

Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and mineralisation of organic matter in the sea*

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SUMMARY: It is frequent to observe disagreements between the relationships $R_c = -\Delta O_2/\Delta C$ and $R_n = -\Delta O_2/\Delta N$ found during photosynthesis-mineralisation studies in the ocean and those expected according to the Redfield plankton composition. That is because R_c and R_n depend on the C/N and Carbohydrates/Lipids (*Cbh/Lip*) ratios of the organic matter. Starting from the mean biochemical composition of the main groups of phytoplankton biomolecules and from the stoichiometry of photosynthesis-mineralisation, we establish a new formulation to enable us to calculate R_c and R_n as a function of C/N and *Cbh/Lip* ratios independent of the variance in the N/P ratio. The approach proposed here permits the theoretical limits of R_c and R_n to be calculated. The R_c value can vary between 1 and 1.58 while R_n can vary between 5.8 and infinity with the interrelationships between the ratios being defined by $R_n/R_c = C/N$ which, in its turn, can vary between 3.67 and infinity. For a given R_c the limits of R_n become narrower and vice versa. When C/N ratio is fixed the limits of the R_c and R_n values also become narrower. A graphic representation to check and visualise these limits and other experimental biochemical composition values is developed. According to the average value of the *Cbh/Lip* relationship, 0.82 in carbon, recovered from the literature and for a C/N = 106/16, the estimate mean R_c and R_n values are 1.41 and 9.33 respectively which are coincident with previous ratios given by other authors.

Key words: Redfield ratio, stoichiometry, photosynthesis, mineralisation, organic matter

INTRODUCTION

Variations in oxygen, carbon dioxide and nutrient content of seawater occur during photosynthesis and mineralisation of particulate organic matter. A knowledge of the relationship between these variations is necessary for modelling the penetration of anthropogenic CO₂ in the ocean and/or mixing of water masses. They are also cru-

cial for developing global budgets of the oceanic organic matter in the ocean (Broecker and Takahashi, 1980; Chen and Millero, 1979).

Fleming (1940) established for the first time the ratio $\Delta C: \Delta N: \Delta P = 106:16:1$ for nutrient uptake during photosynthesis. Later on, Redfield et al. (1963) calculated the oxygen produced (or consumed) during the synthesis (or mineralisation) of the organic matter, obtaining the ratio $-\Delta O_2: \Delta C: \Delta N: \Delta P = 138:106:16:1$. A very simple formulation was used in their calculations, in which all carbon was in the form of CH₂O and all nitrogen was NH₃.

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Consequently and according to that relationship, the total oxidation of the organic matter to CO_2 and NO_3^- consumes one mole of oxygen for each mole of carbon, and 2 moles of oxygen for each mole of nitrogen. The Redfield proportion is correct when only carbohydrates are considered, and is also a very good approximation for proteins and nucleic acids. However, as Redfield pointed out, the ratios can vary when more reduced molecules, such as lipids, are considered. Lipids consume about 36% more oxygen than carbohydrates during their oxidation.

Extensive studies of $-\Delta\text{O}_2:\Delta\text{C}$ and $-\Delta\text{O}_2:\Delta\text{N}$ ratios in marine particulate matter by different authors (Jones et al., 1984, Fraga and Pérez, 1990, Williams and Robertson, 1991, Laws, 1991 and Anderson, 1995) revealed differences between the observed ratios and those expected according to the Redfield composition of organic matter. Generally, the $-\Delta\text{O}_2:\Delta\text{C}$ ratio is higher than that expected from Redfield when the percentage of proteins and nucleic acids in planktonic organic matter increases. It is also higher, for a given C/N ratio, when the ratio of lipids/carbohydrates increases. Taking into account that the observed variations can be relatively large, which means that the output of global organic matter budget models can be strongly affected, this paper was focused in defining the limits of the $-\Delta\text{O}_2:\Delta\text{C}$ and $-\Delta\text{O}_2:\Delta\text{N}$ ratios according to the biochemical composition of the phytoplanktonic organic matter. A knowledge of these limits in photosynthesis and mineralisation processes will be a useful tool to control the quality of experimental data, permitting the detection of irregularities in the ratios of dissolved oxygen: nutrients seen in the oceanic waters and identified by the incompatibility of these observational ratios with those expected from plankton biochemical composition.

