

of the total dissolved carbon that is in the form of carbonate ion. Dissolved carbon is present in the ocean in three forms: dissolved carbon dioxide gas ( $\text{CO}_2$ ), bicarbonate ion ( $\text{HCO}_3^-$ ) and carbonate ion ( $\text{CO}_3^{=}$ ). Carbon is one of the few elements in the ocean that can exist in ions having different charges: as  $\text{HCO}_3^-$  ion with a charge of -1; as  $\text{CO}_3^{=}$  ion with a charge of -2. The amount of gaseous  $\text{CO}_2$  in the ocean is very small and will for the sake of simplicity be neglected in the discussions which follow.

The ratio of  $\text{CO}_3^{=}$  to  $\text{HCO}_3^-$  plays an important role in the sea's balance of electrical charge. The major contributors of positively charged ions (cations) in the sea are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ , and  $\text{Ca}^{++}$  (see table 2-5). To find the total number of units of positive charge per kilogram of seawater, we multiply the moles/kg of each cation by its charge and total the results. This yields 0.470 equivalents of charge from  $\text{Na}^+$ , 0.010 equivalents from  $\text{K}^+$ , 0.106 equivalents from  $\text{Mg}^{++}$ , and 0.020 equivalents from  $\text{Ca}^{++}$ . The total is 0.606 equivalents of positive charge per kilogram.\* Since sea water can have no overall charge, the number of equivalents of negatively charged ions (anions) must add up to exactly the same value. If we take the three major anions (chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{=}$ ), and bromide ( $\text{Br}^-$ )), we find that their charges add up to 0.604 equivalents of negative charge per kilogram, so we are short 0.002 equivalents of negative charge per kilogram of sea water. This difference between the sum of the negative charges is balanced mainly by the dissolved carbon ions ( $\text{HCO}_3^-$  and  $\text{CO}_3^{=}$ ). The ratio of these two anions to one another varies in such a way that charge is balanced. When more negative charge is needed to balance the cations present,  $\text{HCO}_3^-$  is converted to  $\text{CO}_3^{=}$ ; when less is needed,  $\text{CO}_3^{=}$  is converted to  $\text{HCO}_3^-$ . The amount of excess positive charge balanced by bicarbonate and carbonate ions is a small part of the total but, as we shall see, a very important residual that holds the key to the carbonate ion distribution within the sea.

In the discussion which follows we neglect the element boron. The presence of boron in sea water requires a small correction in all the calculations outlined here, for it also exists in two forms ( $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ ). In this first look at carbonate chemistry we keep things more simple by considering a hypothetical boron free ocean.

To understand what determines the ratio of carbonate ions to bicarbonate ions in a given unit of sea water, we must recognize two restrictions. First, the total amount of dissolved carbon present in the water cannot be changed as a result of our manipulation of the charges. There is a fixed number of carbon atoms and these must exist in either bicarbonate or carbonate form. Second, the sum of all the bicarbonate and carbonate charges must just balance the excess cations so that the sea water maintains its electrical neutrality. Respectively, these two restrictions can be stated mathematically as:

\*Chemists measure alkalinity in units of equivalents/kg. An equivalent is equal numerically to a mole. One mole of  $\text{Na}^+$  ions carries one equivalent of positive charge; one mole of  $\text{SO}_4^{=}$  ions carries two equivalents of negative charge.

$$[\Sigma\text{CO}_2] = [\text{HCO}_3^-] + [\text{CO}_3^{=}] \quad 2-23$$

where  $\Sigma\text{CO}_2$  stands for total dissolved inorganic carbon, and

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] \quad 2-24$$

where Alk is the alkalinity of the water (that is, the excess positive charge to be balanced by  $\text{CO}_3^{=}$  and  $\text{HCO}_3^-$  ions). The alkalinity is given by:

$$[\text{Alk}] = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{++}] + 2[\text{Ca}^{++}] + \dots \\ - [\text{Cl}^-] - 2[\text{SO}_4^{=}] - [\text{Br}^-] - \dots \quad 2-25$$

If we subtract equation 2-23 from equation 2-24, we find that:

$$[\text{CO}_3^{=}] = [\text{Alk}] - [\Sigma\text{CO}_2] \quad 2-26$$

Thus the carbonate ion content of any unit of sea water sample is equal to its alkalinity (excess positive charge) minus its total dissolved carbon content. Substituting this result in either of the original equations, we obtain:

$$[\text{HCO}_3^-] = 2[\Sigma\text{CO}_2] - [\text{Alk}] \quad 2-27$$

Here we see that the bicarbonate ion content equals twice the total dissolved carbon content minus the alkalinity.

