

CHAPTER 8

Recycling of the Elements

Carbon and Nutrient Cycles



Key Questions

- What determines how reservoirs (such as the atmospheric CO₂ reservoir) respond to imbalances in the flow of material to and from them?
- Which reservoirs and processes are important to the recycling of carbon and other essential nutrients in the Earth system?
- Do feedback mechanisms regulate the amount of atmospheric CO₂?
- How do nutrients limit biological productivity on Earth?

Chapter Overview

The recycling of the elements among the components of the Earth system is key to the continued functioning of Earth as a living planet. Although many elements are critical, none is more central to the workings of the Earth system than carbon. All life is based on carbon; gaseous carbon dioxide is an important greenhouse gas; the acidity of the ocean is regulated by carbon compounds; and the maintenance of an oxygen-rich atmosphere depends on the transfer of carbon to sedimentary rocks. To perform these functions, the *carbon cycle* involves a hierarchy of subcycles that operate on different time scales, ranging from decades (for the replenishment of CO₂ in the atmosphere) to hundreds of millions of years (for the recycling of carbon through sedimentary rocks and for the exchange of carbon within Earth's interior). Both biological and physical processes are involved in the recycling of carbon, and they are so closely intertwined that it becomes difficult to separate the two. In this chapter we trace the movement of carbon as it cycles through the Earth system and we develop additional systems theory notions of *steady state* and *residence time* along the way. We also discuss the *nutrient elements*, because the

rate of carbon recycling depends strongly on the rate of nutrient recycling.

SYSTEMS APPROACH TO THE CARBON CYCLE

Why is Earth the only planet in our solar system that supports life? The direct answer is that Earth is the only planet that has liquid water at its surface. (Jupiter's moon Europa may have water only a few kilometers beneath its icy surface.) But part of the reason Earth is able to maintain liquid water is that our planet has natural recycling systems for the elements essential for life, including carbon, nitrogen, phosphorus, and sulfur. These recycling systems are ultimately linked with the global process of plate tectonics, discussed in Chapter 7. The link between tectonic activity and the carbon cycle is important to the regulation of atmospheric CO₂ concentrations and thus to climate as well.

The winds and ocean currents discussed in Chapters 4 and 5 and the moving lithospheric plates discussed in Chapter 7 make up Earth's circulatory system: They transport energy and material to different parts of the Earth system where they are utilized in biological

and physical processes. This mixing of Earth's fluid and solid parts also helps accomplish an important task: the recycling of the elements. Essential elements are released to the **biosphere** (the part of Earth that supports life, including the oceans, atmosphere, land surface, and soils) as rocks weather, volcanoes erupt, and nitrogen is made available from the atmosphere by chemical transformations stimulated by lightning discharge. Compared with the rates of utilization by the biota, these releases are very slow; they would support only very low rates of biological activity were there not highly efficient nutrient recycling mechanisms. **Nutrients** are substances, normally obtained in the diet, that are essential to organisms. Nutrient elements are incorporated into living tissue during growth and rapidly returned to the soil or ocean on death. This cycle is repeated many times before the elements are lost from the biosphere, mostly as constituents of sedimentary rocks. The situation is much like our recycling of aluminum cans: Recycling substantially reduces our dependence on the extraction of aluminum from Earth and allows us to produce aluminum products much more rapidly. Similarly, element recycling within the biosphere allows for much higher rates of biological productivity.

A number of important recycling systems operate on Earth. We've already discussed the water cycle in Chapter 4. The cycles of the nutrient elements nitrogen and phosphorus

are discussed later in this chapter. The recycling of carbon is especially important: As a major constituent of the greenhouse gases carbon dioxide and methane, it affects not only biological productivity but Earth's climate as well. We focus on the carbon cycle in this chapter because of its overarching importance to the Earth system.

A Journey through the Terrestrial Organic Carbon Cycle

As an introduction to just one part of the global carbon cycle, imagine that we could follow the carbon atom of a CO_2 molecule as it cycled through the terrestrial (land-based) part of the cycle (Figure 8-1). The carbon in CO_2 is **inorganic carbon**—it is not associated with compounds formed by living organisms and it does not contain carbon-carbon or carbon-hydrogen bonds. After spending nearly a decade moving with the winds in the troposphere, the gaseous CO_2 molecule will have visited both the Northern and Southern hemispheres several times. Then one spring, during the annual greening of the Northern Hemisphere (Figure 8-2), the CO_2 molecule passes through a small opening in a leaf, the photosynthetic apparatus of a plant. Through a frenzy of collisions with other molecules and atoms, the oxygen atoms are ripped from the molecule while hydrogen, nitrogen, and other carbon atoms become

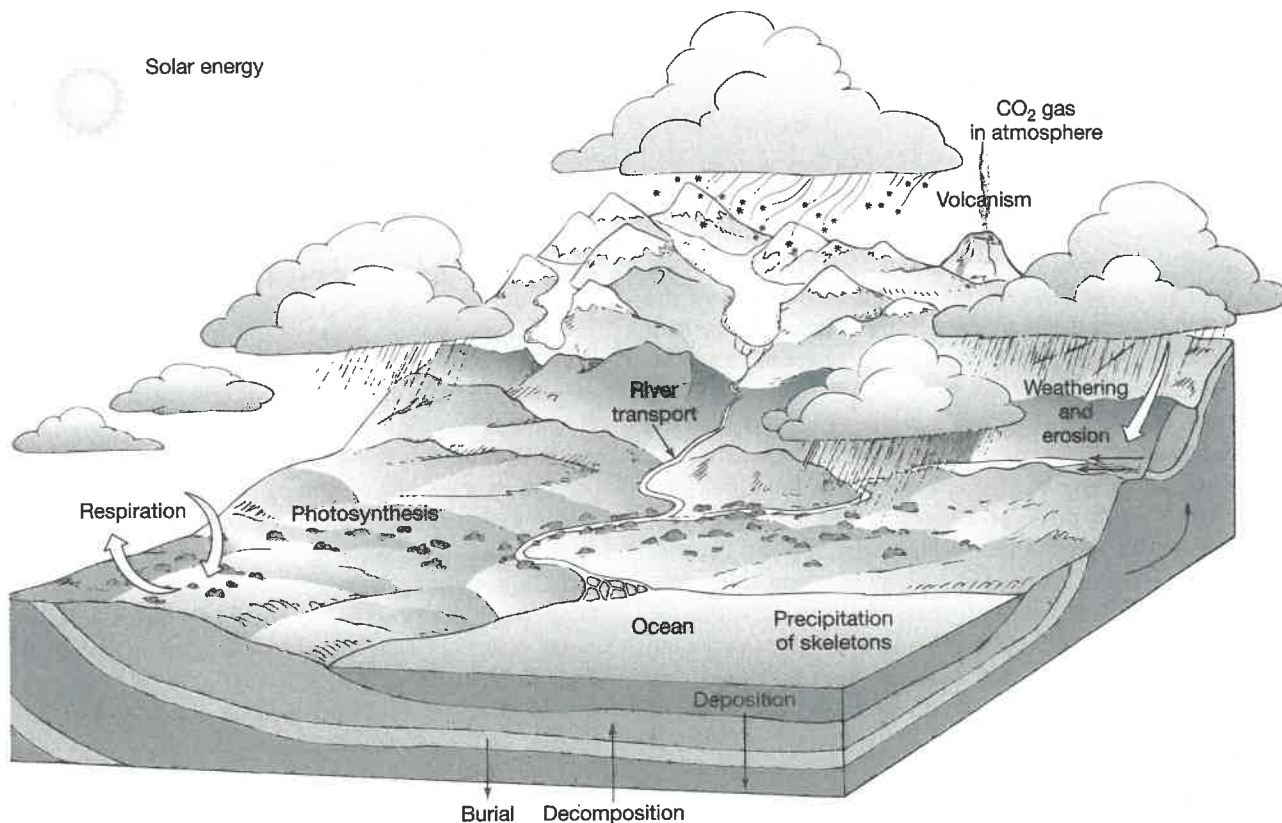


FIGURE 8-1 The global carbon cycle. (Source: From J. P. Davidson, W. E. Reed, and P. M. Davis, *Exploring Earth: An Introduction to Physical Geology*, 1997. Reprinted by permission of Prentice Hall, Upper Saddle River, N.J.)

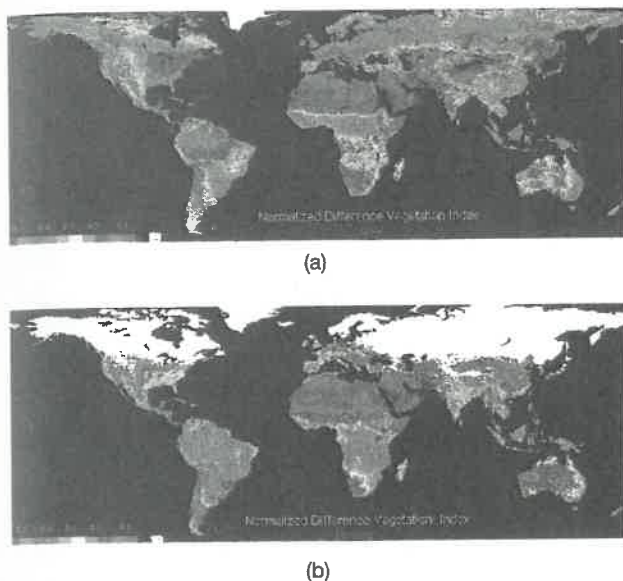


FIGURE 8-2 [See color section] Satellite image of the vegetation coverage of the land surface in the Northern Hemisphere in (a) summer and (b) winter, expressed as an index, with larger values having greater coverage by living vegetation. (Source: Felix Kogan/NOAA/NESDIS/ORA Climate Research and Application Division.)

attached. Our carbon atom, as part of the leaf, is now **organic carbon**. Some leaves are consumed and digested by animals. The carbon in these leaves is then released back to the atmosphere by the animals' respiration as CO_2 .

