

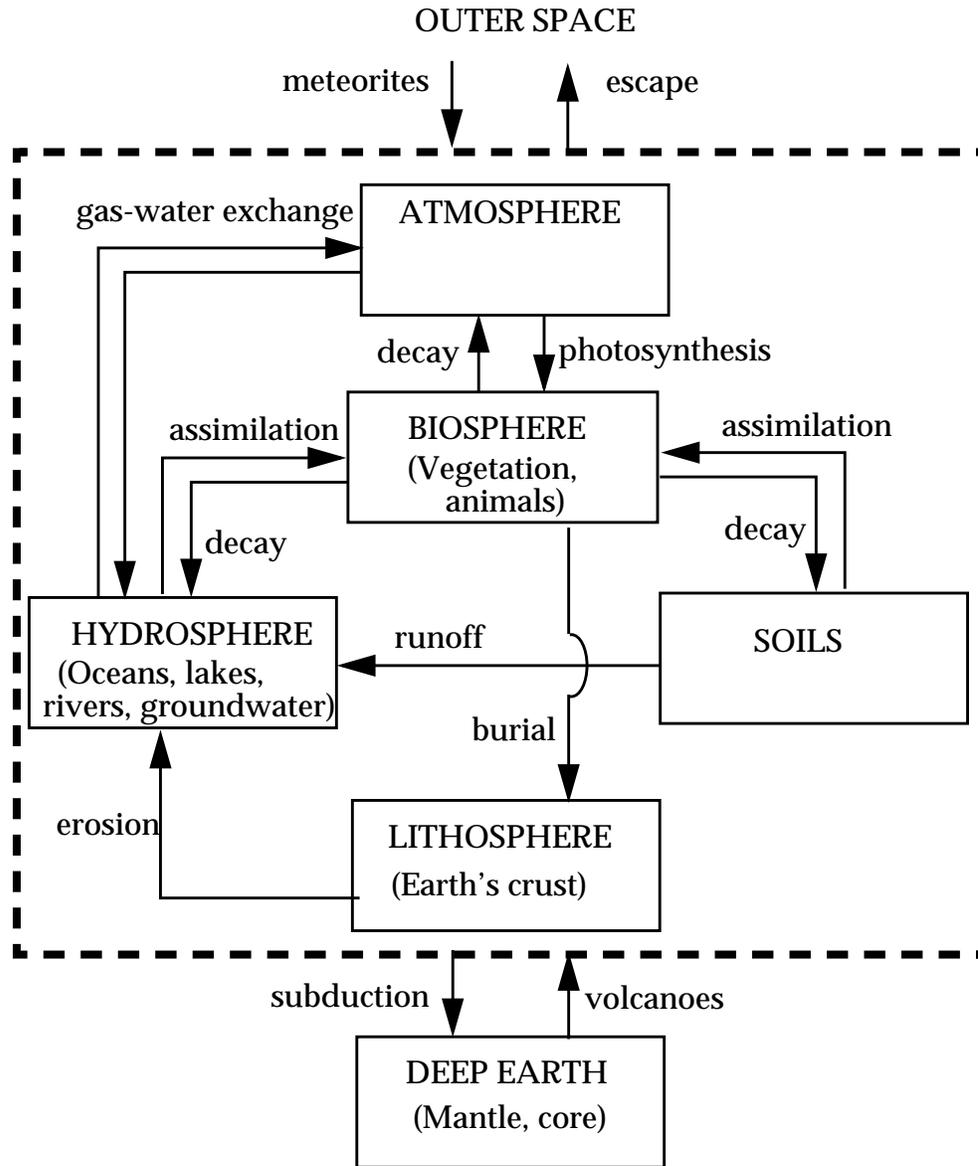
## **CHAPTER 6. GEOCHEMICAL CYCLES**

So far we have viewed the concentrations of species in the atmosphere as controlled by emissions, transport, chemistry, and deposition. From an Earth system perspective, however, the composition of the atmosphere is ultimately controlled by the exchange of elements between the different reservoirs of the Earth. In the present chapter we examine atmospheric composition from this broader perspective, and focus more specifically on the biogeochemical factors that regulate the atmospheric abundances of  $N_2$ ,  $O_2$ , and  $CO_2$ .

### **6.1 GEOCHEMICAL CYCLING OF ELEMENTS**

The Earth system (including the Earth and its atmosphere) is an assemblage of atoms of the 92 natural elements. Almost all of these atoms have been present in the Earth system since the formation of the Earth 4.5 billion years ago by gravitational accretion of a cloud of gases and dust. Subsequent inputs of material from extraterrestrial sources such as meteorites have been relatively unimportant. Escape of atoms to outer space is prevented by gravity except for the lightest atoms (H, He), and even for those it is extremely slow (problem 6. 3). Thus the assemblage of atoms composing the Earth system has been roughly conserved since the origin of the Earth. The atoms, in the form of various molecules, migrate continually between the different reservoirs of the Earth system (Figure 6-1). *Geochemical cycling* refers to the flow of elements through the Earth's reservoirs; the term underlines the cyclical nature of the flow in a closed system.

The standard approach to describing the geochemical cycling of elements between the Earth's reservoirs is with the box models that we introduced previously in chapter 3. In these models we view individual reservoirs as "boxes", each containing a certain mass (or "inventory") of the chemical element of interest. The exchange of the element between two reservoirs is represented as a flow between the corresponding boxes. The same concepts developed in chapter 3 for atmospheric box models can be applied to geochemical box models. The reservoirs may be those shown in Figure 6-1 or some other ensemble. Depending on the problem at hand, one may want a more detailed categorization (for example, separating the hydrosphere into oceans and freshwater), or a less detailed categorization (for example, combining the biosphere and soil reservoirs).



**Figure 6-1 Reservoirs of the Earth system, and examples of processes exchanging elements between reservoirs. The dashed line encloses the "surface reservoirs".**

Most of the mass of the Earth system is present in the deep Earth, but this material is largely isolated from the *surface reservoirs*: atmosphere, hydrosphere, biosphere, soil, and lithosphere (Figure 6-1). Communication between the deep Earth and the surface reservoirs takes place by volcanism and by subduction of tectonic plates, processes that are extremely slow compared to those cycling elements between the surface reservoirs. The abundance of an element in the atmosphere can therefore be viewed as determined

by two separable factors: (a) the total abundance of the element in the ensemble of surface reservoirs, and (b) the partitioning of the element between the atmosphere and the other surface reservoirs.

## 6.2 EARLY EVOLUTION OF THE ATMOSPHERE

Supply of elements to the surface reservoirs was set in the earliest stages of Earth's history when the crust formed and volcanic outgassing transferred material from the deep Earth to the atmosphere. The early Earth was a highly volcanic place due to energy released in its interior by radioactive decay and gravitational accretion. Present-day observations of volcanic plumes offer an indication of the composition of the outgassed material. It was mostly H<sub>2</sub>O (~95%), CO<sub>2</sub>, N<sub>2</sub>, and sulfur gases. There was no O<sub>2</sub>; volcanic plumes contain only trace amounts of O<sub>2</sub>, and examination of the oldest rocks on Earth show that they formed in a reducing atmosphere devoid of O<sub>2</sub>. The outgassed water precipitated to form the oceans. Carbon dioxide and the sulfur gases then dissolved in the oceans, leaving N<sub>2</sub> as the dominant gas in the atmosphere. The presence of liquid water allowed the development of living organisms (self-replicating organic molecules). About 3.5 billion years ago, some organisms developed the capacity to convert CO<sub>2</sub> to organic carbon by photosynthesis. This process released O<sub>2</sub> which gradually accumulated in the atmosphere, reaching its current atmospheric concentration about 400 million years ago.

