

Response to comments of Dr. Fiz Fernandez Perez

First, and foremost, the authors are most grateful to the five colleagues that have provided their constructive comments.

Therefore, we now are quite busy making major revisions to our manuscript towards the revised version to be re-submitted and published as a regular article in Ocean Science. Meanwhile we are also studying the various other articles that were recommended in the five comments of the colleagues.

Perhaps it is useful to mention the rationale for submission of the discussion paper that invites such comments. Recently, it was noticed that one colleague had a different view on one aspect of Alkalinity than another colleague. However, each was convinced the own personal view was the only correct view. For a long time indeed there only was one alkalinity concept in the literature. Yet given the above apparent different views, it was deemed helpful to submit a discussion paper that invites colleagues to provide feedback towards eventually arriving at one commonly agreed exact definition of alkalinity.

Next Prof. Middelburg promptly by email sent his article Middelburg et al. (2020) and from this, and the further information provided by him, all of us learnt and came to realize that in fact there are several definitions of Alkalinity in the literature.

There exist at least three definitions as follows:

- a. what we called Oceanic Alkalinity, more or less the same as Charge Balance Alkalinity after Middelburg et al. (2020).
- b. Titration Alkalinity
- c. Total Alkalinity, after Dickson (1981)

Moreover, for those authors wishing to also take into account the effects of biological uptake/release of sulphate, magnesium, strontium and so forth, and combinations thereof, more versions of the definitions of Alkalinity do arise and do exist in the literature.

Middelburg et al. (2020) review the various approaches and definitions in the literature, in a non-judgmental style. From this style, it is now realized that every author, or team of authors, has the academic freedom of speech to write and publish their own approach and definitions. For example, for the effect of photosynthesis and its opposed respiration, numerous approaches are mentioned yielding calculative factors ranging from 1.06 to 1.36, where yet another approach relying on AOU for assessing such organic matter dynamics is also mentioned.

This notion that there exist several concepts and their definitions of alkalinity, and each is fine, is somewhat of a paradigm shift, this versus the preceding notion of there being one alkalinity that can be measured by titration.

Next, we may, or may not, soon observe the classical response of the scientific community, after Kuhn (1962). Briefly, after such paradigm shift, (almost) everyone states that, yes, they knew this for a long time, has always stated this. In this case, some or several ocean chemists would say they always knew that there are several concepts/definitions of alkalinity. Quite nicely, Kuhn (1962) was soon proven correct once two major revolutions

had taken place: 1) the double helix structure of DNA as per Watson and Crick (1963), and continental drift (evidence of geomagnetic reversals) after Vine and Matthews (1963).

\*) Morley 1963 manuscript, also on geomagnetic reversals, first rejected by Nature, next rejected by J.Geophys.Res.: "*such speculation makes interesting talk at cocktail parties but it is not the sort of thing that ought to be published under serious scientific aegis*"

## General Comments

*Below we have copied all comments of the reviewer, and below each comment/correction have written our response in italic print.*

Stating that there is some confusion in the literature, the authors propose to recover in an operational way the classical definition of total alkalinity in seawater, based on the charge balance defined as the difference between the sum of fully dissociated strong cations and fully dissociated strong anions. They call it oceanic alkalinity (OA) and propose that it be determined by acid titration.

*In retrospect we now are aware that there is a real difference between oceanic alkalinity (OA) and Alkalinity based on acid titration.*

In the marine environment, biological mineralization of organic matter generates very small amounts of sulfate and phosphate. While the latter would have no effect on OA, the former would have a very small effect on the order of OA accuracy.

*Agree.*

However, both are considered in the classical operational definition of total alkalinity (TA) of Dickson et al. (1981), based on acid titration of seawater using the balance of hydrogen ion acceptor and donor species.

*To the best of our knowledge, the classical operational definition of total alkalinity (TA) of Dickson (1981), does NOT take into account the release of sulfate due to biological mineralization of organic matter. It does take into account the fact that at the endpoint of nominal pH=4.5 some portion of the total dissolved sulfate has absorbed some of added hydrogen ions resulting in some presence of HSO<sub>4</sub><sup>-</sup> at this endpoint.*

In order to achieve full consensus among ocean scientists the authors suggest to remove the theoretical difference between the two definitions, OA and TA, motivates the authors to question the role of sulfate, phosphate and nitrite species in the TA definition, and of the relevant sulfate formation during organic matter mineralization processes.

*In retrospect we now do realize that in fact there is a theoretical difference between the two definitions, OA and TA. Otherwise the roles of sulfate, phosphate and nitrite species in the TA definition were questioned in our discussion paper with an eye to soliciting feedback (comments, corrections) from the readership. The relevant sulfate formation during organic matter mineralization processes was also discussed in our paper, where it was mentioned that, there unfortunately is no dissolved tracer for detecting the role of sulphur, this in*

*contrast to other contributors C, N, P of alkalinity, that can be assessed from dissolved tracers DIC, nitrate, phosphate.*

The classic definition of TA (Dickson et al. 1981) has been in operational use for four decades by the scientific community with hundreds of thousands of measurements reported in international databases and certified reference materials (CRMs) used for quality control. TA is well established in the scientific community, in terms of its theoretical definition, and there is a strong family of computer software based on CO2SYS (Lewis and Wallace 1998). There are some practical problems that the scientific community has been evaluating, such as the effect of organic acids in the determination of TA, or a more precise knowledge of the total borate concentration, or those related to the establishment of a pH scale based on the concentration of 'free' hydrogen ions. They all impact the internal consistency of the seawater carbonate system at levels very close to the accuracy of TA and DIC measurements.

*Agree with all the above. Otherwise, with regards to the classic definition of Dickson (1981) it is realized that this is based on two inherent assumptions:*

- (i) the zero proton concept (after Sillen, 1959 lecture as published in 1961);*
- (ii) the distinction of proton donors versus proton acceptors on the basis of the dissociation constants K values being higher or lower than  $10^{-4.5}$  value.*

*Fraga and Alvarez-Salgado (2005) do give recognition to the Dickson (1981) article, yet next decide to use another approach instead following Millero (1995). This choice is interesting as presumably there would be no need to invoke arbitrarily established inherent assumptions. The interesting paragraphs of the Fraga and Alvarez-Salgado (2005) article are copied below, as follows:*

*Dickson (1981) gave his own operational definition of TA: “The total (or titration) alkalinity of a natural water sample can be regarded as a measure of the proton deficit of the solution relative to an arbitrarily defined zero level of protons”. Since the carbonic and boric acid systems are the main contributors to the TA of a natural sample, Dickson (1981) reasonably established that the operational endpoint of the TA titration should be the pH at which:*

$$[H^+] = [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] \quad (3)$$

*This equation can be simplified to:*

$$[H^+] \sim [HCO_3^-] + 2 \times [CO_3^{2-}] \quad (4)$$

*This endpoint is at a pH ~4.4. Hence, Dickson (1981) arbitrarily defined that any acid with a pKA < 4.5 is a proton donor; consequently, it does not accept protons during the TA determination. Based on Dickson's (1981) definition, Millero (1995) provides the following operational definition of alkalinity: “The total (or titration) alkalinity (TA) of a natural water sample is arbitrarily (or operationally) defined as the concentration (in eq kg<sup>-1</sup>) of all bases able to accept a hydrogen ion at the equivalence point of the carbonic acid system species”. In this work we have strictly applied this definition, without considering the arbitrarily established zero level of protons imposed by Dickson (1981). For a standard seawater sample of salinity 35.0 and temperature 25°C, the equivalence point of a TA determination occurs at a pHSWS of ~4.25 (hydrogen ion activity,  $a_H = \sim 10^{-4.4}$ ).*

However, these are not the elements discussed by the authors in the manuscript. They propose to eliminate in the definition of TA certain chemical species (whether or not in ionic form) so that the definition of TA and OA are equivalent.

