LIMNOLOGY and OCEANOGRAPHY

Total alkalinity change: The perspective of phytoplankton stoichiometry

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Abstract

Many biogeochemical processes change total alkalinity: this has been reported for carbonate precipitation and dissolution, uptake and release of various nitrogen-containing compounds, uptake of phosphate, sulfate reduction combined with methane oxidation. However, the list is not exhaustive. Here we discuss additional processes, namely the uptake of Mg, K, Ca by phytoplankton, and calculate their contribution based on the explicit conservative expression for TA and an extended (compared to Redfield's C : N : P) stoichiometry of phytoplankton. These additional contributions are of the same order of magnitude as that of phosphate uptake and thus much smaller than the contribution from nitrate uptake and of opposite sign to the contribution by nitrate and phosphate uptake.

Total alkalinity (TA; Dickson 1981) and dissolved inorganic carbon are the two conservative quantities of the marine carbonate system (*see*, e.g., Zeebe and Wolf-Gladrow 2001) and, as a consequence, are the standard parameters used in all models of the marine carbon cycling. Surface ocean changes in TA lead to changes in dissolved CO_2, $[CO_2 (aq)]$, and the corresponding equilibrium pressure of CO_2, pCO_2, the drivers for air–sea CO_2 exchange. The impacts of several biogeochemical processes on TA have been discussed by Wolf-Gladrow et al. (2007). However, the list of processes considered (carbonate precipitation and dissolution, uptake and release of various nitrogen-containing compounds, uptake of phosphate, sulfate reduction combined with methane oxidation) is not exhaustive. Here we consider additional processes namely the uptake of Mg, K, Ca by phytoplankton, involving ions that fully dissociated in seawater (hereafter referred to as "strong ions") and calculate their contribution based on the explicit conservative expression for TA (Wolf-Gladrow et al. 2007) and an extended (compared to Redfield's C : N : P) stoichiometry of phytoplankton. These additional contributions are of the same order of magnitude as the contribution of phosphate uptake and thus much smaller than those of nitrate uptake and of opposite sign to the contribution from nitrate and phosphate uptake.

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Materials and methods

Extended Redfield stoichiometry

Alfred Redfield (1934, 1958, 1963) showed that the molar ratios of carbon, nitrogen, and phosphorous (C : N : P) in bulk plankton samples are, on average, approximately C : N : P = 106 : 16 : 1. These are the "classical" or "canonical" Redfield ratios. He further pointed out the similarities with the molar ratio of dissolved nitrate and phosphate in seawater, except in surface layers where these two nutrients are taken up by phytoplankton, or in anoxic water masses as, for example, in the Black or the Baltic Sea.

Deviations from the canonical C : N : P ratios have been observed by Sambrotto et al. (1993), Anderson and Sarmiento (1994), Arrigo et al. (1999), Körtzinger et al. (2001), and others. Furthermore, laboratory experiments have shown that these ratios in phytoplankton differ between species and vary with growth conditions (Burkhardt and Riebesell 1997; Geider and La Roche 2002). Fixed values of C : N : P are commonly used in marine biogeochemical models in combination with box or general circulation models and earth system models to simulate the oceanic global carbon cycle (Sarmiento and Toggweiler 1984; Bacastow and Maier-Reimer 1990), allowing to reduce the number of prognostic variables. This approach provides a reasonable approximation of the nutrient and carbon cycles, especially when processes such as denitrification or nitrogen fixation are not taken into account. In recent years, however, several models with variable stoichiometry have been developed [REcoM-2 by Hauck et al. (2013); PISCES-QUOTA by Kwiatkowski et al. (2018); OPEM v1.1 by Pahlow et al. (2020)].

Since the early 1990s, knowledge of the Redfield ratios in phytoplankton has been extended by including other elements. This was motivated by the recognition that other

elements, in particular trace metals, are also relevant in understanding and simulating plankton dynamics and the associated carbon uptake and cycling. The most extended stoichiometry for phytoplankton — to our knowledge — has been provided by Ho et al. (2003) based on laboratory experiments with 15 phytoplankton species. The authors give the following expression for the *average* stoichiometry (phosphorus normalized quotas, i.e., mol of element per mol P, and excluding hard parts such as shells and skeletons)

$$(C_{124}N_{16}P_1S_{1.3}K_{1.7}Mg_{0.56}Ca_{0.5})_{1000}$$
$$Sr_{5.0}Fe_{7.5}Zn_{0.80}Cu_{0.38}Co_{0.19}Cd_{0.21}M_{0.03}.$$