METHOD

Composition of the main groups of phytoplankton biomolecules

Classes of biomolecules are commonly defined operationally based on the methods used during their chemical separation. Nevertheless, Fraga and Pérez (1990) grouped the different phytoplankton biomolecules according to their qualitative elemental composition. Table 1 summarises the main groups of biomolecules according to this criterion. The same authors gave an explanation to calculate the mean composition of each group that we detail here briefly.

All organic and inorganic phosphorus compounds of phytoplankton cells were included in the phosphorus compound group (*Pho*), which is mainly composed of nucleic acids but also includes inorganic phosphate, phospholipids, phosphoproteins and sugar phosphates (Miyata and Hattori, 1986).

The protein group (*Prt*) contains all nitrogen compounds excluding those that also have phosphorus, which were previously included in the *Pho* group. The *Prt* group is almost exclusively formed by proteins. Nevertheless, free amino acids and chlorophylls which represent 7% and 4% of the whole group respectively, are also included. However, MgO from chlorophylls ($\text{C}_{46}\text{H}_{52}\text{O}_5\text{N}_4\text{Mg}$) was removed because it only represents a very small fraction (0.15%) and does not affect consumed oxygen during oxidation. The mean elemental composition of proteins, excluding chlorophyll, obtained by our own amino acid analysis, is $\text{C}_{138}\text{H}_{217}\text{O}_{45}\text{N}_{39}\text{S}$ which is very similar to the avera-

TABLE 1.- Mean elemental composition of each main group of biomolecules

| | | Formula weight (g) | C% in weight |
|-------------------------------------|--|--------------------|--------------|
| Proteins ⁽¹⁾ | $\text{C}_{147}\text{H}_{228}\text{O}_{46}\text{N}_{40}\text{S}$ | 3323.8 | 53.12 |
| Phosphorus compounds ⁽²⁾ | $\text{C}_{45}\text{H}_{76}\text{O}_{31}\text{N}_{12}\text{P}_5$ | 1436.0 | 37.64 |
| Carbohydrates | $\text{C}_6\text{H}_{10}\text{O}_5$ | 162.14 | 44.45 |
| Lipids ⁽³⁾ | $\text{C}_{53}\text{H}_{89}\text{O}_6$ | 822.3 | 77.42 |
| Prt+Pho ⁽⁴⁾ | $\text{C}_{177}\text{H}_{279}\text{O}_{66}\text{N}_{48}\text{P}_3\text{S}$ | 4260.5 | 49.90 |

(1) Chlorophylls are included in proportion 4% in weight.

(2) All phosphorus compounds, both organic and inorganic, are included

(3) Phospholipids are excluded.

(4) Proteins + phosphorus compounds in the ratio Prt/Pho = 3.94 in weight, in order to give a ratio N/P = 16, in moles.

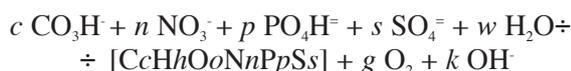
ge composition ($C_{138}H_{217}O_{45}N_{36}S$) extracted from several authors (Fowden, 1954; Ogino, 1963; Cowey and Corner, 1966; Chau *et al.*, 1967; Chuecas and Riley, 1969). The difference of three atoms of nitrogen between both compositions is because the amidic nitrogen linked to the glutamic and aspartic amino acids was considered by Fraga and Pérez (1990) in their analysis. This amidic nitrogen represents 6% of the total nitrogen in phytoplankton proteins.