So to understand how the carbonate ion content of sea water varies from place to place, all we need to know is how the alkalinity of the water and how the total dissolved carbon content of the water vary.

As we have already seen, the total dissolved carbon content of sea water varies because plants extract carbon from surface sea water and because the remains of these plants (or of the animals they support) sink into deep parts of the oceans where they are largely destroyed. Two processes are at work: organic tissue formation and destruction and hard-part formation and destruction. The formation of organic tissue consumes carbon and hence changes the  $\Sigma\text{CO}_2$  of the water. This carbon loss has no effect on the alkalinity of the water because none of the ionic concentrations appearing in the equation defining alkalinity change. However the incorporation and release of nitrogen by organic matter does make small changes in alkalinity. When organically bound nitrogen is released during respiration, the  $\text{NO}_3^-$  ion so produced adds to the anionic charge and reduces the alkalinity of the deep water. Correspondingly, the removal of the  $\text{NO}_3^-$  ion to form organic matter increases the alkalinity of surface water.

Removal of  $\text{CaCO}_3$  from the water changes both concentration of the total dissolved carbon and the alkalinity. Organisms use carbon to form  $\text{CaCO}_3$  and thus remove it from the water. The alkalinity of the water changes because when  $\text{CaCO}_3$  is formed,  $\text{Ca}^{++}$  ion (one of the contributors to the net positive charge) is removed. Each mole of  $\text{CaCO}_3$  formed results in the extraction of 2 moles of positive charge; thus the creation of  $\text{CaCO}_3$  changes the alkalinity

*not strictly true! off cp. known as down*

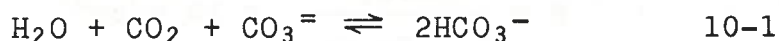
Resistance to the large scale usage of nuclear power runs high. Despite the considerable talk of solar power, its fraction of the "pie" will remain small until a major breakthrough in technology comes which will permit electrical energy to be produced at a competitive price. In a world pushed to grow enough food and fiber it is difficult to believe that vegetation will become a major source of energy. And so it goes; the end to the dominance of fossil fuels is surely many decades away.

Another ingredient to CO<sub>2</sub> production estimates comes from the fact that per unit of energy delivered to the user quite different amounts of CO<sub>2</sub> are delivered to the atmosphere depending on the kind of fuel used (see table 10-2). Methane, which has the lowest CO<sub>2</sub> production to energy delivery ratio, is used as a reference. For oil the ratio of CO<sub>2</sub> produced to energy delivered is 1.3 times greater, for coal it is 1.7 times greater and for synthetic fuels (methane and liquid hydrocarbons manufactured from coal) and for oil derived from tar sands and shales the ratio averages 2.5. Thus we see that, as we run out of natural gas and oil and begin to use other fossil fuel sources, the amount of CO<sub>2</sub> produced per unit energy consumed will rise dramatically.

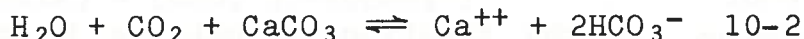
Finally, it should be mentioned that as the population increases and as fuel prices rise the temptation to even further reduce the planet's standing forest stocks will dramatically rise. Forests will be converted to farms and forests will be cut for fuel. We currently have more carbon in our forests than in our oil plus natural gas reserves.

#### CAPACITY OF THE SEA FOR FOSSIL FUEL CO<sub>2</sub> UPTAKE

The distribution of the CO<sub>2</sub> produced by man's activities between the air and the sea is a function of both thermodynamic (i.e., capacity) and kinetic (i.e., rate) factors. We will consider the capacity factors first. Although CO<sub>2</sub>, like any other gas, dissolves in the sea, were simple solution the only mechanism for its uptake then the CO<sub>2</sub> produced by man would remain almost entirely airborne. The ocean would take up only about 3% of that added to the air. Significant amounts of CO<sub>2</sub> enter the ocean only because of the reactions:



and



The CO<sub>3</sub><sup>=</sup> in reaction 10-1 is that which is dissolved in the ocean. The CaCO<sub>3</sub> in reaction 10-2 is that in the sediments on the sea floor. If present in great enough quantities these natural bases will eventually neutralize the man-made carbonic acid.