It is instructive to compare the evolution of the Earth's atmosphere to that of its neighbor planets Venus and Mars. All three planets presumably formed with similar assemblages of elements but their present-day atmospheric compositions are vastly different (Table 6-1). Venus has an atmosphere ~100 times thicker than that of Earth and consisting mostly of CO<sub>2</sub>. Because of the greater proximity of Venus to the Sun, the temperature of the early Venus was too high for the outgassed water to condense and form oceans (see section 7.5 for further discussion). As a result CO<sub>2</sub> remained in the atmosphere. Water vapor in Venus's upper atmosphere photolyzed to produce H atoms that escaped the planet's gravitational field, and the O atoms left behind were removed by oxidation of rocks on the surface of the planet. This mechanism is thought to explain the low H<sub>2</sub>O concentrations in the Venusian atmosphere. On Earth, by contrast, the atmosphere contains only 10<sup>-5</sup> of all water in the surface reservoirs (the bulk is in the oceans) so that loss of water to outer space is extremely slow and is

compensated by evaporation from the oceans.

The atmosphere of Mars is much thinner than that of the Earth and consists principally of CO<sub>2</sub>. The smaller size and hence weaker gravitational field of Mars allows easier escape of H atoms to outer space, and also allows escape of N atoms produced in the upper atmosphere by photolysis of N<sub>2</sub> (escape of N atoms is negligible on Earth). Although the mixing ratio of CO<sub>2</sub> in the Martian atmosphere is high, its total abundance is in fact extremely low compared to that of Venus. It is thought that CO<sub>2</sub> has been removed from the Martian atmosphere by surface reactions producing carbonate rocks.

**Table 6-1 Atmospheres of Venus, Earth, and Mars**

	Venus	Earth	Mars
Radius (km)	6100	6400	3400
Mass of planet (10 <sup>23</sup> kg)	49	60	6.4
Acceleration of gravity (m s <sup>-2</sup> )	8.9	9.8	3.7
Surface temperature (K)	730	290	220
Surface pressure (Pa)	9.1x10 <sup>6</sup>	1.0x10 <sup>5</sup>	7x10 <sup>2</sup>
Atmospheric composition (mol/mol)			
CO <sub>2</sub>	0.96	4x10 <sup>-4</sup>	0.95
N <sub>2</sub>	3.4x10 <sup>-2</sup>	0.78	2.7x10 <sup>-2</sup>
O <sub>2</sub>	6.9x10 <sup>-5</sup>	0.21	1.3x10 <sup>-3</sup>
H <sub>2</sub> O	3x10 <sup>-3</sup>	1x10 <sup>-2</sup>	3x10 <sup>-4</sup>

### 6.3 THE NITROGEN CYCLE

Nitrogen (as N<sub>2</sub>) accounts for 78% of air on a molar basis. Figure 6-2 presents a summary of major processes involved in the cycling of nitrogen between surface reservoirs. Nitrogen is an essential component of the biosphere (think of the amino acids) and the atmosphere is an obvious source for this nitrogen. Conversion of

the highly stable  $N_2$  molecule to biologically available nitrogen, a process called *fixation*, is difficult. It is achieved in ecosystems by specialized symbiotic bacteria which can reduce atmospheric  $N_2$  to ammonia ( $NH_3$ ). The  $NH_3$  is assimilated as organic nitrogen by the bacteria or by their host plants, which may in turn be consumed by animals. Eventually these organisms excrete the nitrogen or die; the organic nitrogen is eaten by bacteria and mineralized to ammonium ( $NH_4^+$ ), which may then be assimilated by other organisms.

Bacteria may also use  $NH_4^+$  as a source of energy by oxidizing it to nitrite ( $NO_2^-$ ) and on to nitrate ( $NO_3^-$ ). This process is called *nitrification* and requires the presence of oxygen (*aerobic* conditions). Nitrate is highly mobile in soil and is readily assimilated by plant and bacteria, providing another route for formation of organic nitrogen. Under conditions when  $O_2$  is depleted in water or soil (*anaerobic* conditions), bacteria may use  $NO_3^-$  as an alternate oxidant to convert organic carbon to  $CO_2$ . This process, called *denitrification*, converts  $NO_3^-$  to  $N_2$  and thus returns nitrogen from the biosphere to the atmosphere.

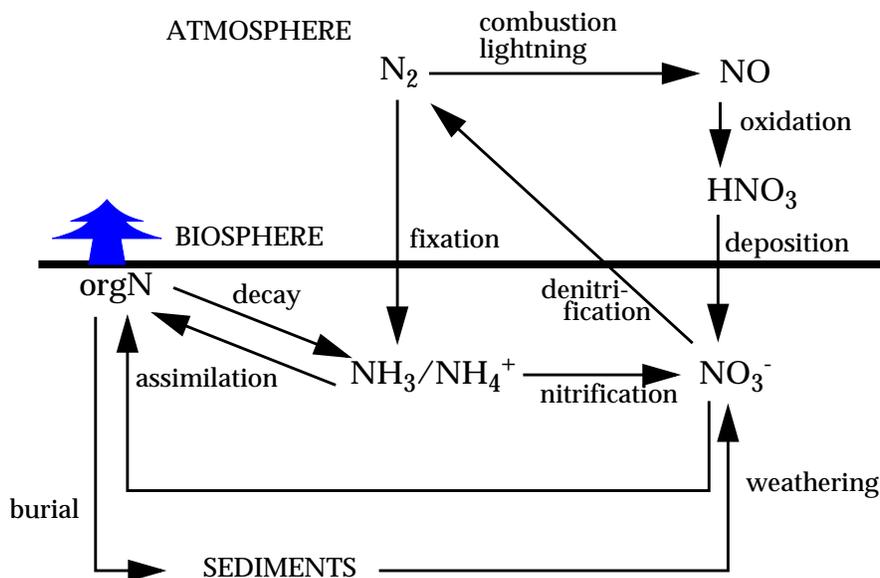


Figure 6-2 The nitrogen cycle: major processes

An additional pathway for fixing atmospheric  $N_2$  is by high-temperature oxidation of  $N_2$  to NO in the atmosphere during

combustion or lightning, followed by atmospheric oxidation of NO to  $\text{HNO}_3$  which is water-soluble and scavenged by rain. In industrial regions of the world, the fixation of  $\text{N}_2$  in combustion engines provides a source of nitrogen to the biosphere that is much larger than natural  $\text{N}_2$  fixation, resulting in an unintentional fertilization effect.

Transfer of nitrogen to the lithosphere takes place by burial of dead organisms (including their nitrogen) in the bottom of the ocean. These dead organisms are then incorporated into sedimentary rock. Eventually the sedimentary rock is brought up to the surface of the continents and eroded, liberating the nitrogen and allowing its return to the biosphere. This process closes the nitrogen cycle in the surface reservoirs.