Summer passes, fall arrives, and the leaf that contains the carbon atom has not been eaten. The nourishing substances and water that the leaf has received from the tree have ceased to flow. The leaf is released from the branch and settles to the ground. Other leaves fall on top, burying it in a thick mat of decaying matter. The carbon atom is part of the soil, where it will remain for about the next 50 years. By the end of that time, bacteria and fungi will have decomposed the organic matter that contains the atom. The chemical reactions that result transform the carbon atom once again into a gaseous CO_2 molecule, which escapes back to the atmosphere.

This life cycle of a carbon atom is repeated nearly 500 times on average before a "leak" occurs. Once in a while, before the organic matter that contains the carbon atom decomposes, the soil erodes and is transported by rivers to the oceans. There it settles with the other particles to the seafloor and is buried by subsequent sediments or carried with its underlying oceanic plate deep into a subduction zone. Under elevated temperatures and pressures the carbon atom may be converted into gaseous carbon atoms and escape to the surface, or be converted into a component of sedimentary or metamorphic rock.

The carbon atom may spend millions of years in the sedimentary/metamorphic rock reservoir, as mountain belts form, thrusting deeply buried rocks to Earth's surface and beyond to great elevations. Eventually our carbon

atom will be transferred from its burial place within Earth's interior to the surface. Here environmental forces, both biological and physical, will cause the sedimentary rock containing the carbon atom to disintegrate during the process of weathering. In this process, the organic carbon reacts with oxygen from the atmosphere and forms (inorganic) CO_2 , which escapes as a gas to the atmosphere. The weathering process, then, is the connecting link in the long path this particular carbon atom has taken—from the atmosphere, to the plant, to the soil, to the sediment, to the sedimentary rock, and back to the atmosphere.

The path the carbon atom has taken encompasses the *terrestrial organic carbon cycle*, operating on time scales that are short (years to decades) and those that are long (centuries and millennia to multimillion years). If instead of being incorporated into a plant leaf the carbon atom had entered the ocean and been converted to organic carbon by marine algae, it would have become part of the *marine organic carbon cycle*. There are also a host of processes not involving organic carbon that compose the *inorganic carbon cycle*. These various parts of the carbon cycle are discussed below.

Carbon Reservoir Dynamics

Carbon resides in many reservoirs at or near Earth's surface (Figure 8-3), ranging in size from the relatively tiny amount of carbon in atmospheric methane to the tremendous amount of carbon stored in sedimentary rocks. One of our ultimate goals is to understand how this system of reservoirs responds to perturbations. We will use the response to the release of carbon dioxide from the burning of fossil

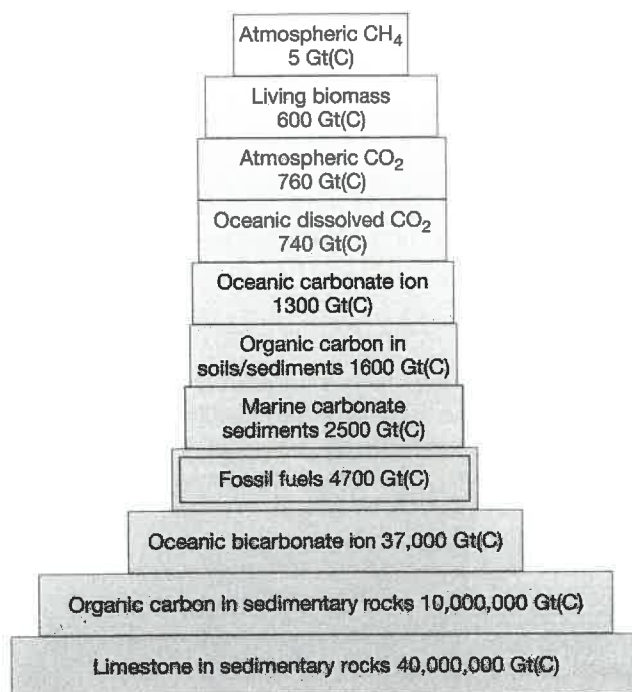


FIGURE 8-3 Reservoirs of carbon at or near Earth's surface circa 1995.

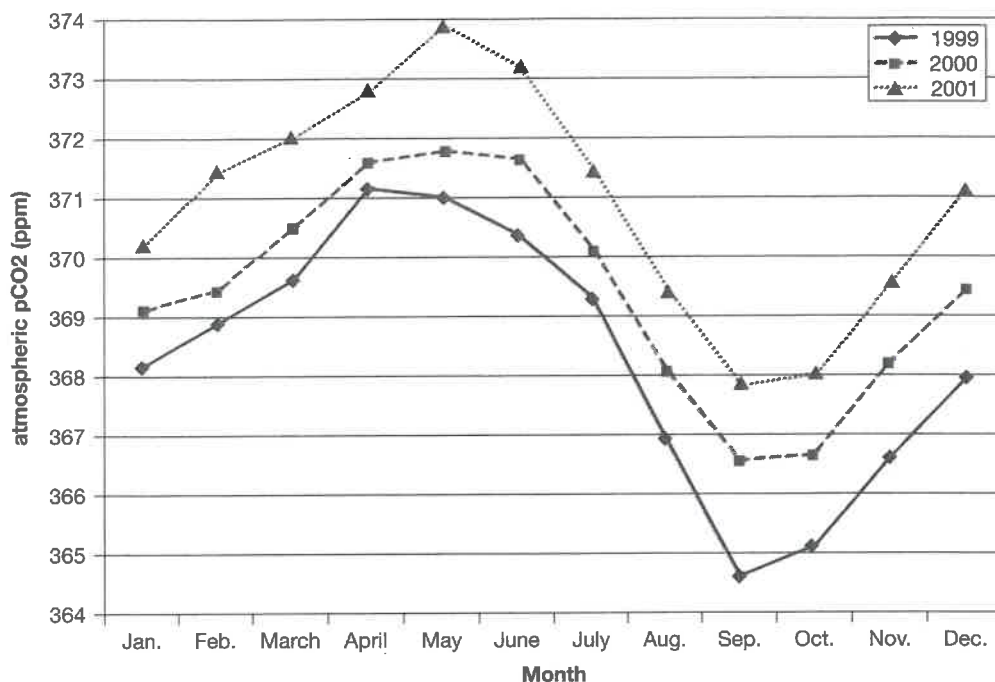


FIGURE 8-4 Seasonal fluctuations in atmospheric CO₂ from the Mauna Loa Observatory for 1999–2001. The gradual increase due to fossil-fuel burning and deforestation accounts for the offset from year to year. (Source: Data courtesy Oak Ridge National Laboratory, <http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm>.)

fuels as an example of the dynamics of the carbon cycle and of material recycling systems in general.

Figure 8-4 shows the seasonal fluctuations in the atmospheric CO₂ level for three years (1999–2001) measured from atop Mauna Loa, Hawaii. We saw a similar graph in Figure 1-2. In Figure 8-4, however, we focus on the natural seasonal cycle rather than the gradual increase in CO₂ from fossil-fuel burning and deforestation. The CO₂ content falls during the Northern Hemisphere summer, when photosynthesis (and the growth of leaves) surpasses respiration and decomposition. It then rises during the late fall to early spring, when respiration and decomposition of the previous season's crop of leaves exceeds photosynthesis. Because Hawaii is in the Northern Hemisphere (17° N), measurements made at Mauna Loa reflect the annual cycle in that hemisphere (see Chapter 1 for further discussion). Let us cast these observations in terms of systems theory.

RESERVOIRS From the systems point of view, the atmosphere is a *reservoir* of carbon in the form of CO₂ (Figure 8-5). Reservoirs are typically characterized in terms of the amount of material they are holding at any particular time.

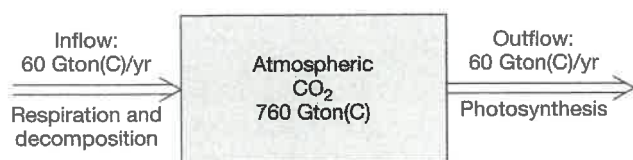


FIGURE 8-5 The atmospheric carbon (i.e., CO₂) reservoir, showing inflows and outflows.

Their sizes are commonly expressed either in mass units or volume units. (Chemists often use *moles*; refer to the Box “Useful Concepts: The Concept of the Mole” if you need a refresher.) In Figure 8-5, the amount of carbon is expressed in gigatons (Gt) of carbon, or Gt(C). A gigaton is 1 billion metric tons, and 1 metric ton is 1000 kg. With the notation Gt(C), we are keeping track of the mass of only the carbon atoms, not the other atoms to which they are attached.

Reservoirs are temporary repositories for material that flows through them, and their sizes change in response to imbalances between inflow and outflow, typically expressed in unit mass, unit volume, or moles per unit time. The *inflow* to the atmospheric CO₂ reservoir is the combination of the processes of respiration and decomposition. This inflow can be expressed in units of gigatons of carbon per year. The *outflow* from this reservoir is photosynthesis, and the rate of outflow is also expressed as gigatons of carbon per year.

STEADY STATE If the rates of inflow and outflow were such that the atmospheric CO₂ level remained at a constant value with time, we would say that *steady state* had been achieved. **Steady state** is a condition in which the state of a system component is constant with time. Steady state could be achieved if no inflow and no outflow existed, that is, if both processes ceased. A constant level could also be maintained if the rate of inflow of CO₂ into the atmosphere equaled the rate of outflow.

Any imbalance in these rates leads to a change in the level of atmospheric CO₂. When the inflow exceeds the outflow, the atmospheric CO₂ level rises. (This situation is analogous to the Northern Hemisphere winter condition.)

USEFUL CONCEPTS

The Concept of the Mole

Atoms and molecules are typically measured in units called moles. A *mole* (abbreviated mol) of a substance is defined as the amount of that substance that contains the same number of atoms or molecules (or any other particle) as the number of atoms in 12 g of ^{12}C . There are 6.02×10^{23} atoms in 12 g of ^{12}C ; this number is called *Avogadro's number*, after the Italian chemist Amedeo Avogadro. A mole of any type of particle contains Avogadro's number of these particles. In concept, a mole is no different than, say, a dozen; it simply converts a number that would be cumbersome into one that is more practical. Even when we use moles, global-scale reservoirs such as that of atmospheric CO_2 are huge. There are presently about 6×10^{16} moles of CO_2 in the atmosphere.