Carbohydrates group (*Cbh*) was mainly formed by hexose polymers which consume one mole of oxygen per mole of carbon during oxidation. Desoxisugars, such as fucose and rhamnose which consume 1.08 moles of oxygen per mole of carbon, is a relatively small fraction (4.4%) of the total carbohydrates.

Triglycerides are the main constituents of the Lipids group (*Lip*) representing about 85% of the group. These triglycerides are formed of fatty acids with a mean of 17.3 carbons and 1.9 double bonds. Phospholipids were excluded because they belong to the phosphorus compounds group. The oxidation degree of this group ($C_{53}H_{89}O_6$) given by Fraga and Pérez (1990) is slightly higher than that of $C_{40}H_{47}O_5$ given by Laws (1991), due to the higher insaturation degree of fatty acids and to the inclusion of xantophylls, which represent about 6%.

Oxidation of the organic matter

Through balancing the formula of photosynthesis-remineralisation



it is possible to calculate the oxygen consumed during the total oxidation of organic matter (Ríos *et al.* 1989)

$$-\text{O}_2 = (4c + h - 2o + 5n + 5p + 6s) / 4 \quad (1)$$

If the oxidation is to NH_4^+ instead of to NO_3^- the term $+ 5n$ must be substituted by $- 3n$.

Then by using (1) it is possible to know the oxygen consumed during the oxidation of each group of biomolecules in Table 1 and the corresponding relationships between oxygen consumption and carbon and nitrogen regenerated. These relationships are defined as $R_C = -\Delta\text{O}_2/\Delta\text{C}$ and $R_N = -\Delta\text{O}_2/\Delta\text{N}$, respectively.

RESULTS

The R_C , R_N and C/N ratios for each group of biomolecules in Table 1 are given in Table 2. According to Table 2, R_C and R_N ratios for protein and phosphorus compounds do not differ appreciably between them, which means that the oxygen consumed during the oxidation of the total organic matter will not be affected by the proportion of *Prt* and *Pho*, and therefore, will be independent of the N/P ratio of the organic matter. Consequently, both groups can be included in a single group of *Prt+Pho*, simplifying greatly the calculations of the R_C and R_N ratios of the whole particulate matter, because only three groups of biomolecules will be involved.

Considering that

$$(\text{Prt+Pho}) + \text{Lip} + \text{Cbh} = 1 \quad (2)$$

where (*Prt+Pho*), *Lip*, and *Cbh* is the fraction of carbon content for each group of biomolecules, therefore

$$R_C = R_{CP}(\text{Prt+Pho}) + R_{CL} \cdot \text{Lip} + R_{CH} \cdot \text{Cbh} \quad (3)$$

then combining equations 2 and 3, and substituting (*Prt+Pho*) by $(\text{C/N})_p/(\text{C/N})$:

TABLE 2.- Relationship between oxygen consumed by each mole of carbon or nitrogen oxidized by each group of biomolecules and C/N ratio in atoms. Organic nitrogen oxidized to nitrate.

| Group | $R_C = -\Delta\text{O}_2/\Delta\text{C}$ | $R_N = -\Delta\text{O}_2/\Delta\text{N}$ | C/N |
|----------------------|--|--|-----------|
| Protein | 1.582±0.005 | 5.81±0.04 | 3.68±0.03 |
| Phosphorus compounds | 1.55±0.02 | 5.8±0.3 | 3.8±0.2 |
| Carbohydrates | 1.00±0.01 | | |
| Lipids | 1.363±0.007 | | |
| Prt+Pho | 1.576±0.007 | 5.81±0.08 | 3.69±0.06 |

$$R_c = (R_{CP} - R_{CH})(C/N)_p/(C/N) + Lip (R_{CL} - R_{CH}) + R_{CH} \quad (4)$$

or

$$R_c = (R_{CP} - R_{CL})(C/N)_p/(C/N) + Cbh (R_{CH} - R_{CL}) + R_{CL} \quad (5)$$

where R_{CP} , R_{CH} and R_{CL} are the R_c ratios for (*Prt+Pho*), *Cbh*, and *Lip*, respectively and $(C/N)_p$ is the C/N ratio of (*Prt+Pho*).