*Admittedly, in retrospect it is recognized that TA and OA are not, or at least not exactly, equivalent. In the revised manuscript we correct this.*

Previously Middelburg et al. (2020) have discussed about the concept of OA (Ocean Alkalinity) based on alkalinity charge balance (CBA) following a previous article by Soetaert et al. (2007) where it is evaluated how natural processes (biological or not) affect differently CBA and TA. In fact, the differences in TA and CBA shown by Soetaert et al. (2007) are identical to those shown by Wolf-Gladrow et al. (2007) systematically questioned in the present manuscript. Both papers, the one by Soetaert et al. (2007) as well as the one published in 2020 in Reviews of Geophysics by Middelburg et al. are, surprisingly, neither cited nor discussed at any point in the entire manuscript.

*Soetaert et al. (2007) as well as the one published in 2020 in Reviews of Geophysics by Middelburg et al. are available to us and will be cited and discussed in the revised manuscript.*

Dealing with many aspects of very little effect on alkalinity, the article must address a multitude of processes, which makes it lengthy and, in some ways, wordy. The manuscript analyzes in great detail different articles concerning the biological processes that generate small amounts of sulfate from organic matter, to finally propose that this contribution is so small as to be negligible. It is true that many articles do not evaluate or ignore the sulfate contribution considering mainly nitrate and phosphate, but there are several classic articles (Chen 1978; Kanamori and Ikegami 1982; Fraga and Alvarez-Salgado where it is evaluated from the biochemical composition of organic matter, with S:P ranges varying from 1 to 2.8). This suggests that the sulfate generation suggested by Wolf-Gladrow et al. (2007) and reflected in TA dynamics in other papers (Carter et al. 2014 and Lauvset et al. 2020) has to be taken into account although its impact on sulfate concentration is practically negligible and therefore on OA.

*Agree. We are grateful for the cited additional articles (Kanamori and Ikegami 1982; Fraga and Alvarez-Salgado, Carter et al. 2014 and Lauvset et al. 2020) that will be discussed and some of these already mentioned in our responses.*

In fact, I believe that the effort to unify the definition of ocean alkalinity is probably futile because while the titration-based definition is clearly proven, and in general use and consistent with other measures of the marine carbonate system, the OA proposal based on the definition of strong anions has certain weaknesses. There are ionic species such as chloride, nitrate or sulfate that clearly fall into that category, but others such as bisulfate, fluoride, nitrite, or  $\text{H}_2\text{PO}_4^-$  since they may consume a small percentage of the acid load that is realized during titration of seawater that reaches pH=3. The definition itself has a significant asymmetry since also certain majority cations considered 'strong' have significant interactions with  $[\text{OH}^-]$  but this has no impact on the differences between OA and TA.

*Surely the OA concept may have weaknesses, but is well known in notably the textbook of Broecker and Peng (1982). Latter textbook is deemed to have been and still being very influential in oceanography. Moreover, those wishing to derive changes in the concentration*

*of dissolved  $\text{Ca}^{2+}$  due to formation/dissolution of  $\text{CaCO}_3$ , in fact do, wittingly or not, use the Ocean Alkalinity approach that next by salinity normalization and correction for organic matter formation/decomposition via nitrate adjustment, does yield a result with regards to changes of dissolved  $\text{Ca}^{2+}$  concentration.*

Consequently, the current manuscript, despite the debate it generates, proposes a definition of alkalinity that is not operative and is not clearly supported despite the important discussion on a significant list of articles that suffers from the lack of the most relevant ones.

*In retrospect we agree that OA is not, or not exactly, compatible with Alkalinity based on acid titration. On the other hand, we are convinced that the OA concept is operative and surely is also supported. We are grateful for on the one hand the appreciation of a significant list of articles in the discussion paper, and on the other hand for the notion that several most relevant articles had been overlooked. The latter omissions are now being remedied in doing the major revisions of the manuscript.*

### **Specific comments**

*First and foremost, we are most grateful for the meticulous effort to proofread and provide these many comments and corrections.*

Line 15: Change "interactions... with alkalinity" to "contributions... to alkalinity". Alkalinity is not a chemical species that interacts with any other.

*We agree.*

Line 22: "Oceanic Alkalinity can be determined by acid titration of a seawater sample, this leading to an ensuing value of Titration Alkalinity." While Middelburg et al (2020) show that both definitions do not lead to identical alkalinity values, de Baar et al. state the opposite.

*Indeed, we were simplifying too much, there is for each seawater sample a difference between OA and the value obtained from acid titration. This difference is largely due to (i) the role of sulphate absorbing some of the added hydrogen ions, (ii) similarly fluoride absorbing some of the added hydrogen ions, and finally (iii) the role of the various species of phosphate. This will be discussed and incorporated into the revised manuscript.*

Line 27: "To the best of our knowledge, this perceived role is mistaken". No reason or argument is shown when many other authors have evaluated experimentally or theoretically the contribution of phosphate. (e. g, Kim et al. 2006, and Kanamori and Ikegami 1982, Fraga and Alvarez-Salgado 2005)

*Given the now awareness (see above) that there are quite some different definitions of Alkalinity in the literature, and that each is fine in accordance with academic freedom of speech, it is now realized that there are several approaches to describing and evaluating the role of phosphate species. In the major revisions of the manuscript, we now are including an approach of literature review focusing on how every article is dealing with the role of phosphate species.*

Line 30-33 "Moreover, the role of sulphate is not verifiable, because the small amount of biological assimilation of sulphate cannot be discerned from measurement of the very large

background concentration value of dissolved sulphate". The need to include the sulfate ion, and specifically the bisulfate ion in the alkalinity titration equation comes from the very small formation of  $\text{HSO}_4^-$  contributing importantly (30%) to the concentration of total hydrogen ions affecting the alkalinity determination which is performed between  $\text{pH}=3$  to  $\text{pH}=4$ .

