

# Perspectives in Environmental Chemistry

Edited by  
**DONALD L. MACALADY**

Colorado School of Mines

## CHAPTER 12

### Why Carbon Dioxide from Fossil Fuel Burning Won't Go Away

PIETER P. TANS

**ABSTRACT.** The carbon dioxide added to the combined atmosphere–ocean–biosphere as a result of the combustion of fossil fuels will not leave that system, which we call the mobile reservoirs, for an extremely long time. The extra carbon will keep moving back and forth between the mobile reservoirs in response to climatic and biological processes. Therefore, future anthropogenic greenhouse forcing of the earth's climate will be controlled primarily by the total amount and the rate of fossil fuel burning. Humankind may have a measure of control on the storage of carbon by the terrestrial biosphere.

#### INTRODUCTION

Carbon dioxide in the atmosphere influences the earth's radiative balance and, hence, its surface temperature and climate. In this chapter we will concern ourselves with the question of how the atmospheric concentration of  $\text{CO}_2$  is determined and how it may change as a result of human activities. Carbon at the surface of the earth is held in reservoirs that differ in capacity by many orders of magnitude. Figure 12.1 shows the major carbon reservoirs and the rates at which carbon is transferred from one form of storage to another. Two features immediately attract attention. The oceans hold much more carbon than the atmosphere, while their carbon inventory in turn pales in comparison with the amount present in sedimentary rocks. The second feature concerns the fluxes of carbon between the various reservoirs. The exchange between the atmosphere and the biosphere and between the atmosphere and the oceans is vigorous, whereas other fluxes are much smaller. Looking at the relative sizes of the reservoirs of carbon, it might at first sight seem surprising that the burning of fossil fuels by our industrialized society could be a problem because there appears to be plenty of capacity for the uptake of  $\text{CO}_2$  from the atmosphere into other reservoirs, especially the oceans. We will see that the earth's capability to absorb from the atmosphere the excess  $\text{CO}_2$  produced from fossil fuels is limited on a timescale of interest to human society.

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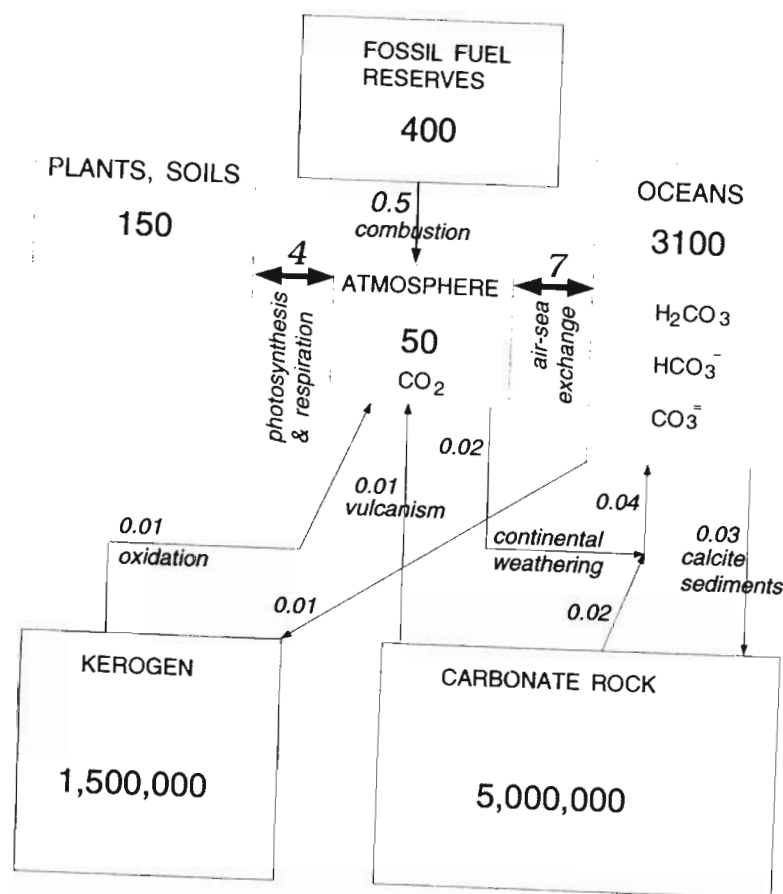


Figure 12.1. Diagram of the global carbon cycle. Quantities in reservoirs are in units of  $10^{15}$  mol C, and fluxes are in  $10^{15}$  mol C  $\text{yr}^{-1}$ .

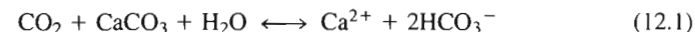
This chapter is arranged as follows. First the carbon cycle is put in a geological perspective. The earth's fossil fuel reserves accumulated as a result of biological activity over many millions of years, and it will take on the order of a million years for the man-made perturbation to completely disappear. Next, the ocean carbonate equilibria are defined so that we can understand (a) why the oceans contain so much more carbon than the atmosphere and (b) what limits their capacity to take up additional carbon. Attempted explanations of "recent" natural variations of the atmospheric  $\text{CO}_2$  concentration, as recorded in air bubbles in ice cores during the last few hundred thousand years, are all based on the impact on the oceanic carbonate system of changes in ocean circulation, sea level, and biological processes. Evidence is presented that the present increase of  $\text{CO}_2$  is, beyond any reasonable doubt, due to man's burning of fuels for energy, and elements of a prognosis for  $\text{CO}_2$  are given if the world proceeds to burn all fossil fuel reserves.

## THE CARBON CYCLE ON GEOLOGICAL TIMESCALES

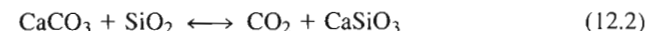
The atmosphere, biosphere, and oceans combined contain only an insignificant amount of carbon compared to that in limestone and silicate rocks. The first three reservoirs we will call the mobile reservoirs. An approximate residence time for carbon in the mobile reservoirs can be obtained by dividing the total amount by the total flux, it is of the order of 100,000 years. Likewise, the residence time in the rock reservoirs is about 150 million years, the timescale of the erosion-sedimentation cycle. On a timescale longer than a million years, the amount of carbon in the mobile reservoirs is governed by the requirement that the input of eroded continental materials equals the rate of sedimentation. Carbonic acid,  $\text{H}_2\text{CO}_3$ , formed from  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , is the dominant global weathering acid, and the rates of chemical weathering are controlled, to a first order of approximation, by the partial pressure of  $\text{CO}_2$  in the atmosphere.

Biological organisms produce  $\text{CO}_2$  concentrations in soils that are orders of magnitude higher than in the atmosphere. Via this mechanism, soils enhance the rate of weathering, but their presence is not necessary for chemical weathering reactions to take place (Holland, 1978). In the oceans the removal rates of cations and carbon are to a large extent controlled by the concentration of carbonate ( $\text{CO}_3^{2-}$ ) ions, with higher concentrations leading to greater removal rates. Presently,  $\text{CaCO}_3$  minerals are produced by shell-forming organisms in surface ocean waters in much greater quantity than the rate of input of carbon to the oceans. Much of this  $\text{CaCO}_3$  falls toward the bottom, together with organic debris. The solubility of  $\text{CaCO}_3$  increases with pressure and with lower temperature. Deep waters are also more acidic, due to the oxidation of organic material. The concentration of carbonate ions is suppressed at higher acidity levels (see below). As a result, deep waters are corrosive to  $\text{CaCO}_3$ , so that only a relatively small fraction of the mineral present in surface environments survives in deep ocean sediments.

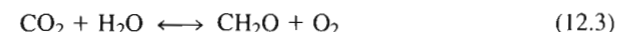
The weathering and burial of carbonate minerals ( $\text{CaCO}_3$ ,  $\text{CaMg}(\text{CO}_3)_2$ ) does not affect the total amount of carbon in the mobile reservoirs on the million year timescale. The overall reaction is



Dissolution of one  $\text{CaCO}_3$  removes one carbon from the rock reservoirs and adds it to the oceans and atmosphere, but it is removed again upon formation of  $\text{CaCO}_3$ . The amounts added and removed in this way have to be about equal in a million years because the calcium cycle is approximately balanced (see below). Transformations that are effective in regulating the total carbon content of the mobile reservoirs are (Berner, 1990)



and



Reaction (12.2) represents the thermal decarbonation at high temperature and depth of  $\text{CaCO}_3$  as a result of magmatic and metamorphic processes, where  $\text{CaSiO}_3$  stands for

a generic calcium silicate mineral. (Magnesium can undergo a similar transformation.) The  $\text{CO}_2$  thus produced is released to the atmosphere by volcanic processes. It is used up again in the reverse process during the weathering of the calcium silicate once the rock has come to the surface. In reaction (12.3),  $\text{CH}_2\text{O}$  represents a generic carbohydrate (organic material formed as a result of photosynthesis) that escapes oxidation and gets buried in sediments. Called kerogen, it is a component of most sedimentary rocks. It is oxidized after the rocks have returned to the surface. The carbon in fossil fuel deposits could be considered part of this reservoir, and it is reduced further than carbohydrate, but it forms only a tiny fraction of the total amount of kerogen in sedimentary rocks. Processes (12.2) and (12.3) greatly influence the amount of carbon in the mobile reservoirs because there can be enormous time delays between production and consumption of  $\text{CO}_2$ , and the storage capacity in sedimentary and metamorphic rocks is very large.