One mole of ^{12}C weighs exactly 12 g. However, 1 mol of H weighs only approximately 1 g, and 1 mol of ^{16}O weighs approximately 16 g. These weights are defined as the mass numbers of the given isotopes. The mass number of an isotope is the total number of protons plus neutrons

in the nucleus. Equivalently, atomic weight is the weight of 1 mol of a particular isotope. For an element with more than one stable isotope, the precise atomic weight (as opposed to the mass number) of the element is determined from the relative amounts of the various isotopes.

Expressing quantities of substances in moles rather than in mass units (e.g. grams) can be useful when we are studying chemical reactions. Consider the chemical reaction for the formation of salt (sodium chloride, NaCl):



This equation shows that one atom of sodium (Na) will react with one atom of chlorine (Cl) to form one molecule of NaCl . Therefore, 1 mol of Na will react with 1 mol of Cl to form 1 mol of NaCl . To express this equation in mass units, we would need to use the atomic weights of sodium and chlorine. If we did, we would find that 22.99 g of Na reacts with 35.45 g of Cl to produce 58.44 g of NaCl —a more cumbersome calculation.

When the outflow exceeds the inflow, the level falls (analogous to the Northern Hemisphere summer condition).

In the record of atmospheric CO_2 variations in Figure 8-4, we see that one maximum and one minimum is reached each year. At these times the fluxes are in balance. The system is not really in steady state at these times, however, because the reservoir size is unchanging only for an instant. Averaged over longer times, though, the *natural* cycle of CO_2 is thought to be close to steady state, despite seasonal imbalances. Because of anthropogenic disturbances, the atmospheric CO_2 level is not currently at steady state, as demonstrated by the steady rise in CO_2 over the past several decades.

Steady state can be maintained over time only if the rates of inflow and/or outflow are sensitive to changes in

the size of the reservoir. In systems terminology, this means that there must be couplings that link the reservoir size to the processes that govern inflow and outflow (see Chapter 2). Consider what would happen if a reservoir in steady state were perturbed by an addition of material. If the coupling governing inflow was negative or if that governing outflow was positive (i.e., inflow decreased or outflow increased), the reservoir would return to its original state. One such negative feedback loop exists between the photosynthetic rate of plants and atmospheric CO_2 . As CO_2 levels go up, plants photosynthesize more rapidly; this effect has been called *CO_2 fertilization* (Figure 8-6). But as they do, CO_2 levels tend to fall, because CO_2 is consumed by plants during photosynthesis. Thus, the terrestrial biota tend to stabilize atmospheric CO_2 levels.

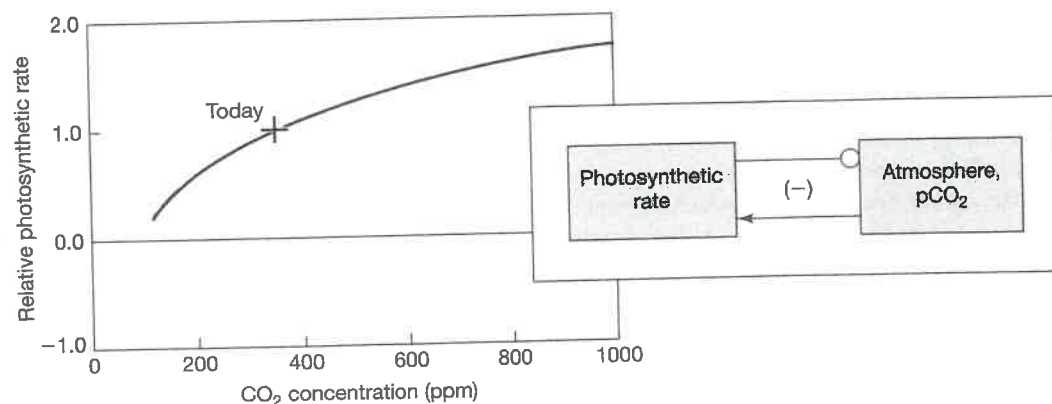


FIGURE 8-6 Effect of changes in CO_2 concentration on the photosynthetic rate of typical plants. Photosynthetic rates are relative to the value for today's atmospheric CO_2 level. Inset represents the negative feedback loop that results from this dependence.

RESIDENCE TIME To help us monitor the recycling of elements through the Earth system, the concept of residence time can be useful. **Residence time** is defined as the average length of time a substance spends in a given reservoir that is at steady state. We can calculate the residence time by dividing the reservoir size at steady state by the inflow or outflow rate:

$$\text{residence time} = \frac{\text{reservoir size at steady state}}{\text{inflow rate or outflow rate}}$$

If reservoir size has units of mass and the inflow and outflow rate is in mass per time, then the quotient has units of time.

We can determine the residence time of the atmospheric carbon reservoir from the size of that reservoir, which Figure 8-3 gives as 760 Gton(C), and from the rate of respiration and decomposition (the inflow rate) or the rate of photosynthesis (the outflow rate), both of which are given as 60 Gton(C)/yr. Thus, if we assume steady state, the residence time of carbon in the atmosphere with respect to these processes is 760 Gton(C)/60 Gton(C)/yr = 12.7 yr. This means that carbon in the atmosphere is replenished about once per decade.

We can also think about residence time as an indicator of how long a reservoir takes to respond measurably to large imbalances in inflow or outflow. In our atmospheric carbon example, if photosynthesis were to cease but respiration and decomposition were to continue at their current rate, the atmospheric CO₂ level would double in about a decade. Thus, the residence time, defined at steady state, becomes the **characteristic response time** when a system is *not* at steady state. The concept of a characteristic response time is similar to that of a half-life in radioactive decay (see Chapter 5). Stated formally, a disturbance from steady state (in a system where the rate of removal is proportional to the amount of disturbance) diminishes to 1/e (about 38%) of its original size in one characteristic response time.

Oxidized and Reduced Carbon

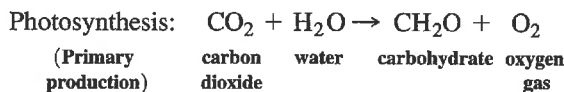
The many identities that carbon assumes in the Earth system can be lumped into two general categories: oxidized carbon and reduced carbon. **Oxidized carbon** is carbon that is combined with oxygen. Examples of oxidized carbon include the carbon in the skeletons of some organisms and in atmospheric CO₂. **Reduced carbon** is carbon that is combined mainly with other carbon atoms, hydrogen, or nitrogen. Organic carbon is a form of reduced carbon. Perhaps a more familiar pair of reduced and oxidized substances is metallic iron and its oxidation product, rust (iron oxide). In the presence of oxygen gas at Earth's surface, reduced substances, such as organic carbon and metallic iron, tend to be highly chemically reactive. Oxidized substances, such as CO₂ and rust, tend to be more inert.

In the next few sections, we explore the organic and inorganic carbon cycles. We begin with the organic carbon

cycle as it operates on land—the terrestrial organic carbon cycle, which we already introduced in our journey through the carbon cycle. We then move to the oceans, where both oxidized and reduced carbon recycling are important on short time scales. Finally, we consider the longer-time-scale cycles, which involve geological processes.

THE SHORT-TERM ORGANIC CARBON CYCLE

The short-term organic carbon cycle involves processes ranging from those we can observe and appreciate on a daily to seasonal time scale (see Figure 8-2), such as the processes of photosynthesis and respiration, to processes of decomposition that are somewhat slower (Figure 8-7). The key step in this cycle is the conversion of inorganic carbon (atmospheric CO₂) to organic carbon by the process of **photosynthesis**. We are not so much interested in the process itself but rather in its impact on the global cycle, which is generally expressed as primary productivity. **Primary productivity** is the amount of organic matter produced by photosynthesis in a unit time over a unit area of Earth's surface. That amount depends on the population size of **primary producers**—that is, plants (or other types of photosynthesizers or even chemosynthesizers) that provide energy other organisms can use. The relationship is not simple, however, because some primary producer species are much more productive than others. In its simplest representation, primary production involves a chemical reaction between CO₂ and water to form organic matter and oxygen:



Here, organic matter is represented by CH₂O, the simplest *carbohydrate*, or compound of carbon, hydrogen, and oxygen. In reality the molecules making up organic matter are much larger than this simple carbohydrate, and they contain small amounts of many other elements, including nitrogen and phosphorus. For our purposes, however, this simpler representation suffices.

Photosynthesis does not occur spontaneously at Earth's surface but instead requires an input of energy from the Sun. Plants, algae, and bacteria have evolved pigments that are able to capture the energy of sunlight and convert it to chemical energy, part of which is stored in living tissues. This chemical energy is then utilized by other organisms that cannot utilize solar energy directly. Such organisms, including animals, are called **consumers**.