*In the discussion paper were described separately the two roles of sulphate.*

*Firstly, in section 4.1.1. the well-known fact that once the titration endpoint (second equivalence point) is reached at nominal  $\text{pH}=4.5$  endpoint, that some small portion of the  $\text{SO}_4^{2-}$  ion (as existed at  $\text{pH}=8$ ) has absorbed a hydrogen ion to become  $\text{HSO}_4^-$ . For the example salinity  $S=35$  there has evolved about  $90 \mu\text{mol.kg}^{-1}$   $\text{HSO}_4^-$  species. The total sum  $\text{SO}_4^{2-}$  plus  $\text{HSO}_4^-$  remains the same value as it was at  $\text{pH}=8$  of the untitrated original seawater sample, this concentration value is  $0.02824 \text{ mol.kg}^{-1}$  or  $28240 \mu\text{mol.kg}^{-1}$  of which at the endpoint some  $90 \mu\text{mol.kg}^{-1}$   $\text{HSO}_4^-$  species, that is equal to  $(90/28240) = 0.003187 = 0.3187\%$ . On the other hand, this  $90 \mu\text{mol.kg}^{-1}$   $\text{HSO}_4^-$  is highly significant in context of an overall Alkalinity value in the order of  $2250\text{-}2400 \mu\text{mol.kg}^{-1}$ . For an Alkalinity value of  $2400 \mu\text{mol.kg}^{-1}$  this amounts to some  $(90/2400) = \sim 0.038 = 3.8\%$ . Otherwise it is understood that a typical  $\text{pH}$  value of the endpoint (second equivalence point) is in the order of say about  $\text{pH}=\sim 4.25$  to  $\text{pH}=\sim 4.5$  for any titrated seawater sample. Surely the titration procedure does continue to about  $\text{pH}=3$  where likely indeed the concentration of  $\text{HSO}_4^-$  has further increased more than an order of magnitude, presumably corresponding with the 30% mentioned by the reviewer. The continuing titration to as far as  $\text{pH}=\sim 3$  is in our understanding very useful if not in fact essential to be able to define accurately by curve fitting the endpoint at  $\text{pH}=4.25\text{-}4.5$  but any type of Alkalinity equation in the literature is taking this latter endpoint, and not  $\text{pH}=3$ .*

*Secondly in text section 4.1.2. is mentioned that several authors have for the formation (photosynthesis) and reverse decomposition of organic matter, not only taken into account nitrogen uptake/release, and in addition phosphate uptake/release but moreover also sulphate uptake/release. This latter role is in our view very distinct from the above as in our text section 4.1.1. In the revised manuscript, we discuss this and make it clearer that such difference exists.*

Line 34 "but insignificant versus the accuracy of the measurements of Titration Alkalinity"  $\text{pK}(\text{Nitrite})=3.2$  below 4.5. So its contribution to TA is practically the same as that of nitrate, although it is not a strong acid (like nitric), it is  $500 (10^{2.7})$  times stronger than  $\text{CO}_{2(\text{aq})}$  ( $K_1$ ). On the other hand, if the theoretical incorporation of nitrite is not incorrect, there is no room for discussion of its inclusion in the alkalinity equation, whether it is significant or not.

*Agree. Otherwise, in the discussion paper was mentioned that shipboard analyses of dissolved nitrate by spectrophotometry in one channel of an Autoanalyzer does also comprise a small amount of the dissolved nitrite, when present in the seawater sample. The ensuing overall nitrate as next inserted in the Oceanic Alkalinity equation (20) in fact is the sum of nitrate plus occasional trace amount nitrite. Therefore, in practice of seagoing oceanography, when only making measurements of nitrate (that in fact is the sum of nitrate plus nitrite) one is doing fine. Moreover, nitrite in a subsample can be determined independently after the method of Strickland and Parsons (1968). However, such additional distinct shipboard analysis of nitrite takes extra effort, and occupies an extra analysis line on the autoanalyzer instrument, and is by no means always pursued in context of oceanographic expeditions.*

Line 36 “the negative sign of  $[H_3PO_4]$  is mistaken.” The  $pK_1$  (=1.8) of  $H_3PO_4$  is very similar to the  $pK$  of  $HSO_4^-$  (=1.0), so theoretically it should be included regardless of the impact of the mineralization of phosphorus compounds present in the organic matter and which are susceptible to be mineralized to  $H_3PO_4$ .

*The now included, intriguing article of Fraga and Alvarez-Salgado (2005) provides extensive considerations on, among others, the role of the phosphate system. There is detailed consideration on the phosphorus compounds present in the organic matter. Our further study of this article towards eventually understanding all this ourselves, would presumably also lead to our complete understanding of the role of the  $H_3PO_4$  species. We will include this extensively in the revised manuscript.*

Line 60 “quantifying the formation/dissolution of  $CaCO_3$  one cannot detect directly the related changes in the concentration of dissolved calcium ( $Ca^{2+}$ ), because these changes are not discernible versus the very large background...”. It seems that nearly 40 years ago **Kanamori and Ikegami (1982)**, none cited in the manuscript) were able to do that.

*Indeed, we will obtain a copy of the Kanamori and Ikegami (1982) article, that as mentioned above, also was recommended by Prof Middelburg and include it in the discussion of the revised manuscript.*

Line 92-93 ‘In order to unravel the various components of the DIC pool, there are four key variables that can be measured directly in a collected sample of seawater’. I guess the authors are unaware that it has also been possible to measure carbonate ion for 14 years (Byrne and Yao, 2008; Guallart et al. 2022).

*Indeed, we were unaware of this ability to directly measure the carbonate ion. By the way and on the other hand, this measurement does not seem to play a large role in the present-day carbonate system measurements. We shall nevertheless incorporate this knowledge in the revised manuscript.*

Line 97-102: This paragraph proposes without clear relation to the previous paragraphs that the exact value of alkalinity is unclear because of the biological role of sulfate and phosphate citing only Wolf-Gladrow et al. 2007. In a review article in the journal 'reviews of Geophysics' Middelburg et al. 2020 (not cited in the manuscript) argued very similarly to Wolf-Gladrow et al. 2007. The Wolf-Gladrow et al. 2007 ratios or similar has been used in Lawset et al. (2020) and Carter et al. (2014) (none cited in the manuscript)

*We are very grateful for the mentioning of these other very relevant articles. The Middelburg et al (2020) paper is already mentioned above. The Lawset et al. (2020) (in fact Lauvset is the correct name) and Carter et al. (2014) we will obtain and study. Please note that overly dissimilar ratios are known from the extended literature so that the discussion on those is still open.*

Line 116. Equation 1. This equation (Redfield et al. 1963) was revolutionary at the time, but not very accurate in the way it expresses the "average" organic matter (OM) mineralized in the aphotic layer of the ocean. It simulates that the OM is composed of phosphoric acid, ammonium and carbohydrates. Although this is not an easy task as it is necessary to know the average biochemical composition of marine plankton, several authors have already expressed this 'stoichiometry' in a form closer to reality (e.g. Fernández-Castro et al. 2019, Alvarez-

Salgado et al. 2014; Hupe and Karstensen 2000; Anderson et al. 1995, Rios et al. 1998, and others). It is advisable to at least use the equation of Anderson et al. (1995) more in line with the biochemistry observed in OM or at least use a condensed form of the Redfield et al. (1963) expression.

