 endpoint the exact difference is 1.026 μmol.kg^{-1}. For the other two examples at slightly lower pH=4.4 or pH=4.25 the exact difference obviously (Figure 4) is slightly less at 1.021 or 1.00 μmol.kg^{-1}.

For the pH=4.4 example, this leads to the following difference (in μmol.kg^{-1}):

$$Alk_{Oceanic} = Alk_{Titration} + 1.021\,[DIP] - 0.0003966\,[SO_4^{2-}] - 0.010457\,[F^-] \qquad (50)$$

or in terms of salinity:

$$Alk_{Oceanic} = Alk_{Titration} + 1.021\,[DIP] - 0.3409\,S \qquad (51)$$

As mentioned above, for each individual seawater sample, the pH values at the beginning and end of the titration may vary, such that for each sample the coefficients in (50) and (51) would vary accordingly. This being stated, it is realized that for the quite common pH=8 of surface waters, and quite narrow pH range of the endpoint at or near pH=4.4 that the per individual sample variations of the coefficients would only slightly deviate from the example coefficients in Eqs. (50) and (51).

Finally, one is aware that the underlying conditional stability constants K* of the sulfate, fluoride, silicate and phosphate constituents in themselves are functions of the salinity. For fluoride this is given in Eq. (40). For sulfate, silicate and phosphate, see the elaborate equations in DOE (1994, Chapter 5). In other words, when applying the above fairly simple equations (50, 51) to other salinities than the here chosen standard S=35, the elaborate equations of the conditional stability constants would need to be incorporated.

7. Biological uptake or release affecting Alkalinity

7.1. Organic matter and skeletal hard parts

As per the classical Redfield approach the photosynthesis/decomposition of organic matter is due to uptake/release of DIC, nitrate and DIP following the C:N:P=106:16:1 stoichiometry. The uptake of 16 μmol NO_3^- that is negatively charged, causes a corresponding increase of Oceanic Alkalinity (Eq. 28), and hence by adjustments among the weak ions also a corresponding increase of the sum of the weak ions (eq. 29). This increase plus the parallel uptake of DIC and DIP is accomodated in the sum of charges of the weak ions (Eq. 29) in combination with overall decreases in the mass balances of DIC (Eq. 2) and DIP (Eq. 14), overall leading to shifts in the concentrations among the weak ion species. The changes taking place can be monitored by changes of the measured concentrations of DIC, NO_3^- and DIP in seawater. Notice that the uptake/release of C and N and P only affect the value of Oceanic Alkalinity due to the factor 16 for nitrate (NO_3^-). The uptake/release of DIP does NOT affect Oceanic Alkalinity, this conclusion resolving the long-standing confusion in the literature (see Supplementary Material S12) where several authors have, incorrectly, applied a factor of (16+1)=17 for the uptake/release of both N and DIP.

Upon acid titration, all the weak ion species become neutralized due to assimilation of added hydrogen ions with a minor exception of DIP. Phytoplankton species may instead of NO_3^- use other nitrogen resources, like NH_4^+, N_2, NO_2^- (Fraga and Álvarez-Salgado, 2005), but here only NO_3^- is considered.

The formation/dissolution of $CaCO_3$ skeletal hard parts results in uptake/release of Ca^{2+} and DIC. For every unit Ca^{2+} [μmol.kg^{-1}] this corresponds to a twofold decreasing/increasing value of Oceanic Alkalinity [μmol.kg^{-1}] (Eq. 28), and hence also decreasing/increasing the value of the sum of weak ions (Eq. 30). This, in combination with the decrease/increase of the DIC pool (Eq. 2) leads to shifts among the weak ions. In many articles, the approach as given in Supplementary Material S5.3. for unraveling biogenic effects towards deriving changes of dissolved Ca^{2+} is done by adjusting the measured Alkalinity, i.e., Titration Alkalinity, by salinity normalization and "correction" for nitrate (e.g., Jones et al., 2021). Quite conceivably it would appear to be more appropriate to first derive Oceanic Alkalinity from Titration Alkalinity as per Eq. (50) and/or (51), and next do the salinity normalization and "correction" for nitrate of Oceanic Alkalinity. When in Eq. (51) entering the standard salinity S=35 and the lowest concentration DIP = 0 μmol.kg^{-1} for oligotrophic oceanic surface waters, the difference between $Alk_{oceanic}$ and $Alk_{titration}$ is in the order of 12 μmol.kg^{-1} merely due to the salinity (i.e., the sulfate and fluoride effects). When entering the highest oceanic concentration DIP = ~3.3 μmol.kg^{-1} (table 2) the difference is in the order of 15.2 μmol.kg^{-1}. This range between 12 and 15 μmol.kg^{-1} would versus an assumed Alkalinity value of for example ~2400 μmol.kg^{-1} amount to some 0.5 to 0.6 %. Given this difference between Oceanic Alkalinity and Titration Alkalinity, this might significantly affect the outcome, i.e., the derived changes of dissolved Ca^{2+} in seawater. Thus far in the literature this application and other applications (see Supplementary Material S5) may, or may not, have used Titration Alkalinity, where it is now realized that one should use Oceanic Alkalinity. It is not inconceivable that this may have caused significant systematic offsets in some of such past applications, such offsets distinct apart from the regular error propagation (Orr et al., 2018).

Finally, the formation/dissolution of siliceous skeletal hard parts is due to uptake/release of ($Si(OH)_4$ + $SiO(OH)_3^-$), where the latter minor amount of the $SiO(OH)_3^-$ is accommodated in the sum of weak ions (Eq. 29).

7.2. Biological uptake or release of other chemical constituents of seawater affecting Oceanic Alkalinity

One or several of the other chemical constituents of seawater may also be involved in biological uptake/release. With regards to the biological uptake/release of phosphorus and sulfur affecting alkalinity, several examples in the literature of the 1965-2022 era are given in Supplementary Materials S12. One such example is the investigation of the variation of Alkalinity during phytoplankton photosynthesis (Fraga and Álvarez-Salgado, 2005). Latter authors not only considered the 'classical' constituents C, N and P of organic matter, but also sulfur (S) and magnesium (Mg) as building blocks of organic matter. Whereas for C, N and P the changes can be monitored by changes of the measured concentrations of DIC, NO_3^- and DIP in seawater, the very high background concentrations of SO_4^{2-} and Mg^{2+} in seawater (Table 1) would prevent to discern any such biological effect in their total concentration in seawater. Clearly, for a given phytoplankton bloom, detailed knowledge of the biochemical composition of the blooming phytoplankton species is advisable for defining the effects of uptake of SO_4^{2-} and Mg^{2+} on the Alkalinity in the ambient seawater.

For sulfur, Deuser (1970) mentions for the atomic ratio of sulfur to carbon in marine organic matter a range of $0.007 < S:C < 0.025$ based on three literature citations: Vinogradov (1953), Mita (1961) and Matsumoto et al. (1964). Using 0.015 as a mean value, the relationship $S_{bio} = 0.015\ C_{bio}$ is obtained by Deuser (1970). Clearly, assessment of the statistical significance of the value 0.015 is not feasible. Therefore, the validity of subsequent applications of this S:C=0.015 value by Kanamori and Ikegami (1982), cited in turn by Carter et al. (2014), Lauvset et al. (2020) and others, is unknown. Otherwise, given the Redfieldian C:N = 106/16 elemental ratio, the S:C = 0.015 of Deuser (1970) would correspond to a S:N = 0.1 ratio. Here we prefer the S:N ratio because both dissolved sulfate and dissolved nitrate are strong anions, such that biological uptake/release of both affects the value of Oceanic Alkalinity.

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). The latter authors report the range $0.060 < S:P < 1.689$ of the geometric mean values for various plankton species at various irradiance levels. Given the Redfieldian N:P = 16, this would translate to the $0.0038 < S:N < 0.106$ range. Moreover, for each geometric mean value, standard deviations are ranging from 1.2% to 46.8%. Certain groups of phytoplankton, mainly Dinophyceae and Prymnesiophyceae, are able to produce and release large amounts of DMSP, $(CH_3)_2S^+ (CH_2)_2COO^−$, a major form of reduced sulfur in marine particulate matter (Simó et al., 2000). It may constitute up to 10–20% of cellular organic carbon (Matrai and Keller, 1994), becoming a major organic constituent in phytoplankton known to produce large amounts of DMSP (Fraga and Álvarez-Salgado (2005). The S:N = 0.1 ratio derived after Deuser (1970) is at the high end of the range $0.0038 < (S:N) < 0.10$ after Finkel et al. (2006), but still lower than the exceptional S:N = 0.15 after the S:P= 2.4 ratio reported by Matrai and Keller (1994), the latter reported in equivalent terms of N:S = 16:2.4 by Steiner et al. (2021). Hedges et al. (2002) report an extended Redfield stoichiometry $C_{106}H_{117}O_{37}N_{16}PS_{0.4}$ such that the ratio S:N = (0.4 / 16) = 0.025.

For an example assessment, when one would take a hypothesized elemental composition ratio S:N = 0.06 then for all oceanic waters the range of changes of the concentration of dissolved sulfate would be 6% of the range of the concentrations of dissolved nitrate. Latter range of nitrate values being between 0 and 45 μmol.kg^{-1} (Table 2) would imply a parallel range in between 0 and 2.8 μmol.kg^{-1} of biology-driven dissolved sulfate concentration changes. This could in principle be significant for Alkalinity changes.

Magnesium (Mg) is the central ion in chlorophyll, and occurs in an Mg:P ratio ranging from $4.2\ 10^{-3}$ to maximum $233\ 10^{-3}$ in marine phytoplankton (see Supplementary Material S15). The maximum value for Mg uptake/release of 0.770 μmol.kg^{-1} seawater is close to the precision of Alkalinity of 1 μmol.kg^{-1}. This maximum is not discernible versus the very high background Mg concentration of 52820 μmol.kg^{-1} in seawater (Table 1).

Finally, the reduced species hydrogen sulfide, ammonia and nitrite may in certain regions play a role but are not in the scope of this article. This is briefly outlined in Supplementary Material S2.

8. General discussion

8.1. Keep it simple

This article defines and describes Oceanic Alkalinity and Titration Alkalinity in a straightforward approach in keeping with common general chemistry. Our aim is to share this more simple approach with the wider community of scientists and students. As we have explained, the quite specialistic jargon of a small expert community is not necessary. By adhering to common general chemistry, various specialistic concepts are avoided.

Firstly, the free pH scale (pH_{FREE}) is used as it just represents how pH is measured and H+ ions are treated in chemistry. The free pH scale is therefore preferable over the specialistic total pH_T scale and the seawater pH_{SWS} scale, the latter scales only having been applied in publications on the CO_2 system of seawater. Secondly, several preceding articles distinguish between so-called proton acceptors and proton donors among the relevant constituents of seawater. This is quite confusing because in the process of the acid titration, all the relevant constituents of seawater are in fact accepting protons, with one exception being dissolved nitrate that at the pH=4.5 endpoint of the titration still is fully dissociated. Otherwise, one is aware of the general concept of proton donors and proton acceptors in the Brønsted–Lowry acid–base theory, yet here this leads to more confusion than clarification. Thirdly, the arbitrarily established zero level of protons, and this for each relevant seawater constituent, is neither needed nor clarifying with regards to understanding the Alkalinity of seawater.

Historically, for more than 150 years efforts were made to unravel and understand the chemistry of seawater leading to the concept of Alkalinity (see Dickson, 1992). Quite understandably, if not inevitably, this led to the evolution of various more and more specialized concepts and their definitions among only a small group of expert scientists. Today, it is deemed timely to provide to a wider group of scientists and students a more simple, but still exact approach in keeping with common general chemistry.

8.2. Surface ocean versus deep ocean

Given the usually quite dynamic wax and wane of phytoplankton blooms, one realizes that several intracellular constituents would by rapid decomposition (grazing or otherwise) largely be returned to seawater. This would be likely for the Mg atom of chlorophyll *a*, because latter is deemed to be quite unstable once a phytoplankton cell has died (Owens and Falkowski, 1982; Bale et al., 2015). Similarly this holds perhaps for intracellular organic sulfur compounds that would become released in the ambient seawater and will presumably become rapidly oxidized to dissolved sulfate. In other words, any changes in alkalinity in surface waters due to uptake of N, P, S, Mg, Si and so forth may perhaps in time frames of one or a few weeks become nullified due to the rapid turnover of algal biomass in the surface water ecosystem. If so, then an Alkalinity definition based on uptake by algae in surface waters may not necessarily be general enough to also apply in deep waters.

Now for uptake and remineralization of N, P and Si we have deep-water tracers dissolved nitrate, phosphate and silicate that provide some guideline for an Alkalinity equation derived in surface waters being valid also in deep waters. For S as well as Mg, the immense background concentrations of dissolved SO_4^{2-} and Mg^{2+} prevent a similar approach for assessing a general definition to be valid also in deep waters.

8.3. Caveats of the Alkalinity concept

One caveat is that regional deviations occur from the original concept of uniform proportions of the major elements comprising salinity (see Supplementary Material S16). This in turn causes deviations of the Oceanic Alkalinity. Other caveats are the risks of interferences with Titration Alkalinity due to undefined and/or unknown proton acceptors, notably dissolved organic substances and suspended particles (see Supplementary Material S17). The treatment of these is beyond the scope of the present study.

9. Summary

Considering publications of the era of 1965 to the present day, in the early years no distinction was made between different concepts of Alkalinity in oceanic seawater. Here we consider two distinct concepts: Oceanic Alkalinity and Titration Alkalinity. The Oceanic Alkalinity is defined as the small difference between the sum of charges of strong cations and the sum of charges of strong anions, after Broecker and Peng (1982). In any natural untreated seawater sample this small difference is compensated by the sum of charges of the weak anions minus the sum of charges of the weak cations. The Oceanic Alkalinity is the pivotal variable for studying and unraveling biogeochemical processes in the oceans. For a given seawater sample, its value can be obtained by titration of seawater yielding a value of Titration Alkalinity that next must be adjusted by the general relation between Oceanic Alkalinity and Titration Alkalinity.

For Titration Alkalinity an operational definition is adopted after Millero (1995) and Fraga and Álvarez-Salgado (2005) as follows: “*The Titration Alkalinity of a natural water sample is defined as the concentration of all bases able to accept a hydrogen ion at the equivalence point of the carbonic acid system species.”* This definition is here developed in a straightforward approach that is intended to be easily understandable for a wider readership and easily used by marine scientists.

Ideally, the acid titration of all weak ions would yield a value of total consumption of added hydrogen ions that then would equate perfectly with the net sum of the charges of the strong ions in Oceanic Alkalinity. Unfortunately, seawater is not that ideal. At the second CO_2 system equivalence point, being the endpoint of the titration, some of the hydrogen ions of the added acid also are absorbed by small portions of the SO_4^{2-} and F^- anions. On the other hand, at this same endpoint of the titration, among the weak ions the various phosphate anions are not completely neutralized to the neutral H_3PO_4 state. Due to this non-ideal situation there is a small, yet significant, difference between Oceanic Alkalinity and Titration Alkalinity.