Berner and Lasaga (1989) have simulated the atmospheric partial pressure of  $\text{CO}_2$  over the last 600 million years in a simple model which treats the geochemical cycle of carbon only—not that of other elements. An important driving force is plate tectonics, which sets the rate of  $\text{CO}_2$  outgassing caused by decarbonation. High atmospheric  $\text{CO}_2$  levels are assumed to stimulate plant growth, which in turn leads to greater rates of rock weathering. The ratio between the rates of sedimentation of calcite and organic matter is constrained by observations of  $^{13}\text{C}/^{12}\text{C}$  in limestone rocks. This is possible because newly formed kerogen has a lower  $^{13}\text{C}/^{12}\text{C}$  ratio than calcite formed during the same time period. A change in the relative rates of burial will produce a shift in the  $^{13}\text{C}/^{12}\text{C}$  ratio of the mobile reservoirs. Berner and Lasaga's result is that atmospheric  $\text{CO}_2$  has changed by more than an order of magnitude over the last 600 million years, with the present as a period of low  $\text{CO}_2$ .

Although the omission of the geochemical cycles of other elements may not greatly influence the partial pressure of  $\text{CO}_2$  in the atmosphere, it does influence the overall budget of carbon. Broecker (1971) assumed that on geological timescales the atmospheric partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) was controlled by the need for weathering reactions to balance the oceanic removal rate of cations. The atmospheric partial pressure of  $\text{CO}_2$  in turn determined the concentration of dissolved  $\text{CO}_2$  through the Henry's Law solubility constant. Furthermore, Broecker's model also assumes that the concentration of  $\text{CO}_3^{2-}$  ions in seawater controls the removal of carbon from the ocean such that this removal balances the carbon inputs.

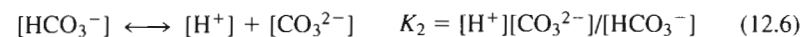
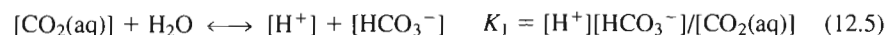
Before we can determine the total amount in the ocean, we need another constraint because C can also be present in the form of bicarbonate ( $\text{HCO}_3^-$ ) ion. Carbonate and bicarbonate ions in seawater provide part of the charge balance. The carbonate alkalinity, defined as  $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ , equals  $[\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{Br}^-] \pm \text{minor species}$ . Therefore, the proportioning of carbon between  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  is determined by the excess of cations over anions other than (bi)carbonate, and in this way by the geochemical cycles of other elements.

Once  $[\text{HCO}_3^-]$  is constrained by this requirement of charge balance, the ocean's pH is also fixed (see next section) as well as the total amount of carbon. The residence time (total amount in reservoir divided by the removal rate) of C in the oceans is short (see Figure 12.1) compared to that of other major elements in seawater, which have residence times of more than a million years. It follows that these elements are so well mixed in the oceans that their ratios are constant, and one variable is sufficient to describe their concentrations. This variable is the salinity, which is a measure of the to-

tal salt content of the water expressed as g/(kg seawater). Important processes determining the concentrations of the various salts are continental weathering, new sea floor formation, hydrothermal venting, sedimentation, ion exchange in newly formed sediments and mid-ocean ridge basalts, and evaporation from semiencloded basins.

## DEFINITION OF THE OCEANIC CARBONATE SYSTEM

Carbon dioxide in the atmosphere is not in thermodynamic equilibrium with the bulk of the oceans. In order to calculate what that equilibrium partial pressure might be, we will first have to introduce the variables that define the oceanic carbonate system. The thermodynamic equilibria we need are:



In writing these equations we have adopted the so-called hydrate convention, which does not distinguish between gaseous dissolved carbon dioxide,  $\text{CO}_2(\text{aq})$ , and its hydrated form carbonic acid,  $\text{H}_2\text{CO}_3$  (Stumm and Morgan, 1981).  $K_0$  is the Henry's Law solubility, and  $K_1$  and  $K_2$  are the first and second dissociation constants of carbonic acid. As defined here they are not proper thermodynamic constants written in terms of activities, but they are practical constants defined in terms of stoichiometric quantities and a particular pH scale. The reason for the use of practical constants is that true thermodynamic activities are difficult to determine in a medium as complex as seawater (e.g., Dickson, 1984). As practical constants, the recently revised values of  $K_0$ ,  $K_1$ , and  $K_2$  (Millero, 1995) are given as a function of temperature and salinity in Table 12.1. At  $25^\circ\text{C}$  and a salinity of 35 g/(kg seawater) the pK values ( $\text{pK} = -\log K$ ) are  $\text{pK}_1 = 5.847$  and  $\text{pK}_2 = 8.916$ . The thermodynamic activities of many species in seawater are quite different from their stoichiometric quantities because of considerable complex formation. An example would be  $\text{HSO}_4^-$ , formed from  $\text{H}^+$  and  $\text{SO}_4^{2-}$ , which ties up part of the "free" hydrogen ions. The stoichiometric quantities are the sum of the free ions and the ions tied up in complexes. Any problems of chemical speciation connected with complex formation are implicitly incorporated into the practical constants themselves because they have been measured (and tabulated) for the particular mix of seawater.

In (12.4)–(12.6) we have five unknowns and three equations. The system is completely determined if we either specify two of those five variables or add two more constraints. We choose the latter, by fixing the total amount of inorganic carbon,  $[\text{CO}_2(\text{aq})] + [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ , commonly written as DIC (dissolved inorganic carbon) or as  $\Sigma\text{C}$ , and the titration alkalinity, written as TA. Both can be routinely measured. TA is defined by

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] \\ & + [\text{NO}_3^-] + [\text{OH}^-] - [\text{H}^+] \pm \text{minor species} \end{aligned} \quad (12.7)$$

On a timescale of a thousand years, both  $\Sigma\text{C}$  and TA can change only very little in the oceans, and therefore it is useful to study the system with the assumption that the alkalinity and total inorganic carbon are constant. The carbonate alkalinity (CA), defined

TABLE 12.1

## Parameters for the Carbonate System in the World's Oceans

The thermodynamic constants given here are as summarized recently by Millero (1995), who incorporated the results of new measurements performed during the last few years. The reference by Millero also presents thermodynamic constants for the dissociation of phosphoric acid, ammonium, silicic acid, and hydrogen sulfide, which have been neglected here. All constants are applicable to concentration units of mol kg<sup>-1</sup> seawater.  $T$  is in degrees Kelvin,  $t$  is in degrees centigrade,  $S$  is salinity in permil, or g/kg seawater,  $\log$  is the logarithm base 10,  $pK = -\log(K)$ ,  $\ln$  is the natural logarithm (base  $e$ ).

Solubility of CO<sub>2</sub>:

$$\ln K_0 = -60.2409 + 9345.17/T + 23.3585 \ln(T/100) + [0.023517 - 0.00023656T + 0.0047036(T/100)^2]$$

## Dissociation constants of carbonic acid:

$$\begin{aligned} \ln K_1 &= 2.18867 - 2275.0360/T - 1.468591 \ln(T) \\ &\quad + (-0.138681 - 9.33291/T)S^{0.5} + 0.0726483S - 0.00574938S^{1.5} \\ \ln K_2 &= -0.84226 - 3741.1288/T - 1.437139 \ln(T) \\ &\quad + (-0.128417 - 24.41239/T)S^{0.5} + 0.1195308S - 0.00912840S^{1.5} \end{aligned}$$

## Dissociation constant of boric acid:

$$\begin{aligned} \ln K_B &= (-8966.90 - 2890.51S^{0.5} - 77.942S + 1.726S^{1.5} - 0.0993S^2)/T \\ &\quad + (148.0248 + 137.194S^{0.5} + 1.62247S) \\ &\quad + (-24.4344 - 25.085S^{0.5} - 0.2474S) \ln(T) + 0.053105S^{0.5}T \end{aligned}$$

Dissociation of water (in the seawater pH<sub>SWS</sub> scale, consistent with the other constants):

$$\ln K_W = 148.9802 - 13847.26/T - 23.6521 \ln(T) + [-5.977 + 118.67/T + 1.0495 \ln(T)]S^{0.5} - 0.01615S$$