Most of the photosynthesis that occurs each year leads to the formation of tissue that is recycled rapidly, including the leaves of trees. This recycling is the cause of the seasonal variations observed in the CO₂ record of Figure 8-4. However, most of the organic carbon that makes up plant tissues has a residence time of many decades. That is because the bulk of the organic carbon in terrestrial plants

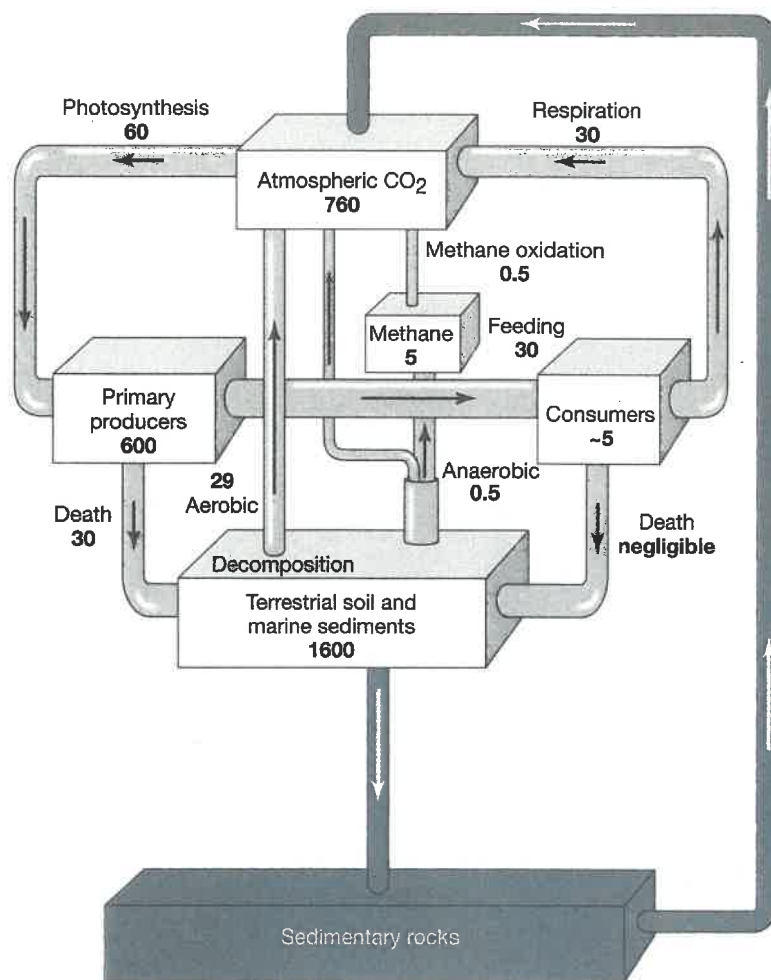
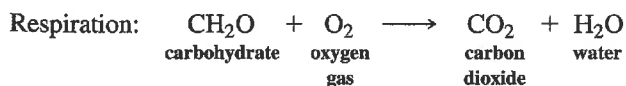


FIGURE 8-7 The short-term, terrestrial organic carbon cycle, showing reservoir sizes, inflows, and outflows. Dark shaded area represents the long-term cycle (see Figure 8-12). Reservoir sizes in Gt(C), fluxes in Gt(C)/yr.

is contained not in the leaves but in the roots and trunks of slow-growing trees. In other words, most of the biomass of primary producers on Earth is contained in tree roots and trunks. **Biomass** is the total mass of organic matter in living organisms in a particular reservoir. In terms of carbon, the total living biomass—the combined biomasses of all primary producers and consumers—is about equal to the atmospheric carbon reservoir (see Figure 8-3).

Consumer biomass is a small percentage (only about 1%) of the biomass of the producers. Consumers derive their metabolic energy from the chemical energy stored in plant tissues by ingesting the tissues and respiring. *Respiration* is the reverse of photosynthesis: It is the chemical reaction between oxygen and organic tissue that yields CO₂ and water:



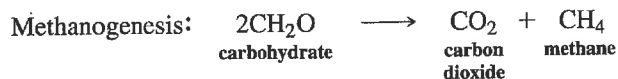
During photosynthesis, plants use solar energy to create tissue. But, like animals, plants produce their metabolic energy through respiration. Hence, respiration is more than just the “breathing” performed by animals. Unlike photosynthesis, respiration would proceed abiotically because it

releases rather than requires energy. However, it would do so very slowly. Organisms are able to accelerate this chemical reaction by the use of *enzymes*, chemical compounds (specifically, proteins) that they synthesize for this purpose.

On land, about half the organic material produced by photosynthesis is respired by animals and by plants themselves. The remaining material is added to the organic-rich upper layers of soil. A host of microscopic bacteria and fungi live in soil. Their metabolic requirements are satisfied through the decomposition of the large store of organic matter that is buried there, fueled by the supply of oxygen from the overlying layers. A biological process that uses oxygen is said to be *aerobic*, and an organism that carries out aerobic metabolism is an *aerobe*. The chemical reaction for this aerobic decomposition is identical to that for respiration.

Because the only source of oxygen is the air, the microorganisms that live well below the surface must be adapted to environments that are devoid of oxygen. A biological process that occurs in the absence of oxygen is said to be *anaerobic*, and an organism that carries out anaerobic metabolism is an *anaerobe*. In the O₂-free environment of deep soil live anaerobic bacteria that decompose organic matter by an overall process known as **methanogenesis**. **Methanogenesis** is an anaerobic form of metabolism that involves multiple

steps, carried out by different bacteria. One step involves fermentation of complex organic materials into simpler forms, including hydrogen (H_2) and acetate that methanogens can then use to form both oxidized carbon (in CO_2) and reduced carbon (methane). The overall process can be represented as:



(Other, more complex compounds can also be used in and produced during anaerobic metabolism, but for the purposes of studying the carbon cycle, this representation is adequate.) The gases CO_2 and CH_4 can escape to the atmosphere. Once there, the CO_2 continues the short-term cycling path described earlier. Methane, however, is chemically unstable in our O_2 -rich atmosphere and is destroyed by a series of oxidation reactions. The carbon contained in

CH_4 combines with O_2 to form CO_2 . With an atmospheric reservoir size of 5 Gton(C) and a supply rate from fermentation of 0.5 Gton(C)/yr (see Figure 8-7), the residence time of CH_4 in the atmosphere is approximately 10 years.

The land surface is continuously stripped of its soil cover by the action of winds and water. On average, about 5 cm of soil is eroded from the land surface every 1,000 years and transported by rivers to the oceans. Although river systems have a substantial capacity for storing sediment in flood plains and deltas, eventually most of the sediment makes its way to the oceans and is deposited on the seafloor. These sediments contain whatever organic matter has survived the trip from land to sea. Thus, there is a transfer of organic carbon from the terrestrial to the marine realm, one that amounts to about 0.1 Gton(C)/yr. However, this transfer is small compared with the flux through the oceanic water column of organic matter produced in the ocean.

A CLOSER LOOK

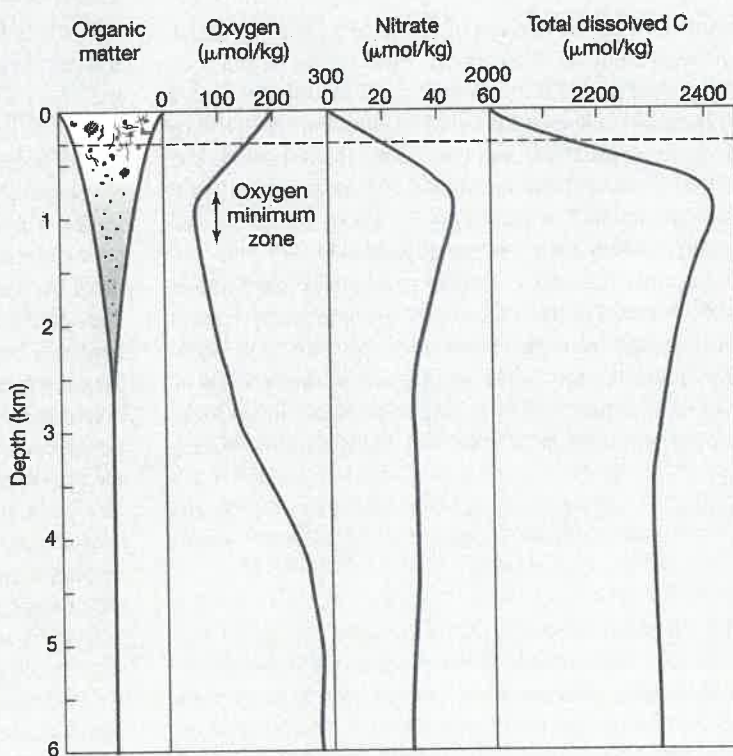
Oxygen Minimum Zone

The decomposition of organic matter settling through the water column consumes oxygen, leading to oxygen depletion. Decomposition also releases nutrients to the water, so nutrient concentrations increase. The lowest oxygen concentrations are achieved at intermediate depths, about 1 km below the surface. This region is known as the *oxygen minimum zone* (Box Figure 8-1). In this zone, dissolved oxygen concentrations reach a minimum as a result of high oxygen demand by aerobic decomposers and low oxygen supply from the surface ocean or from below.

In the waters below the oxygen minimum zone, oxygen content increases with depth. Why is this so, if the source of oxygen is exchange with the atmosphere and production by phytoplankton in the surface ocean?

Recall from Chapter 5 that the circulation of the ocean resembles a giant conveyor belt that brings waters from the surface in the high-latitude North Atlantic and Antarctic oceans to the deep sea. This water is enriched in oxygen as a consequence of having originated at the surface in the high latitudes. Like most gases, oxygen is more soluble in cold water than in warm water. So, gas exchange with the atmosphere leads

to higher gas concentrations in high-latitude surface waters than in low-latitude surface waters. High-latitude surface waters become denser as they cool and get saltier, and sink, moving to lower latitudes at depth. Deep water therefore ends up with more dissolved O_2 than does the water above it. Thus, the oxygen minimum zone owes its existence to the combined operation of the biological pump and the global ocean circulation.

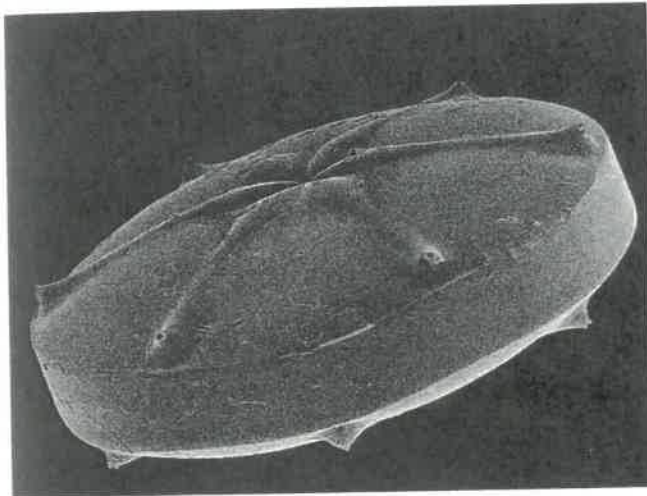


BOX FIGURE 8-1 The effect of the biological pump and thermohaline circulation on the chemical composition of the ocean. Typical vertical profiles of the amount of organic matter, dissolved oxygen, nitrate (a nutrient), and inorganic carbon are shown. Concentrations are in micromoles (10^{-6} mol) per kilogram of seawater.