Is there enough base to neutralize the amount of CO<sub>2</sub> which would be produced if all our fossil fuel reserves were burned? The sea contains a total of about 12 x 10<sup>16</sup> moles of CO<sub>3</sub><sup>=</sup> ion. The upper 10 cm of marine sediments\* contain about 8 x 10<sup>16</sup>

\*We take 10 cm as this is the depth to which burrowing organisms penetrate.

moles of  $\text{CaCO}_3$ . Our combined fossil fuel reserves amount to about  $35 \times 10^{16}$  moles of carbon (see table 10-1). Thus viewed in this way the system could neutralize only about one-half of the carbonic acid man might ultimately produce.

As it turns out, both the estimate of the amount of base in the sea and that in the dynamically available sediment are too low. Our use of the mean amount of  $\text{CO}_3^{=}$  ion in the sea as a measure of its capacity to take up  $\text{CO}_2$  is misleading. Because most of the water in the ocean is deep water, this inventory is heavily biased toward the carbonate ion content of deep water. Actually, the atmosphere "sees" only the carbonate ion in surface-water, which, as shown in chapter 3, ranges from 1.3 times the mean deep water value in regions of cold surface water to as much as three times the deep water value in regions of warm surface water. Hence, the capacity of the sea to neutralize  $\text{CO}_2$  is larger than the value of  $12 \times 10^{16}$  moles given above. As most of the deep water in the ocean is cold it is the  $\text{CO}_3^{=}$  ion of cold surface water which is most important. Hence we should increase our ocean capacity estimate by about 25 percent to a value of  $15 \times 10^{16}$  moles. This is a more realistic estimate of the neutralization capacity of the sea itself.

Our estimate of the neutralization capacity of marine sediments is also low. We assumed that only that amount of  $\text{CaCO}_3$  lying within 10 cm of the sediment-water interface is available for solution on a reasonable time scale (i.e., several thousand years), the reasoning being that molecular diffusion through several centimeters of sediment coupled with the low solubility of calcite would yield extremely low solution rates. Hence, we focus on the layer stirred by organisms. This mixing would continually bring new calcite close to the sediment water interface removing the necessity for a long diffusion path. This reasoning is in error in that as the calcite in the upper 10 cm of sediment is dissolved, organisms would reach down into sediment which had previously been beyond their burrowing range. Indeed calcite would continue to reach the interface as a consequence of their churning until a layer of calcite-free residue 10 cm thick had been generated! The amount of calcite kinetically available then becomes:

$$M = \frac{f_{\text{CaCO}_3}}{1 - f_{\text{CaCO}_3}} \times 10 \text{ g/cm}^2 \quad 10-3$$

where  $f_{\text{CaCO}_3}$  is the fraction of calcite in the original sediment.

In order to obtain a rough estimate of this capacity marine sediments can be divided into two categories: calcite oozes covering about 20% of the sea floor and averaging 85% calcite by mass and red clays covering about 80% of the sea floor and containing negligible calcite. The dynamically available calcite in the carbonate oozes would then be:

$$\begin{aligned} M &= \frac{0.85}{0.15} \times 10 = 57 \text{ g/cm}^2 \\ &= 0.57 \text{ moles/cm}^2 \end{aligned}$$

The total calculated in this way comes out to be about  $40 \times 10^{16}$  moles.

These revised estimates are more promising! The total neutralization capacity is half again the amount of carbon locked up in recoverable fossil fuels. The bulk of this capacity, however, resides in the sediments rather than in the water column. As we shall see, it will take man's  $\text{CO}_2$  several thousands of years to get at this  $\text{CaCO}_3$ .

#### UTILIZABLE CAPACITY - SIMPLIFIED CALCULATION

While the approach we have just taken provides a ready means of getting at the ultimate buffering capacity of the ocean, it says nothing about the amount of this capacity utilizable for any given amount of  $\text{CO}_2$  added to the atmosphere. As we are involved with a reversible chemical reaction, only a fraction of the  $\text{CO}_2$  will be neutralized before an equilibrium distribution is achieved. Once the pressure of  $\text{CO}_2$  in the atmosphere has fallen to the equilibrium pressure, the neutralization will proceed no further.

In the discussions which follow, we will consider separately the cases of neutralization by the carbonate ion in the sea alone and of the sea plus the calcium carbonate in its sediment because the time required for atmosphere and sea to come to equilibrium is many hundreds of years while the time for atmosphere, sea, and sediment to come to equilibrium is many thousands of years. The case for the sea alone will be considered in this section.