*In the discussion paper we did, somewhat in the end in text section 6.1., mention that other, more recent equations do exist, and mentioned merely as one example, the Andersen and Sarmiento 1994, and the reviewing of such type work in the textbook of Sarmiento and Gruber (2006). Also, it was mentioned that the original Redfield, Ketchum and Richards (1963) article did rely mostly on observations in the North Atlantic region (therefore not necessarily representative for all of the world oceans). In the major revisions we will write a more extensive paragraph mentioning more such articles, such as kindly provided. Moreover, we noticed that Fraga and Alvarez-Salgado 2005 also mention Fraga et al. (1998). We intended to give credit to the original work of Redfield, Ketchum and Richards (1963). Yet indeed it would be an improvement to next also mention an equation of a more recent article that is deemed to be more representative for all world ocean basins. Presumably the suggestion of a "condensed form" is consistent with the below cited paragraph of Fraga and Alvarez-Salgado (2005) as follows:*

*Subsequently, Anderson (1995) and Fraga et al. (1998) proposed new formulas, C106H175O42N16P and C106H171O42N16P respectively, which basically correct the over-estimated H and O proportions of the original formula.*

*Here it is noticed that in these new (more condensed) formulas, the relative proportions of key element C, N and P remain the same 106:16:1 as in the original Redfield, Ketchum and Richards (1963) article.*

*Fraga, F., Ríos, A.F., Pérez, F.F. and Figueiras, F.G. (1998). Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea. Sci. Mar., 62: 161–168.*

Line 149. Equation 7 is not an chemical equilibrium expression, this should a mathematical expression. Please replace both opposite arrows by equal one. I believe that the detail shown in this part of the manuscript is somewhat avoidable and that equations 2 to 7 could easily be omitted.

*Agree. We will replace both opposite arrows by equal one symbol (=).*

*Otherwise, the observation that "the detail shown in this part of the manuscript is somewhat avoidable and that equations 2 to 7 could easily be omitted." is in somewhat the same spirit as the following introductory sentence at text lines 96-97 in the discussion paper:*

*"Inevitably, the, often described, dissolved CO<sub>2</sub> system in seawater must first be defined in the introductory section 1.2."*

*It is a matter of choice really, between optimal service to a wider readership, versus being concise. Here we would opt for our original choice to serve a wider readership well beyond the expert colleagues such as the reviewer.*

Line 177 'proton concentration [H<sup>+</sup>]. Change to 'Hydrogen ion concentration'. Interactions between chemical species occur through the exchange of electrons in the valence layer. The proton refers to the elementary particle present in the nucleus of the atom. Therefore, the use of the term proton to refer to H<sup>+</sup> should be avoided. It certainly exists in the classical definition of acid and base by Brønsted (1923) and Lowry, 1923, as the transfer or donation or reception of protons. However, it is still a concept overcome by Lewis (1923) who defines an acid as a chemical species containing an empty orbital capable of accepting an electron pair from a base. It is practically impossible to describe the presence of a free proton as a subatomic particle in a condensed phase such as pure water or seawater. As far as we know, water molecules dissociate by transferring a hydrogen atom with an empty orbital to a neighboring molecule that gives up a pair of electrons from the valence shell of the oxygen atom, generating OH and H<sub>3</sub>O<sup>+</sup>. Let us say that the hydrogen bridge bonds between the water molecules are activated upon a transfer of the hydrogen atom, resulting in the sharing of a pair of electrons given up by the oxygen of the neighboring molecule that yields its electron to the oxygen from which it dissociates. This type of electronic interactions also explains the high ionic mobility of the hydrogen ion in water (Grotthuss mechanism). It is recommended to follow the IUPAC and use the oxonium ion (H<sub>3</sub>O<sup>+</sup>) which was previously called hydronium ion.

*In general the suggested preferable usage of the wording "hydrogen ion" or "hydrogen ion concentration" is appreciated. In revising the manuscript, we will follow this suggestion as much as possible. Otherwise we agree that the wording proton also or primarily refers to the elementary particles, the protons and neutrons that in a suite of combinations constitute the nucleus of atoms of all chemical elements. On the other hand, it is unavoidable to continue to here and there use the word proton, if nothing else because one or another original article in the literature that we are citing, does use this word. Most notably, the reviewer at first had stated a great appreciation of the Dickson (1981) article, as follows:*

*"The classic definition of TA (Dickson, 1981) has been in operational use for four decades by the scientific community with hundreds of thousands of measurements reported in international databases and certified reference materials (CRMs) used for quality control."*

*Here as a matter of fact, Dickson (1981) are mentioning 'proton' many times throughout their article, this including the inherent arbitrary assumption of the 'zero level of protons'.*

*Whereas the naming 'hydrogen ion' or 'proton' is deemed accessible for a wide readership, it is reckoned that systematic use of the wording oxonium ion (H<sub>3</sub>O<sup>+</sup>) surely is not. How far does one want to go with top-notch IUPAC wording at the risk of merely confusing a wider readership not being experts in the latest IUPAC conventions. For example, does one want to go even a step further, and define by also taking into account the existing hydrogen-bonded structure as it exists in seawater (Figure 2.4 at page 65 of Whitfield (1975). Perhaps the best way is to add yet another Supplementary Material where these refinements on oxonium as per IUPAC and previous naming hydronium and hydrogen-bonded network structure can be explained, while in the main text merely using 'hydrogen ion' or 'proton'.*

*Whitfield, M. (1975) Sea Water as an Electrolyte Solution. Chapter 2 in: J.P. Riley and G. Skirrow (eds.) Chemical Oceanography, Volume 1, 2nd Edition, Academic Press, London, New York, San Francisco., pp. 43-171.*

Line 187 'free protons..'. Change by oxonium or hydrogen ions.

*Hydrogen ions is OK and will be used as much as possible.*

Line 255. I wonder if the interactions of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{OH}^-$  to form  $\text{OHCa}^+$  and  $\text{OHMg}^+$  are not equally relevant as that of  $\text{HSO}_4^-$ , and if this does not somewhat invalidate the definition of Alkalinity based on charge balance.

*The Table 3 of the discussion paper for pH=8.07 seawater condition is based on a complete MINEQL simulation that does in its resulting spreadsheet include various species of Ca and Mg. Examples of included such species are  $\text{CaHCO}_3^+$  and  $\text{MgHCO}_3^+$  and  $\text{CaCO}_3(\text{aq})$  and  $\text{MgCO}_3(\text{aq})$  and  $\text{MgH}_2\text{PO}_4^+$  and  $\text{MgHPO}_4(\text{aq})$  and  $\text{CaPO}_4^-$  and  $\text{MgPO}_4^-$ . The spreadsheet does not comprise  $\text{OHCa}^+$  and  $\text{OHMg}^+$ . Presumably such interactions to form  $\text{OHCa}^+$  and  $\text{OHMg}^+$  are not relevant in seawater at pH=8.07 condition, as per the MINEQL simulation. We will in a separate email send this complete MINEQL spreadsheet to the reviewer for his own consideration. The hypothesis of the reviewer may, or may not, have validity, yet thus far we are not able to provide evidence in support of this hypothesis. Otherwise the definition of Oceanic Alkalinity in our discussion paper as the charge balance description merely is an exact copy of such definition by Broecker and Peng (1982).*

Line 326-328 ‘Conversely, one realizes that these latter four systems are not, or virtually not, making a significant contribution to Titration Alkalinity in well oxygenated seawater. However, they are necessary in their analytical determination considering that the pH equivalence is normally determined in the pH range of 3-4 or 3-4.5, and because both bisulfate and HF contribute to capture a 30 and 2% of the acid load, or in other word they contribute to reduce the ‘free’ hydrogen ion concentration. Or in other words, a relevant part of the HCl contribution is mobilized in the increase of their concentrations.