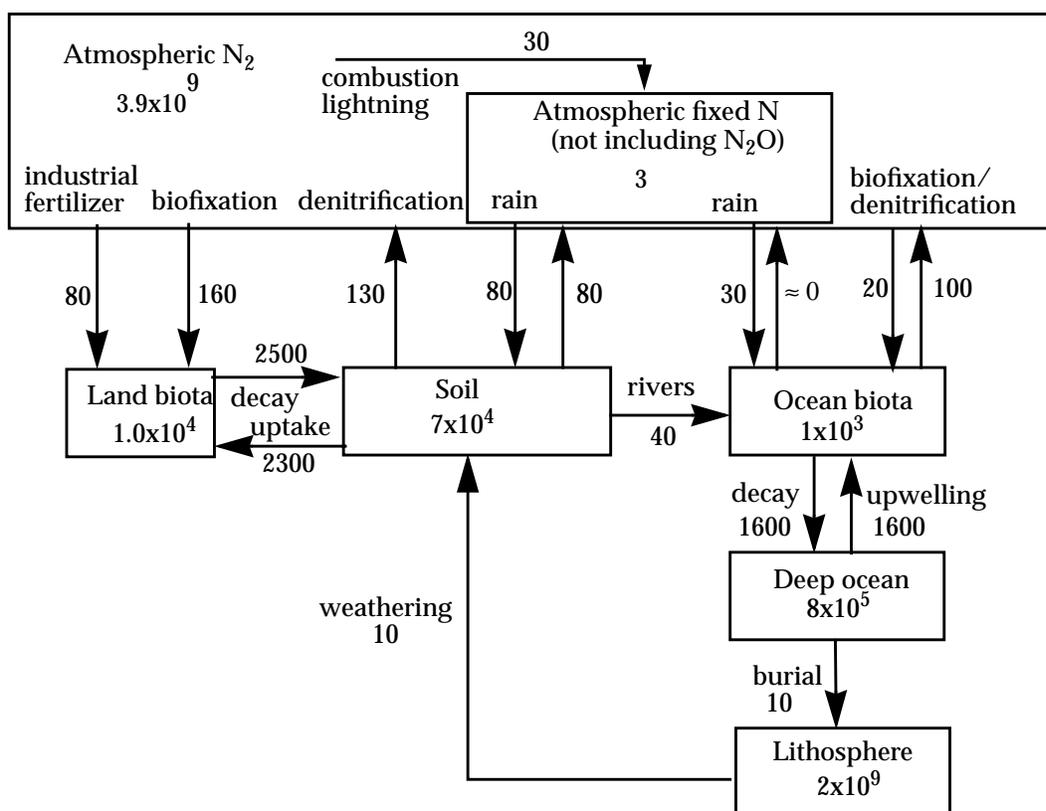


Figure 6-3 Box model of the nitrogen cycle. Inventories are in Tg N and flows are in  $\text{Tg N yr}^{-1}$ . A teragram (Tg) is  $1 \times 10^{12}$  g.

A box model of the nitrogen cycle is presented in Figure 6-3. This model gives estimates of total nitrogen inventories in the major surface reservoirs and of the flows of nitrogen between different reservoirs. The most accurate by far of all these numbers is the mass  $m_{\text{N}_2}$  of nitrogen in air, which follows from the uniform mixing

ratio  $C_{N_2} = 0.78$  mol/mol:

$$m_{N_2} = C_{N_2} \frac{M_{N_2}}{M_{air}} m_{air} = 0.78 \cdot \frac{28}{29} \cdot 5.2 \times 10^{21} = 3.9 \times 10^9 \text{Tg} \quad (6.1)$$

where 1 teragram (Tg) =  $1 \times 10^{12}$  g. Other inventories and flows are far more uncertain. They are generally derived by global extrapolation of measurements made in a limited number of environments. The flows given in Figure 6-3 are such that all reservoirs are at steady state, although the steady-state assumption is not necessarily valid for the longer-lived reservoirs.

An important observation from Figure 6-3 is that human activity has greatly increased the rate of transfer of  $N_2$  to the biosphere (industrial manufacture of fertilizer, fossil fuel combustion, nitrogen-fixing crops), resulting possibly in a global fertilization of the biosphere. This issue is explored in problem 6. 5.

We focus here on the factors controlling the abundance of atmospheric  $N_2$ . A first point to be made from Figure 6-3 is that the atmosphere contains most of the nitrogen present in the surface reservoirs of the Earth. This preferential partitioning of nitrogen in the atmosphere is unique among elements except for the noble gases, and reflects the stability of the  $N_2$  molecule. Based on the inventories in Figure 6-3, the  $N_2$  content of the atmosphere could not possibly be more than 50% higher than today even if all the nitrogen in the lithosphere were transferred to the atmosphere. It appears then that the  $N_2$  concentration in the atmosphere is constrained to a large degree by the total amount of nitrogen present in the surface reservoirs of the Earth, that is, by the amount of nitrogen outgassed from the Earth's interior over 4 billion years ago.

What about the possibility of depleting atmospheric  $N_2$  by transferring the nitrogen to the other surface reservoirs? Imagine a scenario where denitrification were to shut off while  $N_2$  fixation still operated. Under this scenario, atmospheric  $N_2$  would be eventually depleted by uptake of nitrogen by the biosphere, transfer of this nitrogen to soils, and eventual runoff to the ocean where the nitrogen could accumulate as  $NO_3^-$ . The time scale over which such a depletion could conceivably take place is defined by the lifetime of  $N_2$  against fixation. With the numbers in Figure 6-3, we find a lifetime of  $3.9 \times 10^9 / (80 + 160 + 30 + 20) = 13$  million years. In view of this long lifetime, we can safely conclude that human

activity will never affect atmospheric  $N_2$  levels significantly. On a geological time scale, however, we see that denitrification is critical for maintaining atmospheric  $N_2$  even though it might seem a costly loss of an essential nutrient by the biosphere. If  $N_2$  were depleted from the atmosphere, thus shutting off nitrogen fixation, life on Earth outside of the oceans would be greatly restricted.

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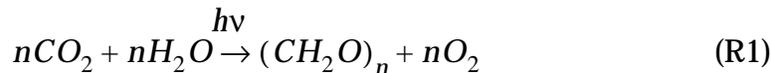
**Exercise 6-1** From the box model in Figure 6-3, how many times does a nitrogen atom cycle between atmospheric  $N_2$  and the oceans before it is transferred to the lithosphere?

*Answer.* The probability that a nitrogen atom in the ocean will be transferred to the lithosphere (burial;  $10 \text{ Tg N yr}^{-1}$ ) rather than to the atmosphere (denitrification in the oceans;  $100 \text{ Tg N yr}^{-1}$ ) is  $10/(10+100) = 0.09$ . A nitrogen atom cycles on average 10 times between atmospheric  $N_2$  and the oceans before it is transferred to the lithosphere.

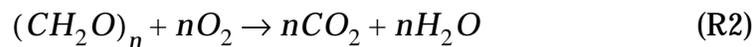
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## 6.4 THE OXYGEN CYCLE

Atmospheric oxygen is produced by photosynthesis, which we represent stoichiometrically as



where  $(CH_2O)_n$  is a stoichiometric approximation for the composition of biomass material. This source of  $O_2$  is balanced by loss of  $O_2$  from the oxidation of biomass, including respiration by living biomass and microbial decay of dead biomass:



The cycling of oxygen by reactions (R1) and (R2) is coupled to that of carbon, as illustrated in Figure 6-4.