There are two crystalline forms of CaCO<sub>3</sub> in the oceans, aragonite and calcite. Their stoichiometric (again, in terms of total concentrations, not thermodynamic activities) solubility products as a function of temperature and salinity are given by:

$$\begin{aligned} pK_{sp}(\text{arag}) &= 171.945 + 0.077993T - 2903.293/T - 71.595 \log T \\ &\quad + S^{0.5}(0.068393 - 0.0017276T - 88.135/T) + 0.10018S - 0.0059415S^{1.5} \\ pK_{sp}(\text{calc}) &= 171.9065 + 0.077993T - 2839.319/T - 71.595 \log T \\ &\quad + S^{0.5}(0.77712 - 0.0028426T - 178.34/T) + 0.07711S - 0.0041249S^{1.5} \end{aligned}$$

As a check, these expressions give at 298.15 K,  $S = 35$ , and  $P = 1$  bar:

$$\begin{aligned} K_0 &= 0.028392 & pK_1 &= 5.8468 \\ pK_2 &= 8.9156 & pK_B &= 8.5819 \\ pK_{sp}(\text{arag}) &= 6.188 & pK_{sp}(\text{calc}) &= 6.369 \\ pK_W &= 13.2107 \end{aligned}$$

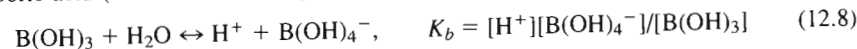
The pressure dependence can be expressed as

$$\ln(K_i^P/K_i^0) = -(\Delta V_i/RT)(P - 1) + (0.5\Delta k_i/RT)(P - 1)^2,$$

in which  $P$  is in bar,  $R = 83.147 \text{ bar cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ,  $K_i^0$  is the thermodynamic constant at 1 bar, and  $\Delta V_i$  (cm<sup>3</sup> mol<sup>-1</sup>) and  $\Delta k_i$  (cm<sup>3</sup> mol<sup>-1</sup> bar<sup>-1</sup>) are the changes in molar volume and molar compressibility of the dissociation and dissolution reactions. They are:

$$\begin{aligned} K_1: \Delta V_1 &= -25.50 + 0.1271t & 10^3\Delta k_1 &= -3.08 + 0.0877t \\ K_2: \Delta V_2 &= -15.82 - 0.0219t & 10^3\Delta k_2 &= 1.13 - 0.1475t \\ K_B: \Delta V_B &= -29.48 - 0.1622t + 0.002608t^2 & 10^3\Delta k_B &= -2.84 \\ K_W: \Delta V_W &= -25.60 + 0.2324t - 0.0036246t^2 & 10^3\Delta k_W &= -5.13 + 0.0794t \\ K_{sp}(\text{arag}): \Delta V_a &= -35.0 + 0.5304t & 10^3\Delta k_a &= -11.76 + 0.3692t \\ K_{sp}(\text{calc}): \Delta V_c &= -48.76 + 0.5304t & 10^3\Delta k_c &= -11.76 + 0.3692t \end{aligned}$$

above as  $2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$ , makes up the majority of the titration alkalinity, but CA itself is not directly measurable. At the pH of seawater the contributions from  $[\text{OH}^-]$  and  $[\text{H}^+]$  are very minor, so that we only need to consider the dissociation of boric acid (a weak acid) and specify  $[\text{NO}_3^-]$ . The borate equilibrium is given by



At 25°C in seawater of salinity 35 we have  $pK_b = 8.582$  (see Table 12.1), which is fairly close to the second dissociation constant of carbonic acid. Since the residence time of boron in the oceans is very long, its total concentration,  $\text{B(OH)}_3 + \text{B(OH)}_4^-$ , is proportional to the salinity. In other words, it is very thoroughly mixed with the other salts that have long residence times in the oceans. The introduction of boron introduced two more variables,  $\text{B(OH)}_3$  and  $\text{B(OH)}_4^-$ , but also two constraints, namely Eq. (12.8) and the total amount of boron, given by

$$\Sigma B = 1.179 \times 10^{-5} S \text{ mol/kg} \quad (12.9)$$

where  $S$  is the salinity expressed as g/kg seawater. The inclusion of boron is necessary to derive the partitioning between  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  from the measured values of the titration alkalinity. Nitrate ion,  $\text{NO}_3^-$ , is an important biological nutrient in seawater and is very low in most surface waters (see Chapter 18, this volume). Its concentration in deep waters is typically about 50  $\mu\text{mol/kg}$  due to the oxidation of biological material. To determine the carbonate system completely, we take for average deep water (Takahashi et al., 1981)  $\Sigma C = 2288 \mu\text{mol/kg}$ ,  $\text{TA} = 2393 \mu\text{equiv./kg}$ , and salinity ( $S$ ) = 34.78.

Now we are finally ready to estimate the atmospheric partial pressure of CO<sub>2</sub> in equilibrium with deep ocean water. The equations describing the carbonate system can best be solved by first solving for  $[\text{H}^+]$  in an iterative manner, which can be done in the following way:

$$\Sigma C = (1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2)[\text{CO}_2(\text{aq})] \quad (12.10)$$

$$\text{CA} = (K_1/[\text{H}^+] + 2K_1K_2/[\text{H}^+]^2)[\text{CO}_2(\text{aq})] \quad (12.11)$$

Dividing Eq. (12.10) by Eq. (12.11) and rearranging gives a quadratic equation for  $[\text{H}^+]$ ,

$$(\text{CA})[\text{H}^+]^2 + K_1(\text{CA} - \Sigma C)[\text{H}^+] + K_1K_2(\text{CA} - 2\Sigma C) = 0 \quad (12.12)$$

and CA is either specified, or found from TA by

$$\begin{aligned} \text{CA} &= \text{TA} - \{K_b/(K_b + [\text{H}^+])\}\Sigma B - [\text{NO}_3^-] \\ &\quad + [\text{H}^+] - [\text{OH}^-] \pm \text{minor species} \end{aligned} \quad (12.13)$$

No great errors are incurred if the contributions of  $\text{H}^+$  and  $\text{OH}^-$  to the alkalinity are neglected, but they can be included by making use of the ion product of water in seawater (Table 12.1). The values of all constants mentioned in this section are given in Table 12.1, so that the reader will be able to reproduce the calculations that follow.

If we bring average deep seawater of the above composition to the surface and warm it to 16°C (the observed average temperature of surface waters), the partial pressure (fugacity, strictly speaking) would be 938  $\mu\text{atm}$ , and the pH would be 7.73. For simplicity, we have assumed the contribution of all minor species including  $[\text{NO}_3^-]$ ,  $[\text{H}^+]$ ,  $[\text{OH}^-]$  to the alkalinity to be zero. The ocean surface would establish a partial

pressure of 938  $\mu\text{atm}$  in air saturated with water vapor at the temperature of 16°C, so that the  $\text{CO}_2$  mole fraction in dry air would be equal to 955  $\mu\text{atm}$ . The actual  $\text{CO}_2$  mixing ratio in the atmosphere during the recent Holocene period was about 280 parts per million ( $\text{ppm} = 280 \mu\text{atm}$  at sea level). The large difference is caused by the activity of biological organisms near the ocean surface. Carbon is used up during photosynthesis, and nutrients (mainly phosphate and nitrate) are incorporated into the organic matter formed. In the process,  $\Sigma C$  in surface water is decreased by about 13%, and the nutrients remaining at the surface are reduced almost to zero.

Incidentally, if we had included the presence of deep water nitrate ( $\text{NO}_3^-$ ) in our above calculation of alkalinity, the equilibrium partial pressure of atmospheric  $\text{CO}_2$  would have been 40% higher yet than 938  $\mu\text{atm}$ . Due to biological processes the global average values for surface waters are (Takahashi et al., 1981)  $\text{TA} = 2311 \mu\text{equiv./kg}$ ,  $\Sigma C = 2002 \mu\text{mol/kg}$ , both normalized to the average ocean salinity of 34.78. At a temperature of 16°C the atmospheric partial pressure in equilibrium with this surface ocean is 278  $\mu\text{atm}$ , and the pH of the water is 8.18, again assuming the contributions of nitrate,  $\text{H}^+$ , and  $\text{OH}^-$  to the alkalinity to be zero. The speciation in this surface water is  $[\text{CO}_2(\text{aq})] = 10 \mu\text{mol/kg}$ ,  $[\text{HCO}_3^-] = 1769 \mu\text{mol/kg}$ , and  $[\text{CO}_3^{2-}] = 223 \mu\text{mol/kg}$ . It is clear why the oceans contain so much more carbon than the atmosphere. The atmosphere is in equilibrium with  $\text{CO}_2(\text{aq})$ , but  $\Sigma C$  in this seawater is about 200 times larger than  $[\text{CO}_2(\text{aq})]$ .