*Here an error did occur for which we apologize. Briefly the paragraph in text lines 318-328 is about phosphate, silicate, hydrogen sulfide and ammonia that each are not making a significant contribution to Alkalinity. Yet in trying to follow as closely as possible the famous equation of Dickson (1981), we did by duly copying this from the Dickson (1981) in the second text line numbered 323 also unintentionally included the  $[\text{HSO}_4^-]$  and  $[\text{HF}]$  that in fact are not among these four minor contributors phosphate, silicate, hydrogen sulfide and ammonia. The reviewer did notice this discrepancy and quite correctly mentions that both bisulfate and HF contribute to capture a 30 and 2% of the acid load, in other words are quite significant. We apologize for this error, and are grateful for the reviewer taking notice. In retrospect it would have been correct to have these two constituents  $[\text{HSO}_4^-]$  and  $[\text{HF}]$  in the tex line 322 and not in the second text line 323. In doing the major revisions of the manuscript we will take this into account.*

Line 347-348 ‘ $\sim 10^{-4.5} \mu\text{mol.kg}^{-1}$ ’ and next lines. The symbol ‘micro’ have to be deleted. Both hydrogen ion and bicarbonate concentration would be around  $31.5 \mu\text{mol.kg}^{-1}$ , being de  $\text{CO}_2(\text{aq})$  nearly  $1968 \mu\text{mol.kg}^{-1}$ .

*Indeed an error of us. Agree and will correct this in revised manuscript.*

Line 359 ‘which the square root is  $\sim 1.4 \times 10^{-4.43}$ ’. That is a pH=4.28.

*Yes, indeed pH=4.28 and quite nicely, this pH=4.28 is actually in good agreement with a value of  $\sim 4.25$  (hydrogen ion activity,  $a_{\text{H}} = \sim 10^{-4.4}$ ) as mentioned by Fraga and Alvarez-Salgado (2005).*

Line 361-22 ‘However, strictly speaking, Dickson (1981) did somewhat simplify by stating  $pH = 4.5$  as the endpoint,...’. This is not true. Dickson sets  $pK$  values to distinguish between chemical species that do or do not contribute to alkalinity, but does not set any endpoint. Moreover, the final  $pH$  will depend on the very chemical and physical characteristics under which the titration is performed, which are usually below  $pH=4.5$ .

*Agree. Dickson (1981) only had defined this  $pH=4.5$  as for making the distinction between proton donors and proton acceptors, and had not stated that  $pH=4.5$  is the endpoint of the titration. This being now understood, it is noticed that in several articles published since the Dickson et al. (1981) article, the value of  $pH=4.5$  is reportedly often given as the  $pH$  value of the endpoint (second equivalence point). Hence, we did fall into the same trap as several others before us.*

Line 365-366 “(The simplification by Dickson (1981) and earlier articles, may, or may not, relate to the fact that initially the end-point was determined by linearization rather than curve fitting of the titration curve.). This is rather speculative and unsubstantiated.

*This can and will now be deleted because, as in the preceding comment and response, the  $pH=4.5$  is NOT given by Dickson (1981) as the  $pH$  value at the endpoint of the titration, and hence is NOT a simplification.*

Line 458 The carbonate ion concentration can also be measured. This means that there are five and not four  $CO_2$  system variables that can be measured.

*Agree, in revising the manuscript this will also be mentioned, with the two citations as kindly provided by the reviewer.*

Line 505- 516 Chen et al. 1982 is very crystal clear in the page 2 of the article ‘To conclude, neglecting the small amount of calcium phosphate dissolution, the release of one mole of  $H_3PO_4$  due to organic matter decomposition decreases TA by one equivalent according to the current method of determining TA. Arthur Chen himself has confirmed this via email. In any case, there is more research and articles not evaluated in the manuscript that show that the contribution of phosphate and even sulfate generated by the oxidation of organic sulfur compounds should be included as alkalinity sinks (Kanamori and Ikegami 1982; Kim et al. 2006, Alvarez-Salgado and Fraga, 2005). In the specific case of Kanamori and Ikegami it is shown experimentally with correlations with  $Ca^{+2}$  observations.

*Indeed, the email message of Prof. Chen is well appreciated and his 1982 article will in the revised version of the manuscript be cited accordingly. With regards to uptake/release of sulfur in organic matter, the articles by Kanamori and Ikegami (1982); Kim et al. (2006), Alvarez-Salgado and Fraga (2005) will be discussed in next version of the manuscript.*

Line 517-524. In relation to Brewer articles: Brewer et al. 1975 “This postulates an effective flux of nitric and phosphoric acids into the deep water. Other redox changes, such as in the oxidation of reduced sulfur, may also contribute protons, but these are more difficult to evaluate” and “The true amount, here referred to as the "potential alkalinity", is unknown. We can attempt to calculate it through the application of additional terms to compensate for proton transfer. The simplest form of this equation would be as in (6):  $\Delta PA = \Delta TA + 1 \Delta NO_3^- + 1 \Delta PO_4^{3-}$ , where  $\Delta PA$  and  $\Delta TA$  are the potential alkalinity and alkalinity differences, in/leq/kg, between two water masses, and  $\Delta NO_3^-$  and  $\Delta PO_4^{3-}$  are the nitrate and phosphate

differences, in micromoles/kg, between the same two water masses.” Why the authors do not cite and comment these piece of literature about that?

*Brewer et al. (1975) will be incorporated in the next version of the manuscript.*

Line 533-534 “Most relevant here is that the uptake or release of phosphate is not mentioned at all, therefore does not affect Oceanic Alkalinity.” This is not fair. The fact that many authors have not considered the impact of the mineralization of phosphorus compounds on alkalinity because of its small magnitude does not mean that these authors consider that it does not affect at all.

*Agree, we now are assembling a sub-chapter that mentions several articles with regards to the role of phosphate being treated/interpreted in such articles, and will refrain from drawing such conclusions. Briefly some articles do mention phosphate uptake/release affecting Oceanic Alkalinity (charge balance alkalinity), others do not. Otherwise one of us (HdB) did in the 1978-1984 period work on the PhD at Woods Hole. In those years in many workshops he did meet and talk with Broecker, and listened to his lectures at such meetings, lectures that mostly were focusing on the Ocean Carbon Cycle including Alkalinity. From all these encounters do tend to remember that Broecker had the view that uptake/release of phosphate would not affect Oceanic Alkalinity, the latter OA as per Broecker and Peng (1982) definition that indeed does not include phosphate.*

Line 533-556. Many authors have considered the variation of the sum of alkalinity + nitrate referred to a fixed or reference salinity as a way to evaluate the changes due to CaCO<sub>3</sub> dissolution without including phosphate. I have done this myself many times, but this does not mean that these same authors consider that there is no phosphate contribution but that it is insignificant. Many times, it has been based on a simplification of the calculations especially if we talk about several decades ago where the numerical calculation was not as affordable as now, or even because there was no quality phosphate data available to substantially improve the results.