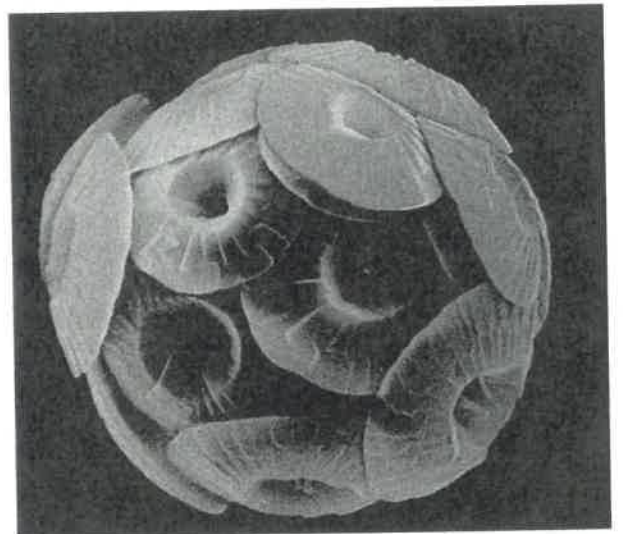
The Marine Organic Carbon Cycle on Short Time Scales

PRODUCERS AND CONSUMERS The dominant primary producers in the ocean are the free-floating, photosynthetic marine microorganisms referred to as *phytoplankton*. (In more general terms, *plankton* are organisms with any type of metabolism that float freely in aquatic environments.) These organisms—primarily *diatoms* (Figure 8-8a)

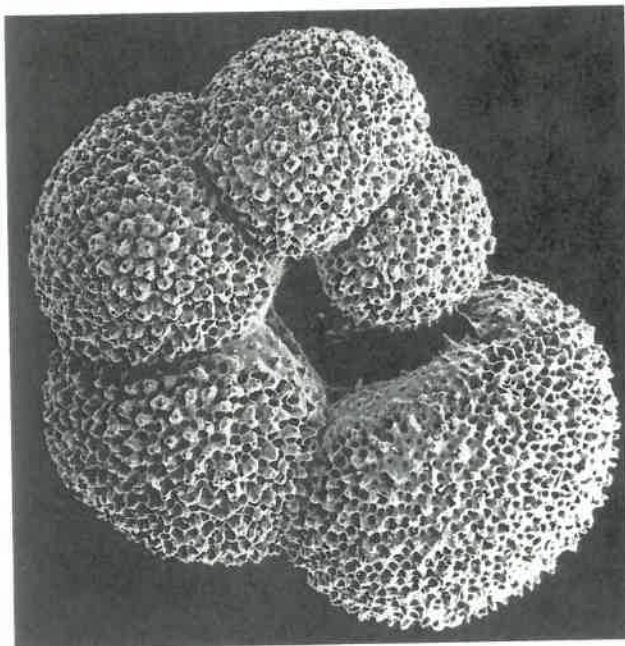
and other algae, such as *coccolithophorids* (Figure 8-8b)—live in the photic zone. The **photic zone** is the uppermost part of the oceanic water column where there is sufficient light for photosynthesis: about the upper 100 m of the water column in the open ocean, and in shallower waters near shore, where water clarity is reduced. It roughly corresponds to the “surface ocean,” which, as we saw in Chapter 5, is the upper part of the ocean mixed by the winds.



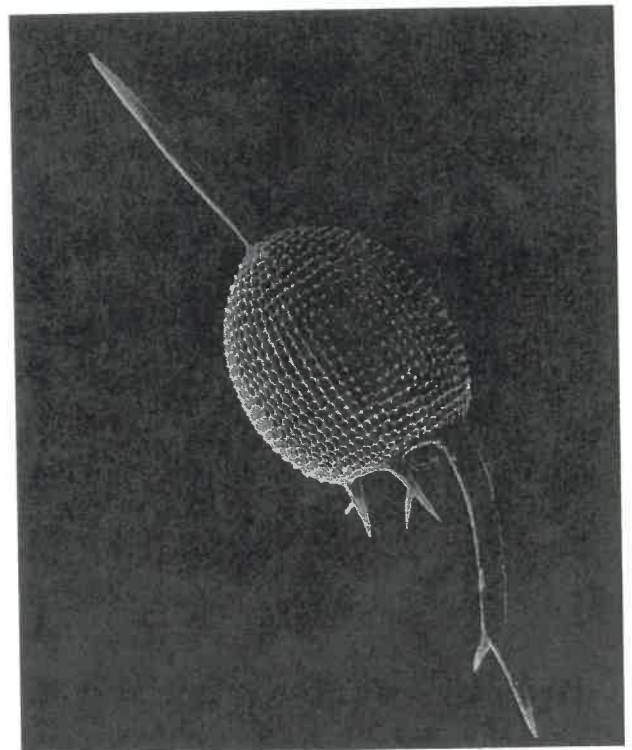
(a)



(b)



(c)



(d)

FIGURE 8-8 [See color section] Shells of typical phytoplankton: (a) diatom (SiO_2 ; approximately $50\ \mu\text{m}$ wide) and (b) coccolithophorid (CaCO_3 ; about $10\ \mu\text{m}$ in diameter). Typical zooplankton: (c) foraminifer (CaCO_3 ; approximately $600\ \mu\text{m}$ in diameter) and (d) radiolarian (SiO_2 ; approximately $50\ \mu\text{m}$ wide). (Source: Renate Bernstein.)

Phytoplankton consume CO_2 and produce O_2 through photosynthesis in much the same way as do land-based plants. Although the gases phytoplankton use and produce are dissolved in seawater, there is continuous gas exchange between the atmosphere and the ocean. Thus, the activities of phytoplankton affect the atmosphere as well as the ocean.

Much of the organic matter produced in the surface ocean by phytoplankton is consumed by zooplankton. **Zooplankton** are free-floating marine consumers, including small invertebrates and microorganisms such as *foraminifera* (Figure 8-8c) and *radiolarians* (Figure 8-8d), that cannot photosynthesize. Zooplankton produce fecal pellets that, together with other large particles of decaying organic matter, settle through the water column to great depths. In contrast to the flux of organic matter from treetops to the ground, though, only about 1% of this material survives the trip to the seafloor. Even then, the material is subject to efficient recycling by aerobic and anaerobic decomposers that live on the seafloor or in the uppermost layers of sediment. As a result, only about 0.1% of the organic matter that settles from the surface ocean is preserved in marine sediments.

Most marine organic matter is decomposed by animals and microbes as it settles through the water column. This decomposition releases CO_2 (the product of both oxygen-breathing animals and microbial respiration) and nutrients to the oceanic deep waters. For marine organisms, nutrients lead to high rates of primary productivity if they are available in the appropriate concentrations. Thus, it is critical to the productivity of the marine biota to get these nutrients back to the surface.

THE BIOLOGICAL PUMP The overall effect of photosynthesis in shallow waters, of the settling of organic matter, and of decomposition in deep waters is the transfer of CO_2 and nutrients from the surface waters to the deep ocean. This process is known as the **biological pump**

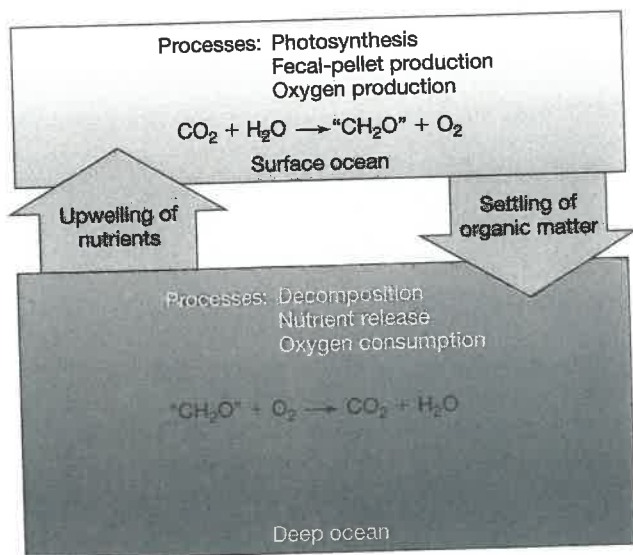


FIGURE 8-9 The marine biological pump.

(Figure 8-9). It is balanced by upwelling (Chapter 5), which brings nutrients and carbon-rich waters back to the surface, replenishing the nutrients and carbon removed by the biological pump.

The biological pump has a profound effect on ocean chemistry. As a result of its operation, surface waters are measurably depleted in carbon and severely depleted in phosphate and nitrate (the major nutrient elements) relative to deep waters. If the biological pump were to cease—for example, as the result of a mass extinction—the ocean would assume a more uniform composition in a few thousand years, as ocean mixing homogenized the ocean.

NUTRIENT LIMITATION Some elements are classified as nutrients for marine phytoplankton because they are essential for growth and exist at suboptimal concentrations; an increase in their concentration leads to higher rates of primary productivity. Other elements are *toxic* to marine life—that is, they are poisonous to certain organisms—because their concentrations in seawater are above the optimum for growth. (Even nutrient elements can be toxic if their concentrations become too high.) There is great variability in the concentration of many elements throughout the world's oceans. Each element, depending on its concentration, can be either a nutrient or a toxic substance. The situation is analogous to the parabolic growth curves for daisies as discussed in Chapter 2 (Figure 2-9a), except that element concentration substitutes for temperature. For each element, there is some optimum concentration that favors biological productivity.

Marine phytoplankton incorporate many nutrient elements into their tissues in ratios that appear to be nearly identical in all species. These ratios are called **Redfield ratios**, in honor of Alfred C. Redfield, the oceanographer who first described this phenomenon. Even more remarkably, the ratios of many of these elements in seawater is nearly identical to that in phytoplankton. For example, the elemental ratio of carbon:nitrogen:phosphorus is very nearly 106:16:1 (Table 8-1). A chicken-or-egg question arises: Does the composition of seawater determine the composition of organisms that live in the sea, or does the composition of marine organisms determine the composition of seawater? To answer this question, we must consider the distribution of primary productivity in the oceans.