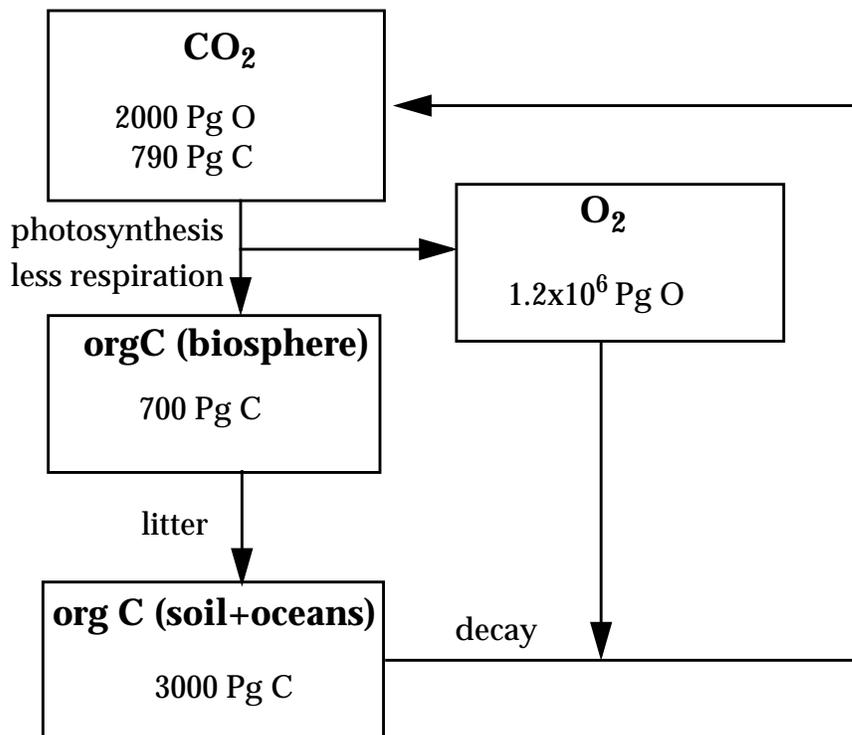


Figure 6-4 Cycling of O<sub>2</sub> with the biosphere; orgC is organic carbon. A petagram (Pg) is  $1 \times 10^{15}$  g.

To assess the potential for this cycle to regulate atmospheric O<sub>2</sub> levels, we need to determine inventories for the different reservoirs of Figure 6-4: O<sub>2</sub>, CO<sub>2</sub>, and orgC. Applying equation (6.1) to O<sub>2</sub> and CO<sub>2</sub> with  $C_{O_2} = 0.21$  v/v and  $C_{CO_2} = 365 \times 10^{-6}$  v/v (Table 1-1), we obtain  $m_{O_2} = 1.2 \times 10^6$  Pg O and  $m_{CO_2} = 2000$  Pg O = 790 Pg C (1 petagram (Pg) =  $1 \times 10^{15}$  g). The total amount of organic carbon in the biosphere/soil/ocean system is estimated to be about 4000 Pg C (700 Pg C in the terrestrial biosphere, 2000 Pg C in soil, and 1000 Pg C in the oceans).

Simple comparison of these inventories tells us that cycling with the biosphere cannot control the abundance of O<sub>2</sub> in the atmosphere, because the inventory of O<sub>2</sub> is considerably larger than that of either CO<sub>2</sub> or organic carbon. If photosynthesis were for some reason to stop, oxidation of the entire organic carbon reservoir would consume less than 1% of O<sub>2</sub> presently in the atmosphere and there would be no further O<sub>2</sub> loss (since there would be no organic carbon left to be oxidized). Conversely, if respiration and decay were to stop, conversion of all atmospheric

CO<sub>2</sub> to O<sub>2</sub> by photosynthesis would increase O<sub>2</sub> levels by only 0.2%.

What, then, controls atmospheric oxygen? The next place to look is the lithosphere. Rock material brought to the surface in a reduced state is weathered (oxidized) by atmospheric O<sub>2</sub>. Of most importance is sedimentary organic carbon, which gets oxidized to CO<sub>2</sub>, and FeS<sub>2</sub> (pyrite), which gets oxidized to Fe<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The total amounts of organic carbon and pyrite in sedimentary rocks are estimated to be 1.2x10<sup>7</sup> Pg C and 5x10<sup>6</sup> Pg S, respectively. These amounts are sufficiently large that weathering of rocks would eventually deplete atmospheric O<sub>2</sub> if not compensated by an oxygen source. The turnover time of sedimentary rock, that is the time required for sedimentary rock formed at the bottom of the ocean to be brought up to the surface, is of the order of 100 million years. The corresponding weathering rates are 0.12 Pg C yr<sup>-1</sup> for rock organic carbon and 0.05 Pg S yr<sup>-1</sup> for pyrite. Each atom of carbon consumes one O<sub>2</sub> molecule, while each atom of sulfur as FeS<sub>2</sub> consumes 19/8 O<sub>2</sub> molecules. The resulting loss of O<sub>2</sub> is 0.4 Pg O yr<sup>-1</sup>, which yields a lifetime for O<sub>2</sub> of 3 million years. On a time scale of several million years, changes in the rate of sediment uplift could conceivably alter the levels of O<sub>2</sub> in the atmosphere.

This cycling of O<sub>2</sub> with the lithosphere is illustrated in Figure 6-5. Atmospheric O<sub>2</sub> is produced during the formation of reduced sedimentary material, and the consumption of O<sub>2</sub> by weathering when this sediment is eventually brought up to the surface and oxidized balances the O<sub>2</sub> source from sediment formation. Fossil records show that atmospheric O<sub>2</sub> levels have in fact not changed significantly over the past 400 million years, a time scale much longer than the lifetime of O<sub>2</sub> against loss by weathering. The constancy of atmospheric O<sub>2</sub> suggests that there must be stabilizing factors in the O<sub>2</sub>-lithosphere cycle but these are still poorly understood. One stabilizing factor is the relative rate of oxidation vs. burial of organic carbon in the ocean. If sediment weathering were to increase for some reason, drawing down atmospheric O<sub>2</sub>, then more of the marine organic carbon would be buried (because of slower oxidation), which would increase the source of O<sub>2</sub> and act as a negative feedback.

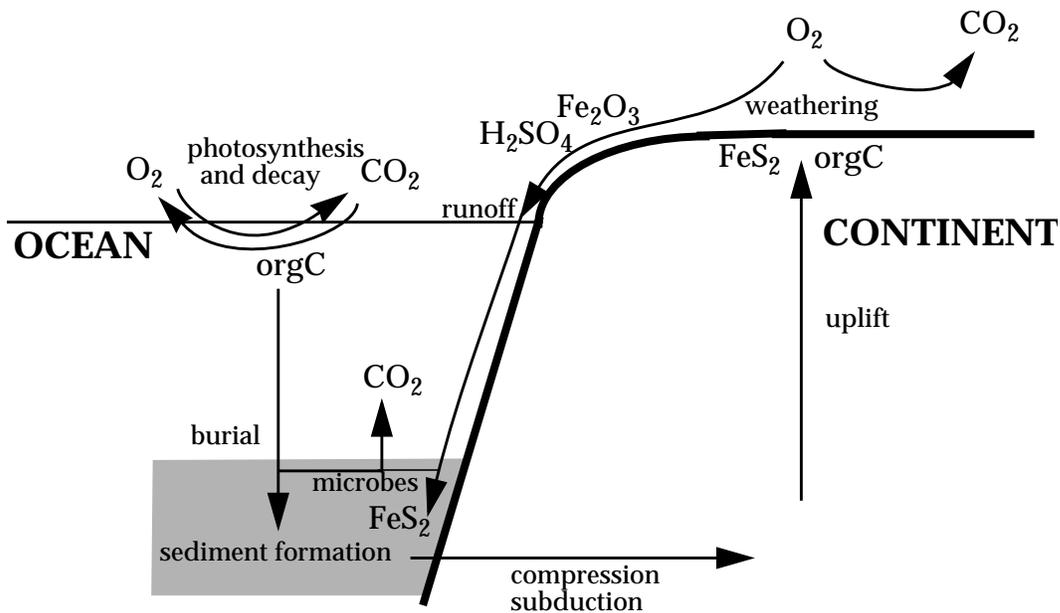


Figure 6-5 Cycling of  $O_2$  with the lithosphere. The microbial reduction of  $Fe_2O_3$  and  $H_2SO_4$  to  $FeS_2$  on the ocean floor is discussed in problem 6. 1.

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**Exercise 6-2** The present-day sediments contain  $1.2 \times 10^7$  Pg C of organic carbon. How much  $O_2$  was produced in the formation of these sediments? Compare to the amount of  $O_2$  presently in the atmosphere. How do you explain the difference?