The exact difference of values of Oceanic Alkalinity and Titration Alkalinity can be accurately quantified. The endpoint pH value of the titration prescribes the exact values of partial proton assimilation by SO_4^{2-} and F^-. Moreover, the endpoint pH defines the exact value of incomplete proton assimilation by the original (pH=~8) charged $H_2PO_4^-$ and HPO_4^{2-} and PO_4^{3-} anions. For an example seawater sample at standard salinity (S=35) and temperature (T=25°C) and initial pH=8 and final pH=4.4 endpoint of the titration, the exact difference in μmol.kg^{-1} is defined in the following relationship:

$$\mathrm{Alk_{Oceanic}} = \mathrm{Alk_{Titration}} + 1.021\ [\mathrm{DIP}] - 0.0003966\ [\mathrm{SO_4^{2-}}] - 0.010457\ [\mathrm{F^-}] \qquad (50)$$

or in terms of salinity (S):

$$\mathrm{Alk_{Oceanic}} = \mathrm{Alk_{Titration}} + 1.021\ [\mathrm{DIP}] - 0.3409\ \mathrm{S} \qquad (51)$$

For each individual seawater sample, the initial pH defines the speciation of DIP before titration (for SO_4^{2-} and F^- the initial pH does not matter, see Figures 3 and 4). Similarly, the endpoint of titration is at its own unique pH value, that is dominated by the second dissociation of the CO_2 system, such that the pH value will in general be very close to pH=4.4. Therefore, in some applications a scientist may be satisfied to adopt the pH=8 and pH=4.4 begin and end values such that the coefficients in above equations can simply be applied. Other scientists may choose to pursue the more precise calculation based on the unique pH values before the titration and at the endpoint of titration of each individual seawater sample, yielding slight adaptations of these coefficients. Finally, one should be aware that the underlying conditional stability constants K* of sulfate, fluoride and phosphate in themselves are functions of the salinity. In other words, when applying the above fairly simple equations (50 and 51) to other salinities than the here chosen standard S=35, the elaborate equations of the conditional stability constants would need to be incorporated yielding more elaborate versions of Eqs. (50) and (51).

The formation/decomposition of organic matter by photosynthesis/respiration is commonly decribed by Redfield stoichiometry C:N:P=106:16:1. The uptake/release of dissolved nitrate yields a corresponding increase/decrease of Oceanic Alkalinity. As result, the complementary sum of charges of weak ions must also increase/decrease. The latter (i) consideration, in combination with (ii) the parallel uptake/release of both DIC and DIP into organic matter and hence (iii) the mass balances of DIC and DIP, lead to changes including shifts in the various charges of the weak ions, notably the charged species of the DIC and DIP pools, but surely also significant shifts of the H^+ and OH^- ions and hence the pH value of seawater. However, the uptake/release of both DIC and DIP does NOT affect Oceanic Alkalinity.

Data availability statement

All data are available in this article with its accompanying Supplementary Materials.

Author contributions

All three authors contributed to the gradual development of the manuscript. Eventually HdB combined all text sections into one manuscript that was improved by several rounds of comments and corrections of MH and EMJ.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Tables

Table 1. The standard mean chemical composition of seawater with salinity = 35 after PICES (2007; their Chapter 5, Table 2). For the derivation (eq. 28) of a typical value 2400 μmol.kg^{-1} of Oceanic Alkalinity, the double charged ions count twice, and the non-charged B is not taken into account. See also similar compilations by Broecker and Peng (1982; B&P; their Table 2-5 at page 64), Bakker (1998; Table 2-1 at page 11) and Zeebe and Wolf-Gladrow (Z&WG; 2001; their Table 1.2.7 at page 47). See Supplementary Material S12 for deviations from the concept of uniform proportions of the major elements comprising salinity, and as a result, regional deviations of Oceanic Alkalinity.

	PICES	**PICES**	**B&P 1982**	**Bakker (1998) and Z&WG(2001)**
Ion	**mol.kg^{-1}**	**μmol.kg^{-1}**	**mol.kg^{-1}**	**mol.kg^{-1}**
Cl^-	0.54586		0.547	0.5455
SO_4^{2-}	0.02824	28240	0.028	0.0282
Br^-	0.00084		0.001	0.0008
F^-	0.00007	70		0.0001
B	0.000416			
Na^+	0.46906		0.470	0.4678
Mg^{2+}	0.05282	52820	0.053	0.0533
Ca^{2+}	0.01028	10280	0.010	0.0103
K^+	0.01021		0.010	0.0099
Sr^{2+}	0.00009	90		0.0001

Table 2. Typical concentrations (μmol.kg^{-1}) of DIC and major nutrients in surface and deep waters of the 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

Table 3. Example of the chemical speciation of dissolved phosphate (total 1.52 µmol.kg^{-1}) in surface seawater after De Baar and Gerringa (2008). Relevant are the summation values in bold 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) but with best value 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 the ANT XXIV-3 expedition (2008) with RV Polarstern in the Southern Ocean part of the Atlantic Ocean (Van Heuven et al. 2011a; Neven et al., 2011). The salinity and concentrations of nitrate, phosphate, silicate used were measured during the expedition. The measured values of Alkalinity and DIC (Van Heuven et al., 2011a) were used with CO2Sys to calculate the pCO_2 = 360 µatm and pH = 8.07. Latter pH value was used as input variable in Mineql+.

MgH_2PO4^+	0.00941µmol.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 %

Table 4. Concentrations (A) and charges (B) of phosphate species at pH = ~8 and at three example pH values for the second equivalence point of the Alkalinity titration: (i) nominal pH = 4.5; (ii) pH=4.4 endpoint of the dominant reaction: $[H^+] \sim [HCO_3^-] + 2\times[CO_3^{2-}]$ (Fraga and Álvarez-Salgado, 2005); (iii) pH_{SWS}=4.25 endpoint for the hydrogen ion activity, $a_H = \sim10^{-4.4}$ (Fraga and Álvarez-Salgado 2005). Conditional stability constants are defined versus the pH_{FREE} scale.

A. For total dissolved phosphate (DIP) = 1 μmol.kg^{-1}

	pH = ~8	**pH = 4.5**	**pH=4.4**	**pH_{SWS}=4.25**
Hydrogen ion concentration (mol.kg^{-1}**)**	10^{-8}	$3.16228\ 10^{-5}$	$3.98107\ 10^{-5}$	$5.62341\ 10^{-5}$
Factor increase of H^+ ion versus pH=8	1	3162	3981	5623
$H_2PO_4^-$ (μmol.kg^{-1})	0.022	0.97374	0.9790	0.9704
HPO_4^{2-} (μmol.kg^{-1})	0.962	0.02625	0.02096	0.01471
PO_4^{3-} (μmol.kg^{-1})	0.016	$1.05\ 10^{-6}$	$0.666\ 10^{-6}$	$0.331\ 10^{-6}$
H_3PO_4 (μmol.kg^{-1})	$1.06\ 10^{-6}$	$1.612\ 10^{-3}$	$2.041\ 10^{-3}$	$2.857\ 10^{-3}$
Summation (μmol.kg^{-1})	1.00	1.00	1.00	1.00

B. The charges (μmol.kg^{-1}) of the phosphate species and the summation total charge for total dissolved phosphate = 1 μmol.kg^{-1}. See Supplementary Material S9 for underlying approximate calculus at the endpoint example pH values

	pH = ~8	**pH = ~4.5**	**pH=4.4**	**pH_{SWS}=4.25**
$H_2PO_4^-$ (μmol.kg^{-1})	0.022	0.9737	0.9790	0.9704
HPO_4^{2-} (μmol.kg^{-1})	1.92	0.0525	0.0419	0.0294
PO_4^{3-} (μmol.kg^{-1})	0.048	$3.15\ 10^{-6}$	$1.998\ 10^{-6}$	$0.993\ 10^{-6}$
H_3PO_4 (μmol.kg^{-1})	nil	nil	nil	nil
Summation Total charge (μmol.kg^{-1})	1.99	1.02624	1.0209	0.9998

Figures

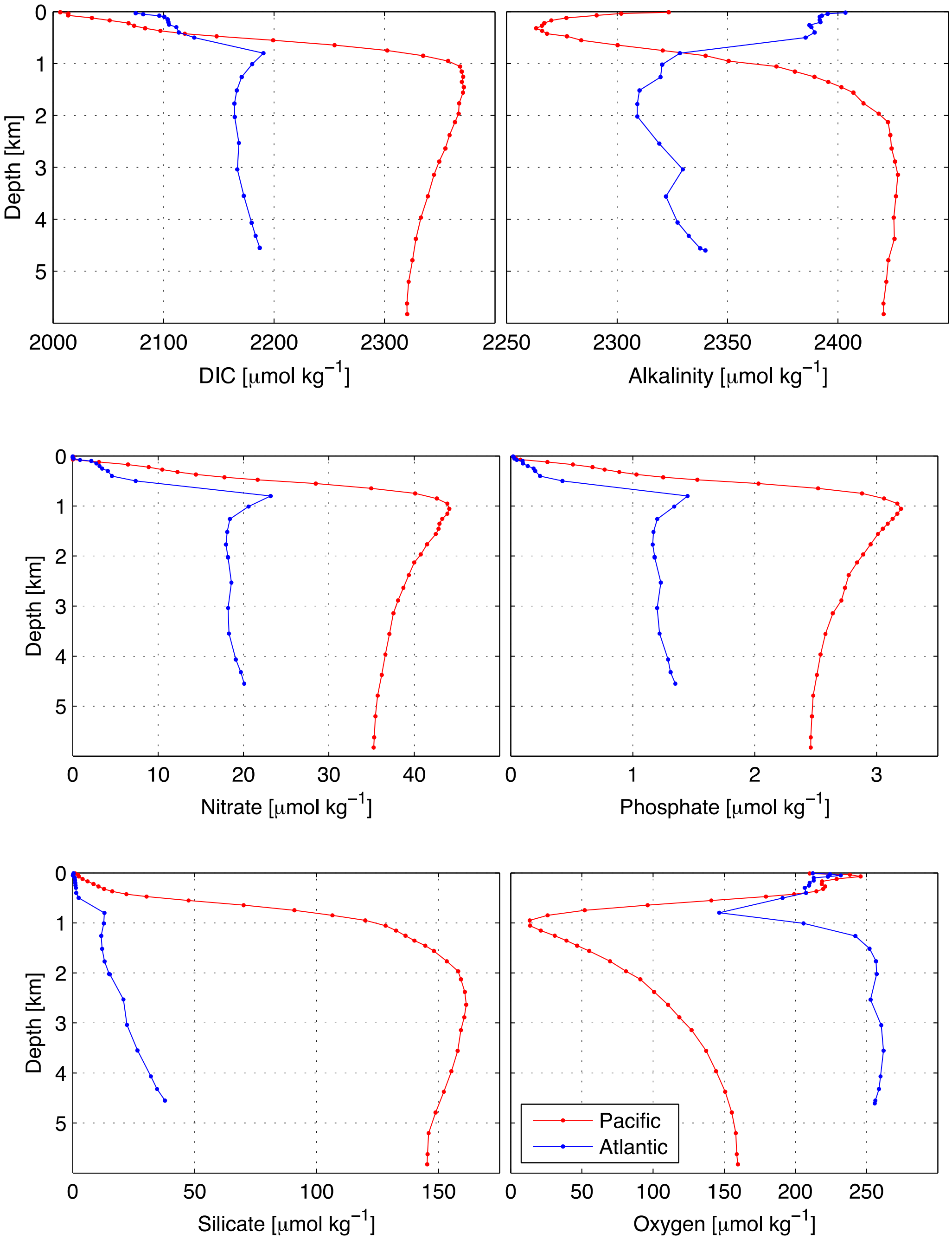

Figure 1. Vertical distributions of DIC, Alkalinity, nitrate, phosphate, silicate and oxygen in the Northwest Atlantic Ocean (blue connected dots; to 4.5 km depth) versus the Northeast Pacific Ocean (red connected dots; to 5.8 km depth). Higher DIC in deep Pacific versus deep Atlantic is due to respiration of organic matter plus 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 (31^{0}45.92'N 64^{0}04.95'W at 13 June 2010), after Rijkenberg et al. (2014), available at www.geotraces.org. Data for North Pacific is from RV Melville cruise 318M2004 along WOCE line PO2, station 119 (30.00^{0}N,159.70^{0}W at 4 August 2004), available in GLODAPv2 via CCHDO (https:// cchdo.ucsd.edu/cruise/ 318M200406). Figure adapted after De Baar et al. (2017b).

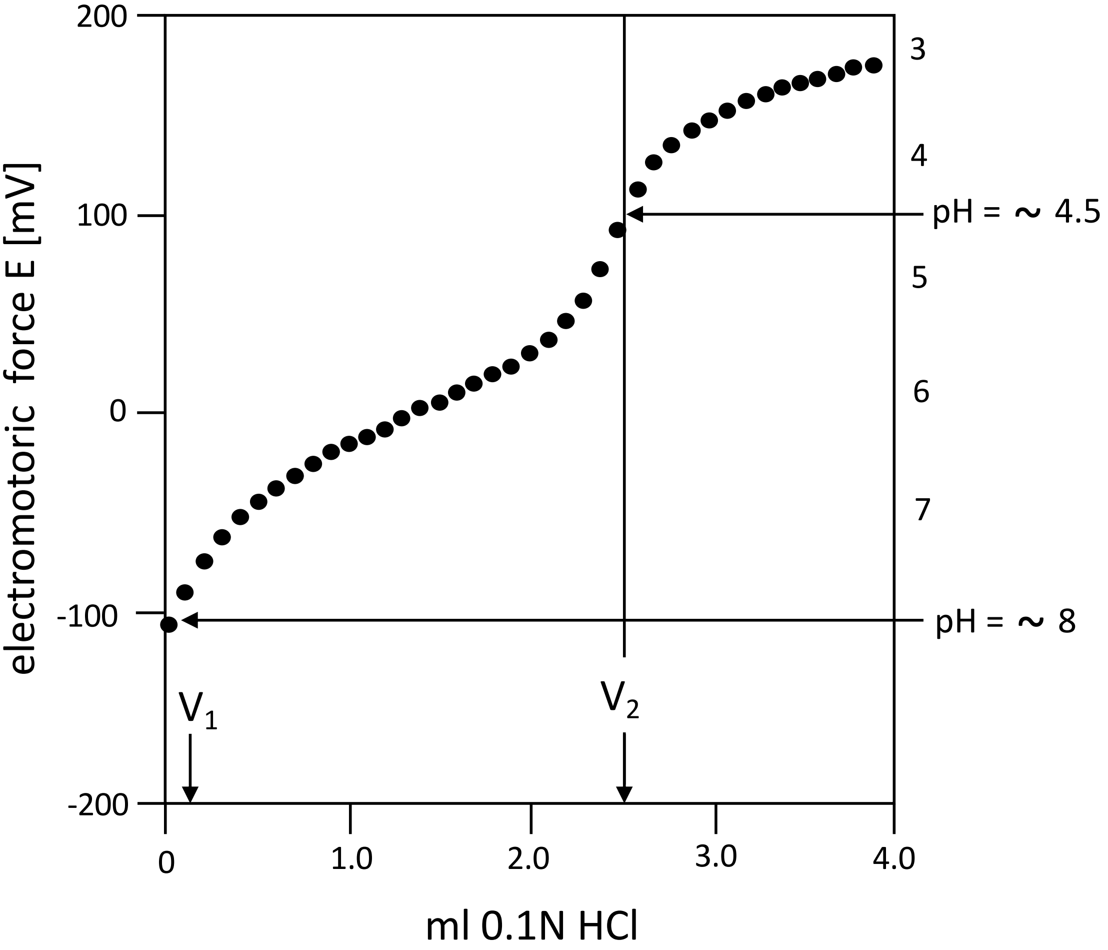

Figure 2. Sketch of a "typical" titration curve with V_1 and V_2 indicated at the x-axis. Redrafted after Stoll (1994) based on data of Johansson and Wedborg (1982) with software kindly provided by Margareta Wedborg. The electromotoric force E [mV] at the left hand vertical scale relates with the pH at the right hand vertical scale via the Nernst equation (see Supplementary Material S7). The added volume V_1 marks the equivalence point of the conversion of the CO_3^{2-} ion to the HCO_3^- ion state. The added volume V_2 marks the equivalence point of the conversion of the HCO_3^- ions to the H_2CO_3/CO_2 (aqueous) state and represents Titration Alkalinity. Some small portion of the at V_2 converted HCO_3^- ions had at V_1 been produced from the CO_3^{2-} ion. Thus overall the latter double charged CO_3^{2-} ion has throughout the titration consumed 2 hydrogen ions, such that Alkalinity = $2[CO_3^{2-}] + [HCO_3^-]$ + some lesser contributions + some minors, in the original seawater sample. The difference (V_2-V_1) multiplied by the 0.1N HCl strength represents the value of DIC. However nowadays the DIC is determined independently by coulometry (Johnson et al., 1987). As result the value V_1 for the term (V_2-V_1) is not needed anymore. Hence it suffices to only determine the value of V_2 (representing Titration Alkalinity) by non-linear curve fitting of only the second part of the overall titration curve. For this and details of Titration Alkalinity see further in Supplementary Material S6. Relevant also are the Supplementary Materials S1 and S7. A similar titration curve is the Figure 1 of Edmond (1970). See also Figure 15-5 at page 370 in Skoog et al. (2014).