*Agree, the difference of using a value 16 for only nitrate, or 17 for nitrate plus phosphate is not that large. Also, in general, for a long time quite some laboratories were not able to produce data of dissolved phosphate as accurate as data of dissolved nitrate. Here, once again, the very interesting article of Fraga and Alvarez-Salgado (2005) provides a relevant paragraph. Quite remarkably Brewer et al (1975) is cited for  $\Delta TA / (\Delta P_T + NO_3^-) = -1$  as if the contribution of phosphate is in fact not accounted for. On the other hand, for Broecker and Peng (1982) it is explicitly stated that a simplified version was presented. Here in fact by saying 'simplified' the authors Fraga and Alvarez-Salgado (2005) do in fact also attribute a choice (of simplification) by Broecker and Peng (1982), but this is also suggestive and we cannot ask Broecker anymore.*

*Based on this definition, Brewer et al. (1975) established that TA increases (decreases) 1 eq per mol of NO<sub>3</sub><sup>-</sup> and P<sub>T</sub> consumed (produced) during the synthesis (early degradation) of the organic tissues of marine phytoplankton, i.e.  $\Delta TA / (\Delta P_T + NO_3^-) = -1$ , and defined the conservative chemical parameter “potential alkalinity” (TAP) as the sum of TA + [NO<sub>3</sub><sup>-</sup>] + [P<sub>T</sub>]. Note that considering the pK<sub>A</sub>'s of the phosphoric acid system, P<sub>T</sub> is not able to accept 1.016 eq of H<sup>+</sup> per mol of P at pH<sub>SWS</sub> 4.25 (see the balance of charges  $\epsilon_{4.25}$  in table 1). Culture experiments conducted by Brewer and Goldman (1976) and*

*revisited by Goldman and Brewer (1980) confirmed the experimental validity of TA<sub>P</sub>. On the basis of those experiments, Broecker and Peng (1982) presented the following simplified version of Brewer et al.'s (1975) equation:  $\Delta TA/\Delta NO_3^- = -1$ , which frequently appears in the literature. In any case, these relationships between TA and NO<sub>3</sub><sup>-</sup> or TA, NO<sub>3</sub><sup>-</sup> and P<sub>T</sub> assume that the organic constituents of marine phytoplankton are neutral; that is, they do not play any part in the hydrogen ion balance of seawater. But, how accurate is this assumption?*

Line 620-621 ‘Thus, for normal seawater in the world oceans, the H<sub>3</sub>PO<sub>4</sub> term in the Titration Alkalinity Eq. (24) is merely theoretical and practically at best leading to confusion for some readers.’ It is correct that the concentration of H<sub>3</sub>PO<sub>4</sub> is very small in the final part of the titration curve (pH between 3 and 4.5), representing only 0.006% of the hydrogen ion concentration, while for HSO<sub>4</sub> and HF it is 30% and 2% respectively. However, this does not mean that this is an error, it simply means considering that a small part of the acid added during titration will be consumed to produce H<sub>3</sub>PO<sub>4</sub> even in very very small quantities.

*Agree.*

Line 622 ‘Another cause of confusion is the negative sign for the [H<sub>3</sub>PO<sub>4</sub>] term in Eq. (24).’ The negative value is intrinsic, for the reasons given above, to the definition of total or titrated alkalinity being fully consistent with the CO2SYS software for a global community that has been used to check the quality of observations made globally for more than 4 decades.

*This we still do not fully understand, but will try to reach this higher level of understanding in the future.*

Line 636. “In other words, the negative sign of [H<sub>3</sub>PO<sub>4</sub>] in the Eq. (24) is mistaken and yet another reason”. Again, just because this term is very small and negligible does not mean that its sign is an error. This argument is flawed.

*Same as above, we still do not fully understand, but will try.*

Line 690-692 “The exact determination of all these changes can be done by a computer chemical speciation program, for example MINEQL, or the CO2SYS algorithms that are tailored for the key variables of the CO<sub>2</sub> system in seawater.” Certainly, these algorithms are fully compatible with Dickson's (1981) definition of alkalinity and less so with the one based on the charge budget alkalinity (CBA) supported by the authors.

*Agree.*

Line 704 “This sub-chapter is one of two pivotal sections” After of reading the half of the manuscript, the hypothesis of the manuscript is present. This is based on a somewhat forced reading of some classic articles and ignoring others such as Soetaert et al. 2007 and Middleburg et al. 2020 where the objective of the manuscript is treated with much greater detail and precision.

*In retrospect it would have been more convenient for the reader, thus also for the reviewer, to have mentioned this paragraph on competing hypothesis more up-front in the beginning of the discussion paper. Otherwise, the second sentence of the Abstract does more or less already*

*state the objectives towards resolving the confusion and come to full agreement among ocean scientists. Indeed, the final published articles of Soetaert et al. 2007 and Middleburg et al. 2020 do describe their objectives much better. In producing the next version of our manuscript there is the opportunity to aim for the same greater detail and precision.*

Line 725-727 However, Wolf-Gladrow et al. (2007) have presumably overlooked the later paper by Chen et al. (1982) which rejects, and thus effectively retracts, the earlier suggestion that phosphate uptake/release does affect ocean alkalinity by Chen et al. (1978)." Chen et al. do not reject the role of phosphate (personal communication), so Wolf-Gladrow et al. are not wrong. See also Soetaert et al. 2007.

*Agree, this also on basis of the recent email message of Prof. Chen. Soetaert et. al. (2007) have assessed the effect of biogeochemical processes on pH. In their Table 3, their equation 33, is listed that the combined uptake of nitrate and phosphate during photosynthesis yields an increase of Total Alkalinity as per their coefficients  $\gamma^N + \gamma^P$  in a generalized photosynthesis equation, akin to our equation (1) that then would yield the coefficients  $\gamma^N + \gamma^P = 16 + 1 = 17$ .*

Line 775 ‘Therefore, nitrite does not significantly affect the value of Titration Alkalinity’. Since nitrite ion can associate with hydrogen ions to a concentration-dependent extent at pH below 4.5 (nitrite can consume part of the hydrogen ions supplied during titration), it must be incorporated into the titrated alkalinity as indicated by Wolf-Gladrow et al. 2007. See also Soetaert et al. 2007.

*Agree. See also an above response on this topic of nitrite.*

Line 842 ‘where the hydrogen ion concentration is expressed on the “free” scale’. Here it is very well expressed, not "proton concentration".