With a total mass of  $5.14 \times 10^{21} \text{ g}$  and a preindustrial  $\text{CO}_2$  mixing ratio of 280 ppm, the atmosphere holds  $280 \times 10^{-6} \times 5.14 \times 10^{21}/29 = 50 \times 10^{15} \text{ mol C}$ . If the oceans contained only dissolved  $\text{CO}_2$  in equilibrium at the surface with an atmosphere of 280  $\mu\text{atm}$ , and no carbonate or bicarbonate, their total C content could be roughly estimated as follows. The solubility at 16°C is 0.036 mol/kg-atm. The average ocean depth is 4 km, and the area covered by the oceans is  $350 \times 10^6 \text{ km}^2$ . The total amount of  $\text{CO}_2$  dissolved in water would then be about  $14 \times 10^{15} \text{ mol C}$ , less than one-third of the atmospheric amount. However, when bicarbonate and carbonate are included, the upper 70 meters of the oceans alone hold about the same amount of carbon as the atmosphere.

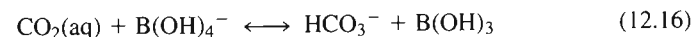
We can now comprehend an important feature of the carbonate system—namely, why an increase in atmospheric  $\text{CO}_2$  does not result in the same proportional increase in ocean carbon at equilibrium. If atmospheric  $p\text{CO}_2$  is forced to increase by 10%,  $\text{CO}_2(\text{aq})$  in the surface layer of the ocean will also go up by 10% if equilibrium with the atmosphere is maintained. What happens to  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ? Dividing Eq. (12.5) by Eq. (12.6) we obtain

$$K_1/K_2 = [\text{HCO}_3^-]^2/([\text{CO}_2(\text{aq})][\text{CO}_3^{2-}]) \quad (12.14)$$

Equation (12.14) is always obeyed. Since  $\text{CO}_2(\text{aq})$  is only a minor species and most of the carbon is present as bicarbonate, we will assume, to a first order of approximation, that the latter does not change. Then, from Eq. (12.14),  $[\text{CO}_3^{2-}]$  will have to decrease by 10% when  $[\text{CO}_2(\text{aq})]$  increases by that much. What happens is that most of the invading  $\text{CO}_2$  reacts with  $\text{CO}_3^{2-}$  to form  $2\text{HCO}_3^-$ .  $\text{HCO}_3^-$  then finds itself increased by a relative amount  $223 \times 2 \times 10\%/1769 = 2.5\%$ , not too inconsistent with our initial assumption. Equation (12.14) represents the thermodynamic equilibrium equation of the reversible reaction



In our approximate treatment the total amount of carbon has changed from the original 2002  $\mu\text{mol/kg}$  to  $11 + (1769 + 44) + (223 - 22) = 2025$ , adding dissolved  $\text{CO}_2$ , bicarbonate, and carbonate in that order. Thus, for a fractional increase of  $p\text{CO}_2$  of 10%,  $\Sigma C$  has increased by only  $23/2002 = 1.1\%$ . A more precise calculation, using the constants of Table 12.1, gives 11, 1800, and 210  $\mu\text{mol/kg}$ , respectively, for  $[\text{CO}_2(\text{aq})]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$ , summing to  $\Sigma C = 2021$ . In the more precise calculation the increase of  $\text{HCO}_3^-$  is more than exactly twice the decrease of  $\text{CO}_3^{2-}$  because not only reaction (12.15), but also the following reaction with borate, has taken place, in competition with reaction (15):



The detailed equilibrium calculations indeed show that  $\text{B}(\text{OH})_4^-$  has decreased by the amount required. The increase in total carbon is still close to 1%.

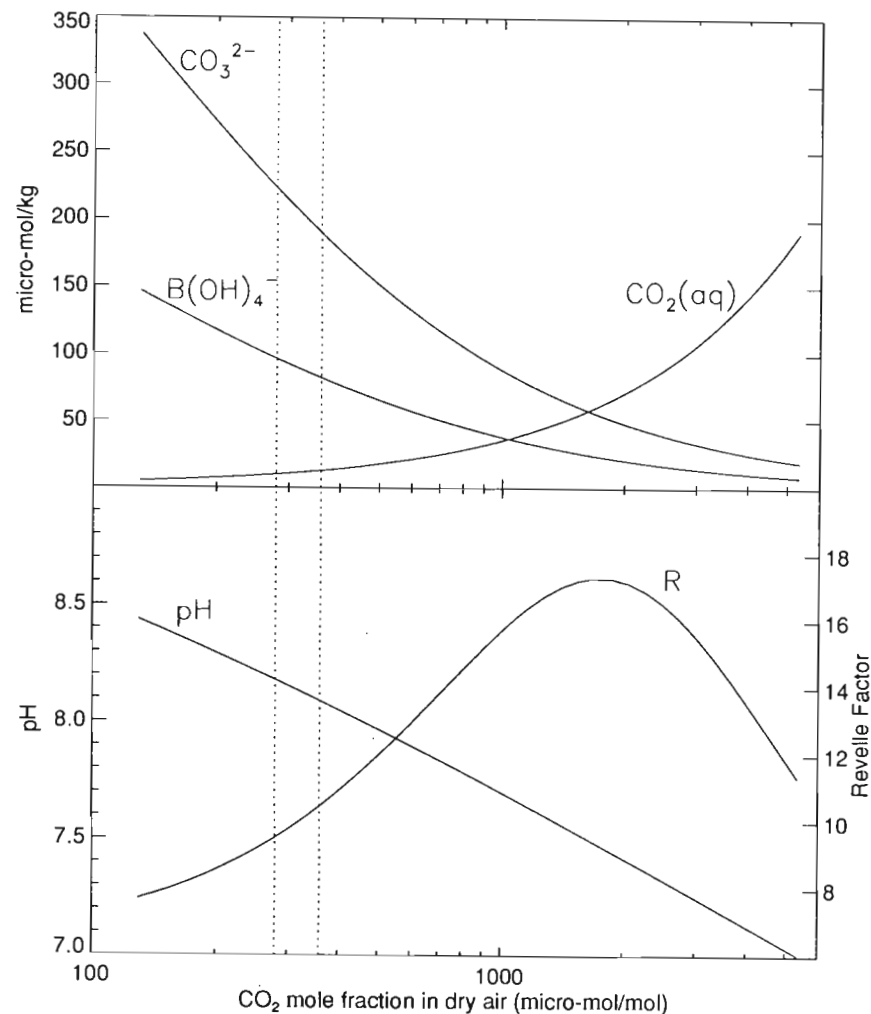
The largest contribution to the oceanic capacity for absorbing  $\text{CO}_2$  gas is due to reactions (12.15) and (12.16). On average, the sum of the concentrations of  $\text{CO}_3^{2-}$  and  $\text{B}(\text{OH})_4^-$  present in today's oceans, at an average temperature of 4°C, is about 110  $\mu\text{mol/kg}$ . With an ocean area of  $350 \times 10^6 \text{ km}^2$  and an average depth of 4 km, this translates into an absorbing capacity for  $\text{CO}_2$  of about  $150 \times 10^{15} \text{ mol C}$ . This reasoning is not correct, however. The capacity of surface waters is greater than that of deep water because of biological activity, and the atmosphere "sees" only the surface waters. The sum of  $\text{CO}_3^{2-}$  and  $\text{B}(\text{OH})_4^-$  in surface waters, at an average temperature of 16°C, is approximately 300  $\mu\text{mol/kg}$  (see Figure 12.2). Provided that biological activity keeps the chemistry of surface waters different from that of deep waters, this would lead to a total ocean absorbing capacity of about  $420 \times 10^{15} \text{ mol C}$ .

It does not matter that at greater depths the capacity would then be exceeded in the event that all fossil fuel reserves are burned. That will only result in very high concentrations of  $\text{CO}_2(\text{aq})$  and high  $p\text{CO}_2$  in deep waters, but that would be invisible to the atmosphere. The  $420 \times 10^{15} \text{ mol C}$  is small compared to the total amount of inorganic carbon in the oceans, which is about  $3100 \times 10^{15} \text{ mol C}$ . It is comparable to estimates of the total amount of recoverable fossil fuels, which is  $400 \times 10^{15} \text{ mol C}$ , give or take a factor of two, and not including shales and tar sands (Perry and Landsberg, 1977). Once the ocean's absorbing capacity has been exceeded, any further  $\text{CO}_2$  additions to the atmosphere will remain as gaseous and dissolved  $\text{CO}_2$ , and the atmosphere will have to retain 75% of the excess addition.