Taking into account that the C/N ratios of *Prt* and *Pho* are very similar (Table 2), it is possible to calculate the content of *Prt+Pho* group in carbon moles starting from the total organic nitrogen content in moles of the particulate matter

$$C_{(Prt+Pho)} = 3.69 N$$

Using the data of Table 2, (4) and (5) become:

$$R_c = 2.125/(C/N) + 0.36 Lip + 1.00$$

and

$$R_c = 0.786/(C/N) - 0.36 Cbh + 1.36$$

respectively.

Phytoplankton biochemical composition is commonly referred to in the literature as ratios between

several biochemical groups (see Table 3). In this way, carbohydrate and lipid contents are given as the ratio *Cbh/Lip* at many times, and for this reason it could be useful to determine R_c and R_N starting from the C/N ratio and from the *Cbh/Lip* ratio, expressed in carbon units, of the particulate organic matter. Combining (4) and (5) and rearranging:

$$R_c = (R_{CH} + (R_{CL} - R_{CH})/(1+Cbh/Lip))(1 - (C/N)_p/(C/N)) + R_{NP}/(C/N)$$

where R_{NP} is R_N of (*Prt+Pho*).

Assigning the corresponding values of Table 2 to the constants, we obtain:

$$R_c = (1.00 + 0.36/(1+Cbh/Lip))(1 - 3.69/(C/N)) + 5.81/(C/N) \quad (6)$$

Ternary plots and ranges of variation of R_c and R_N

Taking into account that the phytoplankton values of R_c and R_N only depend on C/N and *Cbh/Lip* ratios, the mean values can be calculated by using in (6) the average values of C/N and *Cbh/Lip*. For that propose we chose the classic value of $C/N = 6.625$ (Fleming, 1940) which is

TABLE 3.- Σ Carbohydrate/ Σ Lipid ratio in carbon given by different authors. When the ratio was in weight we multiplied by 0.574 to transform it to carbon units.

| Location | Num. of samples | C-Cbh/C-Lip | Authors |
|------------------------|-----------------|-------------|-----------------------------|
| | 3 | 0.92* | Antia et al. (1963) |
| Villefranche-sur-Mer | 46 | 1.20 | Nival et al. (1976) |
| Kiel Bight | 42 | 0.90 | Smetacek et al.(1979) |
| North Sea | 60 | 1.38 | Lancelot-Van Beveren (1980) |
| Peruvian coast (0-50m) | 54 | 0.86 | Hendrikson et al. (1982) |
| Pacific (5m) | 41 | 0.94 | Tanoue et al. (1982) |
| Antarctic (0,100m) | 53 | 0.47 | " " |
| Antarctic (0-75m) | 45 | 0.40 | Tanoue (1985) |
| Ría de Vigo | 20 | 1.25** | Ríos and Fraga (1987) |
| Villefranche-sur-Mer | 10 | 1.23*** | Claustre et al. (1989) |
| Plymouth | 8 | 1.50 | Fernández et al. (1992) |
| Ría de Vigo | 378 | 0.81 | Ríos (1992) |
| Antarctic (0-100) | 7 | 0.17 | Robins et al. (1994) |
| North Atlantic | 39 | 0.51 | Fernández et al.(1994) |
| Average | 14 | 0.82 | |

* During the exponential growth
 ** Calculated from elemental composition
 *** Inverse of the Lip/Cbh geometric average