*Thank you.*

Line 860-863 “This is well above the accuracy of Titration Alkalinity. In other words, a small (~0.3 %) portion of the sulphate has absorbed some protons and this is accounted for by the term  $[\text{HSO}_4^-]$  in the overall Eq. (24) of Titration Alkalinity. In summary, all chemical oceanographers fully agree that sulphate is a strong anion in natural seawater (pH=~8) but has absorbed some protons at pH=4.5.” It is correct that sulfate absorbs 30% of the hydrogen ions added during the alkalinity titration. I do not fully agree that sulfate is a strong anion. The authors seem to relativize the characterization of strong anion as a function of pH. It is strong at pH=~8 but not at pH=4.5. Does this not call into question the definition of alkalinity as a function of the sum of strong cations minus strong anions since it is pH dependent? What about cations: many of them present high percentages in terms of  $\text{OH}^-$  of  $\text{CaOH}^+$  or  $\text{MgOH}^+$  associations and that at pH=~8 can mean a few tenths of micromol/kg which are much larger magnitudes than those given in the manuscript in relation to phosphate.

*As far as we understand, Alkalinity when listing all the constituents that contribute to Alkalinity, these constituents are in principle described at the original pH condition of the not yet titrated seawater sample. Text lines 829-854 describe the situation at an example pH=~8 of natural untreated surface seawater and arrive at very low  $\text{HSO}_4^- = 2.82 \cdot 10^{-3} \mu\text{mol.kg}^{-1}$  that is well below the precision of  $\sim 1 \mu\text{mol.kg}^{-1}$  of an Alkalinity value. Next in separate following paragraph text lines 855-863 the very different situation at the nominal pH=4.5 endpoint of the titration is described. As a matter of fact, in our very first text line 828-829 of this chapter*

4.1. we have stated exactly the same as the reviewer's statement "It is strong at pH= $\sim$ 8 but not at pH=4.5" where we use different wording but still exactly the same meaning.

Otherwise it is mentioned in the paper that natural seawater, for example old deep waters, or in the core of the oxygen minimum zone, can have a lower pH. Obviously the lower the pH of the untreated natural seawater sample, the relatively higher will be the concentration of  $\text{HSO}_4^-$

With regards to  $\text{CaOH}^+$  or  $\text{MgOH}^+$  associations see above response on basis of spreadsheet of MINEQL. We would be keen to become informed more precisely on the suggestion that at pH= $\sim$ 8 these can exist at a few tenths of micromol/kg. Would there be a citation on this?

Line 872-3 "These stoichiometric relationships of C/N/P/Si are based on the oceanic distributions of dissolved constituents in seawater." Stoichiometry refers to the molar ratio of a chemical reaction or a 'set of them' meaning a process of biochemical transformations involved in the formation or mineralization of the MO. Oceanic distributions show relationships or ratios (no stoichiometric relationships) between nutrient concentrations and these do not necessarily reflect each other. In fact, for N/P there seems to be some agreement with the eq1 but not for C/Si or C/P.

*This is exactly what we had stated, the stoichiometric relationships indeed are NOT the same as the oceanic distributions but instead are BASED on the oceanic distributions of dissolved constituents in seawater. On the other hand, the Redfield-Ketchum-Richards equation as in our equation (1) at text line 116, or for that matter any improved version of this equation, does at the left-hand side of the equal sign arrows (for a reaction that can go both directions), list a suite of dissolved constituents in seawater, and at the right hand side of the equal sign arrows, the indeed stoichiometry of organic matter. Overall this equation (1) is a chemical reaction, or is it not? Finally, this nitty-gritty fine tuning of terminology perhaps might be quite extremely perfectionistic, more than deemed necessary.*

*The english language version of Wikipedia is, in general, deemed to be excellent when trying to find out the meaning of words. For the lemma Stoichiometry is stated in the first sentence: "Stoichiometry refers to the relationship between the quantities of reactants and products before, during, and following chemical reactions"*

880-882 "In contrast, the dissolved constituents DIC, nitrate, phosphate (and silicate), due to ocean mixing processes that serve as an averaging tool, have already arrived at a mutual stoichiometry (Equation 1) that is very accurate with very low standard deviations." This suggests to me that the authors do not have a complete understanding of how eq.1 is obtained, and that they are unaware of the state of the art in this matter. There are two ways: by analyzing anomalies in the mixing of water masses (ref.- Takahashi et al. 1985, Anderson and Sarmiento 1994; Alvarez-Salgado et al. 2014, Hupe and Kartensen 2000; Fernandez-Castro et al. 2019, and many others), or by studying the mean composition of organic matter (Laws 1991, Anderson 1995; Fraga et al. 1998; Rios et al. 1998,...). Moreover, the standard deviations are not 'low' but rather in the order of 10 to 20% depending on the methodology and the geographical area.

*The original equation (1) of Redfield, Ketchum and Richards (1963) is obtained from the dissolved constituents DIC, nitrate, phosphate. The mentioned subsequent Takahashi et al. (1985), Anderson and Sarmiento (1994); Alvarez-Salgado et al. (2014), Hupe and Kartensen*

(2000); Fernandez-Castro et al. (2019), and many others, presumably are also based on dissolved constituents, with or without their anomalies in the mixing of water masses. The other, or opposite or complementary approach is by studying the composition of organic matter, that is the right-hand term of equation (1), and as per the mentioned assessments by Laws (1991), Anderson (1995); Fraga et al. (1998); Rios et al. (1998). With regards to the standard deviations, for some dissolved tracers the relationships can be very tight, as we know for trace metals versus major nutrients, but admittedly for the dissolved constituents DIC, nitrate, phosphate, and/or the organic matter C/N/P stoichiometry, we had not actually verified this in the various articles. This we can and will do as basis for the revisions of the manuscript.

886-893: This paragraph is not relevant for the objective of the manuscript.

*We will take this comment in consideration when doing revisions of the manuscript.*

894-901: In this paragraph, the authors seem to argue that the stoichiometric ratio in which plankton utilize the various elements should be reflected in the ratio of concentrations present in the water. They seem to extrapolate what happens with the N:P ratio in a rough way and with other micro or trace elements in a clearly incorrect way since many of the elements (or major elements) present in seawater are not related to biological activity but to other geochemical processes of very long-time scale.

*Here we had taken the S:P ratio value in organic matter as assumed by Wolf-Gladrow et al. (2007) and from this calculate what this would imply for the decrease/increase of dissolved sulphate as result of formation/decomposition of organic matter. We do NOT state that this represents the overall concentration of in this case sulphate in seawater. In fact we know that this overall sulphate concentration is very high, such that the calculated loss or gain due to formation/decomposition of organic matter is not discernible in the overall dissolved concentration. We also do recognize the highest concentration value of phosphate in the oceans at maximum  $\sim 3.3 \mu\text{mol.kg}^{-1}$  and from this derive that the maximum loss or gain of dissolved sulphate due to organic matter formation or decomposition would be in the order of  $\sim 7.9 \mu\text{mol.kg}^{-1}$ . Indeed, this is very small compared to the overall total dissolved sulphate that indeed is controlled by geochemical processes of very long time-scale. In textbooks there are tables of the residence time in the oceans of all constituents of salinity (Table 1 of the discussion paper) and surely for sulphate this is a very long residence time indeed, in the order of 10 million years (Seawater, 1995).*