The relationship between the fractional changes of  $p\text{CO}_2$  and total carbon is often called the buffer factor or Revelle factor, after Roger Revelle, who played a seminal role in the first modern measurements of the global oceanic and atmospheric carbon system. The Revelle factor ( $R$ ), defined by

$$\Delta p\text{CO}_2/p\text{CO}_2 = R \Delta \Sigma C / \Sigma C$$

depends on  $\Sigma C$  and temperature and is about equal to 10 for the present global average surface ocean. In the previous paragraph we have seen that the ocean's ability to absorb additional carbon depends mostly on the concentrations of  $\text{CO}_3^{2-}$  and  $\text{B}(\text{OH})_4^-$  in surface waters. These amounts will decrease as more and more  $\text{CO}_2$ , generated by the burning of fossil fuels, is absorbed. As a result the Revelle factor, which is approximately equal to the concentration of total inorganic carbon divided by the concentration of carbonate ions, will increase as  $\text{CO}_3^{2-}$  gets converted, and it gradually becomes harder for the oceans to keep absorbing  $\text{CO}_2$ . This is shown in Figure 12.2, in

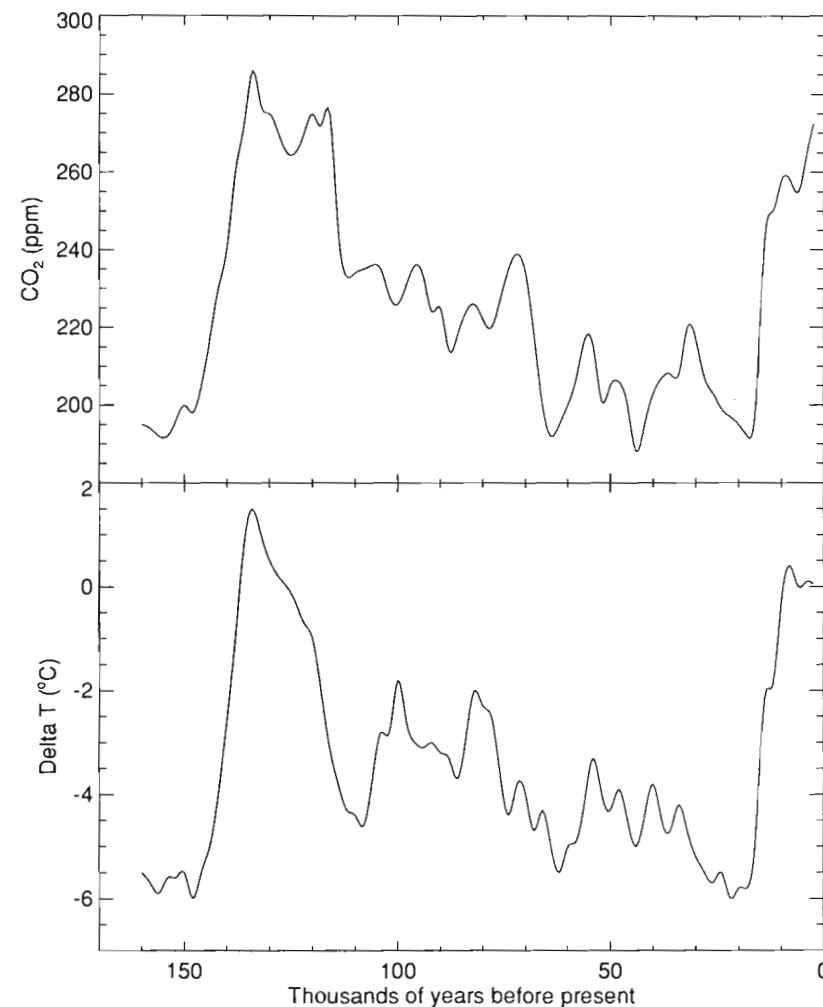


**Figure 12.2.** The response of surface ocean waters at 16°C to increasing atmospheric concentrations of  $\text{CO}_2$ , which is plotted on a logarithmic scale. The dissolved  $\text{CO}_2(\text{aq})$  increase is directly proportional to  $p\text{CO}_2$  (Henry's Law). The decreases of  $\text{CO}_3^{2-}$  and  $\text{B}(\text{OH})_4^-$  have been calculated with the constants of Table 12.1. In the lower panel, pH is referred to the left axis, and the Revelle factor,  $R$ , (see main text) is referred to the right axis. The vertical dotted lines indicate the preindustrial (280 ppm) and the 1995 level of  $\text{CO}_2$  (360 ppm).

which  $[\text{CO}_3^{2-}]$ ,  $[\text{B}(\text{OH})_4^-]$ ,  $[\text{CO}_2(\text{aq})]$ ,  $R$ , and pH of average surface water are plotted as a function of  $p\text{CO}_2$ . The ocean reaches equilibrium with the atmosphere after only a relatively small amount has been absorbed, namely a fractional  $\Sigma C$  increase of  $1/R$  times the atmospheric increase. At the high  $p\text{CO}_2$  values expected when mankind continues to burn fossil fuels, most of the added  $\text{CO}_2$  will eventually remain as dissolved  $\text{CO}_2$ . There will not be enough  $\text{CO}_3^{2-}$  and  $\text{B}(\text{OH})_4^-$  left in the oceans to react with.  $R$  starts decreasing again at very high  $p\text{CO}_2$  values because  $\text{CO}_2(\text{aq})$ , which is proportional to  $p\text{CO}_2$ , then becomes an increasingly important component of  $\Sigma C$ .

## NATURAL VARIATIONS ON THE TIMESCALE OF ICE AGES

Significant changes in the atmospheric mixing ratios of trace gases have occurred over the last glacial-interglacial cycle (Figure 12.3). During the last decade, convincing evidence of these changes has been obtained from samples of air trapped in ice in Greenland and Antarctica. For a recent review, see Raynaud et al. (1993). Over this geologically short time span there is no requirement that the inputs and outputs from the mobile reservoirs are in balance, and  $p\text{CO}_2$  and  $[\text{CO}_3^{2-}]$  are free to vary. Furthermore, significant rearrangements between the mobile reservoirs of atmosphere, oceans, and



**Figure 12.3.** History of temperature and atmospheric  $\text{CO}_2$  as recorded in the Vostok ice core, Antarctica.  $T$  is plotted as the difference from modern temperatures. (Data from Raynaud et al., 1993).

terrestrial biosphere could have had an impact on the  $p\text{CO}_2$  level that has been recorded in the ice cores.

The fact that organisms keep the surface values of the carbonate system different from the bulk of the oceans provides a potentially powerful mechanism to control  $p\text{CO}_2$  of the atmosphere on the timescale of thousands of years. The concentrations of phosphate and nitrate, which are the nutrients for the primary photosynthetic producers (phytoplankton), are close to zero in the surface layer over most of the tropical and temperate zones of the oceans. This surface layer is fairly shallow, about 70 m or so, and therefore comprises only a few percent of all ocean water. Deep waters receive a steady rain of organic debris from the sunlit surface layer. The organic material slowly decomposes, increasing the nutrient levels at depth and adding to the total pool of inorganic carbon,  $\Sigma\text{C}$ . Only at high latitudes in both hemispheres are the nutrient concentrations at the sea surface significantly different from zero. The high latitudes are also the regions where deep water can outcrop to the surface and where most of the new deep water formation occurs.

The quantities of nutrients in inorganic form contained in this newly formed deep water are of crucial importance to the carbon balance. Chemical oceanographers call these "preformed" nutrients, as opposed to the deep water nutrients that are derived later from the decomposition of the falling organic debris. If all the nutrients of newly formed deep water are tied up in organic material ("zero preformed nutrients"), the gradual carbon increase resulting from organic decomposition will start from approximate equilibrium with the atmosphere and will continue until the average nutrient content of deep water has been reached. The carbon increase of new deep water with an intermediate initial (or preformed) nutrient concentration also starts from approximate equilibrium with the atmosphere, but will be less before the nutrient level of average deep water has been reached.

Thus, with zero preformed nutrients the atmosphere will be further removed from equilibrium with deep water than with nonzero preformed nutrients. The atmosphere is a minor carbon reservoir compared to the deep seas, so we can assume that the carbon content of the deep seas remains constant. Therefore, atmospheric  $\text{CO}_2$  has to be lower with fuller biological nutrient utilization in surface waters. This can be formulated in yet another way: What matters for the atmospheric concentration is whether the oceanic nutrients reach the depths while taking carbon with them (as organic debris) or not (as preformed nutrients).

The mechanism outlined in the previous paragraph has often been called the "biological pump" because inorganic carbon and nutrients are continuously removed from the surface layer, falling to the depths due to gravity. Some proposed explanations for the difference in atmospheric  $\text{CO}_2$  during an ice age ( $\sim 200$  ppm) and an interglacial period ( $\sim 280$  ppm) are based on hypotheses about glacial-interglacial differences in the effectiveness of the biological pump and different nutrient distributions in the oceans. The oceans must have been involved because they are the largest of the mobile carbon reservoirs, and the time scale of ice ages is tens of thousands of years. There is ample time for the atmosphere and oceans to arrive at some form of steady state or equilibrium. In many of these hypotheses, special attention has been given to high latitudes because we know that in today's oceans those are the places in which nutrients are not close to zero at the surface.