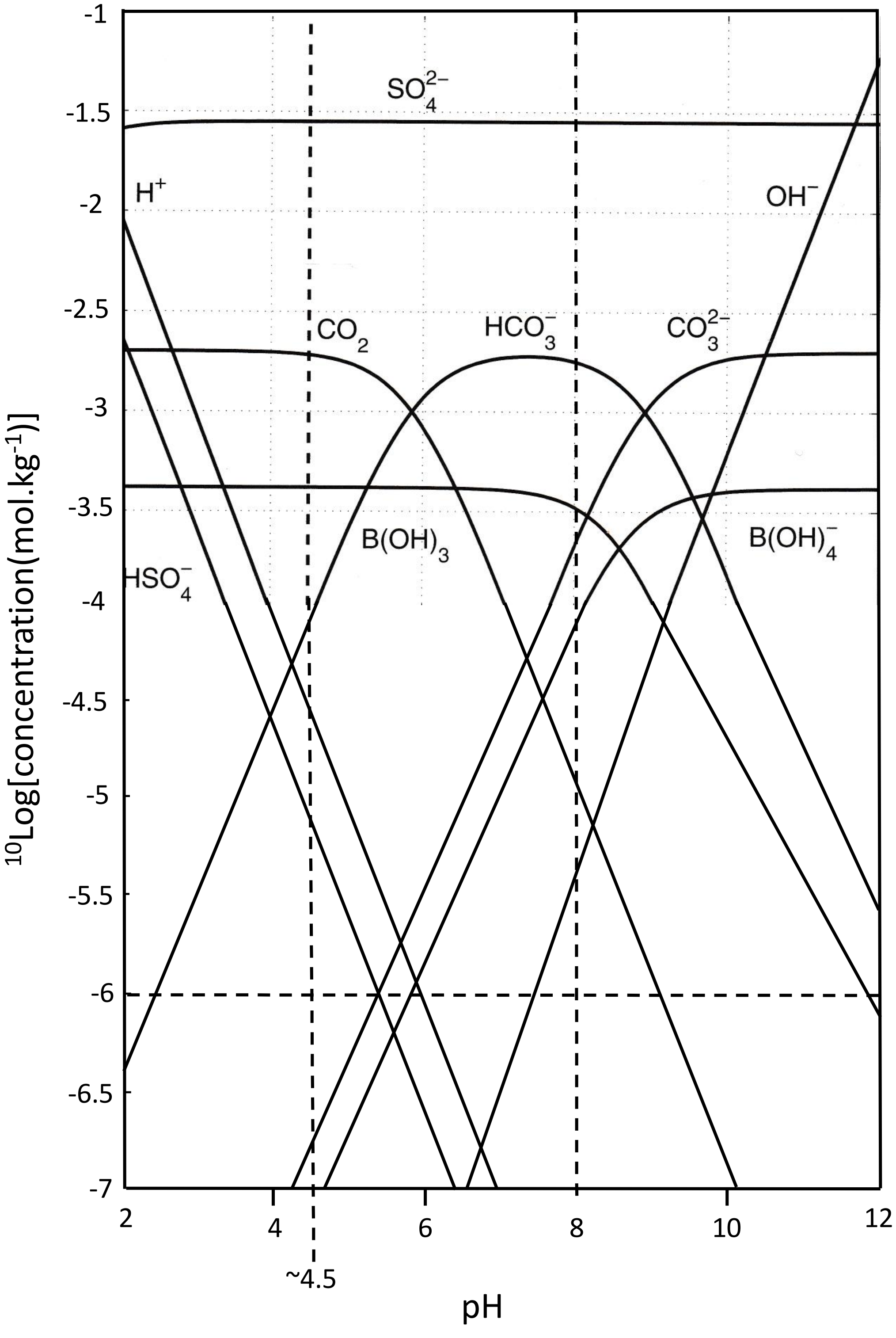

Figure 3. Bjerrum plot of the major constituents with respect to Alkalinity. Redrafted with downward extensions, after the upper graph of the Figure 1.2.11. of Zeebe and Wolf- Gladrow (2001). The vertical dotted line at pH=8 represents a typical pH of surface seawater. The vertical dotted line at pH=~4.5 represents the nominal pH value of the equivalence point of the conversion of the HCO_3^- ions to the CO_2^* $_{(aqueous)}$ state. The horizontal dotted line at the 10^{-6} mol.kg^{-1} = 1 μmol.kg^{-1} concentration represents the approximate reproducibility of the determination of Alkalinity. An earlier version of a Bjerrum plot is Figure 2 of Edmond (1970).

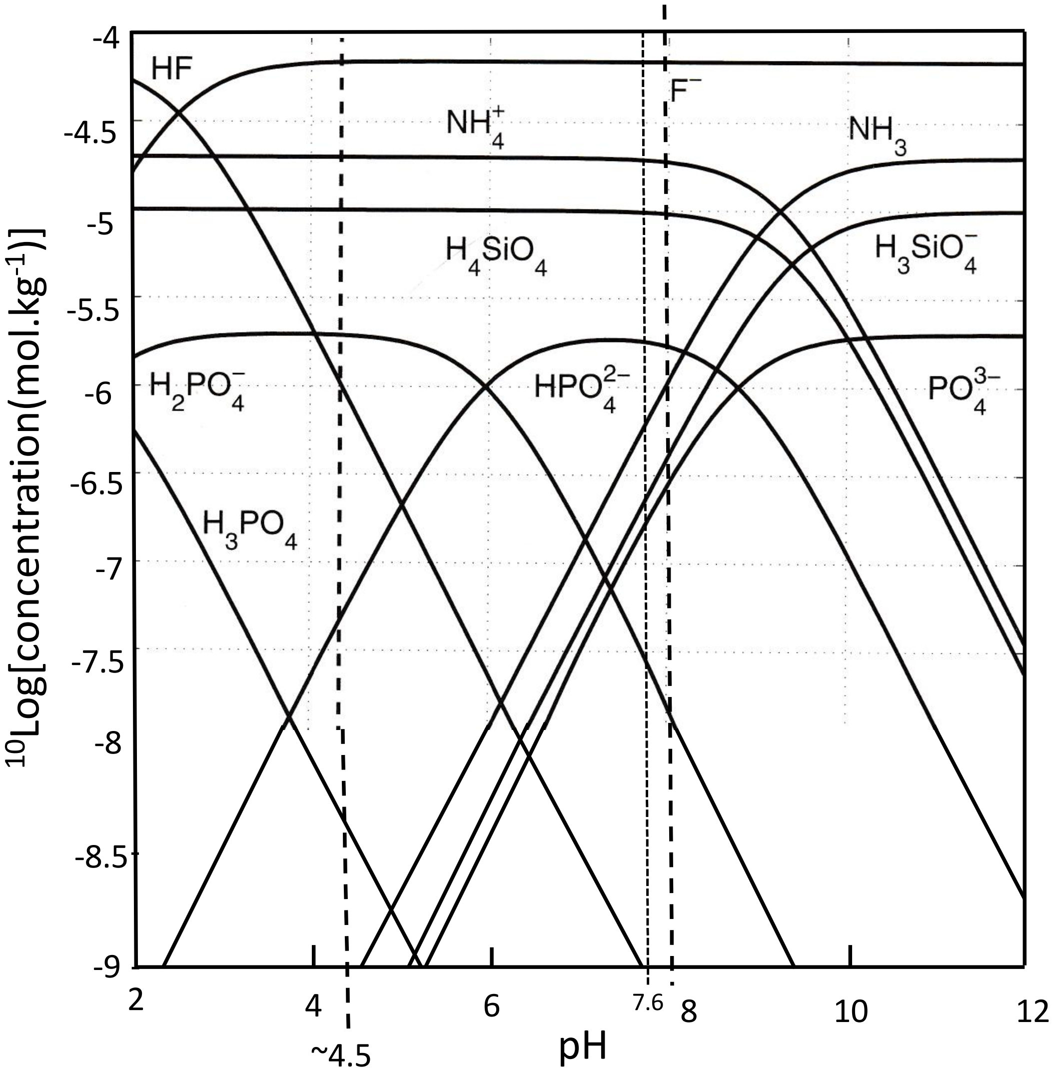

Figure 4. Bjerrum plot of the minor constituents with respect to Alkalinity. Redrafted with downward extensions after the lower graph of the Figure 1.2.11 of Zeebe and Wolf- Gladrow (2001). The vertical dotted line at pH = 8 represents a typical pH of surface seawater. The adjacent vertical dotted line at pH = 7.6 represents the more or less lowest value in oceanic seawater.The vertical dotted line at pH = ~4.5 represents the nominal pH value of the equivalence point of the conversion of the HCO_3^- ions to the $CO_2^*{}_{(aqueous)}$ state. Total silicate (H_4SiO_4 + $H_3SiO_4^-$) is depicted at 10^{-5} mol.kg^{-1} = 10 μmol.kg^{-1} that is representative for the concentration range zero to 170 μmol.kg^{-1} in the oceans (Table 2; Figure 1). The total dissolved inorganic phosphate is depicted at DIP = $10^{-5.7}$ mol.kg^{-1} = 2 μmol.kg^{-1} that is representative of the concentration range zero to 3.3 μmol.kg^{-1} in the oceans (Table 2; Figure 1). (This is akin to the Bjerrum plot in Figure 2 of Edmond (1970) where the positioning of the label $H_2PO_4^-$ at left hand side in the plot appears to be somewhat puzzling.)

Supplementary Material

Oceanic Alkalinity and Titration Alkalinity: a novel straightforward approach in keeping with common general chemistry

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S1) Conditional stability constants and pH scales

The concentration c_i of a dissolved ion i in water is best expressed in unit of molality. In general chemistry, molality is a measure of the amount of solute relative to a given mass of solvent (Lewis and Randall, 1923). The commonly used unit for molality is the moles per kilogram [mol.kg^{-1}]. This contrasts with the definition of molarity which is based on a given volume of solution, e.g. [mol.L^{-1}]. Molality only depends on the masses of solute and solvent, which are unaffected by variations in temperature and pressure. Therefore molality is the preferred intrinsic unit in general chemistry. Molality is the suitable unit for oceanic waters that are subject to significant ranges of temperature and pressure.

For chemical equilibrium reactions, the more fundamental thermodynamic stability constant K is defined versus the activities a_i of the reactants. For example, for the reactants q and r and product p in the reaction q + r = p the thermodynamic stability constant is

$$K = (a_p) / \{(a_q)\ (a_r)\} \qquad \text{(Eq. S1.1)}$$

The activity a_i of a solute i may differ from its concentration c_i [mol.kg^{-1}] due to electrostatic interactions between the dissolved solutes in the solution. This deviation between a_i and c_i is defined by the dimensionless activity coefficient γi as follows: $a_i = \gamma_i .\ c_i$

This leads to

$$K = \gamma_p\ [c_p] / \{\gamma_q\ [c_q]\ \gamma_r\ [c_r] \qquad \text{(Eq. S1.2)}$$

In aqueous conditions of (theoretical) infinite dilution the various dissolved constituents are infinitely far apart such that there is no mutual interaction and then the activity a_i equals the concentration [i], such that activity coefficient $\gamma_i = 1$. In practice, for example in destilled water, this is a quite suitable approach. However, seawater comprises a suite of dissolved constituents with very high concentrations (Table 1). The corresponding dissolved ions have quite strong interactions.

By transfer of the activity coefficients to the left hand side one obtains the conditional stability constant that incorporates these activity coefficients:

$$\{(\gamma_q \text{ x } \gamma_r) / \gamma_p\} \text{ x } K = K^* = [c_p]/\{[c_q]\ [c_r] \qquad \text{(Eq. S1.3)}$$

where [c] is the concentration [mol.kg^{-1}].

Conditional stability constants of seawater are functions of salinity, temperature and pressure. For the experimental determination of Alkalinity at laboratory conditions of 20°C or 25°C and 1 atm it suffices to only focus on the dependence on salinity. Notation for conditional stability constants is K* or K' where all the reactants and products are expressed in square brackets as stoichiometric concentrations [µmol.kg^{-1}].

The activity coefficients are functions of the ionic strength of the solution, here the seawater. The molar ionic strength I of a solution is a function of the concentration of all ions present in that solution:

$$I = 1/2\ \Sigma\ c_i z_i^2 \qquad \text{(Eq. S1.4)}$$

where one half is part of this equation because we are including both cations and anions. The c_i is the molar concentration of ion i [mol.kg^{-1}], z_i is the charge number of that ion. Notice that double charged ions, for example Mg^{2+} or SO_4^{2-} yield fourfold higher contributions, this due to the quadratic function z_i^2.

For seawater at standard salinity S=35 (Table 1) the ionic strength I is calculated as: I = 0.72276, or rounded 0.72

As a more general function of salinity the ionic strength is defined as:

$$I = \{19.924S\}/\{1000 - 1.005S\} \quad \text{(Eq. S1.5)}$$

At the very high ionic strength of seawater there are multiple strong interactions between all charged ions in seawater and as result the activity coefficients γ_i deviate strongly from 1 (for example, see Zeebe and Wolf-Gladrow (2001; their Table 1.1.3; see also Plummer and Sundquist, 1982).

The determinations of the actual values of conditional stability constants K* and activity coefficients γ_i in seawater are quite complicated. The very extensive literature on such experimental determinations and ensuing derivations is beyond the scope of this article and supplements. Otherwise, such various complications, presumably have led to the development of four different pH scales for seawater (Table S1.1):

Table S1.1. pH scales after Velo et al. (2010). For the free scale we use the notation pH_{FREE} in order to avoid confusion with the subscript F for fluoride.