TABLE 4.- Maximum and minimum values that R_N can take for the possible R_C values, and maximum and minimum values that can take R_C for a given R_N

| R_C | R_N minimum | R_N maximum | R_N | R_C minimum | R_C maximum |
|-------|------------------|------------------|-------|------------------|------------------|
| 1 | ∞ | ∞ | 100 | 1.02 | 1.37 |
| 1.1 | 23 | ∞ | 20 | 1.12 | 1.42 |
| 1.2 | 12.8 | ∞ | 10 | 1.27 | 1.48 |
| 1.3 | 9.2 | ∞ | 9 | 1.31 | 1.49 |
| 1.4 | 7.4 | 30 | 8 | 1.36 | 1.51 |
| 1.41 | 7.3 | 24 | 7 | 1.44 | 1.54 |
| 1.5 | 6.4 | 8.6 | 6 | 1.55 | 1.57 |
| 1.58 | 5.8 | 5.8 | 5.8 | 1.58 | 1.58 |

very close to that found in further analysis of marine particulate organic matter (Tanoue and Handa, 1979, Copin-Montegut and Copin-Montegut, 1983; Ríos, 1992). The *Cbh/Lip* ratio in phytoplankton populations shows a higher variability, depending on many factors such as dominant species, physiological state, presence of silicium, nutrient concentrations, light availability and water temperature (Strickland *et al.*, 1969; Darley, 1977; Taguchi *et al.*, 1987; Ríos, 1992). Table 3 summarises the *Cbh/Lip* ratios given by several authors for marine particulate organic matter. We use the average ratio (0.82) of all data gathered in Table 3 expressed in carbon units. Therefore, using $C/N = 6.625$ and $Cbh/Lip = 0.82$, the corresponding mean R_C and R_N values for the oxidation or photosynthesis of plankton organic matter with mean composition, are 1.41 and 9.33 respectively.

Following Nival *et al.* (1976) the biochemical composition of the particulate organic matter can be easily represented by lineal functions in ternary plots. Figure 1 shows such ternary plots, where each side of the triangle represents the proportion of carbon, in weight or moles, of the three groups of biomolecules (*Cbh*, *Lip* and *Prt+Pho*). The use of carbon units is independent of the N/P ratio, however when the weight of each substance is chosen, we need to know the N/P ratio previously. Consequently, the use of carbon units makes a general formulation possible in which the N/P ratio can take any value. On the other hand, in this type of graphic representation the lines defining the R_C and N/C values are parallel at constant intervals. Besides, the N/C ratio can be represented in a vertical axis because the respective isopleths are horizontal. All R_N lines meet at *Cbh-Lip*

axis and $R_C = 0$ line intersection. The horizontal continuous line represents all the possible mix of proteins, phosphorus compounds, carbohydrates and lipids that fulfils $C:N = 106:16$. The point on this line is located at the intersection of $R_C = 1.41$ and $R_N = 9.33$ lines, and therefore represents the mean biochemical composition of the phytoplankton containing 59% of proteins plus phosphorus compounds, 24% of carbohydrates and 17% of lipids, with an elemental composition $C_{106}H_{171}O_{42}N_{16}P$.

Theoretically, the R_C range could vary from 1.00, when all carbon is in carbohydrates, to 1.58 when carbon is exclusively in proteins plus phosphorus compounds. When all nitrogen is in proteins plus phosphorus compounds $R_N = 5.81$, while $R_N = \infty$ when only carbohydrates and lipids are considered. Considering that $C/N = R_N/R_C$ it is possible to calculate the limits of R_C and R_N by using (6) and assigning to *Cbh/Lip* the extreme values of 0 and ∞ which correspond to *Cbh*=0 and *Lip*=0, respectively. Then,

for $R_C > 1.36$;