Several mechanisms have been postulated as potential causes of shifts in preformed nutrients. Knox and McElroy (1984) explored in a simple ocean model how the effi-

ciency of nutrient utilization, driven by secular changes in the insolation at high latitudes, could alter the  $\text{CO}_2$  content of the atmosphere. Sarmiento and Toggweiler (1984) considered both changes in high latitude productivity and in the rate of thermohaline overturning in the oceans. A simultaneous increase in productivity and a decrease in the rate of overturning would reinforce each other because organisms are given more time to decrease the surface nutrient concentrations. Siegenthaler and Wenk (1984) stress the importance of the rate of mixing of deep water with cold, high-latitude surface waters. An attractive feature of all the above mechanisms is that they could alter atmospheric  $\text{CO}_2$  at a fast enough rate to explain the observed rapid variations. The ice core record suggests that changes of the atmospheric  $\text{CO}_2$  content took place at sustained rates of up to  $5 \times 10^{15}$  mol C per century. Faster increases may have occurred for short periods, but are not visible at the resolution of the ice record. Another common feature of these hypotheses is that they predict very low oxygen concentrations for deep water during glacial times, which should have led to widespread anoxia. There is no evidence in the sediments that this actually occurred, casting considerable doubt on the likelihood of the above mechanisms.

Mangini and collaborators proposed that rapid outgassing of  $\text{CO}_2$  from the oceans could have been triggered by an intensification of deep water formation at the beginning of a warm period. This would bring  $\text{O}_2$  to the oxygen-poor deep waters causing the oxidation of soluble  $\text{Mn}^{2+}\text{CO}_3^{2-}$  to insoluble  $\text{Mn}^{4+}\text{O}_2$ , which then deposits in the sediments and releases  $\text{HCO}_3^-$  and  $\text{H}^+$ . As a result, the  $\text{CO}_3^{2-}$  concentration would drop and the partial pressure of  $\text{CO}_2(\text{aq})$  would rise. Some evidence for such occurrences has been found in deep sea sediment cores and Mn crusts (Mangini et al., 1991).

Another hypothesis not involving the biological pump was presented by Opdyke and Walker (1992). They noted that most of the present  $\text{CaCO}_3$  deposition takes place on coral reefs and in shallow waters generally and that it is occurring at a rate ( $\sim 2.0 \times 10^{13}$  mol/yr) higher than its long-term average during the Pleistocene period ( $\sim 0.8 \times 10^{13}$  mol/yr). Their hypothesis is that during interglacial warm periods sea level is higher, so that carbonate precipitation can occur on the continental shelves. During glacial intervals sea level is low, and the carbonate deposits are exposed and eroded. The average deposition over a full glacial cycle can then be close to the long-term Pleistocene average. The net reaction for this process has already been given in Eq. (12.1). The driving force is sea level, and therefore climate, with atmospheric  $\text{CO}_2$  responding. The hypothesis would imply an (asymmetric) sawtooth-like history of atmospheric  $\text{CO}_2$  due to short interglacials separated by much longer glacial intervals. A look at the ice core record of  $\text{CO}_2$  faintly suggests that such a pattern might indeed be present.

Recently, Archer and Maier-Reimer (1994) proposed yet another intriguing hypothesis for the cause of the glacial-interglacial  $\text{CO}_2$  changes. We have seen at the beginning of this chapter that only a small fraction of the calcite reaching the sediments survives dissolution. The oceans are self-regulating with respect to the calcite flux. All deep waters are corrosive to calcite. If the calcium content of the oceans rises, due to increased erosion on the land for instance, the carbonate ion content will rise and the  $\text{CO}_2$  partial pressure will drop (same as the two paragraphs above). The increased carbonate ion content implies that the deep waters are less corrosive to calcite or that the portion of the ocean floor bathed in waters that dissolve calcite decreases. Therefore, more of the calcite reaching the ocean floor will be preserved, increasing the calcium output until balance with the higher inputs of calcium is reestablished.



What Archer and Maier-Reimer observed is that the oxidation of organic carbon in ocean sediments promotes the dissolution of calcite, due to the addition of the respired  $\text{CO}_2$  to the sedimentary pore water. They employed a three-dimensional ocean model in steady state for the calcium fluxes. In their model the total preservation of calcite is regulated by two contributions, namely, "regular" dissolution in undersaturated waters and enhanced dissolution through respiratory  $\text{CO}_2$  in sediments rich in organic material. Therefore, if the ratio of organic carbon to calcite reaching the sediments increases, the steady-state contribution to calcite weathering of the "regular" process has to decrease, implying a higher carbonate ion concentration and a lower partial pressure of  $\text{CO}_2$ .

Any hypothesis trying to explain the glacial-interglacial  $\text{CO}_2$  changes leads to a number of other consequences that should have left their signature in the sedimentary record. Examples are the  $^{13}\text{C}/^{12}\text{C}$  ratio, the cadmium content as a proxy record of nutrient concentrations, the types of organisms buried, and the preservation record of  $\text{CaCO}_3$ . The precise and detailed time history of the  $\text{CO}_2$  change in the ice cores relative to the timing of the climate change is also an important piece of the evidence. The evidence is still confusing at this time, and no completely satisfactory explanation has yet been advanced.

## THE PRESENT

There is no doubt that the current increase in atmospheric  $\text{CO}_2$  is mainly due to the burning of fossil fuels. During the early 1990s,  $0.5 \times 10^{15}$  mol was injected into the atmosphere annually (Marland and Boden, 1991). This is an order of magnitude larger than any imbalance between the mobile C reservoirs inferred from the ice core record, although it must be kept in mind that the slow process of air capture in the ice has produced a smoothing of the record (Raynaud et al., 1993). Also, the present level of atmospheric  $\text{CO}_2$ , about 360 parts per million in 1995, is much higher than at any time during the last several hundred thousand years, and it appeared suddenly during this century, coincident with the rapid rise of fossil fuel consumption.

The isotopic evidence is also consistent with fossil fuels.  $^{14}\text{C}/\text{C}$  ratios were lowered from the 19th century until 1950 when atmospheric testing of nuclear bombs injected a large amount of  $^{14}\text{C}$ . Fossil fuels contain no  $^{14}\text{C}$ , in contrast to other conceivable sources of atmospheric  $\text{CO}_2$  such as biomass or ocean carbon.  $^{13}\text{C}/^{12}\text{C}$  ratios are similarly being lowered, with the trend continuing to the present, which proves that the source of carbon has to be depleted in  $^{13}\text{C}$ . This would have to be either fossil fuels or contemporary organic carbon. The photosynthetic process discriminates slightly against the assimilation of  $^{13}\text{C}$  relative to  $^{12}\text{C}$ . As a result, organic matter has a lower  $^{13}\text{C}/^{12}\text{C}$  ratio than atmospheric  $\text{CO}_2$ . Fossil fuels have the same low isotopic  $^{13}\text{C}/^{12}\text{C}$  signature, having been derived from organic matter. (The same applies to kerogen, which plays an important role in the carbon balance on long geological timescales.) It appears likely from the detailed recent time history of  $\text{CO}_2$  and  $^{13}\text{C}/^{12}\text{C}$  that during the second half of the 19th century and the first half of the 20th century there was appreciable loss of carbon, up to  $0.1 \times 10^{15}$  mol/yr, from terrestrial ecosystems and soils to the atmosphere (Enting and Pearman, 1987), whereas at present the observations indicate that the biosphere has to act globally as a net sink of C (Francey et al., 1995; Ciais et al., 1995).

Further evidence for the present (im)balance of sources and sinks of the global carbon cycle comes from the spatial distribution of  $\text{CO}_2$  in the atmosphere. Its mixing ratio is higher in the Northern Hemisphere than in the Southern Hemisphere. The atmosphere is stirred quite vigorously by winds, and the average transport time from one hemisphere to the other is about one year. The higher concentration in the Northern Hemisphere is being actively maintained by a distribution of sources and sinks; the Northern Hemisphere has stronger sources than sinks and the Southern Hemisphere has stronger sinks. Ninety percent of fossil fuel combustion takes place in the Northern Hemisphere.