Scale	**pH definition**
Free	$pH_{FREE} = -\log [H^+]_{FREE}$
Total	$pH_T = -\log[H^+]_T = -\log([H^+]_F \cdot(1+[SO_4^{2-}]/K_S)) \approx -\log([H^+]_F + [HSO_4^-])$
Seawater	$pH_{SWS} = -\log[H^+]_{SWS} = -\log([H^+]_F \cdot(1+[SO_4^{2-}]/K_S + [F^-]/K_F)) = -\log([H^+]_F + [HSO_4^-] + [HF])$
NBS	$pH_{NBS} = -\log a_H$

Notice that the latter NBS scale is defined versus the activity a_H of the hydrogen ion.The free proton concentration scale pH_{FREE} for seawater is defined versus the concentration $[H^+]$ and deemed the most consistent with common general chemistry, and therefore the preferred scale (Waters et al., 2013, 2014). In our article this scale pH_{FREE} is thus used. The stoichiometric concentration $[H^+]$ is related to the activity a_H as follows:

$$a_H = \gamma_H \times [H^+] \quad \text{(Eq. S1.6)}$$

where γ_H is the activity coefficient that is a function of the salinity, temperature and pressure of the seawater. In seawater at S = 35, T = 25°C and p = 1 atm, values in the order of 0.6 to 0.7 have been reported (Zeebe and Wolf-Gladrow (2001; their Table 1.1.3).

In previous publications on Alkalinity and acid titration either the specialistic total scale pH_T or the specialistic seawater scale pH_{SWS} are commonly used (Millero, 1995; DOE, 1994; Zeebe and Wolf-Gladrow, 2001; PICES, 2007; Velo et al., 2010). The difference between the total and the seawater scales is numerically small, in the order of ~0.01 pH units at salinity S=35 (Velo et al., 2010). For example, in order to convert -approximately- from the pH_{SWS} scale to the pH_T scale a value of 0.015 is applied (see Chapter 5, footnote 5 at page 14, in PICES, 2007).

All conditional stability constants K* that are used in our article are defined versus the free proton concentration scale pH_{FREE}.

In DOE (1994) and PICES (2007), quite often the * symbol is left out. Obviously when all reactants are expressed as stoichiometric concentrations in square brackets then the given K is in fact a conditional stability constant K*, and not a thermodynamic constant K.

The aqueous cation $H^+_{(aq)}$ is the recommended notation for the hydrogen ion or proton in aqueous solution. This notation is deemed best, overruling the knowledge that in water the H^+ cation is linked to surrounding water molecules, such that it exists as the hydronium ion H_3O^+ or even, the more extended, hexahydrate $H^+(H_2O)_2(H_2O)_4$ state. In the alkalinity literature the simple $H^+_{(aq)}$ or H^+ notations are indeed commonly used.

The alkalinity literature does mention both the wording proton as in the classical article by Dickson (1981), as well as the wording hydrogen ion. Here are mentioned both wordings "proton" and "hydrogen ion", the choice largely following the cited reference. (Obviously, the proton concept in aqueous solution differs greatly from the proton concept in nuclear chemistry, that is, the nucleus of a chemical element in general comprising both protons $H^+_{(nuclear)}$ and neutrons.)

References: see main article

S2) On Alkalinity interactions with reduced chemical species

S2.1 Chemical thermodynamic equilibrium and deviations thereof

In well oxygenated seawater, the reduced species hydrogen sulfide, ammonia and nitrite should not exist according to the laws of chemical thermodynamics. However, as result of biological processes, these species can be introduced in the ambient seawater and may exist as short-lived intermediates. When avoiding exposure of a seawater sample to the high-oxygen atmosphere and doing determinations quickly after sampling, these reduced forms may be found occasionally in the samples from the biologically active upper euphotic zone and usually in the oxygen minimum zone.

When a collected seawater sample is stored during some time before being analyzed for Titration Alkalinity, there is a risk that the reduced constituents, which originally were present, have in fact become oxidized due to exposure to atmospheric oxygen. If so, then the insertion of the independently (quickly stabilized) measured value(s) of sulfide, ammonia and nitrite in the complete equation 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 under an oxygen-free atmosphere.

In deep, poorly ventilated basins (e.g., Cariaco Trench and 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. In truly anoxic seawater basins, for example the deeper waters of the Black Sea, the concentrations of sulfide and ammonia may be very high.

S2.2 Contribution of sulfide and ammonia to Titration Alkalinity

For anoxic seawater basins, the concentrations of sulfide would be significant in the Titration Alkalinity equation. In the anoxic deeper waters of the Black Sea, the concentration of total sulfide is more than 400 μmol.kg^{-1} at ~2100 m depth (Luther, 1991). The equilibrium constants of the reactions of H_2S and HS^- are:

$$K^*_{1S} = [H^+]\,[HS^-]/[H_2S] \qquad \text{(Eq. S2.1)}$$

$$K^*_{2S} = [H^+]\,[S^{2-}]/[HS^-] \qquad \text{(Eq. S2.2)}$$

where the $pK^*_{1S} = 7$ and the $pK^*_{2S} = 12$ after Dickson (1981). Within the deep anoxic Black Sea the pH can be as low as pH=7.6-7.7 (Figure 3 of Kondratiev et al., 2017). As a matter of fact, the sulfide system here is the major control on the pH. For seawater in general in the range $7 < pH < 8$ (Hiscock and Millero, 2006), in above Eq. (S2.1) at pH=8 the $[HS^-]$ would be about tenfold the $[H_2S]$, whereas at pH=7 there would be a fifty/fifty distribution of $[HS^-]$ and $[H_2S]$. For the deep Black Sea with the total sulfide = 400 μmol.kg^{-1} and pH=7.65 the single charged $[HS^-]$ = 327 μmol.kg^{-1} and the remaining $[H_2S]$ = 73 μmol.kg^{-1}. For the same sample, the double charged species would be $[S_2^-] = 4.5\ 10^{-5}$ μmol.kg^{-1} and is deemed negligible.

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 most ammonia exists in the NH_4^+ state, but about 5 % 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 number of protons absorbed in this conversion of NH_3 to NH_4^+ contributes 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 μmol.kg^{-1} precision of Titration Alkalinity. In an extreme oxygen minimum zone, the overall ammonia concentration may be as high as 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} which still is less than the precision of Titration Alkalinity, but in combination with other such minor species may be slightly significant.

Within the anoxic deep water column of the Black Sea, the dissolved ammonia steadily increases with depth to about 40 μmol.kg^{-1} at 350 m depth (Codispoti et al., 1991) and ultimately more than 90 μmol.kg^{-1} at the greatest depth of about 2000 m (Friederich et al., 1990). Obviously, in these extreme anoxic conditions, ammonia plays a significant role in the determination of Titration Alkalinity.

These contributions for anoxic water conditions can be included by further expanding Eq. (48) of Titration Alkalinity, as follows:

$$\begin{aligned} Alk_{Titration} = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] - [H^+] \\ & + 0.97\,[DIP] + 0.0003966\,[SO_4^{2-}] + 0.01324\,[F^-] + [HS^-] + 2[S^{2-}] + [NH_3] \qquad \text{(Eq.S2.3)} \end{aligned}$$

S2.3 Contribution of nitrite to Oceanic Alkalinity

It has been suggested that dissolved nitrite may also contribute to Alkalinity (Wolf-Gladrow et al., 2007). Therefore, at least in theory, nitrite would become part of the overall Eq. (28) of Oceanic Alkalinity. At pH=8.0 both nitrate and nitrite are fully dissociated strong anions. Shipboard analyses of dissolved nitrate by spectrophotometry in one channel of an Autoanalyzer does also comprise the small amount of the dissolved nitrite, if present at all. The ensuing overall nitrate (Σ $[NO_3^-] + [NO_2^-]$) as inserted in the Oceanic Alkalinity equation (28) in fact is the sum of nitrate plus occasional trace amount of nitrite. The latter nitrite 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:

$$K^* = 10^{-3.25} = [NO_2^-]\,[H^+] / [HNO_2] \qquad \text{(Eq. S2.4)}$$

with pK*=3.25 (Fraga and Álvarez-Salgado, 2005). Then at pH = 4.5 one derives $[NO_2^-] / [HNO_2] = 10^{1.25} = 17.8$ such that $[HNO_2]=0.056\ [NO_2^-]$. Thus, at pH = 4.5 the percentage HNO_2 is merely 5.6%, the remaining 94.4% 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 are typically in the 0-0.3 μmol kg^{-1} range. At the upper limit 0.3 μmol kg^{-1} the 5.6% HNO_2 after titration to pH = 4.5 would be merely 0.015 μmol kg^{-1}. The corresponding proton consumption is well below the precision ±1 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 (where neither O_2 nor H_2S is present) in the 50-100 m depth range of the Black Sea, nitrite is also very low, except at one station 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 0.025 to 0.035 μmol kg^{-1} but still below the precision of the Titration Alkalinity. Moreover, all the above assumes that between sampling and the titration for alkalinity, none of the nitrite has meanwhile become oxidized to nitrate. This is valid only when the seawater sample is treated under O_2-free atmospheric conditions, i.e., in a glove box environment of N_2 gas only. Nevertheless, for the sake of completeness, the equation (28) of Oceanic Alkalinity can be expanded by mentioning the nitrite ion, as follows:

$$\begin{aligned}\text{Oceanic Alkalinity} = {} & [Na^+] + [K^+] + 2{\cdot}[Ca^{2+}] + 2{\cdot}[Mg^{2+}] + [Sr^{2+}] \\ & - [Cl^-] - 2{\cdot}[SO_4^{2-}] - [Br^-] - [F^-] - [NO_3^-] - 0.944\,[NO_2^-] \qquad \text{(Eq.S2.5)}\end{aligned}$$

References: see main article

S3) The GEOSECS expeditions

Professor W.S. Broecker was one of the leading scientists having initiated, implemented and interpreted the GEOSECS Program (Geochemical Ocean Sections Study). This was the first ever program doing large-scale ocean sections of the CO_2 system, ancillary parameters, notably the major nutrients, and other ocean variables in the Atlantic, Pacific and Indian Oceans. The measurements by acid titration of both DIC and Titration Alkalinity were done with the method of Edmond (1970). For the GEOSECS program some further refinements of the acid titration method for determination of both DIC and Titration Alkalinity were made by Bradshaw et al. (1981). The expeditions took place in 1972-1973 in the Atlantic Ocean, in 1973-1974 in the Pacific Ocean, and in 1977-1978 in the Indian Ocean. Overall, more than 6000 seawater samples were analyzed for DIC and Titration Alkalinity. Moreover, independent measurements of DIC were made by gas chromatography and pCO_2 by infrared gas analyses. The resulting datasets, including all the derived calculated values of the different CO_2 chemical species, were published in three Hydrographic Data Reports Volumes 1, 3 and 5, as well as three Atlases comprising the graphics of Sections and Profiles Volumes 2, 4 and 6, and Volume 7 comprising Shore-Based Data and Graphics. (GEOSECS 1981-1987). The major findings were described in an overview chapter by Campbell (1983). During GEOSECS the precision of Titration Alkalinity was reported at 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 that time.

References: see main article

S4) Various stoichiometries of the Redfield equation

The Redfield equation as presented in the main text

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

There are three major nutrient chemical elements: carbon (C), nitrogen (N) and phosphorus (P). The coefficients C:N:P=106:16:1 represent the stoichiometry of the reaction and at the time were largely based on the distributions of DIC, NO_3^- and DIP in the North Atlantic Ocean. The resulting organic biomass $[(CH_2O)_{106}(NH_3)_{16}(H_2PO_4)]_{\text{organic biomass}}$ is energetically rich and hence serves as a food and energy source for bacteria and animals in the reverse reaction (1), that is known as remineralization or respiration. Due to respiration/mineralization of organic biomass in subsurface waters, dissolved oxygen is depleted in intermediate and deep waters, with lowest concentrations in the regional Oxygen Minimum Zone (OMZ) at about 1000 m depth (Figure 1).

Various refined versions of Eq. (1) with adjusted values of the stoichiometry coefficients have been reported. Variations in ocean distributions of 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). Adjusted values of the stoichiometric constants have been derived and advocated. There are several ways, notably (i) by analyzing anomalies in the mixing of water masses (for example, Takahashi et al. 1985, Anderson and Sarmiento 1994; Alvarez-Salgado et al. 2014, Hupe and Karstensen 2000; Fernandez-Castro et al. 2019), or (ii) by studying the mean composition of organic matter (for example, Laws 1991, Anderson 1995; Fraga et al. 1998; Ríos et al. 1998). Hedges et al. (2002) report an extended Redfield stoichiometry $C_{106}H_{117}O_{37}N_{16}PS_{0.4}$ that additionally includes a value for sulfur. Sarmiento and Gruber (2006; page 116) reviewed several such more recent estimations and arrived at a stoichiometric formula for the "best guess" of the new ratios, as follows:

$$106\ \mathrm{DIC} + 122\ \mathrm{H_2O} + 16\ \mathrm{HNO_3} + 1\ \mathrm{H_3PO_4} + 78\ \mathrm{H_2O} \rightleftarrows [(\mathrm{C_{106}H_{175}O_{42}N_{16}P}]_{\text{organic biomass}} + 150\ \mathrm{O_2} \qquad \text{(Eq. S4.1)}$$

This equation is based on, among others, the new formulas $C_{106}H_{175}O_{42}N_{16}P$ as well as $C_{106}H_{171}O_{42}N_{16}P$ by Anderson (1995) and Fraga et al. (1998), respectively, which correct the overestimated H and O proportions of the original formula (1) (Fraga and Alvarez-Salgado, 2005). In principle, every scientist has the freedom to select from these various stoichiometry relationships, the relationship that is deemed to be the most appropriate. Quite nicely, as long as one is focusing merely on the bio-essential elements C, N and P, the stoichiometry of most of these equations is identical at C:N:P=106:16:1. Moreover, for the key questions of the current paper on Alkalinity, the exact stoichiometry is not at all an issue.

References: see main article

S5) 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 citations exist in the literature, but our objective is not an exhaustive review of all such applications. For correct applications one would need to use the Oceanic Alkalinity and not the Titration Alkalinity. When in equation (53) entering the 'typical' standard salinity S=35 and the lowest concentration DIP = 0 μmol.kg^{-1} for oligotrophic oceanic surface waters, the difference between Alk$_{\text{oceanic}}$ and Alk$_{\text{titration}}$ is in the order of 12 μmol.kg^{-1} merely due to the salinity (i.e., the sulfate and fluoride effects). When entering the highest oceanic concentration DIP = ~3.3 μmol.kg^{-1} (Table 2) the difference is in the order of 15.2 μmol.kg^{-1}. This range between 12 and 15 μmol.kg^{-1} would versus an assumed Alkalinity value of for example ~2400 μmol.kg^{-1} amount to some 0.5 to 0.6 %. Given this difference between Oceanic Alkalinity and Titration Alkalinity, this might significantly affect the outcome, for example, the derived changes of dissolved Ca^{2+} in seawater, or a calculated pCO_2. Thus far in the literature this application and other applications may, or may not, have used Titration Alkalinity, where it is now realized that one should use Oceanic Alkalinity. It is not inconceivable that this may have caused significant systematic offsets in some of such past applications, such offsets distinct apart from the regular error propagation (Orr et al., 2018).

S5.1. Solubilities of calcium carbonates crystalline states aragonite and calcite

By far the 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 ($\Omega_{\text{aragonite}}$) and calcite ($\Omega_{\text{calcite}}$) (Figure S4.1). For aragonite, this saturation state is defined as follows (for calcite it is similar):

$$\Omega_{\text{aragonite}} = \{[Ca^{2+}]_{sw} \text{ x } [CO_3^{2-}]_{sw}\} / K^*_{\text{SP aragonite}} \qquad \text{(Eq. S5.1)}$$

where $[Ca^{2+}]_{sw}$ and $[CO_3^{2-}]_{sw}$ are the concentrations in ambient seawater and $K^*_{\text{SP aragonite}}$ 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 biotic $CaCO_3$ minerals aragonite and calcite and abiotic $CaCO_3$ mineral ikaite each have such saturation state 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, in the sea-ice environment (Dieckmann et al., 2008 and references 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 due to its higher solubility relative to calcite. Thus, aragonite is most vulnerable to dissolution. Seawater is undersaturated when $\Omega_{\text{aragonite}} < 1$, 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; Li et al., 1969; Takahashi, 1975), where in general the upper oceanic water column is supersaturated, and the deeper, older waters tend to be undersaturated (Figure S5.1.). Nowadays, there is the ongoing emission of fossil fuel CO_2, its uptake by the oceans and ensuing decreasing time trend of $[CO_3^{2-}]$ in seawater. This has led to 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.