Where are rates of primary productivity greatest in the oceans? We now have a sophisticated way of answering this

TABLE 8-1 Redfield Ratios

Element	Relative Number of Atoms in Living Phytoplankton
Carbon	106
Nitrogen	16
Phosphorus	1
Iron	0.01

question, by satellite. With a color scanner, researchers can quantify the color of seawater from space (Figure 8-10). The color of the ocean surface is strongly influenced by the density of phytoplankton, which contain photosynthetic pigments. In the early 1960s and 1970s, oceanographers began to study the relationship between the concentration of these pigments and the abundance and productivity of near-surface-dwelling phytoplankton. The researchers found that regions of the ocean that have low concentrations of *chlorophyll* (a green pigment that is the dominant pigment in algae) are biological deserts, with low abundances of organisms and low nutrient concentrations. In contrast, more productive waters tend to have high chlorophyll concentrations.

Although we might expect that the warm, sunny low-latitude oceans would be most conducive to phytoplankton growth, the satellite patterns reveal that the waters with the highest productivities are the cold waters of the high-latitude Atlantic, Pacific, and Southern oceans. The reason is that the thermocline is weak or nonexistent at these latitudes because surface waters are just as cold as the deep waters there. Thus, wind-driven mixing of nutrient-rich deep waters up to the surface occurs much more readily at high latitudes than at low latitudes, where mixing is inhibited by the strong temperature and density gradients (Chapter 5). Apparently the inhibitory effects of cold temperatures and low light availability experienced by organisms that live at high latitudes are more than compensated for by an enhanced nutrient supply.

The satellite images also indicate high productivity in regions of upwelling. As we saw in Chapter 5, many of these regions occur along the western continental margins. There the wind-driven surface currents cause offshore



FIGURE 8-10 [See color section] The concentration of photosynthetic pigments as determined by the Coastal Zone Color Scanner (CZCS) on the Nimbus 7 satellite. Pigment concentrations are indirect indicators of rates of primary production. (Source: Gene Feldman, NASA GSFC/SPL/Photo Researchers.)

transport, which allows nutrient-rich waters from intermediate depths to well up to the surface. Other upwelling regions occur where surface currents diverge (for example, along the equator, due to the action of the trade winds and the Coriolis effect). Surface divergence also allows intermediate-depth waters to rise and replace the water transported away at the surface. Finally, the coastal regions of the continental shelves tend to be highly productive because of nutrient inputs from rivers (often strongly enhanced by anthropogenic inputs of nitrogen and phosphorus) and localized upwelling driven by the topography of the seafloor.

Nutrient supply therefore seems to be a major limitation on the productivity of the surface ocean. Except in upwelling regions, phosphate and nitrate concentrations in surface waters are driven essentially to zero as a result of intense uptake by phytoplankton. Deep waters begin as surface waters, depleted in nutrients, at high latitudes. These waters increase in nutrient concentration as nutrients are released by decomposing organic matter that rains down from the overlying water column (the biological pump). In the North Atlantic, the effect of this “rain” on the composition of the water is small, because the water mass is young and has not had time to build up a large supply of organic matter. Farther along the path of ocean general circulation, the aging water mass begins to show its increasing influence on the biological pump. Accordingly, the nutrient contents of deep North Pacific waters (the oldest waters in the ocean) are much greater (Figure 8-11a), and the O_2 contents much lower (Figure 8-11b), than those of the North Atlantic. Thus, the explanation for the observed similarity in nutrient elemental ratios between seawater and marine organisms—the Redfield ratios—is that the nutrient composition of the world’s oceans is dominated by the production and decomposition of organic matter. In other words, the composition of marine organisms determines the composition of seawater.

THE LONG-TERM ORGANIC CARBON CYCLE

The processes we have discussed thus far affect the atmospheric CO_2 balance on time scales shorter than a century. On longer time scales, these processes must be very closely in balance: Because the fluxes involved are so large, persistent imbalances would lead to intolerable fluctuations in atmospheric CO_2 . Geological processes become the important controls on atmospheric CO_2 on longer time scales (Figure 8-12). The fluxes of carbon involved in these processes are small, and the reservoirs involved are large. Together these two adjustments in scale mean that the importance of the geological processes affecting the sedimentary reservoir and the atmosphere are influential only on long time scales (on the order of 1,000 years to 1 million years).

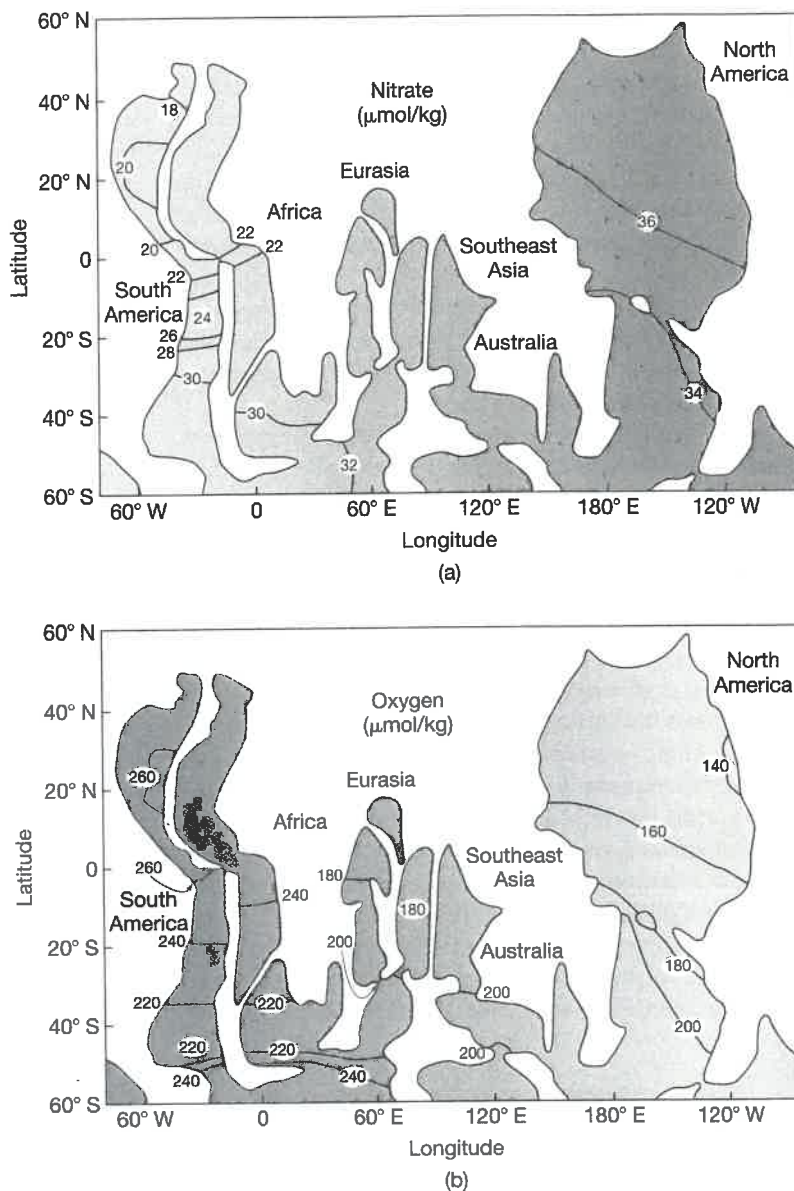


FIGURE 8-11 Concentrations of dissolved (a) nitrate and (b) O_2 in the deep ocean, in micromoles per kilogram of seawater. Maps are drawn for a water depth of 4000 m. At this depth the mid-ocean ridges appear as mountain ranges, and the continental outlines are substantially modified. (Source: W. S. Broecker and T.-H. Peng, *Tracers in the Sea*, New York: Eldigio Press, Columbia University, 1982, p. 31.)

Carbon Burial in Sedimentary Rocks

The flux of land-derived and marine sediments to the seafloor fills sedimentary basins, many of which flank the margins of the continents. The continuous supply of sediment to these basins leads to the burial of previously deposited material. Eventually, as the process continues, sediments become buried to a depth of a few kilometers below the seafloor and become lithified. The organic carbon associated with these sediments is then entombed in sedimentary rock until weathering liberates the material to the biosphere.

CARBON LEAKS AND OXYGEN REPLENISHMENT This organic carbon burial represents a leak of material from the short-term organic carbon cycle (see Figure 8-12). It is this leak, rather than photosynthesis alone (which is nearly balanced by respiration and decay), that maintains the O_2

content of the atmosphere. Oxygen is continuously removed from the atmosphere by chemical reactions with reduced materials (especially organic matter) that are preserved in rocks exposed at Earth's surface and with reduced volcanic gases such as hydrogen, sulfur dioxide, and carbon monoxide. The loss of O_2 is very slow, but the O_2 concentration would reach zero in a few million years if that gas were not supplied from other sources. Oxygen is replenished by the leak of organic matter into the sedimentary rock reservoir. For every carbon atom that enters this reservoir as organic carbon, one oxygen molecule is left behind. This is because the O_2 liberated during the photosynthesis of that carbon was not utilized during respiration or decomposition, and thus the gas remains in the atmosphere.