*Answer.* One molecule of  $O_2$  is produced for each organic C atom incorporated in the sediments. Therefore, formation of the present-day sediments was associated with the production of  $(32/12) \times 1.2 \times 10^7 = 3.2 \times 10^7$  Pg  $O_2$ . That is 30 times more than the  $1.2 \times 10^6$  Pg  $O_2$  presently in the atmosphere! Where did the rest of the oxygen go? Examination of Figure 6-5 indicates as possible reservoirs  $SO_4^{2-}$  and  $Fe_2O_3$ . Indeed, global inventories show that these reservoirs can account for the missing oxygen.

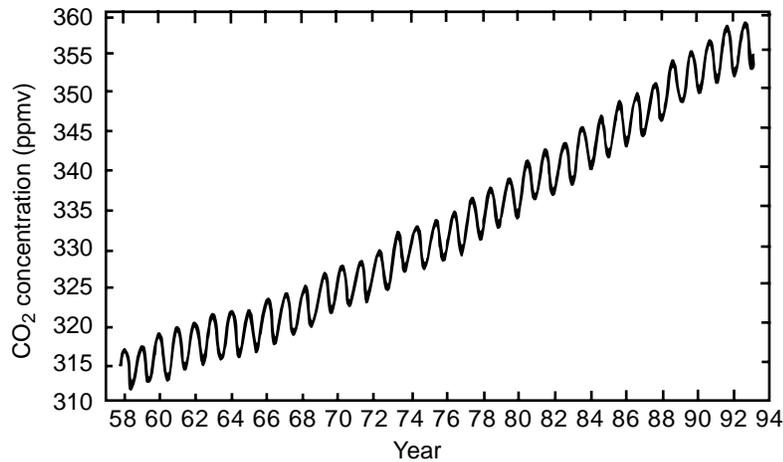
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## 6.5 THE CARBON CYCLE

### 6.5.1 Mass balance of atmospheric $CO_2$

Ice core measurements show that atmospheric concentrations of  $CO_2$  have increased from 280 ppmv in pre-industrial times to 365

ppmv today. Continuous atmospheric measurements made since 1958 at Mauna Loa Observatory in Hawaii demonstrate the secular increase of CO<sub>2</sub> (Figure 6-6). Superimposed on the secular trend is a seasonal oscillation (winter maximum, summer minimum) that reflects the uptake of CO<sub>2</sub> by vegetation during the growing season, balanced by the net release of CO<sub>2</sub> from the biosphere in fall due to microbial decay.



**Figure 6-6** Trend in atmospheric CO<sub>2</sub> measured since 1958 at Mauna Loa Observatory, Hawaii.

The current global rate of increase of atmospheric CO<sub>2</sub> is 1.8 ppmv yr<sup>-1</sup>, corresponding to 4.0 Pg C yr<sup>-1</sup>. This increase is due mostly to fossil fuel combustion. When fuel is burned, almost all of the carbon in the fuel is oxidized to CO<sub>2</sub> and emitted to the atmosphere. We can use worldwide fuel use statistics to estimate the corresponding CO<sub>2</sub> emission, presently 6.0 ± 0.5 Pg C yr<sup>-1</sup>. Another significant source of CO<sub>2</sub> is deforestation in the tropics; based on rates of agricultural encroachment documented by satellite observations, it is estimated that this source amounts to 1.6 ± 1.0 Pg C yr<sup>-1</sup>.

Substituting the above numbers in a global mass balance equation for atmospheric CO<sub>2</sub>,

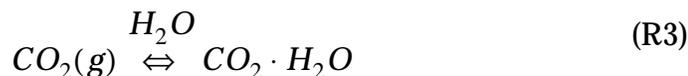
$$\frac{dm_{CO_2}}{dt} = \sum \text{sources} - \sum \text{sinks} \quad (6.2)$$

we find  $\Sigma \text{sinks} = 6.0 + 1.6 - 4.0 = 3.6 \text{ Pg C yr}^{-1}$ . Only half of the CO<sub>2</sub> emitted by fossil fuel combustion and deforestation actually

accumulates in the atmosphere. The other half is transferred to other geochemical reservoirs (oceans, biosphere, and soils). We need to understand the factors controlling these sinks in order to predict future trends in atmospheric  $\text{CO}_2$  and assess their implications for climate change. A sink to the biosphere would mean that fossil fuel  $\text{CO}_2$  has a fertilizing effect, with possibly important ecological consequences.

### 6.5.2 Carbonate chemistry in the ocean

Carbon dioxide dissolves in the ocean to form  $\text{CO}_2\cdot\text{H}_2\text{O}$  (carbonic acid), a weak diacid which dissociates to  $\text{HCO}_3^-$  (bicarbonate) and  $\text{CO}_3^{2-}$  (carbonate). This process is described by the chemical equilibria:



with equilibrium constants  $K_{\text{H}} = [\text{CO}_2\cdot\text{H}_2\text{O}]/P_{\text{CO}_2} = 3\times 10^{-2} \text{ M atm}^{-1}$ ,  $K_1 = [\text{HCO}_3^-][\text{H}^+]/[\text{CO}_2\cdot\text{H}_2\text{O}] = 9\times 10^{-7} \text{ M}$  ( $pK_1 = 6.1$ ), and  $K_2 = [\text{CO}_3^{2-}][\text{H}^+]/[\text{HCO}_3^-] = 7\times 10^{-10} \text{ M}$  ( $pK_2 = 9.2$ ). Here  $K_{\text{H}}$  is the *Henry's law constant* describing the equilibrium of  $\text{CO}_2$  between the gas phase and water;  $K_1$  and  $K_2$  are the first and second *acid dissociation constants* of  $\text{CO}_2\cdot\text{H}_2\text{O}$ . The values given here for the constants are typical of seawater and take into account ionic strength corrections, complex formation, and the effects of temperature and pressure.

The average pH of the ocean is 8.2 (problem 6. 6). The alkalinity of the ocean is maintained by weathering of basic rocks ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ) at the surface of the continents, followed by river runoff of the dissolved ions to the ocean. Since  $pK_1 < \text{pH} < pK_2$ , most of the  $\text{CO}_2$  dissolved in the ocean is in the form of  $\text{HCO}_3^-$  (Figure 6-7).