However, when a numerical model of the atmosphere with properly calibrated transport is used to calculate the north-south gradient of  $\text{CO}_2$  resulting solely from the burning of fossil fuels, the calculated gradient is much larger than what is observed. Therefore, there must be sinks of  $\text{CO}_2$  in the Northern Hemisphere that partially compensate for the fossil fuel source. Based on observations of the north-south gradient of the  $^{13}\text{C}/^{12}\text{C}$  ratio, Keeling et al. (1989) concluded that the sink had to be mostly in the northern oceans. Tans et al. (1990) studied observations of the difference of the partial pressure of  $\text{CO}_2$  in the ocean surface and the atmosphere, which is the thermodynamic driving force of any net flux between those reservoirs. They concluded that the difference was insufficient to sustain a large northern oceanic sink. Therefore, they hypothesized that there has to be substantial  $\text{CO}_2$  uptake in forests at temperate latitudes.

It has been demonstrated in many different experiments under controlled conditions that increased  $\text{CO}_2$  is generally beneficial to plant growth (see, for instance, Allen et al., 1987). The increased productivity may result in more standing biomass above and below ground and can also lead to increasing amounts of organic matter in soils. It is, however, very difficult to measure this directly because of the tremendous heterogeneity of ecosystems and microclimates. Furthermore, there are other anthropogenic influences that could either counteract or enhance any effects of increased  $\text{CO}_2$  in different areas. Examples are increased concentrations of  $\text{O}_3$ , acid rain, fertilization by low amounts of nitrate deposition, and so on. From an experimental viewpoint the effect on whole ecosystems over a decade or longer is unknown (Mooney et al., 1991). Additional, longer-term processes such as species competition would have to be taken into account. An assessment of net carbon uptake by forest ecosystems based on recent national and regional studies of carbon inventories, carbon fluxes, and land-use statistics concluded that deforestation at low latitudes is still causing emissions of  $0.13(\pm 0.04) \times 10^{15}$  mol  $\text{CO}_2$   $\text{yr}^{-1}$  into the atmosphere, but that carbon storage in temperate forests is increasing by  $0.06(\pm 0.02) \times 10^{15}$  mol C  $\text{yr}^{-1}$  (Dixon et al., 1994). However, this last study did not consider any potential effects of  $\text{CO}_2$  fertilization.

## FUTURE SCENARIOS FOR $\text{CO}_2$

The odds are very strong that the combustion of fossil fuels will continue to overwhelm other imbalances in the carbon cycle well into the next century. In 1990 the consumption of energy by 1.2 billion people in the developed world was  $9 \times 10^{12}$  W, while the other 4.1 billion people together used  $4.5 \times 10^{12}$  W. Suppose that the developed world manages to lower, through increased conservation and efficiency, its per capita con-



sumption of energy every year by 2% so that in 2025 it would be half of the 1990 number. Then that part of the world would still consume  $5.3 \times 10^{12}$  W in the year 2025 if the population increased to 1.4 billion. In the same time the number of people in the less developed countries might have grown to 6.9 billion, assuming a growth rate of 1.5% per year. If we also assume that their economic well-being improves and that, as a result, they will buy more energy at an increase rate of 2% per year, their total consumption would be  $15 \times 10^{12}$  W in 2025. Global energy consumption would then have increased by 50% compared to 1990, while per capita consumption in the developed countries would still be almost twice that in less developed countries.

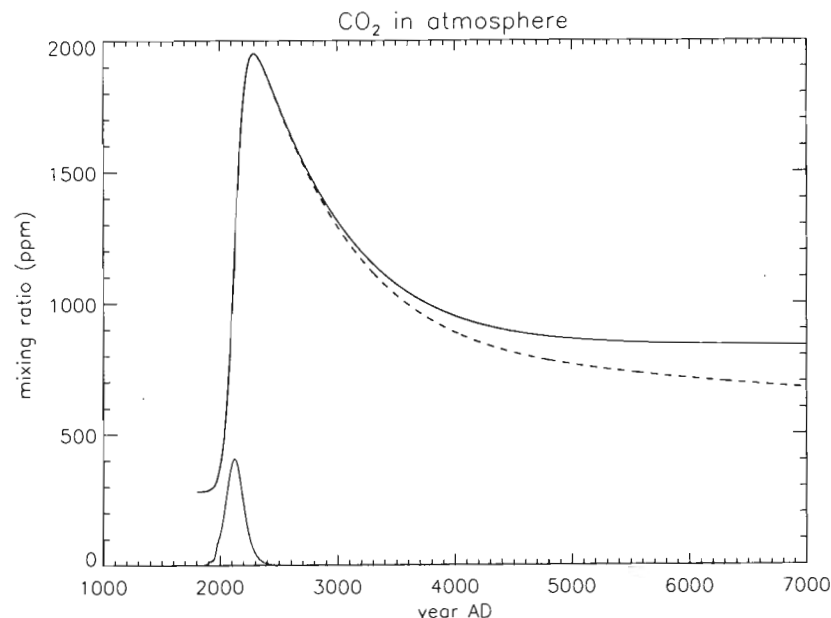
In other words, there is ample room for substantial further increases in energy use, and it would be highly desirable as well, in view of the existing great inequities in the use of global natural resources. With current technology, most of the increased energy demand will be met by the burning of coal, oil, and natural gas. Even if an alternative energy source would be economically competitive at this moment, it would still take several decades of investment and replacement of energy infrastructure before fossil fuel burning would cease to be our major source of energy.

In discussing future CO<sub>2</sub> scenarios we will initially neglect the role of the terrestrial biosphere. Without performing any detailed model calculations, a few general observations can then be made, both about the transient effects during the next few centuries and about the long-term prospects. First the latter. The mixing time of the deep oceans is of the order of a thousand years. On that timescale the amount of CO<sub>2</sub> in the atmosphere will come to chemical equilibrium with the oceans (mediated by the biological pump; see the section on the ice ages), and even more slowly with the sediments underlying them.

The atmospheric level would then be determined by four factors: the total net amount added to the ocean-atmosphere system, the ocean's neutralizing capacity as determined by the concentrations of dissolved carbonate and borate ions, the effectiveness of the biological pump, and the amount of CaCO<sub>3</sub> in ocean bottom sediments that will be dissolved. For the long term it does not matter much whether it takes one century or five centuries to burn the fossil fuels—only the total amount burned is important. This result was already obtained by Keeling and Bacastow (1977) in an early study of the impact of industrial gas emissions on the atmosphere.

If we neglect the dissolution of sedimentary calcite on the ocean floor for the moment, a fraction of the CO<sub>2</sub> emitted would remain in the atmosphere "indefinitely," determined by equilibrium with the carbonate system in the oceans. At this time approximately 5% of the global fossil fuel resources have been consumed, and a fraction of about 15% will remain permanently in the atmosphere if there is no change in ocean calcium. This long-term airborne fraction would gradually increase from 15% to 75%, at which point the ocean's neutralizing capacity will have become exhausted. Current observations of the atmospheric CO<sub>2</sub> increase show that about half of the industrial emissions remain in the atmosphere. This number is higher than the long-term airborne fraction because the time is too short to reach equilibrium with deeper ocean waters, and the terrestrial biosphere also plays a role.

However, there will likely be an adjustment of the ocean's calcium content. Recall that the surface waters are supersaturated with respect to CaCO<sub>3</sub> mineral, but that the deep waters are not. We have seen that an increase in  $p\text{CO}_2$  will decrease  $\text{CO}_3^{2-}$ . Therefore, a greater portion of the seafloor than at present will be bathed in waters that are undersaturated. The fraction of the sea floor that was previously overlain with wa-



**Figure 12.4.** Long-term projection of atmospheric CO<sub>2</sub> with a five-box model of the carbon cycle similar to Keeling and Bacastow (1977). The five reservoirs are the atmosphere, ocean surface waters, the deep oceans, living biomass, and soil carbon. It is assumed that all recoverable fossil fuel reserves are burned ( $400 \times 10^{15}$  mol C) in a temporal pattern as indicated (not to scale) on the bottom axis, with an initial increase rate of 2% per year during the first decades of the 21st century. The solid curve results if it is assumed that the terrestrial biosphere does not absorb or lose carbon, that the biological pump (see main text) remains as today, and that there is no calcite dissolution of deep ocean sediments. For the dashed curve, calcite dissolution does take place until the present product of  $[\text{CO}_3^{2-}]$  and  $[\text{Ca}^{2+}]$  in deep water is restored, with a time constant of 1000 years.

ters supersaturated with respect to CaCO<sub>3</sub>, but not any longer, becomes susceptible to calcite dissolution. This will have the effect of lowering the partial pressure of CO<sub>2</sub> [see reaction (12.1)]. There are some uncertainties regarding the kinetics of this process in real-life bottom mud.