Their $C:P = 124:1$ is somewhat higher than the canonical Redfield ratio, whereas $N:P = 16:1$ is identical to the canonical value. According to the stoichiometry provided by Ho et al. (2003), phytoplankton cells contain more sulfur and potassium than phosphorus. The amounts of magnesium and calcium are almost the same, about half of the amount of phosphorous. The elements Sr and Fe are more than a factor 100, and Zn, Cu, Co, Cd, and Mo a factor 1000 smaller than the phosphorous content and thus can be neglected here. The TA change by assimilation of trace metals could, however, be estimated with the same approach as for the more abundant elements discussed here. Note that the amount of Na and Cl in cells was not determined by Ho et al. (2003, p.1151) as, in their study, cells were rinsed with NaCl or synthetic ocean water before analysis.

The stochiometry by Ho et al. (2003), and indeed the work here, also does not include the production of hard parts (biominerals covering the cell walls) in phytoplankton, primarily biogenic silica in diatoms and calcium carbonate in coccolithophores, because (1) the formation of biogenic silica does not change TA (Wolf-Gladrow et al. 2007). (2) While alkalinity is reduced by 2 mol per mol of $CaCO_3$ precipitated (Wolf-Gladrow et al. 2007), the molar ratio between particulate inorganic carbon (PIC; $CaCO_3$) and particulate organic carbon (POC) in coccolithophorids is highly variable and dependent on growth conditions (light, nutrient limitations, Zondervan 2007) as well as species present. A recently published meta-analysis of experimental data (Sheward et al. 2023) gives a mean PIC : POC of 0.89 ± 0.53 with high intraspecific variability (up to a factor of 2). Furthermore, the meta-analysis by Sheward et al. (2023) is limited to studies on *Emiliania* (now *Gephyrocapsa*) *huxleyi*.

TA and its explicitly conservative expression

TA has been defined by Dickson (1981) as the difference between proton (H^+) acceptors and donors (Dickson et al. 2007):

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

$$(1)$$

whereby the square brackets indicate concentrations in gravimetric units (mol kg^{-1}). This definition provides the basis for the determination of TA by titration with a strong acid—usually HCl—and thus TA is also referred to as titration alkalinity.

Based on Dickson's definition of TA and on the principle of electroneutrality (charge balance), Wolf-Gladrow et al. (2007) derived the following expression for TA

$$\begin{aligned} [Na^+] &+ 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] + \dots - [Cl^-] - [Br^-] \\ &- [NO_3^-] - \dots - TPO_4 + TNH_3 - 2\,TSO_4 - THF - THNO_2 \\ &= TA_{ec}, \end{aligned}$$

$$(2)$$

where $TPO_4 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$, $TNH_3 = [NH_3] + [NH_4^+]$, $TSO_4 = [SO_4^{2-}] + [HSO_4^-]$, $THF = [F^-] + [HF]$, and $THNO_2 = [NO_2^-] + [HNO_2]$ corresponding to the total phosphate, ammonia, sulfate, fluoride, and nitrite, respectively. TA_{ec} is called the explicit conservative expression for TA because each single term is conservative (*see* Wolf-Gladrow et al. 2007 for more details).

Phytoplankton take up the largest amounts of elements in the form of anions, namely, HCO_3^-, NO_3^-, HPO_4^{2-}. To keep charge neutrality of cells, they have to either release other anions or take up cations. Releasing anions, as for example, Cl^-, in exchange of HCO_3^- is observed in erythrocyctes where the direction of exchange is frequently reversed. However, in growing phytoplankton cells, this is not a viable option because the initially available internal Cl^- would be depleted very quickly. Compensation through the uptake of cations such as Na^+ is also unlikely as for similar reasons (i.e., accumulation of Na^+ in cells). Wolf-Gladrow et al. (2007) hypothesized that the electroneutrality is likely kept through uptake of H^+ or the release of OH^-, whereby the former is more plausible given the widespread use of proton pumps in phytoplankton. This was termed *the nutrient-H^+-compensation principle* (Wolf-Gladrow et al. 2007).

The TA estimates given here are also based on the assumption that the nutrient-H^+-compensation principle is valid and similar, for cations, to the uptake of NH_4^+ compensated by H^+ release (or OH^- uptake) by the cells leading to a *decrease* of TA (Wolf-Gladrow et al. 2007), a result that is consistent with results and interpretation of experiments where phytoplankton was grown on NH_4^+ (Brewer and Goldman 1976; Goldman and Brewer 1980).