S5.2. 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, researchers have tried to unravel the uptake of one or another of these three species 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. Here the $[CO_2]$ and $[HCO_3^-]$ in the ambient seawater were calculated by CO2Sys software from measurements of DIC and Alkalinity (Van Heuven et al., 2011a).

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., 2011a), $[HCO_3^-]$ 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.

S5.3. Unraveling biogenic effects on Oceanic Alkalinity

Changes in DIC (ΔDIC) and Alkalinity (ΔA) result from physical and biological processes, such as salinity changes ($\Delta DIC_{\text{salinity}}$, $\Delta A_{\text{salinity}}$) from freshwater inputs and mixing of different water masses, photosynthesis and respiration ($\Delta C_{\text{organic}}$, $\Delta A_{\text{organic}}$) 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:

$$\Delta DIC = \Delta DIC_{\text{salinity}} + \Delta DIC_{\text{organic}} + \Delta DIC_{CaCO3} \qquad \text{(Eq. S5.2)}$$

$$\Delta A = \Delta A_{\text{salinity}} + \Delta A_{\text{organic}} + \Delta A_{CaCO3} \qquad \text{(Eq. S5.3)}$$

By salinity normalization (Jones et al., 2021) to S=35 or better an average salinity value of the region of investigation, the major effect of salinity on Alkalinity is taken care of. Next, the changes in DIC due to photosynthetic fixation of DIC and production of organic matter ($\Delta DIC_{\text{organic}}$) can be determined from changes in salinity-normalized dissolved nitrate (NO_3^-) and the classical C/N Redfield ratio of 106/16 = 6.6. Thus, 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 parallel decreases ΔDIC of 1 μmol kg^{-1} and ΔDIP of 1/106 = 0.0094 μmol kg^{-1} do not affect Alkalinity, but instead are accomodated by re-arrangements among the weak ions (see Eq. 29). The $\Delta A_{\text{organic}}$ is therefore estimated from $\Delta DIC_{\text{organic}}$ 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 $\Delta A_{\text{organic}}$ is entered into the salinity-normalized version of above equation (S5.3) 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 $\Delta A_{\text{organic}}$ 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+}, a value that is too small to be easily discernible by direct measurement of the very large background concentration of 10280 μmol kg^{-1} in seawater (Table 1).

Notice that in this section S5.3. there is mention of Alkalinity . This should be Oceanic Alkalinity, based on a measured value of Titration Alkalinity that subsequently is adjusted to Oceanic Alkalinity by relation (50) or (51); see text sections 6. and 7. in the main article. Unfortunately, to the best of our knowledge, thus far many articles in the literature on oceanic seawater are based on Titration Alkalinity.

S5.4. Internal consistency of CO_2 system measurements in seawater

Titration Alkalinity is among the CO_2 system variables that can be measured, the others being the DIC, pH and pCO_2, and by some laboratories, the CO_3^{2-} ion. The overall CO_2 system is such that when two variables are measured, all other variables and concentrations can be calculated. Next, when a third (and fourth, and fifth) variable is also measured, the system is overdetermined and this allows to verify for internal consistency of all measurements and constants. For example, when primarily measuring DIC and Titration Alkalinity, one may calculate pH and/or pCO_2 and compare this with the measured values of pH and/or pCO_2. Obviously, the various equilibrium constants (Section 2), notably their uncertainties, also play a role here (Millero et al., 2006, see also their table 1). Over the years, excellent efforts have been pivotal for greatly improving the accuracy of the CO_2 system in seawater (e.g., Millero et al., 1993a,b; Lueker et al., 2000; Chen eet al., 2015; Patsavas et al., 2015; Salt et al., 2016; Raimondi et al., 2019).

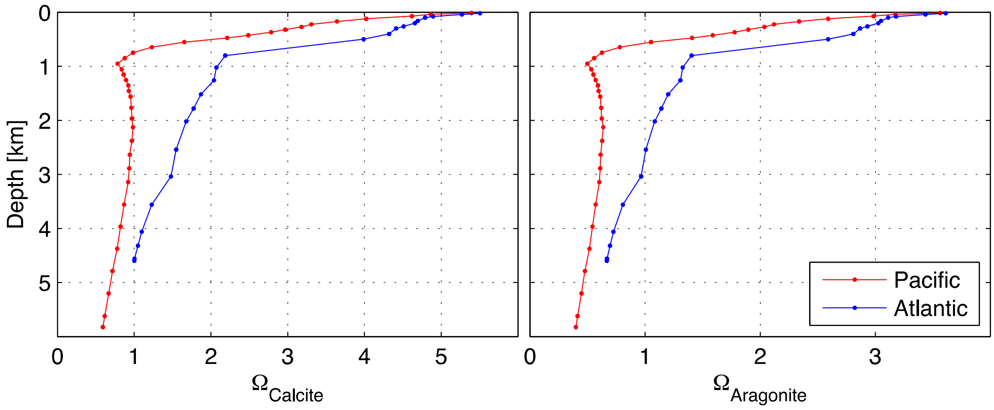

Figure S5.1. Vertical distributions of $\Omega_{Calcite}$ and $\Omega_{Aragonite}$ (Eq. S5.1) in the Northwest Atlantic Ocean (blue connected dots; to 4.5 km depth) versus the Northeast Pacific Ocean (red connected dots; to 5.8 km depth). For station positions and sampling dates see caption of Figure 1.

References: see main article

S6) Operational methodologies of Titration Alkalinity

Notice that our manuscript and supplements avoid the wording 'total' and instead use 'titration' as in Titration Alkalinity. The operational procedures have been described by Millero (1993), PICES (2007), Mintrop et al. (2000), Van Heuven et al. (2011a), Van Heuven (2013), among several others. Closed cells (PICES, SOP3a), or open cells (PICES, SOP3b) or a calibrated burette can be used and each represents the volume V_0 of the seawater sample (Eq. 23). Various authors use titration cells with various volumes V_0, for example nominal ~115 ml that in fact is determined very accurately (Stoll et al., 1993). Millero et al. (1993a) report for different cells, the volumes were determined to ± 0.03 cm^3, and actual cell volumes in the range of V_0 = 210 - 240 ml (see Millero et al., 1993a, their Table 1). Mintrop et al. (2000) when intercalibrating three different methods of determination of Alkalinity, report for (i) closed cell titration as well as (ii) open cell titration (using the VINDTA) and (iii) two end-point method (after Perez and Fraga, 1987), nominal cell volumes of (i) ~200 ml or (ii) ~100 ml as well as (iii) a calibrated 250 ml Knudsen pipette. Similarly much effort goes into assuring the exact concentration of the 0.1 N hydrochloric acid. For example a most accurate value of 0.09982 ± 0.00003 (versus nominal molarity 0.09979) is reported in Mintrop et al. (2000). The dilute hydrochloric acid is fortified by addition of 35 gram NaCl per Liter to match the ionic strength of seawater. Certified Reference Materials (CRM's) of Alkalinity in seawater are being analyzed routinely. For the CRM's and much more highly valuable technical details see also PICES (2007). .

In the 1980's and 1990's in context of TTO and JGOFS/WOCE the closed cell titration method was commonly used, see for example Bradshaw et al. (1981), Brewer et al., (1986). This acid titration was applied for determination of both DIC and Alkalinity, where in Figure 2, the difference (V_2 - V_1) multiplied by the 0.1N HCl strength represents the value of DIC; the V_2 determines Titration Alkalinity as per Eq (23).

In the 2000s the novel Marianda (Versatile INstrument for the Determination of Titration Alkalinity) VINDTA 3C came into use for the determination of Total Alkalinity and Total Dissolved Inorganic Carbon in seawater. This comprises two, in itself independent, instruments, namely (i) an open cell titration unit for Titration Alkalinity and (ii) a coulometry unit for DIC. Methods for the VINDTA 3C can be found in Mintrop et al. (2000); Hartman et al. (2011); Van Heuven (2013; Chapter 3 at pp. 31-56), among others. Nowadays many oceanography laboratories use the VINDTA instrumentation.

For the non-linear curve fitting of the Titration Alkalinity curve (Figure 2) there is no need anymore to fit the complete curve. This is because the value of V_1 as previously required to determine the difference (V_2-V_1) as a measure of DIC, has become obsolete because nowadays DIC is far more precisely determined by the independent coulometry method. Therefore the non-linear curve fitting can be restricted to only the about second half of the titration curve (Figure 2; an interval from ~1.5 ml acid addition to final 4 ml acid addition) to determine V_2 precisely for the most precise determination of Titration Alkalinity. This second part of the titration curve (Figure 2) has the typical S-shape of a monoprotic acid that can be described by the mathematical sigmoid function (Skoog et al., 2014). In the seawater sample one therefore considers the carbonic acid as a monoprotic entity, as follows:

$$H_2CO_{3(aq)} \rightleftarrows H^+_{(aq)} + HCO_3^-{}_{(aq)} \qquad (5)$$

with the corresponding conditional equilibrium constant:

$$K^*_1 = [H^+]\,[HCO_3^-] \,/\, [CO_2^*] \qquad (14)$$

In the real seawater sample, the second equivalence point indicated by V_2 (Figure 2) is dominated by the above reaction (5), but several other constituents of seawater (Figures 3 and 4) also somewhat affect the exact position of this equivalence point. Therefore the mathematical sigmoid function can be fitted by a non-linear fitting routine for a hypothetical acid HA as per the equilibrium reaction:

$$HA \rightleftarrows H^+ + A^- \qquad \text{(Eq. S6.1.)}$$

with a stability constant $^*K_A$ that is determined by the curve fitting. This $^*K_A$ is affected by the minor constituents in seawater, i.e., does in principle slightly deviate from the K^*_1 in the above equation (14). Once the curve fitting over the interval 1.5 ml - 4.0 ml has arrived at the minimal overall offset between the datapoints and the mathematical curve function, one has obtained the best value of hypothetical $^*K_A$ and more of practical use the best value of V_2 and hence as per Eq. (23) the best value of Titration Alkalinity.

For the traditional non-linear curve fitting of the complete Titration Alkalinity curve, the screen shot of Hartman et al. (2011; their page 23) demonstrates quite large residuals in the first part of the titration curve, i.e. the non-linear curve fitting procedure is challenged by the first equivalence point where volume V1 (see our Figure 2) represents the equivalence point of conversion of the CO_3^{2-} ion to the HCO_3^- ion state. This V1 and its quite large residuals are not needed when only fitting the second part of the titration curve to only obtain V2 (see our Figure 2) that represents Titration Alkalinity.

Overall our approach is more straightforward than the thus far method of fitting the complete titration curve with a more complicated fitting procedure (e.g., Johansson and Wedborg, 1982; Millero, 1993; PICES, 2007). Moreover, in our approach, the derived value of Titration Alkalinity also comprises any undefined constituents such as in some articles indicated by so-called ellipses (...) symbols 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" (PICES, 2007; Middelburg et al. (2020). Such undefined constituents have for example been hypothesized to be some organic entities somehow affecting the value of Titration Alkalinity. Validation of such hypothesis of organic constituents affecting Titration Alkalinity would obviously require additional independent measurements of the concentration and acid/base properties of such organic molecules (see also Supplementary Materials S17 and S18). Otherwise, as a matter of fact, our above approach is somewhat akin to an apparent suggestion made previously, that presumably carbonic acid can be treated as a mixture of two monoprotic acids in order to simplify the curve fitting of the complete titration curve (Dickson as cited by Johansson and Wedborg, (1982).

Finally, for the traditional non-linear curve fitting of the complete Titration Alkalinity curve (Figure 2) one is referred to the pioneering articles by Dickson (1981) and Johansson and Wedborg (1982); as well as the article by Millero, 1993. Moreover Mintrop et al. (2000) applied the same FORTRAN curve fitting software provided by Millero (1993). This also in the VINDTA software with stability constants also after Prieto and Millero (2002). See also Fraga and Perez (1987). Also there is a detailed description in PICES (2007).

References: see main article

S7) Nernst equation and various sources of error

The Nernst equation and several sources of error of Titration Alkalinity are described, after Johansson and Wedborg (1982), Brewer et al. (1986) and Stoll (1994). When using pH-electrodes during a potentiometric titration it is assumed that the pH electrode in principle follows Nernstian behavior:

$$E = E_0 + (RT/F) \cdot \ln(H^+) \qquad \text{(Eq. S7.1.)}$$

where

E = Electromotive force in milliVolt (mV) measured by the electrode relative to E_0 (mV)
(in the literature this is sometimes defined as e.m.f. for electromotive force)
E_0 = an arbitrary level depending on the electrode used (mV)
R = Gas constant 8.3144 (J $mol^{-1}K^{-1}$) where K is Kelvin
T = Temperature (K)
F = Faraday constant $9.6485*10^4$ (C mol^{-1})
(H^+) = activity of hydrogen ions

Johansson and Wedborg (1982) defined the Nernst equation somewhat differently

$$E = Ek = k. \log [H] \qquad \text{where } k = RT \ln 10/F \qquad \text{(Eq. S7.2.)}$$

Theoretically, the slope of the linear equation S6.1. would be 59.16 mV at 25˚C (Brewer et al., 1986) or 58.16 mV at 20˚C (Stoll, 1994) with every change in pH unit (10-fold increase of H+ activity). Deviations from this theoretical slope may occur and are a frequent concern during potentiometric titration (Brewer et al., 1986). In context of the Transient Tracers in the Oceans program (TTO 1981, 1983), for the shipboard and shore-based titrations, the practical electrode slopes were determined meticulously (Brewer et al., 1986; their Table 18.3). Effects of deviations from the theoretical response on the derived values of Alkalinity (and DIC) were discussed. In summary, the small deviations from the theoretical response were judged to not constitute sufficient evidence of non-ideal behavior, and, therefore, for all calculated values from the cruise, the Nernstian slope was assumed. Stoll (1994) mentions that deviations from the ideal theoretical response of 58.16 mV at 20˚C can be straightforward denoted by the slope factor f as follows:

$$E = E_0 + (RT/F) \cdot \ln(H^+) \cdot f \qquad \text{(Eq. S7.3.)}$$

Stoll (1994) reported that during JGOFS 1989-1990 cruises, the slope factor f was never deviating from the ideal value, within the error of its determination (0.001). Otherwise, theoretical calculated effects on the Titration Alkalinity due to various errors were given (Table S7.1):

Table S7.1. An example of the theoretical calculated effects on Titration Alkalinity due to errors in the slope factor f, the normality N1 of the titration acid, the volume V0 (ml) of the titrator cell and the temperature t (˚C) of the thermostated waterjacketed titrator cell (taken from Stoll, 1994). Each titration cell has its own volume, typically in the order of 116 ml. The cell temperature was kept constant at 20 ± 0.2 ˚C (Stoll et al., 1993). Obviously, for any assumed larger errors of f or V0 of the titrated seawater samples, the error of Titration Alkalinity would be larger (Table 3 in Chapter 2 of Stoll, 1994).