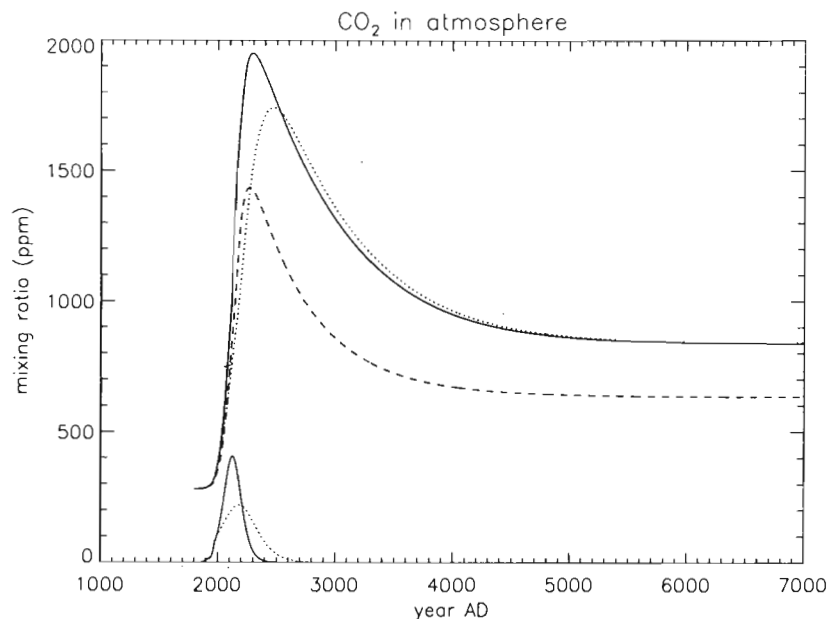
A possible time course of these events is sketched in Figure 12.4. The solid line assumes the burning of "all" fossil fuel reserves and no calcite dissolution, and the ocean-atmosphere system reaches a new equilibrium with "permanently" enhanced levels of CO<sub>2</sub>. If we assume, on the other hand, that calcite dissolution is affected and we restore the calcium balance between inputs and outputs on a timescale of 1000 years (by requiring the product of  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  in deep waters to be restored to present values on that time scale), we obtain the dashed curve. The atmospheric response to calcite dissolution is slow because there are several delays: The enhanced CO<sub>2</sub> has to reach deeper waters first, the deep water calcium balance has to adjust, and then the deep water signal has to reach the atmosphere again.

Thus, we can expect that the CO<sub>2</sub> generated from the burning of fossil fuels will—slowly, over thousands of years—cause a greater amount of Ca to be mobilized in the oceans, which will lower the  $p\text{CO}_2$  of the atmosphere. A new quasi-steady state develops, in which the supply of calcium to the oceans equals the loss and in which the

amounts of mobile carbon and mobile calcium are above their preanthropogenic levels. Left to itself, the atmosphere–ocean system will ultimately return to preindustrial conditions through silicate weathering (reaction (12.2)) and through the burial of carbon in reduced form, as in reaction (12.3), and as it was initially in fossil fuel deposits. This, however, will take millions of years.

The calcite dissolution process has no influence on the CO<sub>2</sub> transient expected during the coming centuries. If all the fossil fuel reserves are burned over the next few centuries, the atmospheric CO<sub>2</sub> concentration will go through a transient which could reach maximum levels of five to ten times the preindustrial concentration. How rapidly the transient will rise, and how high the maximum will be, depends sensitively on the rate of fossil fuel consumption relative to the rate of deep sea mixing, as well as on what happens with land plants and soils.

A possible course of events is shown in Figure 12.5. The solid line is the same as in Figure 12.4, whereas the dotted line projects the atmospheric concentrations if the same total amount of fossil fuels is burned more slowly. If the CO<sub>2</sub> transient goes near the high end of the possible range, the CO<sub>3</sub><sup>2-</sup> concentrations of surface waters will drop low enough that they may become undersaturated with respect to CaCO<sub>3</sub> (Figure 12.2). For calcite this will happen at  $p\text{CO}_2 \approx 2650 \mu\text{atm}$ ; and for aragonite, which is



**Figure 12.5.** Additional long-term scenarios of atmospheric CO<sub>2</sub>. The solid curve is the same as in Figure 12.4. All curves assume no change in the effectiveness of the biological pump and no dissolution of deep sea calcite sediments. The dotted curve is different from the solid curve only in the initial rate of increase of fossil fuel burning, 1% per year during the first half of the 21st century (as indicated on the bottom axis), with the total amount burned as in Figure 12.4,  $400 \times 10^{15}$  mol C. For the dashed curve the fossil fuel consumption pattern is the same as for the solid curve, but the global productivity of terrestrial ecosystems is assumed to respond to increased CO<sub>2</sub> in a way similar to Michaelis–Menten kinetics (Allen et al., 1987). Respiration remains proportional to total biomass. These assumptions lead to continued storage of carbon in biomass above today's amounts as long as atmospheric CO<sub>2</sub> remains higher than today.

the other form of crystalline CaCO<sub>3</sub> but about twice as soluble, it will occur at  $p\text{CO}_2 \approx 1360 \mu\text{atm}$ . (The relative abundance of aragonite is only a few percent, however). This could mean a serious threat to the existence of many shell-forming organisms, but it would also put a cap on the maximum atmospheric CO<sub>2</sub> increase.

Thus far the terrestrial biosphere has been left out of our discussion of the future course of anthropogenic CO<sub>2</sub> because it represents one of the more uncertain facets of the problem. Gain or loss of carbon in terrestrial ecosystems will, respectively, decrease or increase the net amount of CO<sub>2</sub> added to the atmosphere–ocean system as described in the previous paragraphs. The total amount of carbon stored in standing biomass has been estimated as  $70 \times 10^{15}$  mol and organic C in soils as  $120 \times 10^{15}$  mol (Schlesinger, 1991). If these amounts could be doubled as a result of fertilization by increased CO<sub>2</sub>, or possibly due to human manipulation, a sizable fraction of all the fossil fuel CO<sub>2</sub> would be absorbed. A scenario such as this is illustrated as the dashed line in Figure 12.5.

This possibility was first seriously debated by Revelle and Munk (1977). Stimulation of C uptake by the biosphere has an immediate effect on the CO<sub>2</sub> transient we are in, as well as potentially on the long-term increase of atmospheric CO<sub>2</sub>. As discussed above, the atmospheric and oceanic evidence strongly suggests that the biosphere currently absorbs CO<sub>2</sub>. Thus it is clear that the biosphere exerts an important influence on today's CO<sub>2</sub> levels, and is likely to continue to do so in the future. An important difference between carbon storage in the deep oceans versus trees and soils is that the latter form of storage remains close to the atmosphere and would appear to be vulnerable to climate change and to continuing human intervention.

The doubling mentioned above is entirely speculative. No credible predictions have been made, but ecologists tend to expect the opposite for the near future, namely that the adjustment of ecosystems to climate change and other perturbations will cause a loss of carbon stored, at least temporarily, which would exacerbate the atmospheric CO<sub>2</sub> problem (Woodwell et al., 1994).

Finally, another crucial uncertainty with regard to the future course of atmospheric CO<sub>2</sub> needs mention. The scenarios pictured in Figures 12.4 and 12.5 assume that the oceanic biological pump keeps working as it does today. If the effectiveness of the pump in lowering the surface values of nutrients and  $\Sigma\text{C}$  decreases, the atmospheric CO<sub>2</sub> level will go up further. The effectiveness of the pump depends on the interplay of primary photosynthesis/grazing with ocean circulation/mixing, all of which are likely to be affected by global climate change. The effectiveness of the biological pump could also increase, but it is close to its maximum efficiency (zero nutrient levels in the surface ocean) at the present time.

## CONCLUSION

The limitations on the uptake of industrially produced CO<sub>2</sub> are seen clearly when the earth system is considered in a geological perspective. Industrial carbon essentially does not leave the ocean–atmosphere–biosphere system for many thousands of years. How much of the extra carbon resides as CO<sub>2</sub> in the atmosphere depends on several processes that govern the partitioning between these three reservoirs. Important are the chemical equilibria in the oceans, how the terrestrial biosphere responds to direct hu-

man perturbations and to global environmental change, and the oceanic biological pump. Of these, only ocean carbon chemistry is well understood. The biological pump is likely to undergo change, but it is currently not apparent that we would have a measure of control over it.

The only obvious controls we have over the level of atmospheric CO<sub>2</sub> are the rate and the total amount of fossil fuel combustion. The deliberate manipulation of terrestrial biological processes could be an effective control process if we knew how to muster it. Our current understanding of long-term biological sources and sinks of carbon is grossly insufficient for that purpose, however. Therefore, it is extremely likely that the earth's climate will be under enhanced greenhouse forcing for thousands of years as a result of the utilization of fossil fuels as our main source of energy. There will also be a more transient period, starting during the era of fossil fuel burning and continuing for several centuries afterwards, during which the enhanced greenhouse forcing due to CO<sub>2</sub> will be roughly twice as strong as during the long aftermath.

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