FORMATION OF FOSSIL FUELS During burial, the organic material in the sediment also undergoes significant

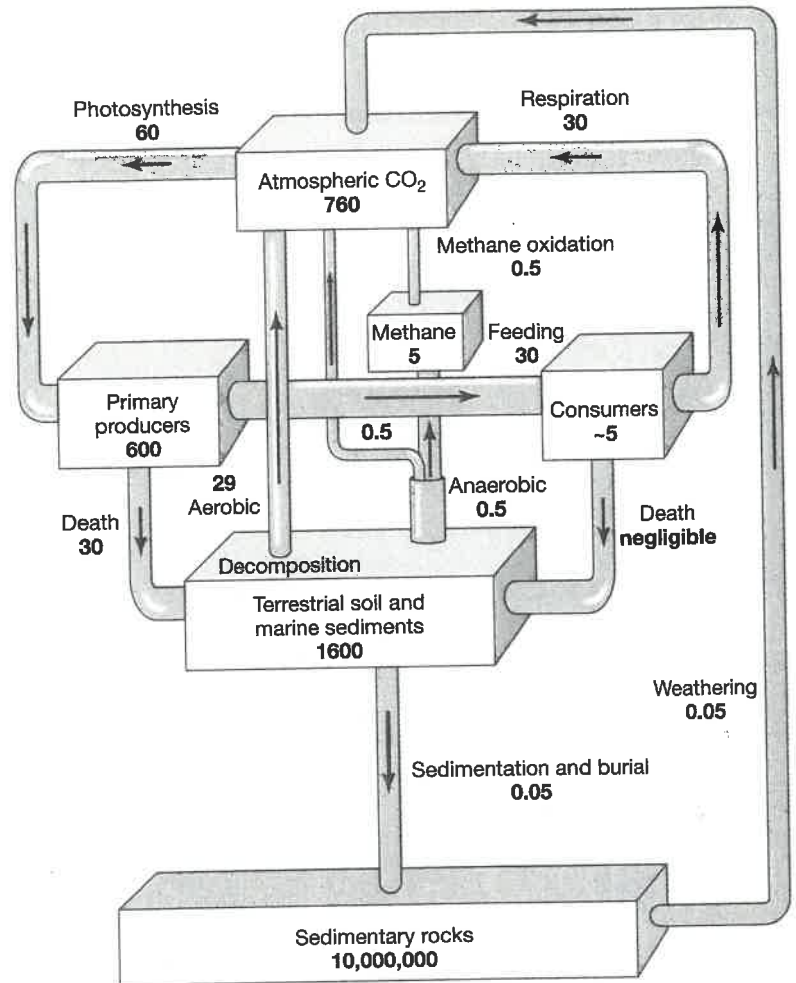


FIGURE 8-12 The combined short-term and long-term organic carbon cycles, showing the geological processes of sedimentation, burial, and weathering. Reservoir sizes in Gt(C), fluxes in Gt(C)/yr.

changes in its structure and chemistry, and fossil fuels may form. Sediments derived from land plants (especially *peat*, which forms in swamps and bogs) accumulate on land or in basins near shore. If the concentrations of terrestrial organic matter are high in these basins, burial processes under high pressures and temperatures can lead to the formation of **coal**. Similarly, high concentrations of organic matter in marine sediments can produce sedimentary rocks that, under high-pressure and high-temperature conditions of burial, serve as sources of **petroleum**. This material is fluid and tends to migrate through the basin until it becomes trapped and accumulates. If the accumulation is sufficient, the petroleum will be an economical source of fossil fuel. More commonly, however, the concentration of organic matter is 1% or less of the total sediment material. As a result, most sedimentary rocks do not represent economically viable energy sources.

THE SEDIMENTARY ORGANIC CARBON RESERVOIR

Sedimentary rocks contain by far the greatest quantity of organic carbon on Earth: approximately 10^8 Gton(C) (see Figure 8-3). Most of the organic carbon is found in *shales*, which are fine-grained sedimentary rocks formed by the

lithification of muds. The residence time for the sedimentary organic carbon reservoir is about 200 million years.

Weathering of Organic Carbon in Sedimentary Rocks

Weathering of the organic carbon in sedimentary rocks is an oxidation process requiring atmospheric O₂, either by direct exposure to the atmosphere or by exposure to groundwaters containing dissolved O₂. The oxidation of this material can be represented by the same schematic chemical reaction that we used previously for respiration and aerobic decomposition. The organic matter reacts with oxygen, releasing carbon dioxide to the atmosphere or groundwater.

In this sense, the mining, pumping, and combustion of fossil fuels represent merely an acceleration of the weathering process. The rocks from which humans have removed these fuels would likely have become exposed at the surface and undergone oxidation to form CO₂ some time in the distant future. Human intervention, however, has speeded up this process by a factor of a million or more for these fossil-fuel deposits. The release of organic matter from sedimentary rocks is occurring much faster than it

can be replaced. Hence fossil fuels represent only a short-term energy source.

Summary of the Organic Carbon Cycle

We have now explored the entire global organic carbon cycle. Pathways exist to recycle carbon from all reservoirs (see Figure 8-12). Every reservoir in this cycle is directly connected to the atmosphere. Thus, the CO_2 concentration of the atmosphere changes continuously in response to changes in the flux of carbon to and from these reservoirs. The responses to these changes are rapid for the large fluxes associated with the biota, soils, and marine sediments but slow for the small fluxes from the sedimentary rock reservoir. This observation will prove to be important in later chapters when we consider the fate of CO_2 added to the atmosphere from the burning of fossil fuels.

THE INORGANIC CARBON CYCLE

The photosynthesis of CO_2 to reduced carbon in organic matter, and its subsequent reoxidation to CO_2 through respiration, decomposition, and weathering, is central to the organic carbon cycle. But there are other sources and sinks for atmospheric CO_2 . Carbon dioxide readily dissolves in rainwater and seawater and then undergoes rapid chemical reactions to other ionic forms of inorganic carbon. The oxidized carbon in these waters is chemically reactive and becomes involved in a number of chemical processes. Because they do not involve organic carbon directly, these processes are together referred to as the *inorganic carbon cycle*.

The important reservoirs of inorganic carbon are the atmosphere, which we have discussed at length; the ocean;

sediments; and sedimentary rocks (see Figure 8-3). The sediment and sedimentary-rock carbon reservoirs consist primarily of limestone. **Limestone** is a rock composed largely of *calcium carbonate* (CaCO_3), generally in the form of the mineral *calcite*. The magnesium-rich carbonate mineral *dolomite*, $\text{CaMg}(\text{CO}_3)_2$, is abundant in older sedimentary rocks.

Carbon Exchange between Ocean and Atmosphere

Carbon dioxide is continuously exchanged between the atmosphere and ocean. The distribution of sources and sinks of CO_2 is tied to the circulation and productivity patterns of the oceans (Figure 8-13). In regions of the ocean where high rates of primary productivity have created surface waters with low CO_2 , CO_2 *diffuses* from the atmosphere to the ocean. In other words, the net flow of CO_2 is down the concentration gradient—from regions of higher CO_2 concentration (in this case, the atmosphere) to regions of lower concentration (the ocean). Conversely, upwelling regions, such as the equatorial Pacific surface waters, have high CO_2 concentrations because deep waters rich in CO_2 (as the result of decomposition associated with the biological pump) have risen to the surface there. In such regions, CO_2 flows from the ocean to the atmosphere. Thus, the oceans serve as both a source and a sink for atmospheric CO_2 .

Before the carbon cycle was disturbed by human activity, the flux of CO_2 from oceanic CO_2 source areas was probably closely balanced by the flux to oceanic CO_2 sinks. This pattern is changing in response to the burning of fossil fuels. As we have seen, the atmospheric CO_2 concentration has been increasing. Regions of the ocean that

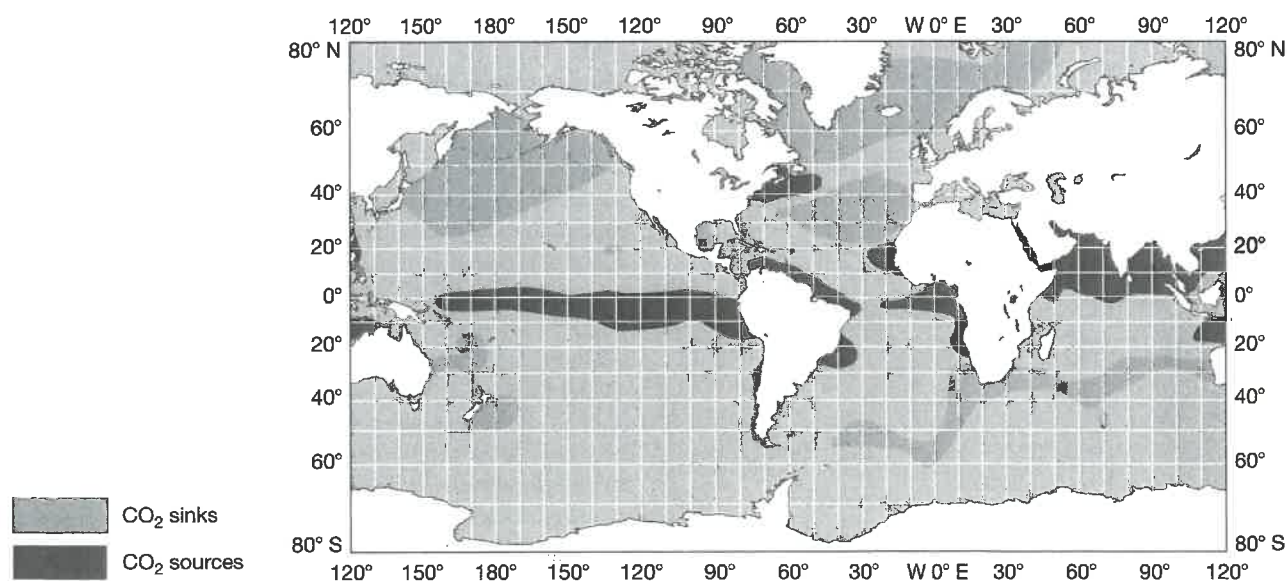
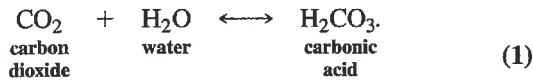


FIGURE 8-13 Oceanic sources (darker shading) and sinks (lighter shading) of atmospheric CO_2 . Sources have CO_2 concentrations larger than those in equilibrium with the atmosphere, whereas sinks have lower-than-equilibrium CO_2 concentrations. (Source: T. Takahashi, *Oceanus* 32, 1989, pp. 22–29.)

were previously weak sources have now become sinks, and the ocean as a whole has become a sink for CO₂.

The Chemistry of Inorganic Carbon in Water

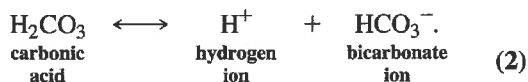
In the oceans, inorganic carbon exists in a number of dissolved forms. When CO₂ dissolves in water (whether it be freshwater or seawater), carbonic acid is generated:



The double arrows in this reaction indicate that the reaction can proceed both forward and backward. The rates of the forward and reverse reactions depend on the concentrations of the *reactants* (on the left-hand side) and of the *products* (on the right-hand side), respectively. If the concentration of the reactants is high, the forward reaction proceeds fast, depleting the concentration of the reactants and enhancing that of the products until the forward rate matches the reverse rate. Conversely, if the concentration of the products is high, the reverse reaction proceeds more rapidly, and the products become depleted (and reactants enriched) until the rates balance. In other words, *chemical equilibrium* is rapidly achieved in such reactions.