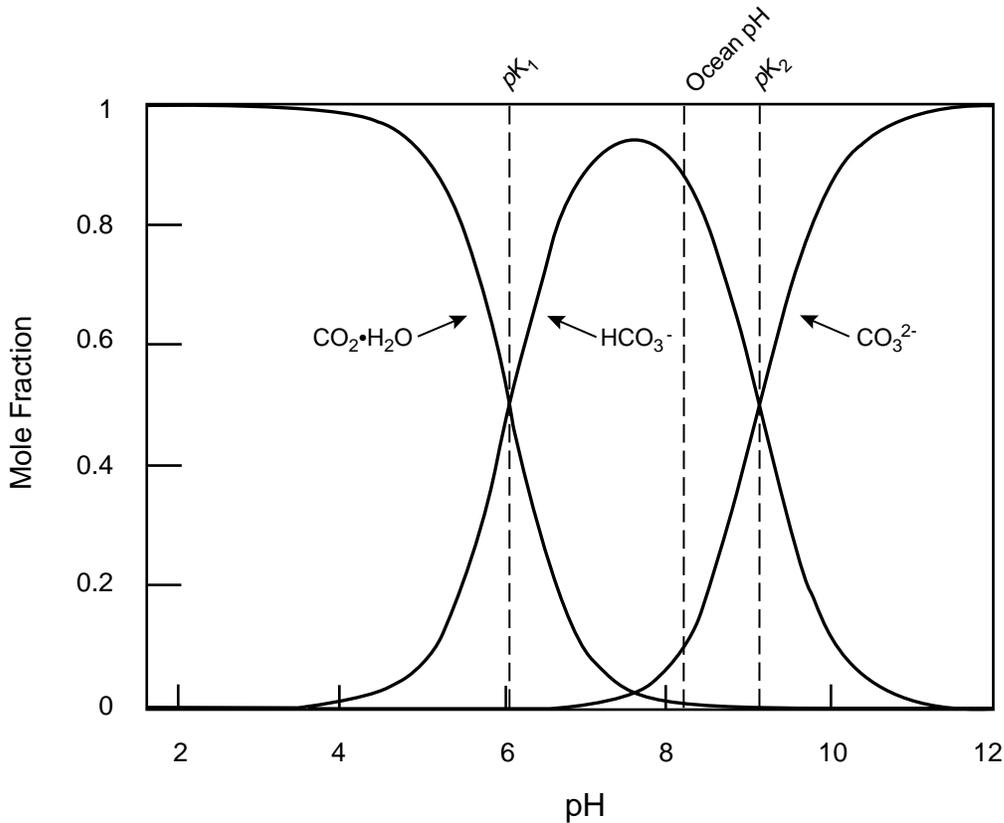


Figure 6-7 Speciation of total carbonate  $\text{CO}_2(\text{aq})$  in seawater vs. pH

Let  $F$  represent the atmospheric fraction of  $\text{CO}_2$  in the atmosphere-ocean system:

$$F = \frac{N_{\text{CO}_2(\text{g})}}{N_{\text{CO}_2(\text{g})} + N_{\text{CO}_2(\text{aq})}} \quad (6.3)$$

where  $N_{\text{CO}_2(\text{g})}$  is the total number of moles of  $\text{CO}_2$  in the atmosphere and  $N_{\text{CO}_2(\text{aq})}$  is the total number of moles of  $\text{CO}_2$  dissolved in the ocean as  $\text{CO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ :

$$[\text{CO}_2(\text{aq})] = [\text{CO}_2 \cdot \text{H}_2\text{O}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (6.4)$$

The concentrations of  $\text{CO}_2$  in the atmosphere and in the ocean are related by equilibria (R3)- (R5):

$$[\text{CO}_2(\text{aq})] = K_H P_{\text{CO}_2} \left( 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} \right) \quad (6.5)$$

and  $N_{CO_2(g)}$  is related to  $P_{CO_2}$  at sea level by (1.11) (Dalton's law):

$$N_{CO_2(g)} = C_{CO_2} N_a = \frac{P_{CO_2}}{P} N_a \quad (6.6)$$

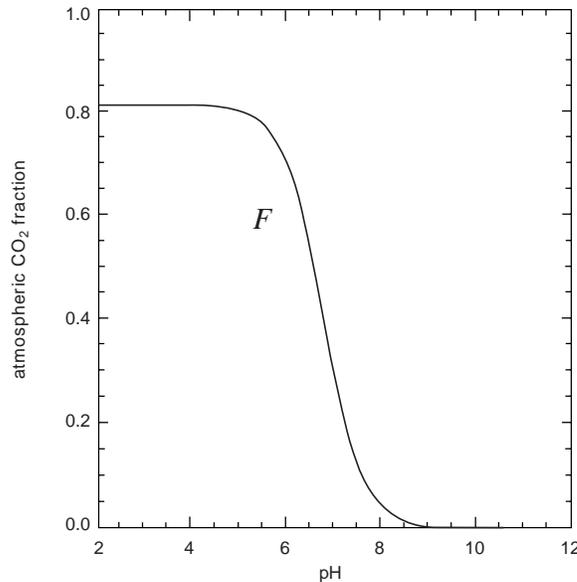
where  $P = 1$  atm is the atmospheric pressure at sea level and  $N_a = 1.8 \times 10^{20}$  moles is the total number of moles of air. Assuming the whole ocean to be in equilibrium with the atmosphere, we relate  $N_{CO_2(aq)}$  to  $[CO_2(aq)]$  in (6.5) by the total volume  $V_{oc} = 1.4 \times 10^{18}$  m<sup>3</sup> of the ocean:

$$N_{CO_2(aq)} = V_{oc} [CO_2(aq)] \quad (6.7)$$

Substituting into equation (6.3), we obtain for  $F$ :

$$F = \frac{1}{1 + \frac{V_{oc} P K_H}{N_a} \left( 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right)} \quad (6.8)$$

For an ocean pH of 8.2 and other numerical values given above we calculate  $F = 0.03$ . At equilibrium, almost all of  $CO_2$  is dissolved in the ocean; only 3% is in the atmosphere. The value of  $F$  is extremely sensitive to pH, as illustrated by Figure 6-8. In the absence of oceanic alkalinity, most of the  $CO_2$  would partition into the atmosphere.

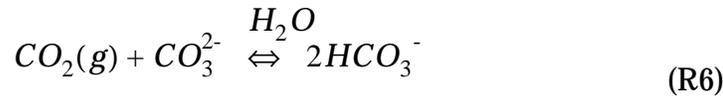


**Figure 6-8** pH dependence of the atmospheric fraction  $F$  of  $CO_2$  at equilibrium in the atmosphere-ocean system (equation (6.8)).

### 6.5.3 Uptake of CO<sub>2</sub> by the ocean

One might infer from the above calculation that CO<sub>2</sub> injected to the atmosphere will eventually be incorporated almost entirely into the oceans, with only 3% remaining in the atmosphere. However, such an inference is flawed because it ignores the acidification of the ocean resulting from added CO<sub>2</sub>. As atmospheric CO<sub>2</sub> increases, [H<sup>+</sup>] in (6.8) increases and hence  $F$  increases; this effect is a *positive feedback* to increases in atmospheric CO<sub>2</sub>.

The acidification of the ocean due to added CO<sub>2</sub> is buffered by the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> equilibrium; H<sup>+</sup> released to the ocean when CO<sub>2</sub>(g) dissolves and dissociates to HCO<sub>3</sub><sup>-</sup> (equilibrium (R4)) is consumed by conversion of CO<sub>3</sub><sup>2-</sup> to HCO<sub>3</sub><sup>-</sup> (equilibrium (R5)). This buffer effect is represented by the overall equilibrium



which is obtained by combining equilibria (R3)-(R5) with (R5) taken in the reverse direction. The equilibrium constant for (R6) is  $K' = [\text{HCO}_3^-]^2 / P_{\text{CO}_2}[\text{CO}_3^{2-}] = K_H K_1 / K_2$ . Uptake of CO<sub>2</sub>(g) is thus facilitated by the available pool of CO<sub>3</sub><sup>2-</sup> ions. Note that the buffer effect does not mean that the pH of the ocean remains constant when CO<sub>2</sub> increases; it means only that changes in pH are dampened.

To better pose our problem, let us consider a situation where we add  $dN$  moles of CO<sub>2</sub> to the atmosphere. We wish to know, when equilibrium is finally reached with the ocean, what fraction  $f$  of the added CO<sub>2</sub> remains in the atmosphere:

$$f = \frac{dN_{\text{CO}_2(\text{g})}}{dN} = \frac{dN_{\text{CO}_2(\text{g})}}{dN_{\text{CO}_2(\text{g})} + dN_{\text{CO}_2(\text{aq})}} \quad (\text{6.9})$$

where  $dN_{\text{CO}_2(\text{g})}$  and  $dN_{\text{CO}_2(\text{aq})}$  are respectively the added number of moles to the atmospheric and oceanic reservoirs at equilibrium.