Results

To combine stoichiometry and the explicit conservative expression for TA one has to make assumptions, if information is lacking, on the chemical form of the various elements taken up by phytoplankton, N, for example, as NO_3^- or NH_4^+. Carbon uptake in the form of CO_2 and/or HCO_3^- by algae has no effect on TA as can be inferred by the absence of

the terms $[CO_2]$ and $[HCO_3^-]$ from TA_{ec} (Eq. 2; *see* also Peng et al. 1987, and Eq. 1 where HCO_3^- uptake is compensated by concurrent H^+ uptake). This is also consistent with the established fact that air–sea CO_2 exchange has no impact on TA.

Nitrogen can be taken up by phytoplankton in various forms and the different impacts on TA have been discussed in detail in Wolf-Gladrow et al. (2007). Here, we will assume that N is taken in the form of nitrate and thus TA is *increased* by the amount of nitrate taken up as can be seen by the term "$-[NO_3^-]$" in TA_{ec} (Eq. 2). This change would be less obvious to derive from Eq. 1, where a nitrate term is absent, but TA increases anyway because of H^+-compensation (Wolf-Gladrow et al. 2007).

Phosphate comes along in the form of four different species from electrically neutral to threefold negative. Based on Eq. 2, for the change in TA it is only important to consider how bulk dissolved phosphate (corresponding to the "$-TPO_4$" term) concentrations in seawater increase (remineralization) or decrease (phytoplankton uptake), that is, phytoplankton uptake of any form of phosphate will lead to an *increase* of TA (Wolf-Gladrow et al. 2007).

Assuming that P, S, K, Mg, Ca are taken up respectively in the form of a phosphate compound, SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+} in the ratios given by the stoichiometry of Ho et al. (2003), with charges balanced by H^+ uptake or release (H^+-compensation principle), the ratio of the change in TA from S, K, Mg, Ca uptake to the TA change due to phosphate uptake can be calculated using TA_{ec} as follows:

$$\Delta TA_{S,K,Mg,Ca} = \left(\underbrace{2 \times 1.3}_{TSO4} \underbrace{-1 \times 1.7}_{K+} \underbrace{-2 \times 0.56}_{Mg2+} \underbrace{-2 \times 0.5}_{Ca2+} \right) \Delta TA_{TPO4}$$
$$= -1.22 \, \Delta TA_{TPO4},$$

(3)

that is, the contribution from K, Mg, and Ca uptake is in the same order of magnitude as the contribution from phosphate uptake, however, with opposite signs. The resulting effect on TA from S, K, Mg, and Ca uptake is small because of partial compensation between terms of different signs.

Discussion

Wolf-Gladrow et al. (2007) provided an alternative formulation for TA, based on Dickson's definition, that allows a straightforward estimate of the impact of plankton nutrient uptake on seawater alkalinity (Eq. 2). The TA change estimates (Eq. 3) rest on the premise that uptake of, respectively, anionic and cationic nutrients, is balanced by the concurrent respective uptake of H^+ or OH^-, (nutrient-H^+-compensation principle) and that the nutrient-H^+-compensation principle should apply to all nutrients in ionic form.

The effect of nitrogen assimilation by phytoplankton on alkalinity has been investigated almost half a century ago in two seminal papers by Peter Brewer and Joel Goldman (Brewer and Goldman 1976; Goldman and Brewer 1980). Their experiments, with three marine phytoplankton species *Phaeodactylum tricornutum*, *Dunaliella tertiolecta*, and *Monochrysis lutheri* showed a simple $1:1$ mol L^{-1} ratio between nitrate uptake and alkalinity increase that could be explained by concurrent uptake of NO_3^- and H^+ (or release of OH^-). Similarly, when grown on NH_4^+, the data were also consistent with a $1:1$ mol L^{-1} ratio between NH_4^+ uptake and alkalinity decrease that could be explained by release of H^+ (or concurrent uptake with OH^-). Goldman and Brewer (1980) further tested the impact of phosphate uptake on TA, however, their data was too noisy to come to any conclusion. To the best of our knowledge no successful experimental attempt to determine how phosphate uptake changes TA has been reported. Although the experiments described by Kranz et al. (2010), using N-fixing cyanobacteria, were meant to address this question, precipitation of $CaCO_3$ in the form of aragonite dominated the observed change in alkalinity. Assuming that the nutrient-H^+-compensation principle is valid for all nutrients taken up by cells, the change of TA caused by uptake of phosphate, sulfate, Mg^{2+}, K^+, and Ca^{2+} according to the stoichimetric ratios of Ho et al. (2003) would be only -0.22 that of phosphate (combined: $\Delta TA_{TPO4} - 1.22$ $\Delta TA_{TPO4} = -0.22 \times \Delta TA_{TPO4}$) and only $-0.22/16 = -0.014$ that of nitrate and thus impossible to observe.