$$2.125 R_C / (R_C - 1) < R_N < 0.785 R_C / (R_C - 1.36)$$

while for $R_C < 1.36$; $2.125 R_C / (R_C - 1) < R_N < \infty$

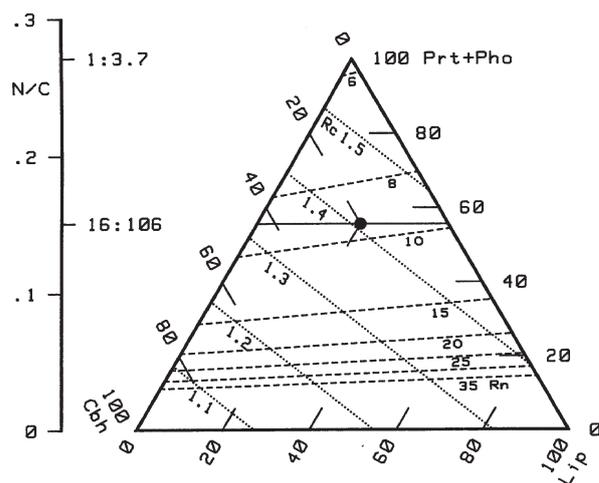


FIG. 1. -Ternary plots that represent the percentages of each group of biomolecules expressed in carbon (carbohydrates, lipids and proteins+chlorophyll+phosphorus compounds) that compose the phytoplankton. The point corresponds to the mean composition of plankton. The dotted lines indicate the location of samples with a mixing composition following the same R_C . The dashed lines represent samples with mixing composition exhibiting the same R_N . The continuous line points out a mixing composition that fulfils $C/N = 106/16$.

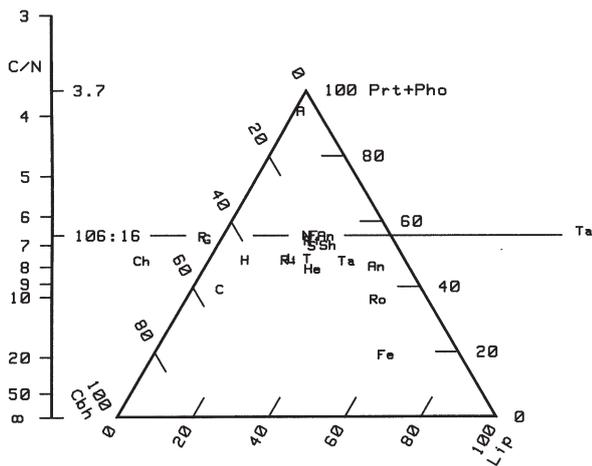


FIG. 2. - Distribution of samples given by different authors, represented on ternary plots as in Fig. 1. (A) Antía *et al.* 1963, (R) Redfield *et al.* 1963, (H) Haug *et al.* 1973, (N) Nival *et al.*, 1976, (G) Sen Gupta *et al.* 1976, (S) Smetacek *et al.* 1979, (L) Lancelot Van-Beveren 1980, (He) Hendrikson *et al.* 1982, (T) Tanoue (1985), (Ta) Takahashi *et al.* 1985, (Ri) Ríos and Fraga, 1987 and Ríos 1992, (C) Claustre *et al.* 1989, (An) Anderson and Sarmiento 1994 and Anderson 1995, (Fe) Fernández *et al.* 1992, (Ro) Robins *et al.* 1994, (Ch) Chen *et al.* 1996, (Sh) Shaffer 1996, (F) Fraga *et al.* (this paper).

This differentiation is necessary because the higher limit of R_N occurs when protein content $\square 0$ and consequently $R_N \square \infty$ (see also Figure 1). Similarly, the limits for R_C for a given R_N are:

$$R_N / (R_N - 2.125) < R_C < 1.36 R_N / (R_N - 0.785)$$

The limits of R_C and R_N are given in Table 4 according to all possible values derived from the plankton composition.