	Titration Alkalinity (μmol dm^{-3})
f + 0.001	- 1
f - 0.001	0
N1 + 0.0001	+2
N1 - 0.0001	- 3
V0 + 0.1	- 3
V0 - 0.1	+2
t +1	- 3
t - 1	+2

References: see main article

S8) Citations of the footnote and a table at pages 40 and 41, respectively, of Broecker (1974)

Here is cited what is written in the footnote at page 40:

"* Chemists measure alkalinity in units of equivalents/liter. An equivalent is equal numerically to a mole. A mole of Na^+ ions would carry an equivalent of positive charge; a mole of $SO_4^{- -}$ ions would carry two equivalents of negative charge. In this book we will simplify matters by using moles of charge rather than equivalents as the unit of alkalinity."

The Table at page 41 gives the following information:

"Charge balance in sea water: the excess cation charge is balanced by the dissociation of carbonic acid (H_2CO_3) into bicarbonate (HCO_3^-) and carbonate (CO_3^{--}) ions."

	Positive			**Negative**	
Cation	**Mass, mol/m³**	**Charge mol/m³**	**Anion mol/m³**	**Mass, mol/m³**	**Charge mol/m³**
Na^+	470	470	Cl^-	547	547
K^+	10	10	$SO_4^{- -}$	28	56
Mg^{++}	53	106	Br^-	1	1
Ca^{++}	10	20			
Σ	-	606	Σ	-	604
			HCO_3^- + CO_3^{2-}	-	2
			Σ'	-	606

Reference

Broecker, W.S. (1974). Chemical Oceanography. Harcourt Brace Jovanovich, New York, pp. 40-41 of 214 pp.

S9) Underlying approximate calculus at the endpoint example pH values of Table 4a for K* values versus free pH_F scale

(It should be noted that all calculated values are given with a somewhat excessive suite of numbers beyond the decimal points, this for the readers to be able to verify the correctness of these calculations. However, before publication of the actual article and supplementary materials the values will be rounded.)

$(K^*_{1P})_{\text{Free scale}} = 0.0190998$	$= 0.0191$	(factor 0.78 lower than $(K^*_{1P})_{\text{Total scale}}$)
$(K^*_{2P})_{\text{Free scale}} = 0.852513$ 10-6	$= 0.8525\ 10^{-6}$	(factor 0.78 lower than $(K^*_{2P})_{\text{Total scale}}$)
$(K^*_{3P})_{\text{Free scale}} = 1.26515$ 10-9	$= 1.2652\ 10^{-9}$	(factor 0.78 lower than $(K^*_{3P})_{\text{Total scale}}$)

From looking at the Bjerrum plot of the minor constituents it is obvious that at the pH=~4.5 nominal condition the $H_2PO_4^-$ species is dominant, followed by the HPO_4^{2-} species at almost 100-fold lower concentration. The H_3PO_4 looks to be almost 1000-fold lower than the $H_2PO_4^-$ species. Finally, the PO_4^{3-} looks to be some 10000-fold lower than the $H_2PO_4^-$ species. Therefore, as a first approximation for the endpoint of the titration, the H_3PO_4 and PO_4^{3-} species are ignored. Then it is feasible to solve the following equation:

$K^*_{2P} = [H^+]\,[HPO_4^{2-}]/[H_2PO_4^-]$ ln $(K^*_{2P}) = -13.9750774$ $(K^*_{2P}) = 0.8525\ 10^{-6}$

by substitution. Briefly, total phosphate = 1 μmol.kg^{-1} such that

$[HPO_4^{2-}] + [H_2PO_4^-] = 1$ μmol.kg^{-1}

$0.8525\ 10^{-6}\ [1-HPO_4^{2-}] = [H^+]\ [HPO_4^{2-}]$

$\{0.8525\ 10^{-6} / [H^+]\}$x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

Next are filled in the hydrogen ion concentration $[H^+]$ values for the three pH examples 4.5 and 4.4 and 4.25 as follows:

	pH = ~4.5	**pH=4.4**	**pH$_{SWS}$=4.25**
Hydrogen ion concentration (mol.kg^{-1}**)**	$3.16228\ 10^{-5}$	3.98107 10-5	$5.62341\ 10^{-5}$
Factor increase of hydrogen ion versus pH=8	3162	3981	5623

for pH=4.5 $\{0.8525\ 10^{-6} / 3.16228\ 10^{-5}\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $\{0.8525\ 10^{-6} / 3.98107\ 10^{-5}\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $\{0.8525\ 10^{-6} / 5.62341\ 10^{-5}\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $\{0.0269584\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $\{0.02141384\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $\{0.01515984\}$ x $[1\text{-}HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $0.0269584 - 0.0269584[HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $0.02141384 - 0.02141384[HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $0.01515984 - 0.01515984[HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $0.0269584 = 1.0269584\ [HPO_4^{2-}]$

for pH=4.4 $0.02141384 = 1.02141384\ 02744\ [HPO_4^{2-}]$

for pH=4.25 $0.01515984 = 1.01515984\ 01943\ [HPO_4^{2-}]$

Next:

for pH=4.5 $[HPO_4^{2-}] = 0.02625072$ μmol.kg^{-1}

for pH=4.4 $[HPO_4^{2-}] = 0.0209644$ μmol.kg^{-1}

for pH=4.25 $[HPO_4^{2-}] = 0.01471044$ μmol.kg^{-1}

Next:

$K^*_{2P} = [H^+]\ [HPO_4^{2-}] / [H_2PO_4^-]$ ln $(K^*_{2P}{}^{o}) = -13.9750774$ $(K^*_{2P}) = 0.8525\ 10^{-6}$

$0.8525\ 10^{-6}$ [H2PO4-] = [H+]$[HPO_4^{2-}]$

[H2PO$_4^-$] = {[H+]/$0.8525\ 10^{-6}$}$[HPO_4^{2-}]$

Next:

for pH=4.5 $[H_2PO_4^-] = \{3.16228\ 10^{-5} / 0.8525\ 10^{-6}\}[0.02625072]$

for pH=4.4 $[H_2PO_4^-] = \{3.98107\ 10^{-5} / 0.8525\ 10^{-6}\}\ [0.0209644]$

for pH=4.25 $[H_2PO_4^-] = \{5.62341\ 10^{-5} / 0.8525\ 10^{-6}\}\ [0.01471044]$

Next:

for pH=4.5 $[H_2PO_4^-] = 0.97374929\ \mu mol.kg^{-1}$

for pH=4.4 $[H_2PO_4^-] = 0.97901166\ \mu mol.kg^{-1}$

for pH=4.25 $[H_2PO_4^-] = 0.97035584\ \mu mol.kg^{-1}$

Next verify the summation: $[H_2PO_4^-] + [HPO_4^{2-}]$

for pH=4.5 $0.97374929 + 0.02625072 = 1.000000001$ is 1 $\mu mol.kg^{-1}$

for pH=4.4 $0.97901166 + 0.0209644 = 0.99997606$ is 1 $\mu mol.kg^{-1}$

for pH=4.25 $0.97035584 + 0.01471044 = 0.98506628$ is 1 $\mu mol.kg^{-1}$

Next:

$K^*_{1P} = [H^+]\ [H_2PO_4^-] / [H_3PO_4]$ $\ln(K^*_{1P}) = -3.9580774$ $(K^*_{1P}) = 0.0191$

$[H_3PO_4] = \{[H^+]\ [H_2PO_4^-]\} / 0.0245$

for pH=4.5 $[H_3PO_4] = [3.16228\ 10^{-5}] \times [0.97374929] / 0.0191 = 161.218215\ 10^{-5}\ \mu mol.kg^{-1}$

for pH=4.4 $[H_3PO_4] = [3.98107\ 10^{-5}][0.97901166] / 0.0191 = 204.058322\ 10^{-5}\ \mu mol.kg^{-1}$

for pH=4.25 $[H_3PO_4] = [5.62341\ 10^{-5}][0.97035584] / 0.0191 = 285.685592\ 10^{-5}\ \mu mol.kg^{-1}$

Next:

$K^*_{3P} = [H^+]\ [PO_4^{3-}] / [HPO_4^{2-}]$ $\ln(K^*_{3P}) = -20.4880744$ $(K^*_{3P}) = 1.2652\ 10^{-9}$

$[PO_4^{3-}] = \{[1.6214\ 10^{-9}]/[H+]\}[HPO_4^{2-}]$

for pH=4.5 $[PO_4^{3-}] = \{[1.2652\ 10^{-9}]/[3.16228\ 10^{-5}]\}[0.02625072] = 0.01050268\ 10^{-4}\ \mu mol.kg^{-1}$

for pH=4.4 $[PO_4^{3-}] = \{[1.2652\ 10^{-9}]/[3.98107\ 10^{-5}]\}[0.0209644] = 0.00666257\ 10^{-4}$ $\mu mol.kg^{-1}$

for pH=4.25 $[PO_4^{3-}] = \{[1.2652\ 10^{-9}]/[5.62341\ 10^{-5}]\}[0.01471044] = 0.00330967\ 10^{-4}$ $\mu mol.kg^{-1}$

Next the summation of all four species can be calculated:

$[H_2PO_4^-] + [HPO_4^{2-}] + [H_3PO_4] + [PO_4^{3-}]$

for pH=4.5 $0.97374929 + 0.02625072 + 161.218215\ 10^{-5} + 0.01050268\ 10^{-4} = 1.00161$ is 1.00 $\mu mol.kg^{-1}$

0.0016121821 0.000001050268

for pH=4.4 0.97901166 + 0.0209644 + 204.058322 10^{-5} + 0.00666257 10^{-4} = 0.1002017 is 1.00 μmol.kg^{-1}
0.00204058322   0.000000666257

for pH=4.25 0.97035584 + 0.01471044 + 285.685592 10^{-5} + 0.00330967 10^{-4} = 0.98792 is 1.00 μmol.kg^{-1}
0.00285685592   0.000000330967

In the above it can be seen that a simplified calculation on the basis of at first only the two dominant species gives good approximation for the sum of the two dominant species being very close to the overall sum value = 1 μmol.kg^{-1}. Secondly, the two minor species have been calculated.

Obviously, the procedure can be improved by writing a computer program that by a suite of iterative steps would further refine the concentration values by again and again verifying the overall summation with the given total concentration value 1 μmol.kg^{-1}. Presumably this would not yield a better accuracy within the first two decimal points. In other words, right now for the purpose of our article, we are satisfied with the above total summation of 1.00 μmol.kg^{-1}.

S10) Alternative results of Tables 4a and 4b for phosphate computations versus the total pH_T scale

	pH = ~8	**pH = 4.5**	**pH=4.4**	**pH_{SWS}=4.25**
Hydrogen ion concentration (mol.kg^{-1}**)**	10^{-8}	3.16228 10^{-5}	3.98107 10^{-5}	5.62341 10^{-5}
Factor increase of hydrogen ion versus pH=8	1	3162	3981	5623
$H_2PO_4^-$ (μmol.kg^{-1})	0.022	0.96524	0.97322	0.98098
HPO_4^{2-} (μmol.kg^{-1})	0.962	0.03335	0.02671	0.01906
PO_4^{3-} (μmol.kg^{-1})	0.016	1.701 10^{-6}	1.088 10^{-6}	0.5496 10^{-6}
H_3PO_4 (μmol.kg^{-1})	1.06 10^{-6}	124.586 10^{-6}	158.141 10^{-6}	225.61 10^{-6}
Summation (μmol.kg^{-1})	1.00	1.00	1.00	1.00

Supplementary Alternative Table S4a. For conditional stability constants defined versus the total pH_T scale. For total dissolved phosphate = 1 μmol.kg^{-1} the concentrations of phosphate species are listed.

	pH = ~8	**pH = ~4.5**	**pH=4.4**	**pH_{SWS}=4.25**
$H_2PO_4^-$ (μmol.kg^{-1})	0.022	0.96524	0.97322	0.98098
HPO_4^{2-} (μmol.kg^{-1})	1.92	0.066794	0.0430	0.03812
PO_4^{3-} (μmol.kg^{-1})	0.048	0.000051	0.000026268	0.00006824
H_3PO_4 (μmol.kg^{-1})	nil	nil	nil	nil
Summation Total charge (μmol.kg^{-1})	1.99	1.032	1.016	1.019

Supplementary Alternative Table S4b. For conditional stability constants defined versus the total pH_T scale. For total dissolved phosphate = 1 μmol.kg^{-1} the charges (μmol.kg^{-1}) of the phosphate species and the summation total charge. See Supplementary Material S11 for underlying approximate calculus at the endpoint example pH values.

Supplementary Alternative Table S4. For conditional stability constants defined versus the total pH_T scale. Concentrations (4a) and charges (4b) of phosphate species, at the pH = ~8 and at three example pH values for the (second) equivalence point of the titration as follows:
- the nominal pH = 4.5;
- the pH=4.4 endpoint of the dominant reaction: $[H^+] \sim [HCO_3^-] + 2\times[CO_3^{2-}]$ (Fraga & Alvarez-Salgado, 2005)
- the pH_{SWS}=4.25 endpoint for the hydrogen ion activity, $a_H = \sim 10^{-4.4}$ (Fraga & Alvarez-Salgado 2005)

S11) Underlying approximate calculus at the endpoint example pH values of Table 4a for K* values versus total pH_T scale

(*It should be noted that all calculated values are given with a somewhat excessive suite of numbers beyond the decimal points, this for the reviewers to be able to verify the correctness of these calculations. However, before publication of the actual article and supplementary materials the values will be rounded.)*

From looking at the Bjerrum plot of the minor constituents it is obvious that at the pH=~4.5 nominal condition the $H_2PO_4^-$ species is dominant, followed by the HPO_4^{2-} species at almost 10^2 =100 fold lower concentration. The H_3PO_4 looks to be almost 10^3=1000 fold lower than the $H_2PO_4^-$ species. Finally, the PO_4^{3-} looks to be some 10^4=10000 fold lower than the $H_2PO_4^-$ species. Therefore, as a first approximation for the endpoint of the titration, the H_3PO_4 and PO_4^{3-} species are ignored. Then it is feasible to solve the following equation

$K^*_{2P} = [H^+]\,[HPO_4^{2-}]/[H_2PO_4^-]$ $\ln(K^*_{2P}) = -13.727$ $(K^*_{2P}) = 1.0926\ 10^{-6}$

by substitution. Briefly the total phosphate = 1 μmol.kg^{-1} such that

$[HPO_4^{2-}] + [H_2PO_4^-] = 1$ μmol.kg^{-1}

$1.0926\ 10^{-6}\ [1-HPO_4^{2-}] = [H^+]\ [HPO_4^{2-}]$

$\{1.0926\ 10^{-6} / [H^+]\} x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

Next are filled in the hydrogen ion concentration $[H^+]$ values for the three pH examples 4.5 and 4.4 and 4.25 as follows:

	pH = ~4.5	**pH=4.4**	**pH_{SWS}=4.25**
Hydrogen ion concentration (mol.kg^{-1}**)**	$3.16228\ 10^{-5}$	3.98107 10-5	$5.62341\ 10^{-5}$
Factor increase of hydrogen ion versus pH=8	3162	3981	5623

for pH=4.5 $\{1.0926\ 10^{-6} / 3.16228\ 10^{-5}\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $\{1.0926\ 10^{-6} / 3.98107\ 10^{-5}\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $\{1.0926\ 10^{-6} / 5.62341\ 10^{-5}\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $\{0.0345\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $\{0.02744\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $\{0.01943\}\ x\ [1-HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $0.0345- 0.0345[HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.4 $0.02744- 0.02744[HPO_4^{2-}] = [HPO_4^{2-}]$

for pH=4.25 $0.01943- 0.01943[HPO_4^{2-}] = [HPO_4^{2-}]$

Next:

for pH=4.5 $0.0345 = 1.0345\ [HPO_4^{2-}]$

for pH=4.4 $0.02744= 1.02744\ [HPO_4^{2-}]$

for pH=4.25 $0.01943 = 1.01943\ [HPO_4^{2-}]$

Next:

for pH=4.5 $[HPO_4^{2-}] = 0.03335\ \mu mol.kg^{-1}$

for pH=4.4 $[HPO_4^{2-}] = 0.02671\ \mu mol.kg^{-1}$

for pH=4.25 $[HPO_4^{2-}] = 0.01906\ \mu mol.kg^{-1}$

Next:

$K^*_{2P} = [H^+]\ [HPO_4^{2-}] / [H_2PO_4^-]$ $\ln (K^*_{2P}) = -13.727$ $(K^*_{2P}) = 1.0926\ 10^{-6}$

$1.0926\ 10^{-6}\ [H_2PO_4^-] = [H^+][HPO_4^{2-}]$

$[H_2PO_4^-] = \{[H^+]/1.0926\ 10^{-6}\}[HPO_4^{2-}]$

Next:

for pH=4.5 $[H_2PO_4^-] = \{3.16228\ 10^{-5} / 1.0926\ 10^{-6}\}[0.03335]$

for pH=4.4 $[H_2PO_4^-] = \{3.98107\ 10^{-5} / 1.0926\ 10^{-6}\}\ [0.02671]$

for pH=4.25 $[H_2PO_4^-] = \{5.62341\ 10^{-5} / 1.0926\ 10^{-6}\}\ [0.01906]$

Next:

for pH=4.5 $[H_2PO_4^-] = 0.96524\ \mu mol.kg^{-1}$

for pH=4.4 $[H_2PO_4^-] = 0.97322\ \mu mol.kg^{-1}$

for pH=4.25 $[H_2PO_4^-] = 0.98098\ \mu mol.kg^{-1}$

Next verify the summation: $[H_2PO_4^-] + [HPO_4^{2-}]$

for pH=4.5 $0.96524 + 0.03335 = 0.9985$ is 1 $\mu mol.kg^{-1}$

for pH=4.4 $0.97322 + 0.02671 = 0.99993$ is 1 $\mu mol.kg^{-1}$

for pH=4.25 $0.98098 + 0.01906 = 1.00004$ is 1 $\mu mol.kg^{-1}$

Next:

$K^*_{1P} = [H^+]\ [H_2PO_4^-] / [H_3PO_4]$ $\ln(K^*_{1P}) = -3.71$ $(K^*_{1P}) = 0.0245$

$[H_3PO_4] = \{[H^+]\ [H_2PO_4^-]\} / 0.0245$

for pH=4.5 $[H_3PO_4] = [3.16228\ 10^{-5}] \times [0.96524] / 0.0245 = 124.586\ 10^{-5}\ \mu mol.kg^{-1}$

for pH=4.4 $[H_3PO_4] = [3.98107\ 10^{-5}][0.97322]/0.0245 = 158.141\ 10^{-5}\ \mu mol.kg^{-1}$

for pH=4.25 $[H_3PO_4] = [5.62341\ 10^{-5}][0.98098]/0.0245 = 225.161\ 10^{-5}\ \mu mol.kg^{-1}$

Next:

$K^*_{3P} = [H^+]\,[PO_4^{3-}] / [HPO_4^{2-}]$ ln $(K^*_{3P}) = -20.24$ $(K^*_{3P}) = 1.6214\ 10^{-9}$

$[PO_4^{3-}] = \{[1.6214\ 10^{-9}]/[H^+]\}[HPO_4^{2-}]$

for pH=4.5 $[PO_4^{3-}] = \{[1.6214\ 10^{-9}]/[3.16228\ 10^{-5}]\}[0.03335] = 0.01701\ 10^{-4}$ $\mu mol.kg^{-1}$

for pH=4.4 $[PO_4^{3-}] = \{[1.6214\ 10^{-9}]/[3.98107\ 10^{-5}]\}[0.02671] = 0.01088\ 10^{-4}$ $\mu mol.kg^{-1}$

for pH=4.25 $[PO_4^{3-}] = \{[1.6214\ 10^{-9}]/[5.62341\ 10^{-5}]\}[0.01906] = 0.005496\ 10^{-4}$ $\mu mol.kg^{-1}$

Next the summation of all four species can be calculated:

$[H_2PO_4^-] + [HPO_4^{2-}] + [H_3PO_4] + [PO_4^{3-}]$

for pH=4.5 $0.96524 + 0.03335 + 124.586\ 10^{-5} + 0.01701\ 10^{-4} = 0.99983756$ is 1.00 $\mu mol.kg^{-1}$
0.00124586 0.000001701

for pH=4.4 $0.97322 + 0.02671 + 158.141\ 10^{-5} + 0.01088\ 10^{-4} = 1.00151249$ is 1.00 $\mu mol.kg^{-1}$
0.00158141 0.000001088

for pH=4.25 $0.98098 + 0.01906 + 225.161\ 10^{-5} + 0.005496\ 10^{-4} = 1.00229215$ is 1.00 $\mu mol.kg^{-1}$
0.00225161 0.0000005496

In the above it can be seen that a simplified calculation on the basis of at first only the two dominant species (thus ignoring the other two minor species) gives good approximation for the sum of the two dominant species being very close to the overall sum value = 1 $\mu mol.kg^{-1}$. Secondly, the two minor species have been calculated.

Obviously, the procedure can be improved by writing a computer program that by a suite of iterative steps would further refine the concentration values by again and again verifying the overall summation with the given total concentration value 1.00 $\mu mol.kg^{-1}$. Presumably this would not yield a better accuracy within the first two decimal points. In other words, right now for the purpose of our article, we are satisfied with the above total summation of 1.00 $\mu mol.kg^{-1}$.

S12) On biological uptake of phosphate (and sulfate); examples in literature of the 1965-2022 era

For a long time in most articles there is merely mention of alkalinity, without a clear distinction between what we call Oceanic Alkalinity and Titration Alkalinity. Furthermore, in some literature there are definitions that are not as extensive or exhaustive. It is afterwards difficult to assume whether an omission in the definition is intentional for intended approximation and/or for educational purpose, or due to ignorance at the time, or the then state of the art of measurements. For example, the role of nitrate in Oceanic Alkalinity was only mentioned for the first time after the Brewer and Goldman (1976) article. The role of phosphate for quite some time was below the reproducibility of the acid titration of Alkalinity.

The history of Alkalinity by Dickson (1992) is a valuable source of information. Here, we focus firstly on the modern history as off 1965, and secondly on the interactions of phosphate with Alkalinity. Moreover, where articles also mention the role of sulfate (or other constituents) this will also be cited here.

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 2.3 μM phosphate may be neglected (but in anoxic waters may have to be considered). In those years the Department of Analytical and Marine Chemistry in Göteborg was world-leading in research of Alkalinity, for example see also Hansson and Jagner (1973), Almgren et al. (1997), Hansson (1972), Wedborg (1979), Johansson (1981).

Edmond (1970) further refined the titration method for Titration Alkalinity and DIC that next was used in the ensuing GEOSECS program (Supplementary Material S3). He 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). 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." Otherwise, Edmond (1970) mentions: "The proton condition (Sillen, 1959) requires that at the end-point the proton excess and deficit are balanced." This appears to be similar to an arbitrarily defined zero level of protons, see below (Dickson, 1981) and Wolf-Gladrow et al. (2007).

Broecker (1974) defined the charge balance in seawater in his Table 2-3 (Supplementary Material S8), as we here call Oceanic Alkalinity. It should be noted that the role of nitrate, as realized later, has not yet been mentioned. Gieskes (1974) used the term $3[PO_4^{3-}]$ presumably (but incorrectly) assuming the free PO_4^{3-} state of the original seawater sample at natural pH=8 and presumably (but incorrectly) the fully protonated H_3PO_4 end state at the second equivalence point of the titration. Takahashi (1975) mentions that the Alkalinity 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 represents Titration Alkalinity and the right hand term represents Oceanic Alkalinity. Here again notice that the nutrients nitrate and phosphate were still omitted.

Skirrow (1975) using a suite of chemical equations (Supplementary Material S13) for the formation of organic matter 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 complete Eq. (50) of Titration Alkalinity.

Brewer et al. (1975) assess the changes of dissolved Ca versus such changes predicted from the changes in alkalinity. Given an apparent excess Ca, the effect of oxidative decomposition of organic matter on alkalinity is addressed for an effective flux of nitric and phosphoric acids into the deep water:

"The simplest form of this equation would be: $\Delta P.A. = \Delta T.A. + 1\ \Delta NO_3^- + 1\ \Delta PO_4^{3-}$ where ΔP.A. and ΔT.A. are the potential alkalinity and alkalinity differences, in μeq/kg, between two water masses, and ΔNO_3^- and ΔPO_4^{3-} are the nitrate and phosphate differences, in μmoles/kg, between the same two water masses. The true situation is more complicated than this. Firstly, we have neglected the effects of mixing, and secondly, the nutrient values should be corrected for the pre-formed nitrate and phosphate. Thirdly, the contribution of phosphate is more complex than appears in this simple scheme, due to its multi-proton character and its varying dissociation in seawater. In oceanic terms the alkalinity equivalent of the phosphate (~2 μeq/kg) is, however, quite small. Lastly, we have ignored the flux of protons from other redox reactions. These will probably remain an unknown. Possibly the next significant contribution could come from the oxidation of reduced sulfur. The atom ratio of sulfur to carbon in marine organism is approximately 0.015 (*after Deuser, 1970*). Incorporating this into the Redfield-Ketchum-Richards relationship we have C:N:S:P = 106:16:1.6:1. If all reduced sulfur were oxidized to sulfate two equivalents per mole should be produced, and the sulfur contribution would be 20% of the nitrate contribution. We have no direct evidence for this; the level of the oxidized product, sulfate ion, is extraordinarily high in seawater (2.712 g/kg, 0.02926 molal, at 35‰) and the predicted small changes in concentration (~3 μmoles/kg) would be well nigh impossible to detect. Sulfur species of intermediate oxidation state, such as $S_2O_3^-$, have not been detected."

Firstly, Brewer et al. (1975) refrained from implementing the S:C=0.015 ratio after Deuser (1970). Secondly, in Deuser et al. (1970) one reads that a range is mentioned varying between 0.007 < S:C < 0.025 on the basis of three literature citations of years 1954, 1961, 1964, and then was chosen S:C=0.015 as a likely mean value.

Chen (1978) reckoned that for the decomposition of organic matter the value (of Oceanic Alkalinity) decreases with 17 units, that is the implicit summation of 16 nitrate and 1 phosphate added to seawater. Chen et al. (1982) at first also mention that a decrease of 17 mol kg^{-1} in Alkalinity (i.e., Oceanic Alkalinity) occurs with the decomposition of one mole of organic matter per kg of seawater; this. However next, upon more careful evaluation of the proton balances, Chen et al. (1982) mention that, in theory, the release of H_3PO_4 due to the decomposition of organic matter should have no effect on Alkalinity (i.e., Oceanic Alkalinity). Next they defined what we call Titration Alkalinity in their Equation (3) that does comprise the term $+[HPO_4^{2-}]$. Next they also defined what we now call Oceanic Alkalinity in their Equation (4) that comprises the term $-(NO_3^-)$ and not any phosphate term. However, eventually it is mentioned that the release of one mole of H_3PO_4 due to organic matter decomposition decreases Alkalinity by one equivalent.

The articles of Dickson (1981), Johansson and Wedborg (1982) at the time were major breakthroughs in the research of Alkalinity in seawater. Dickson (1981) defined Total Alkalinity (A_T), as the result of careful consideration (L. Anderson, A. Dickson, D. Dyrssen, D. Jagner, O. Johansson, M. Wedborg) during a visit of A. Dickson to the Department of Analytical and Marine Chemistry in Göteborg in April-May 1980 (Johansson and Wedborg (1982). Presumably, this definition (Dickson, 1981) comprises two inherent arbitrary assumptions (Fraga and Alvarez-Salgado, 2005) as follows; (i) an arbitrarily defined zero level of protons, such that (ii) acids with a dissociation constant $K > 10^{-4.5}$ are considered as proton donors, whilst those bases formed from weak acids with $K \leq 10^{-4.5}$ are considered proton acceptors. In the context of the acid titration procedure to obtain a value of Titration Alkalinity, the pH decreases from pH=~8 to pH=~4.5 such that the wording about so-called "proton donors" may, or may not, lead to confusion. This is because throughout the titration pathway in fact all seawater constituents are either proton acceptors or not affected (i.e., the nitrate ion, e.g. chloride ion). In other words, there are no seawater constituent proton donors during the acid titration for determination of titration alkalinity. Otherwise at page 612 lines 12-13 from above, it is noted that in the 'resultant expression for the alkalinity' there is no $[H_2PO_4^-]$ term, this presumably due to the assigned so-called zero level of protons. The concept of a so-called proton condition is after Butler (1964a), see also Butler (1964b) and Butler (1982). The proton condition in aqueous solutions is deemed to be intended at the time (e.g., Burton 1964a, b; Dickson, 1981) to present an overall summation (i.e., "mass balance") of all protons present, not only the true ("free") protons but in addition also the protons that have been bound to various anions in the context of acid/base equilibria (J. Middelburg, personal communication), the latter bound protons in fact not being the true protons in aqueous solution anymore. Natural seawater is uncharged and the Oceanic Alkalinity is in essence a charge balance approach relying on the requirement of overall neutral electric charge of seawater. This is our preferred approach notably because Oceanic Alkalinity is the pivotal variable for studying and unraveling biogeochemical processes in the oceans. Alternatively, others (notably Dickson, 1981) have taken a proton balance approach (see Middelburg, 2019, its pages 79-80), this comprising the above mentioned assumptions of proton condition and of zero level of protons. In contrast Oceanic Alkalinity does neither need nor rely on any assumption.

Johansson and Wedborg (1982) extensively tested non-linear curve fitting procedures for the potentiometric titration of seawater, and in this context developed a theoretical titration curve (their Table 3) comprising several components including the four species of DIP (see main article BOX 1 Eq. 14). This theoretical titration curve is the basis of Figure 2 in our main article.

Kanamori and Ikegami (1982) on the basis of direct measurements of dissolved Ca, dissolved nitrate, Alkalinity and salinity developed a model to derive the change of dissolved Ca due to the combined dissolution of $CaCO_3$ and decomposition of organic matter generating nitric acid, phosphoric acid and sulfuric acid. For latter decomposition the production of nitrate and phosphate was based on Redfield stoichiometry, in combination with the production of sulfuric acid on the basis of the S:C=0.015 ratio of marine organisms after Deuser (1970). Both this study and the study of Brewer et al. (1975) focus on the relationship between changes of Ca and changes of Alkalinity.

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. Briefly, it makes a difference whether the uptake of phosphate species is, or is not, accompanied by cation uptake (see Supplementary Material S14). Brewer and Goldman (1976) concluded that the "argument (*on the role of P in Alkalinity*) is somewhat academic because the net effect is barely detectable given the precision of our measurement". Next, Goldman and Brewer (1980) concluded that the experimental results were tending to support the notion that uptake of phosphate does 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.