We relate  $dN_{\text{CO}_2(\text{g})}$  to the corresponding  $dP_{\text{CO}_2}$  using equation (6.6):

$$dN_{CO_2(g)} = \frac{N_a}{P} dP_{CO_2} \quad (6.10)$$

We also relate  $dN_{CO_2(aq)}$  to  $d[CO_2(aq)]$  using the volume of the ocean:

$$\begin{aligned} dN_{CO_2(aq)} &= V_{oc} d[CO_2(aq)] \\ &= V_{oc} (d[CO_2 \cdot H_2O] + d[HCO_3^-] + d[CO_3^{2-}]) \end{aligned} \quad (6.11)$$

Since the uptake of  $CO_2(g)$  by the ocean follows equilibrium (R6),  $d[CO_2 \cdot H_2O] \approx 0$  and  $d[HCO_3^-] \approx -2d[CO_3^{2-}]$ . Replacing into equation (6.11) we obtain

$$dN_{CO_2(aq)} = -V_{oc} d[CO_3^{2-}] \quad (6.12)$$

Replacing into (6.9) yields:

$$f = \frac{1}{1 - \frac{V_{oc} P d[CO_3^{2-}]}{N_a dP_{CO_2}}} \quad (6.13)$$

We now need a relation for  $d[CO_3^{2-}]/dP_{CO_2}$ . Again we use equilibrium (R6):

$$[HCO_3^-]^2 = K' P_{CO_2} [CO_3^{2-}] \quad (6.14)$$

and differentiate both sides:

$$2[HCO_3^-] d[HCO_3^-] = K' (P_{CO_2} d[CO_3^{2-}] + [CO_3^{2-}] dP_{CO_2}) \quad (6.15)$$

Replacing  $d[HCO_3^-] \approx -2d[CO_3^{2-}]$  and  $K' = K_H K_1 / K_2$  into (6.15) we obtain

$$\frac{[CO_3^{2-}]}{P_{CO_2}} dP_{CO_2} = - \left( 1 + \frac{4K_2}{[H^+]} \right) d[CO_3^{2-}] \quad (6.16)$$

To simplify notation we introduce  $\beta = 1 + 4K_2/[H^+] \approx 1.4$ ,

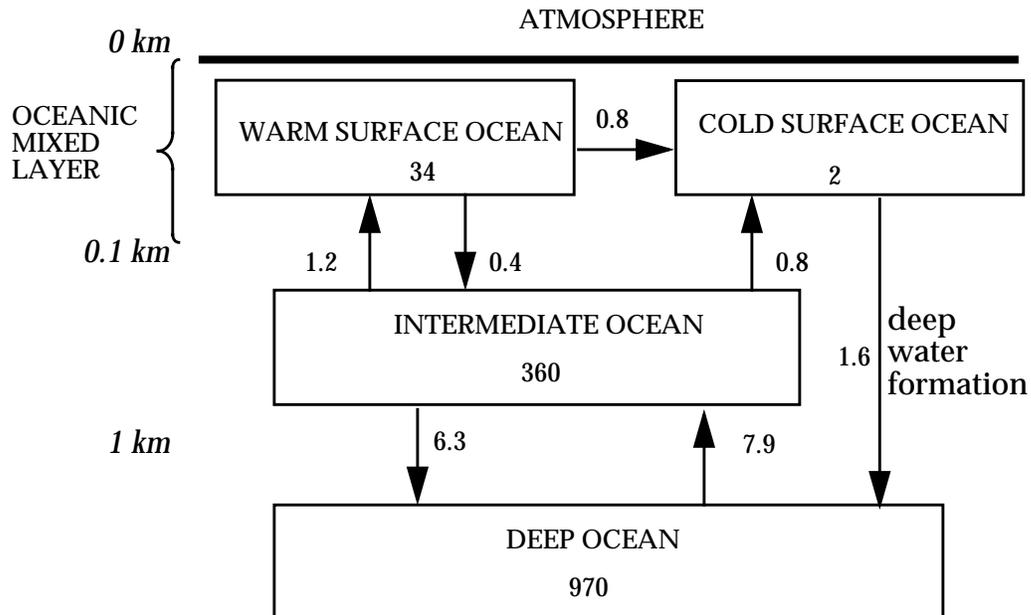
$$\frac{d[CO_3^{2-}]}{dP_{CO_2}} = \frac{-1[CO_3^{2-}]}{\beta P_{CO_2}} = \frac{-K_H K_1 K_2}{\beta [H^+]^2} \quad (6.17)$$

and finally replace into (6.13):

$$f = \frac{1}{1 + \frac{V_{oc} P K_H K_1 K_2}{N_a \beta [H^+]^2}} \quad (6.18)$$

Substituting numerical values into (6.18), including a pH of 8.2, we obtain  $f = 0.28$ . At equilibrium, 28% of  $CO_2$  emitted in the atmosphere remains in the atmosphere, and the rest is incorporated into the ocean. The large difference from the 3% value derived previously reflects the large positive feedback from acidification of the ocean by added  $CO_2$ .

The above calculation still exaggerates the uptake of  $CO_2$  by the ocean because it assumes the whole ocean to be in equilibrium with the atmosphere. This equilibrium is in fact not achieved because of the slow mixing of the ocean. Figure 6-9 shows a simple box model for the oceanic circulation.



**Figure 6-9** Box model for the circulation of water in the ocean. Inventories are in  $10^{15} \text{ m}^3$  and flows are in  $10^{15} \text{ m}^3 \text{ yr}^{-1}$ . Adapted from McElroy, M.B., *The Atmosphere: an Essential Component of the Global Life Support System*, Princeton University Press (in press).

As in the atmosphere, vertical mixing in the ocean is driven by buoyancy. The two factors determining buoyancy in the ocean are temperature and salinity. Sinking of water from the surface to the deep ocean (*deep water formation*) takes place in polar regions where the surface water is cold and salty, and hence heavy. In other regions the surface ocean is warmer than the water underneath, so that vertical mixing is suppressed. Some vertical mixing still takes place near the surface due to wind stress, resulting in an *oceanic mixed layer* extending to ~100 m depth and exchanging slowly with the deeper ocean. Residence times of water in the individual reservoirs of Figure 6-9 are 18 years for the oceanic mixed layer, 40 years for the intermediate ocean, and 120 years for the deep ocean. Equilibration of the whole ocean in response to a change in atmospheric CO<sub>2</sub> therefore takes place on a time scale of the order of 200 years.

This relatively long time scale for oceanic mixing implies that CO<sub>2</sub> released in the atmosphere by fossil fuel combustion over the past century has not had time to equilibrate with the whole ocean. Considering only uptake by the oceanic mixed layer ( $V = 3.6 \times 10^{16}$  m<sup>3</sup>) which is in rapid equilibrium with the atmosphere, we find  $f = 0.94$  from (6.18); the oceanic mixed layer can take up only 6% of fossil fuel CO<sub>2</sub> injected into the atmosphere. Since the residence time of water in the oceanic mixed layer is only 18 years, the actual uptake of fossil fuel CO<sub>2</sub> over the past century has been more efficient but is strongly determined by the rate of deep water formation.

An additional pathway for CO<sub>2</sub> uptake involves photosynthesis by phytoplankton. The organic carbon produced by phytoplankton moves up the food chain and about 90% is converted eventually to CO<sub>2</sub>(aq) by respiration and decay within the oceanic mixed layer. The 10% fraction that precipitates (fecal pellets, dead organisms) represents a *biological pump* transferring carbon to the deep ocean. The biological productivity of the surface ocean is limited in part by upwelling of nutrients such as nitrogen from the deep (Figure 6-3), so that the efficiency of the biological pump is again highly dependent on the vertical circulation of the ocean water. It is estimated that the biological pump transfers 7 Pg C yr<sup>-1</sup> to the deep ocean, as compared to 40 Pg C yr<sup>-1</sup> for CO<sub>2</sub>(aq) transported by deep water formation.