DISCUSSION

The mean value of $R_C = 1.41$ obtained from the mean C/N and Cbh/Lip relationships of the particulate organic matter coincides with the 1.4 value suggested by Laws (1991) and with the 1.42 value calculated from the elemental composition given by Anderson (1995). Similarly, the value of $R_N = 9.33$ obtained here is in agreement with the $R_N = 9.38$ derived from the elemental composition of particulate matter (Anderson, 1995) and the $R_N = 9.1$ (Minster and Boulahdid, 1987) deduced from nutrients data of several oceans. The Redfield ratio ($-O_2:C:N:P$) that corresponds to these mean R_C and R_N values is 149:106:16:1 which is practically the same as that given by Anderson (1995). The appro-

ach proposed here permits the calculation of R_C and R_N as a function of C/N and Cbh/Lip ratios. For an organic matter with a fixed C/N ratio of 106/16 but with varying proportions of carbohydrates and lipids, all possible biochemical composition will be situated along the 16:106 = $N:C$ line inside the ternary plots (Fig. 1), and the limits are $R_C = 1.32$ and $R_N = 8.8$ when lipids = 0% while they are $R_C = 1.48$, $R_N = 9.8$ when carbohydrates = 0%.

The limits and ranges of variation of R_C and R_N allow us to validate observational data from organic matter composition or nutrient ratios in the ocean. All data found in the literature derived from biological studies such as elemental or biochemical composition of organic matter showed values within the limits proposed in this work after transformation following (4), (5) or (6). In other words, they are inside the ternary plots (Figure 2). The values corresponding to the biochemical composition obtained by Nival *et al.* (1976), Smetacek *et al.* (1979), Ríos (1992), Anderson (1995) and Shaffer (1996) are surrounding the mean value (point in Fig 1). Near this point are the values obtained from Lancelot-Van Beveren (1980), Hendrikson *et al.* (1982), Tanoue (1985) and Ríos and Fraga (1987). Biochemical composition with lipids proportions higher than 50% (Fernández *et al.*, 1992; Robins *et al.*, 1994) correspond to the North Atlantic and Antarctic phytoplankton. Haug *et al.* (1973) and Claustre *et al.* (1989) gave the highest carbohydrates proportion, between 40% and 60%, while Antía *et al.* (1963) gave the highest proteins proportion (94%). In most of the biochemical composition shown here, the C/N ratio of the particulate material is higher than 6.625, in agreement with Sambrotto *et al.* (1993) who found high C/N ratios from the consumption of carbon relative to nitrogen. The classic Redfield biochemical composition is outside the ternary plots because its original formulation has no lipids and therefore, the composition should fall on the $Prt-Cbh$ line. However, Redfield considered the proteins as the sum of carbohydrates plus ammonium which is a less reduced form and so, the composition falls out the triangle. The elemental composition given by Chen *et al.* (1996) is also outside the triangle, probably because their hydrogen analysis could be rather low. The composition given by Sen Gupta *et al.* (1976) for the Indian Ocean obtained from dissolved oxygen and nutrient concentrations, is also outside the triangle and very close to the Redfield composition. The composition obtained for the Atlantic and

Indian ocean by Talakashi et al. (1985) is also outside the triangle. However, in this case the calculated biochemical composition was affected by an overestimation of lipids (94%), which was already recognised by the authors, proposing a new biochemical composition for the Atlantic and Indian ocean which is inside the triangle and not far from the Redfield ratios determined by Anderson and Sarmiento (1994) for South Atlantic, Indian and Pacific basins. This signifies that when R_C and R_N values obtained from dissolved oxygen and nutrient concentrations are outside the defined limits of the triangle some process is misunderstood.

To establish the real limits of the R_C and R_N ratios used in studies of photosynthesis and mineralisation processes constitutes an essential step to improve models dealing with global net primary production and models devoted to quantifying the anthropogenic CO_2 incorporation into deep ocean in which it is a crucial task to accurately remove the CO_2 gained by deep waters due to the oxidation of the organic matter (Brewer, 1978; Chen and Millero, 1979, Chen 1993, Wallace, 1995). The use of R_C and R_N ratios in agreement with the real oxidation processes will permit better estimations of anthropogenic penetration into the oceans.

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