Bradshaw et al. (1981) incorporated phosphate into the Titration Alkalinity, as follows:
". . the sample alkalinity with regard to the second equivalence point must be adjusted by adding: $2[PO_4^{3-}]_0$ + $[HPO_4^{2-}]_0$ - $[H_3PO_4]_0$ where the subscript 0 refers to the sample." Also mentioned by Bradshaw et al. (1981) was the notion that phosphate interferes with the, at the time, calculation of DIC from the difference (V2-V1) between the second and the first equivalence points (Figure 2).

Broecker and Peng (1982) mention as follows: "When organically bound nitrogen is released during respiration, 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 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 would 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."

Here 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 parallel gains or losses of phosphate are not mentioned.

Campbell (1983) describes as follows: "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." In this cited text of Campbell (1983) there is no mentioning of either phosphate or sulfate affecting Oceanic Alkalinity; see also Chester (1990).

Peng et al. (1987) mentioned that in their model study, it is assumed that the productivity of calcareous organisms is low in the study area, and the salinity is constant at $35^{o}/_{oo}$. Accordingly in their study the alkalinity is affected only by changes in the nitrate concentration (Brewer and Goldman, 1976).

Zeebe and Wolf-Gladrow (2001; pages 51-52) mention that alkalinity can change due to precipitation/dissolution of $CaCO_3$ and due to uptake/release of nitrate by algae. Otherwise it is referred to their Appendix C.1. that follows Total Alkalinity after Dickson (1981) including its two assumptions (see Section 9), plus a third assumption (hypothesis) that electroneutrality of algal cells which take up charged species is ensured by simultaneous uptake or release of H^+ or OH^-. Latter hypothesis is assumed for the mentioning that uptake of one mole of phosphate implies an increase of alkalinity by one mole. This assumed hypothesis ignores other mechanisms, such as mentioned by Brewer and Goldman (1976; their Table 3) (see Supplementary Material S14).

Fraga and Álvarez-Salgado (2005) report a detailed assessment on the variation of alkalinity during phytoplankton photosynthesis, this including the roles of various nitrogen resources, phosphate, sulfur and magnesium. This leads to their more refined expanded expressions for the effects on alkalinity.

Wolf-Gladrow et. al. (2007) rely on the Total Alkalinity description of Dickson (1981), including its two inherent assumptions, plus a third assumption, their *nutrient-H^+-compensation principle*, that appears to be identical to the above mentioned third assumption/hypothesis on electroneutrality of algal cells of Zeebe and Wolf-Gladrow (2001). All constituents are described with regards to their assumed zero level of protons, yielding their suggested eight proton condition equations (20-27). Uptake/release of 1 mole of phosphate is, due to the third assumption of nutrient-H^+-compensation principle, concluded to yield an increase/decrease of alkalinity by 1 mole per mole P. Relying on cellular carbon:sulfur (C:S) ratio values after Matrai and Keller (1994), and classical C:P = 106:1 eventually is concluded the overall ratios to carbon as C:N:P:S = 106:16:1:2.4 in algae. Again relying on the nutrient-H^+-compensation principle assumption and a factor 2 for sulfur, it is concluded that uptake of nutrient elements N, P and S together with carbon C, yields an increase of Alkalinity by a summation factor 21.8=16+1+4.8 (as per 16 for N, 1 for P and 2x2.4 for S) that is clearly higher than the factor 16 as used in other articles. A similar approach is presented for additional elements Mg, K, Ca (Wolf-Gladrow and Klaas, 2024).

Ayers and Lozier (2012) in a major study for unraveling dynamical controls on the North Pacific carbon sink quantify the effect of biological production in surface waters via the utilization of nitrate (NO_3^-), as follows:
"The uptake of one mol of NO_3^-, accompanied by the parallel uptake of one mol of hydrogen ions, H^+, increases alkalinity by one mol [Brewer et al., 1975; Brewer and Goldman, 1976; Goldman and Brewer, 1980]. Here we estimate nitrate uptake from our NPP estimates using 16N:106C Redfield stoichiometry. The increase in alkalinity due to biological nitrogen utilization opposes its decrease due to $CaCO_3$ precipitation."

Carter et al. (2014) mention as follows:
"Feely et al. (2002) used a variant that relies on the empirical relationship between dissolved calcium concentrations, A_T, and nitrate determined by Kanamori and Ikegami (1982). This variant has the advantage of implicitly accounting for the A_T changes created by the exchange of numerous other components of marine organic matter besides nitrate (e.g., sulfate and phosphate). We thus use the ratio found by Kanamori and Ikegami (1982) to define potential alkalinity: $AP = AT + 1.26 \times [NO_3^-]$. While the empirical Kanamori and Ikegami (1982) ratio of 1.26 may be specific to the elemental ratios of the North Pacific, Wolf-Gladrow et al. (2007) provide a theoretical derivation from Redfield ratios and obtain a similar value of 1.36."

Lerman and MacKenzie (2016) define in their equations (12) and (13) in essence the same as in equation (4) of Takahashi (1975) as reproduced in Eq. (34). Omitted are the terms for nitrate and various phosphate species. In other words, in year 2016 the effect of production/decomposition of organic matter is ignored, this in contrast to (almost) all articles published after the Brewer and Goldman (1976) article was published.

Lauvset et al. (2020) in their equation (8) adopt the coefficient 1.36 after Wolf-Gladrow et al. (2007) for the effect of production/decomposition of organic matter on alkalinity. In their Table 1, an uncertainty estimate of 10% of this 1.36 coefficient is reportedly based on published values of this coefficient (Kanamori & Ikegami, 1982; Wolf-Gladrow et al., 2007). Presumably, the 10% uncertainty estimate is based on comparison of two coefficient values 1.26 (Kanamori and Ikegami, 1982) and 1.36 (Wolf-Gladrow et al., 2007).

Jones et al. (2021) investigated calcium carbonate saturation states along the West Antarctic Peninsula. The changes of dissolved Ca^{2+} were resolved from salinity-normalized Alkalinity, that is adjusted for formation/decomposition of organic matter via nitrate. Steiner et al. (2021) make adjustments for the effect of organic matter production/decomposition on Alkalinity by taking into account nitrate, nitrite, soluble reactive phosphate and sulfate. For sulfate an average ratio N:S = 16:2.4 is applied after Wolf-Gladrow et al. (2007).

References: see main article

S13) Citation of relevant text parts of page 166-167 by Skirrow (1975)

Skirrow (1975) writes as follows:

"Dyrssen and Gunderson (1974) have examined the changes in alkalinity and ΣCO_2 which accompany the simultaneous oxidation of organic matter and the dissolution of calcium carbonate for stations near the Hawaiian Islands. As a slight modification of the Richards (1965) model, they considered that one unit of organic matter (C:N:P = 106:16:1) comprises effectively 89 carbohydrate groups, 16 peptide or amino acid groups and one phosphate ester group according to $(CH_2O)_{89}(NHCO)_{16}C(H_2PO_4)^-$.

Alkalinity, ΣCO_2, O_2, NO_3^- and PO_4^{3-} changes accompanying the formation of organic matter were summarized by

$89\ CO_2 + 89\ H_2O \rightarrow 89\ CH_20 + 89\ O_2$; $\Delta A = 0$; $\Delta CO_2 = -89u$; $\Delta O_2 = +89u$.

$16\ CO_2 + 16\ NO_3^- + 16\ H^+ \rightarrow 16\ NHCO + 32\ O_2$; $\Delta A = +16u$; $\Delta CO2 = -16u$; $\Delta O2 = +32u$; $\Delta NO3- = -16u$

$CO_2 + MHPO_4 + H^+ \rightarrow CH_2PO_4^- + O_2 + M^{2+}$; $\Delta A = 0$; $\Delta CO_2 = -u$; $\Delta O_2 = +u$; $\Delta PO_4^{3-} = -u$

giving overall changes for u units of organic matter production of

$\Delta A = +16u$; $\Delta CO_2 = -106u$; $\Delta O_2 = +122u$; $\Delta NO_3^- = -16u$; $\Delta PO_4^{3-} = -u$

The reverse of these changes was considered to accompany the oxidation of organic matter in the water column."

Here obviously Skirrow (1975) reckons that for the formation of organic matter as per the Redfield Eq. (1), the resulting decrease of 16 units nitrate is the cause of a parallel increase of 16 units Oceanic Alkalinity. The parallel decrease of 1 unit phosphate has zero effect on Oceanic Alkalinity.

Reference

Skirrow, G. (1975). The Dissolved Gases - Carbon Dioxide. Chapter 9 in: Riley J.P., Skirrow G. (eds.) Chemical Oceanography, Academic Press, London, New York, San Francisco, vol. 2, 2nd edn. pp. 166-167.

S14) Citation of a table after Brewer and Goldman (1976)

"Schematic equations for the uptake of phosphate and nitrogen by phytoplankton"

“Assimilation of phosphate species by phytoplankton without accompanying cation uptake

$H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^-$ (1)

$HPO_4^{2-} + 2H_2O \rightleftarrows H_3PO_4 + 2OH^-$ (2)

$PO_4^{3-} + H_3PO_4 \rightleftarrows H_3PO_4 + 3OH^-$ (3)

Assimilation of phosphate species by phytoplankton with accompanying cation uptake

$Mg^{2+} + HPO_4^{2-} \rightleftarrows MgHPO_4^0$ (4)

$Fe^{3+} + PO_4^{3-} \rightleftarrows FePO_4^0$ (5)

Nitrate assimilation by phytoplankton

$106CO_2 + 138O_2 + 16NO_3^- \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16OH^- + 138O_2$ (6)

Ammonia assimilation by phytoplankton

$106CO_2 + 138O_2 + 16NH4^+ \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16H^+ + 106O_2$ (7)”

Please notice that presumably Brewer and Goldman (1976) had written a minor typo in the above equation (3) where at left hand is written the term H_3PO_4 that presumably should have been the term $3H_20$ as follows:

$PO_4^{3-} + 3H_2O \rightleftarrows H_3PO_4 + 3OH^-$ (3)

Reference

Brewer, P.G., and Goldman J.C. (1976). Alkalinity changes generated by phytoplankton growth. *Limnol. Oceanogr.* 21, 108-117.

S15) Magnesium in chlorophyll *a*

The key molecule chlorophyll *a* for photosynthesis by all plants comprises 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. Each molecule of chlorophyll *a* comprises one Mg atom. Jakobsen and Markager (2016) give a wide range of carbon to chlorophyll *a* ratio values (C : Chl *a*; weight:weight) from 6 to 333 in the literature. Assuming this range and given the molar mass of 893.509 $g \cdot mol^{-1}$ of chlorophyll *a*, 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 equation 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 close to the precision of Alkalinity of 1 $\mu mol.kg^{-1}$. This maximum is not discernible versus the very high background Mg concentration of 52820 $\mu mol.kg^{-1}$ in seawater (Table 1).

Reference:

Jakobsen, H. H., and Markager, S. (2016). Carbon-to-chlorophyll ratio for phytoplankton in temperate coastal waters: Seasonal patterns and relationship to nutrients. *Limnol. Oceanogr.* 61, 2016, 1853–1868. doi:10.1002/lno.10338

S16) External sources and sinks for the major constituents of seawater

Seawater of the world ocean basins is subject to 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, (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 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 ºC) 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, 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 a community effort on the basis of measured modern seawater Mg:Ca and Sr:Ca ratio values in more than 1100 samples worldwide. Described are the regional deviations, where indeed riverine supply and hydrothermalism play a major role, besides ocean biological processes. The interactions with Alkalinity are also discussed and in their Figure 3A shown for Ca, Mg and Sr.

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 sciences. This being stated, one must be aware of regional deviations interfering with the original first order approach.

References: see main article

S17) Interferences of dissolved organics and suspended particles with Titration Alkalinity

One caveat is that in the acid titration procedure for determination of Titration Alkalinity there may occur interferences due to dissolved organic moieties acting as proton acceptors. This has been reported and discussed for natural seawater samples (Hernández-Ayon et al., 2007; Kim and Lee, 2009; Ko et al., 2016; 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 some 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 excess Alkalinity. Historically, there have been previous suggestions of interferences by organic substances. One example of such historical suggestion where discrepancies among CO_2 system variables were hypothesized to be due to perhaps unknown (organic) protolytes is described in Supplementary Material S18. Similarly, recently a residual discrepancy was reported that would only be fully accounted for if there exists a small, but meaningful amount (~4 μmol kg^{-1}) of an unidentified and typically neglected contribution to measured Titration Alkalinity, likely from organic bases, that would occur widespread in the open ocean (Fong and Dickson, 2019).

Another caveat is the conceivable risk that some of the hydrogen ions of the acid titration may somehow become involved with surfaces of suspended marine particles. On the one hand, within the deeper midwaters of the oceans, the abundance of suspended particles is quite low. Chanson and Millero (2007) compared filtered and unfiltered samples collected in the open ocean and found no statistical difference of the at-sea shipboard measured Alkalinity. On the other hand, in coastal waters and/or the benthic boundary layer, and plankton blooms in surface waters, the abundance of particles is much higher. Bockmon and Dickson (2014) provided a filtration method of seawater samples that was tested for DIC, pH and Alkalinity. Obviously, it is advisable to remain alert for any artifacts merely due to the filtration step.

References: see main article

S18) Historical example of hypothesis of interferences due to unknown protolytes

During the GEOSECS expeditions in the 1970s the acid titration method was used to determine both DIC and Titration Alkalinity (see Supplementary Information S3). During the Atlantic expedition, DIC was also determined by shipboard gas chromatography, as well as for a suite of selected stored samples, by infrared gas analysis afterwards in the home laboratory (Takahashi and Bainbridge, 1981). The station-by-station average for the difference between the shipboard GC data and shipboard titration data of DIC was reported. The GC based data was in average 15.1 (± 9.7) µmol.kg^{-1} higher than the titration-based data. Offsets were also reported between the shore-based infrared data of DIC and the shipboard DIC data of either GC or titration. This, and various other uncertainties, also in the ensuing Pacific and Indian Ocean expeditions, were deemed to lead to some ambiguity in the data of both DIC and Alkalinity.

Bradshaw and Brewer (1988) reported for the TTO project (Brewer et al., 1985, 1986), that the titration-based DIC results were ~21 µmol kg^{-1} higher than those obtained by gas extraction methods which, unlike the titration method, do not require detailed knowledge of the chemistry of the seawater samples. Possible explanations of these differences were mentioned: an error in the physico-chemical model*;* a persistent contamination problem; or the presence of an unknown protolyte (HX) in natural seawater. The systematic offset appeared to be largest in the surface waters, where the reported very high concentrations of Dissolved Organic Carbon (DOC) by Sugimura and Suzuki (1988) might give rise to higher concentrations of such unknown organic protolytes. Eventually the very high DOC data as reported by Sugimura and Suzuki (1988) was demonstrated to be irreproducible by others (e.g. Sharp, 1993; De Baar et al., 1993; among others). This led to a retraction of the dataset of Sugimura and Suzuki (1988) by Suzuki (1993).

During the JGOFS expeditions in 1989 and 1990, Stoll et al. (1993) used two independent methods for measurement of DIC, the traditional acid titration and the then quite novel coulometric method (Johnson et al., 1987). Latter coulometric method nowadays is the standard method for determination of DIC. For more than 600 seawater samples there was fair agreement, independent of depth, between the two methods (on average 0.6%).

Some years later, Millero et al. (1993) concluded that the previously reported offset in DIC by titration versus DIC by other method(s), for example as reported by Bradshaw and Brewer (1988), after all is independent of depth and instead is deemed to be due to the non-Nernstian behavior of the electrodes. In other words, according to Millero et al. (1993), the offset would not be due to unknown protolytes.

References: see main article