We will first consider the situation for an ocean with uniform chemistry and with no borate. This simplification is useful in that it allows us to understand the big picture without mathematical complexity. The equilibrium equation for reaction 10-1 is as follows:

$$K\alpha = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{=}] p\text{CO}_2} \quad 10-4$$

where  $K$  is the equilibrium constant for reaction 10-1 (see table 3-7) and  $\alpha$  is the solubility of  $\text{CO}_2$  in sea water (see table 3-7).

In our hypothetical borate-free ocean we can write down the following equation relating alkalinity to the concentrations of  $\text{CO}_3^{=}$  and  $\text{HCO}_3^-$ :

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] \quad 10-5$$

Eliminating the  $[\text{HCO}_3^-]$  concentration between the two equations yields:

$$K\alpha = \frac{([\text{Alk}] - 2[\text{CO}_3^{=}])^2}{p\text{CO}_2 [\text{CO}_3^{=}]} \quad 10-6$$

This equation contains only  $[\text{CO}_3^{=}]$  as an unknown.

A rough estimate of what happens when additional  $\text{CO}_2$  is added to our simplified ocean-atmosphere system can be obtained by assuming that the numerator of this expression remains constant.

This approximation yields the following relationship:

$$p\text{CO}_2 [\text{CO}_3^{=}] = p^\circ\text{CO}_2 [\text{CO}_3^{=}]^\circ \quad 10-7$$

Thus to the first approximation for each 10% the  $\text{CO}_2$  content of the atmosphere rises the  $\text{CO}_3^{=}$  ion content of surface water drops by 10%.  $\text{CO}_3^{=}$  ion constitutes between 7% (for cold water) and 12% (for warm water) of the  $\Sigma\text{CO}_2$  in the surface ocean. As the total  $\text{CO}_2$  content rises by the same amount as the  $\text{CO}_3^{=}$  ion content falls (see reaction 10-1) a 10% rise in  $p\text{CO}_2$  will lead to a 0.7% rise in  $\Sigma\text{CO}_2$  for cold surface water and a 1.2% rise in  $\Sigma\text{CO}_2$  for warm surface water.

What we seek is the equilibrium fraction of  $\text{CO}_2$  remaining in the atmosphere. In honor of Charles D. Keeling whose monitoring of the atmospheric  $\text{CO}_2$  forms the foundation for all studies of the fate of fossil fuel  $\text{CO}_2$  we will refer to this fraction as the Keeling fraction,  $f_K$ , where:

$$f_K = \frac{M^*_{\text{atm}}}{M^*_{\text{atm}} + M^*_{\text{ocean}}} \quad 10-8$$

The amount of fossil fuel  $\text{CO}_2$  accumulated in the air,  $M^*_{\text{atm}}$ , is given can be approximated by:

$$M^*_{\text{atm}} = \frac{(p\text{CO}_2 - p^\circ\text{CO}_2)}{p^\circ\text{CO}_2} M^\circ_{\text{atm}} \quad 10-9$$

where  $p^\circ\text{CO}_2$  is the partial pressure of  $\text{CO}_2$  in the air prior to the industrial revolution and  $M^\circ_{\text{atm}}$  is the mass of  $\text{CO}_2$  in the preindustrial atmosphere. The amount of excess  $\text{CO}_2$  taken up by the ocean can be approximated by:

$$M^*_{\text{ocean}} \cong ([\text{CO}_3^{=}]^\circ - [\text{CO}_3^{=}]) V_{\text{ocean}}$$

where  $[\text{CO}_3^{=}]^\circ$  is the mean carbonate ion content of the surface ocean prior to the industrial revolution and  $V_{\text{ocean}}$  is the volume of the ocean. It is the drop in  $\text{CO}_3^{=}$  ion concentration in surface water that provides the measure of the amount of  $\text{CO}_2$  taken into the sea (one mole of  $\text{CO}_3^{=}$  is utilized for each mole of  $\text{CO}_2$  removed from the atmosphere). Thus  $f_K$  is given by the following equation:

$$f_K = \frac{\frac{(p\text{CO}_2 - p^\circ\text{CO}_2)}{p^\circ\text{CO}_2} M^\circ_{\text{atm}}}{\frac{(p\text{CO}_2 - p^\circ\text{CO}_2)}{p^\circ\text{CO}_2} M^\circ_{\text{atm}} + ([\text{CO}_3^{=}]^\circ - [\text{CO}_3^{=}]) V_{\text{ocean}}} \quad 10-11$$