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## Carbon dioxide and metabolism in marine environments<sup>1</sup>

Investigators of community metabolism in aquatic environments have frequently followed changes in the O<sub>2</sub> content of the water. Changes in the carbon dioxide content provide an alternative metabolic record which has also been used. Previous biological applications have often simplified treatment of the marine CO<sub>2</sub> system to the point of losing valuable information, while more rigorous chemical discussions of the marine CO<sub>2</sub> system are often so laborious that they obscure relevant biological interpretations. This comment is meant to focus attention on those aspects of the marine CO<sub>2</sub> system directly relevant to studies of community metabolism. Detailed examples of the use of CO<sub>2</sub> in such studies are reported elsewhere (Smith 1973; Smith and Pesret 1974), as are more rigorous and detailed descriptions of the chemistry of CO<sub>2</sub> in seawater (Skirrow 1965; Park 1969).

Photosynthesis (or respiration) and calcification (or solution) within a closed body of water induce a variety of changes in the absolute and relative concentrations of the CO<sub>2</sub> species present. Photosynthesis and calcification both lower the CO<sub>2</sub> content of the water, while respiration and CaCO<sub>3</sub> solution raise it. Only the precipitation or solution of CaCO<sub>3</sub> significantly alters the total alkalinity of the water; consequently, alkalinity changes can be used to calculate the effects of CaCO<sub>3</sub> reactions on total CO<sub>2</sub> changes. Changes in CO<sub>2</sub> not directly attributable to CaCO<sub>3</sub> reactions represent photosynthesis or respiration and

can be related to organic carbon production or consumption. Both the organic carbon reactions and the CaCO<sub>3</sub>-C reactions are biologically important processes in a variety of marine environments.

The two most convenient parameters to describe the CO<sub>2</sub> content of seawater are pH and total alkalinity. The only major instrumentation required to measure these parameters is a good pH meter. With reasonable care, one can achieve a precision (standard error on duplicate analyses) of about ±0.005 pH units and ±0.005 meq liter<sup>-1</sup>; this precision allows calculation of the total CO<sub>2</sub> content of the water to a precision of about ±0.005 mM (or about 0.25% of the total CO<sub>2</sub> content of seawater). The calculation of CO<sub>2</sub> from these parameters is sufficiently tedious to be best accomplished by computer.

To determine the CO<sub>2</sub> changes as the sample incubates in the system of interest, one calculates the total CO<sub>2</sub> content of the water as described above. The molar change in CO<sub>2</sub> from CaCO<sub>3</sub> reactions equals half the equivalents of total alkalinity change; that CaCO<sub>3</sub>-induced CO<sub>2</sub> change is subtracted from the total CO<sub>2</sub> change, and the remainder equals the net CO<sub>2</sub> change that may be attributed to photosynthesis or respiration.

Alkalinity is the capacity of water to neutralize hydrogen ions. Carbonate alkalinity is the neutralizing capacity of the ionic CO<sub>2</sub> species alone, while total alkalinity includes not only the carbonate alkalinity but also other species (almost entirely boron species) that neutralize hydrogen ions, *minus* the offsetting effect of hydrogen ions present in the solution. Changes in

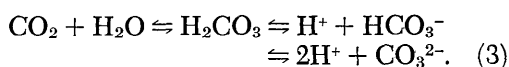
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both carbonate alkalinity (*CA*) and total alkalinity (*TA*) have been used to estimate  $\text{CaCO}_3$  reactions. However, changes in these two alkalinity parameters are equivalent to one another only under conditions of constant pH. The following equations describe the ionic species contributing to each of the two alkalinities:

$$CA = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}); \quad (1)$$

$$TA = CA + (\text{H}_2\text{BO}_3^-) + 2(\text{HBO}_3^{2-}) + (\text{OH})^- - (\text{H})^+. \quad (2)$$

The critical difference between the two kinds of alkalinity can be seen by example. Consider the case of bubbling water with gaseous  $\text{CO}_2$ , which hydrates to form carbonic acid and then dissociates into bicarbonate and carbonate ions:



The addition of  $\text{CO}_2$  has not altered the capacity of the water to neutralize hydrogen ions; for every negative charge added to the water in the form of bicarbonate or carbonate ions, there has also been a balancing hydrogen ion added. Thus bubbling the water with  $\text{CO}_2$  or directly altering the free  $\text{CO}_2$  by any other process does not alter the total alkalinity. On the other hand, the carbonate alkalinity is altered by this reaction, both through the addition of ionic  $\text{CO}_2$  species and through pH-related shifts in the partitioning of  $\text{CO}_2$  species already present in the water.