Taking into account all of the above processes, the best current

estimate from oceanic transport and chemistry models is that 30% of fossil fuel CO<sub>2</sub> emitted to the atmosphere is incorporated in the oceans. We saw in section 6.5.1 that only 50% of the emitted CO<sub>2</sub> actually remains in the atmosphere. That leaves a 20% missing sink. We now turn to uptake by the biosphere as a possible explanation for this missing sink.

#### 6.5.4 Uptake of CO<sub>2</sub> by the terrestrial biosphere

Cycling of atmospheric CO<sub>2</sub> with the biosphere involves processes of photosynthesis, respiration, and microbial decay, as discussed in section 6.4 and illustrated in Figure 6-4. It is difficult to distinguish experimentally between photosynthesis and respiration by plants, nor is this distinction very useful for our purpose. Ecologists define the *net primary productivity* (NPP) as the yearly average rate of photosynthesis minus the rate of respiration by all plants in an ecosystem. The NPP can be determined experimentally either by long-term measurement of the CO<sub>2</sub> flux to the ecosystem from a tower (section 4.4.2) or more crudely by monitoring the growth of vegetation in a selected plot. From these data, quantitative models can be developed that express the dependence of the NPP on environmental variables including ecosystem type, solar radiation, temperature, and water availability. Using such models one estimates a global terrestrial NPP of about 60 Pg C yr<sup>-1</sup>.

The lifetime of CO<sub>2</sub> against net uptake by terrestrial plants is:

$$\tau_{CO_2} = \frac{m_{CO_2}}{NPP} = 9 \text{ years} \quad (6.19)$$

which implies that atmospheric CO<sub>2</sub> responds quickly, on a time scale of a decade, to changes in NPP or in decay rates. It is now thought that increased NPP at middle and high latitudes of the northern hemisphere over the past century may be responsible for the 20% missing sink of CO<sub>2</sub> emitted by fossil fuel combustion (problem 6. 8). Part of this increase in NPP could be due to conversion of agricultural land to forest at northern midlatitudes, and part could be due to greater photosynthetic activity of boreal forests as a result of climate warming. The organic carbon added to the biosphere by the increased NPP would then accumulate in the soil. An unresolved issue is the degree to which fossil fuel CO<sub>2</sub> fertilizes the biosphere. Experiments done in chambers and outdoors under controlled conditions show that increasing CO<sub>2</sub> does stimulate plant growth. There are however other factors limiting NPP, including solar radiation and the supply of water

and nutrients, which prevent a first-order dependence of NPP on  $\text{CO}_2$ .

### 6.5.5 Box model of the carbon cycle

A summary of the processes described above is presented in Figure 6-10 in the form of a box model of the carbon cycle at equilibrium for preindustrial conditions. Uptake by the biosphere and by the oceans represent sinks of comparable magnitude for atmospheric  $\text{CO}_2$ , resulting in an atmospheric lifetime for  $\text{CO}_2$  of 5 years. On the basis of this short lifetime and the large sizes of the oceanic and terrestrial reservoirs, one might think that  $\text{CO}_2$  added to the atmosphere by fossil fuel combustion would be rapidly and efficiently incorporated in these reservoirs. However, as we have seen, uptake of added  $\text{CO}_2$  by the biosphere is subject to other factors limiting plant growth, and uptake of added  $\text{CO}_2$  by the ocean is limited by acidification and slow mixing of the ocean.

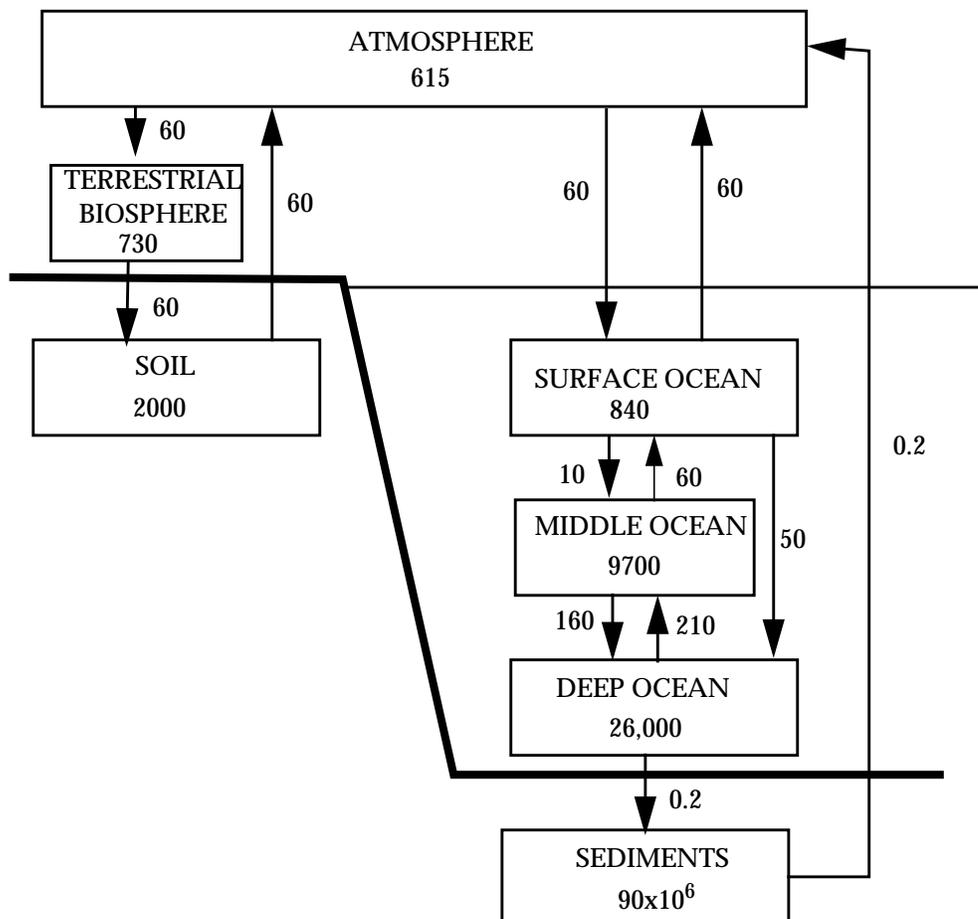


Figure 6-10 The preindustrial carbon cycle. Inventories are in Pg C and flows are in  $\text{Pg C yr}^{-1}$ . Adapted from McElroy, M.B., op.cit.

Even after full mixing of the ocean, which requires a few hundred years, a fraction  $f = 28\%$  of the added  $\text{CO}_2$  still remains in the atmosphere according to our simple calculation in section 6.5.3 (current research models give values in the range 20-30% for  $f$ ). On time scales of several thousand years, slow dissolution of  $\text{CaCO}_3$  from the ocean floor provides an additional source of alkalinity to the ocean, reducing  $f$  to about 7% (problem 6. 9). Ultimate removal of the  $\text{CO}_2$  added to the atmosphere by fossil fuel combustion requires transfer of oceanic carbon to the lithosphere by formation of sediments, thereby closing the carbon cycle. The time scale for this transfer is defined by the lifetime of carbon in the ensemble of atmospheric, biospheric, soil, and oceanic reservoirs; from Figure 6-10 we obtain a value of 170,000 years. We conclude that fossil fuel combustion induces a very long-term perturbation to the global carbon cycle.

*Further reading:*

**Intergovernmental Panel of Climate Change**, *Climate Change 1994*, Cambridge University Press, 1995. Carbon cycle.

**Morel, F.M.M., and J.G. Hering**, *Principles and Applications of Aquatic Chemistry*, Wiley, 1993. Ocean chemistry.

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