*Seawater, its composition, properties and behaviour. 2nd Edition (1995). Volume in the series of The Open University Course Team, Pergamon Press, Table 6.4 at page 106.*

902-915: It is very likely that the stoichiometric ratio S:P=2.4 of Wolf-Gladrow et al. 2007 is in the high range. Not only from Finkel et al. 2006, but also if one considers Kanamori and Ikegami's Alk:NO<sub>3</sub> ratio of 1.26 which would imply an S:P=1.6, right in the upper range of Finkel et al. 2006. As early as 1978 Chen 1978 also uses the ratio S:P=1.6. However, estimation of this ratio is somewhat complex due to the difficulty of assessing the variability of sulfur compounds, such as DMS, in marine plankton. Fraga and Alvarez-Salgado (2005) have evaluated S:P ratios in function of the DMSP produced by the phytoplankton, given values of 2.3, 3.3 and 5.7 micromol of H<sup>+</sup> per mol of mineralized phosphorous which is comparable to the value of 1.4 micromol of H<sup>+</sup> obtained for phytoplankton that does not produce DMSP. Furthermore, arguing that "In other words, hypothetical sulfate concentration

changes of biological origin are not verifiable because they are undetectable" is meaningless given that high sulfate concentrations in water come from non-biological sources.

*Indeed, we had mentioned that the stoichiometric ratio S:P=2.4 of Wolf-Gladrow et al. (2007) is in the high range, as compared to Finkel et al (2006). We will study the findings of Kanamori and Ikegami, as well as the ratio S:P=1.6 of Chen et al (1978). The very interesting article of Fraga and Alvarez-Salgado (2005) will also be studied for the assimilation of sulfur. Moreover, Brewer et al (1975) did mention: "The atom ratio of sulfur to carbon in marine organism is approximately 0.015 [16]. Incorporating this into the Redfield- Ketchum-Richards relationship we have C:N:S:P = 106:16:1.6:1." The given citation [16] by Brewer et al. (1975) is the following: W.G. Deuser, Carbon-13 in Black Sea waters and implications for the origin of hydrogen sulfide, Science 168 (1970) 1575.*

Line 920-922 "Last but not least, throughout the existing literature the Oceanic Alkalinity has always been defined without taking into account this more recently suggested (Wolf-Gladrow et al., 2007) effect of biological uptake/release of sulphate". At least two published articles (Carter et al. 2014; Lauvset et al. 2020) have used ratios ALK:N base in Kanamori and Ikegami and Wolf-Gladrow et al., (2007).

*Agree and will incorporate these articles in the discussion in the revised manuscript.*

Line and 989 and 1027  $+[Sr^{2+}]$  should be  $+2*[Sr^{2+}]$  eq. 20 a 44

*Yes, an omission to be corrected. Thanks for noticing this omission.*

Line 1016 ' $[3PO_4^{3-}]$ ' should be  $3*[PO_4^{3-}]$

*Thanks for noticing this error that we will remedy.*

Line 989-1041. The development of Wolf-Gladrow et al., 2007 is correct. It starts from the zero-charge equilibrium as the electroneutrality condition for seawater (equation 31 in Wolf-Gladrow et al., 2007 and equation 42 in the present work). He then tries to include Dickson's (1981) definition of total alkalinity to obtain his equation 32. In that expression he compares the differences between the charge budget of the strong ions with the total alkalinity. Somewhat similar to the present manuscript is the equation of Soetaert et al. 2007 in their Table 3. Also, Middleburg et al. 2020, equation 7 compares TA with CBA (or also called excess negative charge-ENC of Soetaert et al.). Besides ignoring or not knowing the two articles mentioned above, perhaps the mistake of this manuscript is to try to equate their equation 20, their definition of Oceanic Alkalinity with Total Alkalinity as they are different magnitudes.

*Yes, we now realize and admit that Oceanic Alkalinity is not the same as Titration Alkalinity. Our discussion in the revised manuscript will account for this. On the other hand, both apparently are still in the same order of magnitude.*

1102-1105 'In contrast, the article by Wolf-Gladrow et al. (2007) largely focused on the biomass domain with an assumed requirement of overall neutral electric charge balance of the plankton biomass. The latter various neutral charge balance reasonings for marine plankton are not necessarily valid, and also not necessarily all verifiable.' The paper by Wolf-Gladrow et

al. (2007) did not focus on the overall neutral electric charge balance requirement of the biomass but on that of the water mass.

*This not sure about, but will again carefully read the Wolf-Gladrow et al. (2007) article.*

1111-1112 "With respect to alkalinity Aq these factors +0.21 and -0.21 are wrong." This is not so clear, it may be perhaps somewhat high.

*Given the new paradigm that anyone author is having freedom of speech in an article, these values are not any longer deemed to be wrong. Otherwise as the reviewer concludes, perhaps somewhat high when compared to other values in the literature.*

1177-1181. "Unfortunately, these recent findings of excess Alkalinity in the CRMs appear to be a caveat. Matters are complicated also because different batches of CRMs tend to show different values of such excess Alkalinity. Finally, historically there have been previous suggestions of interferences. Nowadays these are deemed to be merely of historical interest. Nevertheless, one example of such historical suggestion is described in Supplementary Material C." This is an interesting reflection on the work of Sharp and Byrne (2021), although I think it is somewhat exaggerated. That study has not evaluated the impact of the addition of  $\text{HgCl}_2$  to CRMs (~33 micromolar) so some differences might be expected. It also shows that it is possible that the existence of possible amounts of organic matter that can act as weak bases (hydrogen ion acceptors) is likely to be very small in natural waters, lower than those predicted in Fong and Dickson (2019). The usefulness of CRMs is and has been of great relevance for obtaining high quality data from marine carbonate system, and the possible uncertainties of CRMs, if any, should be endorsed in future work.

*In revising our manuscript, we will include mentioning the consideration that perhaps the addition of some  $\text{HgCl}_2$  to CRMs (~33 micromolar) might also play a role. Thanks for this interesting suggestion. In our text lines 1173-1176 we also have highlighted the great importance of the CRM's.*

1190-1191 'Currently, the perceived role of biological uptake or release of dissolved phosphate in the value of Oceanic Alkalinity is often mistaken, which may be due to two articles with great influence in the biogeochemistry community.' It is true that the impact of phosphate formation by biological mineralization of OM does not affect OA as defined by the authors, but it does affect total alkalinity or titrated alkalinity as commonly measured in oceanographic studies, and which are subsequently used along with other marine carbonate system variables to study their variability.

*Agree.*

1196-98 'The perceived role of biological uptake/release of dissolved sulphate from seawater is not verifiable because it cannot be discerned from measurement of the relatively very large background dissolved concentration value of sulphate.' This fact has been observed, and evaluated by several authors since 1978 (Chen 1978; Kanamori, S. and Ikegami, H.1982, Kim et al. 2006, Alvarez-Salgado and Fraga 2006) and used in several articles such as Carter et al. 2014, Lauvset et al. 2019.

*As mentioned in one of the above responses we will further study these articles with an eye to next making revisions in our manuscript.*