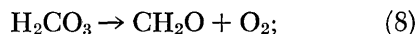
The precipitation of  $\text{CaCO}_3$  can be represented by any one of several equations, two of which are given below:



The degree to which equation 4, equation 5, or some other equation describes calcification is both complex and variable. The direct depression of *CA* attributable to the reaction described by equation 5 is half that attributable to the reaction of equation 4. The pH shift accompanying the reaction described by equation 5 will also alter carbonate speciation, hence *CA*.

On the other hand, either of the above equations demonstrates that *TA* is lowered by two equivalents for each mole of  $\text{CaCO}_3$  precipitated. Thus, there is a clear and simple stoichiometric relationship between *TA* and calcification: calcification lowers the total  $\text{CO}_2$  content of seawater one mole for each mole of  $\text{CaCO}_3$  precipitated, and the total  $\text{CO}_2$  content of seawater is therefore lowered by 0.5 moles for each equivalent of *TA* reduction. This simple stoichiometry does not exist between *CA* and calcification because of the dependence of *CA* on the exact reaction used to describe the precipitation of  $\text{CaCO}_3$ .

The following equations describe carbohydrate formation from the various available  $\text{CO}_2$  species and demonstrate that there is no change in total alkalinity associated with organic carbon production:



Equations 6 and 7 describe a balance between utilization of hydrogen ions (raising *TA*) and utilization of ionic  $\text{CO}_2$  species (lowering *TA*)—for no net change in *TA*. Yet the reactions do result in *CA* shifts—a further reason for using *TA* rather than *CA* to estimate  $\text{CO}_2$  changes induced by  $\text{CaCO}_3$  reactions.

Processes other than  $\text{CaCO}_3$  or organic carbon reactions may interfere with the interpretations of apparent  $\text{CO}_2$  changes as described here. Liberation of ammonia from amino acids would raise total alkalinity, while precipitation of nutrient salts such as  $\text{CaPO}_4$  would lower it (Gaines and Pilson 1972). However, in most oxygenated seawater the total contribution of nonconservative, non- $\text{CO}_2$  species to *TA* is sufficiently small (Edmond 1970) that such changes can be neglected. The data of Gaines and Pilson demonstrate that this assumption is not justified in anoxic systems, and other apparent anomalies can also be found (Davies and Kinsey 1973).

In open systems, there may be exchange of gaseous  $\text{CO}_2$  across the air-sea interface. However, available data (Kanwisher 1963; Teal and Kanwisher 1966; Smith 1973) suggest that gas exchange is ordinarily far less serious for  $\text{CO}_2$  estimates of metabolism than for  $\text{O}_2$  estimates. As has already been discussed, gas exchange does not affect total alkalinity—hence the estimates of  $\text{CaCO}_3$  reactions.

Several workers have measured a single  $\text{CO}_2$ -related parameter to record organic carbon metabolism in seawater. Beyers (1966 and several other papers) and others have measured empirical relationships between pH and the total  $\text{CO}_2$  content of both seawater and freshwater, while Teal and Kanwisher (1966) have used similar empirical relationships between  $\text{CO}_2$  partial pressure in the water and the total  $\text{CO}_2$  content of that water. Park et al. (1958) calculated the relationship between pH and total  $\text{CO}_2$  at a constant alkalinity. Such relationships between changes in any single  $\text{CO}_2$ -related parameter and total  $\text{CO}_2$  changes depend either implicitly or explicitly on a constant total alkalinity, and thus a constant buffer capacity, of the water. For any system in which significant  $\text{CaCO}_3$  precipitation or solution occurs, this assumed dependence is invalid. As calcification or solution occurs, the alkalinity is altered, and estimates of the  $\text{CO}_2$  content based on a single parameter become progressively more in error. Moreover, single-parameter methods of evaluating the total  $\text{CO}_2$  content of the water give no information about the pathways of  $\text{CO}_2$  flux in biologically active systems. It is misleading to consider changes in a single  $\text{CO}_2$  parameter, which may be an index for the sum of organic carbon metabolism plus  $\text{CaCO}_3$

reactions, and  $\text{O}_2$ , which is related to organic carbon metabolism.

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