The largest uncertainties in estimating TA changes are likely due to the fact that the amounts of S, K, Mg, and Ca — which are all of the same order of magnitude as P — and their interspecific variations are less well understood. Furthermore, the contributions of these elements can vary quite a bit between different phytoplankton species (Ho et al. 2003). Magnesium (Mg^{2+}) with its central role in light harvesting and an essential constituent for chlorophyll is a case in point. C : Chl in marine phytoplankton is highly variable (Cloern et al. 1995) with extreme values of < 10 g C g Chl^{-1} (Geider 1987) to > 300 g C g Chl^{-1} (Falkowski et al. 1985) whereby the higher values are observed during growth limitation (by either light and/or nitrate). Healthy growing cells show C : Chl ratios in the range of 30–40 g C g Chl^{-1} (Cloern et al. 1995). To estimate the amount of Mg in algal chlorophyll we first convert the units g C g Chl^{-1} to g C g $C_{Chla}{}^{-1}$. For this purpose, one has to know how much C and other elements are included in chlorophyll. The commonly used chlorophyll a standard for HPLC and fluorometric chlorophyll measurements (from which the above ratios are derived) has the empirical formula $C_{55}H_{72}MgN_4O_5$ and molecular weight 893.5 g mol^{-1} (Sigma-Aldrich) of which 660.6 g mol^{-1} are the chlorophyll *a*-associated carbon (C_{Chla}). The ratio $893.5/660.6 \approx 1.35$ implies ratios between about 41 and 55 g C g $C_{Chla}{}^{-1}$ (or mol C mol $C_{Chla}{}^{-1}$) in healthy phytoplankton cells. Assuming similar composition and C : Mg molar ratios

in phytoplankton chlorophyll a (55 : 1) one would expect a C : Mg ratio 55 times lower than the C C_{Chla}^{-1}; that is 2200–3000 mol C mol Mg^{-1}. This molar ratio can be further converted to a molar ratio of about 0.056–0.042 mol Mg mol P^{-1} by using the C : P ratio of 124 : 1 mol C mol P^{-1} (Ho et al. 2003). This is about one order of magnitude lower than the observed Mg : P stoichiometry of 0.56 mol Mg mol P^{-1} given by Ho et al. (2003). Thus, most of the magnesium in phytoplankton has to be contained in or bound to other compounds. In addition to its role in chlorophyll, Mg is involved in phosphate compounds and in phosphate and nucleic acid metabolism as well as enzymes associated to carbon assimilation and metabolism (Fraústo da Silva and Williams 2001).

Last but not least, we would like to address the question whether the impact of minor — compared to C and N — elements on TA should be included in ocean global biogeochemical models (OGBMs): The effects of P, S, K, Mg, Ca on TA are of similar size and substantially smaller than those of calcification/carbonate dissolution and nitrate uptake/remineralization. The simulation of calcification and dissolution of carbonates in OGBMs is still unsatisfying for various reasons, to name only a few:

1. Carbonates are precipitated by various groups of organisms including, in the open ocean, coccolithophorids, foraminifera, and pteropods and numerous multicellular organisms in coastal and shelf regions, including fish (Wilson et al. 2009). The ecologies of these groups are quite different and not well enough understood to predict their distribution, abundances and dynamics.
2. Calcium carbonate can be precipitated in form of calcite or aragonite which differ in stability against dissolution; further, some organisms precipitate high Mg carbonates that dissolve even before aragonite (Woosley et al. 2012).
3. This is compounded by the fact that observations and data-based analyses hint at dissolution of carbonates above their estimated saturation horizons (Milliman et al. 1999; Sulpis et al. 2021), possibly through the presence of acidic micro-environments in larger planktonic aggregates or in the guts of metazoans.

Given these large uncertainties in current simulations of the oceanic TA (Hinrichs et al. 2023; Planchat et al. 2023) and the probably small joint effect—compared to calcification and nitrate uptake—from P, S, K, Mg, Ca in soft tissue on TA, as well as our poor knowledge of Na^+, Cl^- content and variability in phytoplankton, it seems too premature to include their contributions in OGBMs.

Data availability statement

The paper does not contain own measurements and all data used (especially the extended stoichiometry from Ho et al. 2003) are given in the text.

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Conflict of Interest
None declared.