Like many substances that dissolve in water, carbonic acid molecules break apart, or *dissociate*, into ions. Ions are charged atoms or molecules. Ions with negative charges are referred to as **anions**. Ions with positive charges are referred to as **cations**. When carbonic acid dissociates, carbon-bearing anions and hydrogen cations are formed. The relative abundance (concentration) of the carbon anions is thus linked to the *pH* of seawater (see the Box "Useful Concepts: pH"), which is a measure of the concentration of hydrogen ions in solution.

CARBONIC ACID, BICARBONATE, AND CARBONATE ION EQUILIBRIUM Returning to the discussion of the forms of inorganic carbon in water, we see that the dissociation of carbonic acid involves the release of one or both of its hydrogen atoms to yield carbon-oxygen anions. When the first hydrogen atom is lost, *bicarbonate ion* (HCO₃⁻) is formed:



If the H⁺ concentration were to decrease (i.e., the pH increased), more carbonic acid would dissociate to balance the equilibrium between the two forms (the reaction would proceed to the right). If, instead, seawater were to become acidic, this equilibrium would shift to the left, forming carbonic acid at the expense of bicarbonate ion.

The release of the second hydrogen ion converts bicarbonate ion in the previous reaction to *carbonate ion* (CO₃²⁻):



(Note that we have previously used the term "carbonate" to refer to calcium and magnesium carbonate minerals.) For a given hydrogen ion concentration (pH), the relative amounts of bicarbonate and carbonate ions are adjusted until equilibrium is achieved. As pH decreases from alkaline to acidic, the concentration ratio of carbonate to bicarbonate ion also decreases.

Perturbation of this equilibrium (e.g., by the diffusion of anthropogenic CO₂ from the atmosphere to the ocean) changes the pH of seawater. These changes in pH affect the relative concentrations of carbonic acid, bicarbonate ion, and carbonate ion in the following way: CO₂ dissolves, forming carbonic acid (reaction 1); the carbonic acid dissociates, forming bicarbonate and hydrogen ions (reaction 2), which causes the pH to drop. Hydrogen ion then reacts with carbonate ion, forming another bicarbonate ion (the reverse of reaction 3). The overall chemical reaction describing the uptake of anthropogenic CO₂ is the sum of these three reactions (reactions 1, 2, and the reverse of 3):



Thus, the ocean's capacity to take up CO₂ derived from fossil fuels is enhanced relative to what it would be if it simply equilibrated with the atmosphere, because it is converted to other forms of inorganic carbon. There is a limitation on the amount that can be taken up, however: the amount of carbonate ion in the ocean, which is smaller than the total available fossil fuel. If we continue to utilize fossil fuels, the oceans' capacity to take it up will become depleted, and a larger fraction will remain in the atmosphere.

Chemical Weathering

A similar chemistry applies when atmospheric CO₂ dissolves in raindrops, making them naturally acidic. As we noted earlier, the unpolluted pH of rainwater is generally between 5 and 6. Rocks exposed at Earth's surface undergo chemical attack from this rain of dilute acid, a process known as *chemical weathering*.

Crustal rocks are composed mainly of two types of minerals: carbonates and silicates. Carbonate minerals, such as calcite, contain carbon in combination with oxygen and other elements. Calcite and dolomite are the most abundant carbonates at Earth's surface, occurring as the dominant minerals in limestones and dolostones and as minor minerals in a host of other rock types. These minerals have fairly simple chemical formulas: CaCO₃ and CaMg(CO₃)₂, respectively. Silicate minerals contain compounds of silicon and oxygen. They tend to have rather complicated compositions. They are most abundant in igneous rocks but are also common minerals in sedimentary and metamorphic rocks. (See Chapter 6 for a further discussion of rocks and minerals.)

In discussing the carbon cycle, we are most interested in the weathering of the calcium-bearing minerals, because calcium ions released by weathering are used by organisms

IT ISN'T CLEAR WHY YOU NEED THIS

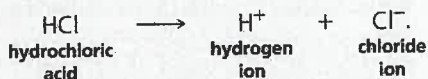
CaCO₃ → Ca²⁺ + CO₃²⁻

USEFUL CONCEPTS

pH

The hydrogen ion H^+ is the smallest of all cations. The small size and ionic charge make hydrogen ions extremely reactive: They tend to infiltrate solids, breaking bonds and causing the molecules that make up the solids to dissolve. Solutions (liquids with dissolved material) with high concentrations of hydrogen ions are called acids. Vinegar and hydrochloric acid are common acids. Solutions with low concentrations of hydrogen ions are called bases (or alkalis). Baking soda and lye dissolved in water are common bases.

Strong acids are solutions that completely dissociate: When dissolved in water, the anions separate completely from the hydrogen cations. This dissociation leads to high hydrogen ion concentrations. For example, the strong acid hydrochloric acid (HCl) dissociates to form hydrogen ions and chloride ions:

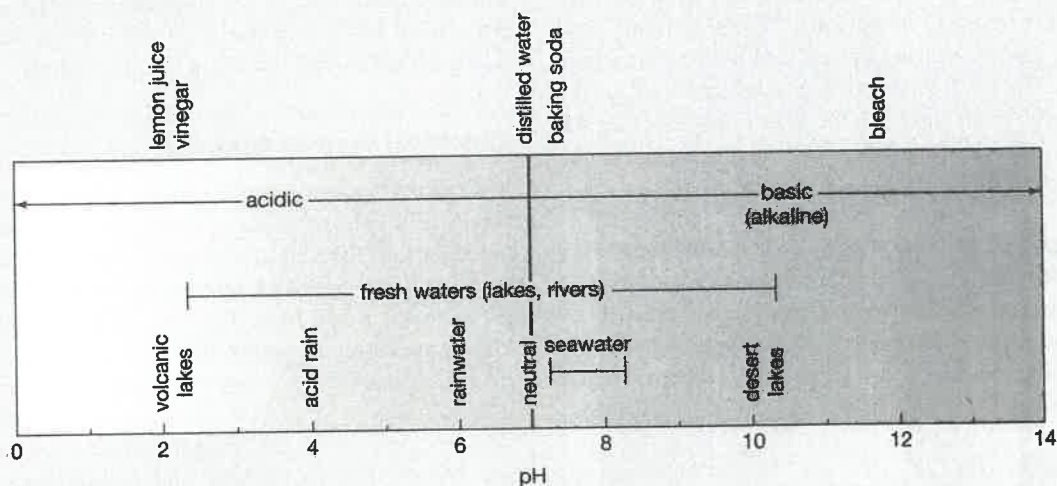


Other strong acids include nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Weak acids, such as boric acid (H_3BO_3) and carbonic acid (H_2CO_3), only partially dissociate when dissolved in water.

The concentration of dissociated hydrogen ions (expressed in moles per liter of solution) determines the acidity of the solution. Acidity is commonly measured by the pH scale, which is a logarithmic scale. The pH of a solution is a close approximation of the negative of the logarithm (to the base 10) of the hydrogen ion concentration, $[H^+]$ (in moles per liter):

$$pH = -\log [H^+]$$

(We say "approximation" because chemists define pH in terms of the activity of hydrogen, which is the concentration of hydrogen ions available for chemical reaction. A small fraction of the hydrogen ions are involved in electrostatic interactions with other ions.) For example, a solution with a hydrogen ion concentration of 10^{-4} mol per liter would have a pH of 4, because the logarithm of 10^{-4} is -4 . At room temperature, pure water is defined as having a neutral pH, or a pH of exactly 7. Solutions with a pH less than 7 are acids, whereas solutions with a pH greater than 7 are bases (Box Figure 8-2). The pH of the surface and deep oceans is slightly basic—about 8 and 7.5, respectively. Rainwater that is in equilibrium with atmospheric CO_2 has a slightly acidic pH, between 5 and 6. Most lakes, rivers, and streams range in pH from about 6 to 9, that is, from slightly acidic to mildly basic.



BOX FIGURE 8-2 The pH scale.

in the construction of calcium carbonate shells and skeletons. Important calcium-bearing silicates include *anorthite*, $CaAl_2Si_2O_8$, and *hornblende*, $NaCa_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$. However, we will use *wollastonite* ($CaSiO_3$), which has a much simpler formula, to represent calcium silicates. It is the relative amounts of calcium and silicate that matter to our discussion of chemical weathering, not the detailed compositions of the weathered minerals.

When exposed to rain, both carbonates and silicates weather chemically, although the carbonates dissolve much more rapidly (Figure 8-14). Chemical weathering neutralizes the acidity of carbonic acid in much the same way that an antacid neutralizes the acidity of your stomach:

Carbonate weathering:





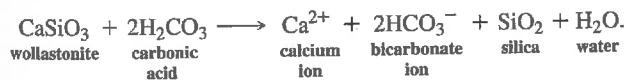
(a)



(b)

FIGURE 8-14 Differential weathering of (a) granite and (b) limestone. The granite headstone is a few years older than the limestone tombstone. (Sources: (a) Bill Aron/Photo Researchers and (b) Mark Burnett/Photo Researchers)

Silicate weathering:



In both weathering reactions, the products include Ca^{2+} and HCO_3^- . Silicate weathering also yields dissolved silica (SiO_2), which, together with Ca^{2+} and HCO_3^- , is transported to rivers and ultimately to the oceans. Silicate weathering consumes twice as much dissolved CO_2 (in the form of carbonic acid) as does carbonate weathering. This fact will prove important later in this chapter when we attempt to balance the carbon cycle.

Carbonate Mineral Deposition

The oceans eventually receive the products—soil particles and dissolved materials—of the chemical and physical weathering and erosion of the land surface. Most of the particulate material is deposited near the mouths of rivers in deltas, beaches, and other deposits near shore. In contrast,

the dissolved materials mix with seawater and, if their residence times are longer than the ocean's mixing time, are distributed throughout the world's oceans. The constant flux of dissolved materials from land to sea would gradually increase the saltiness of seawater by dilution were it not for processes that continuously remove material from the sea (see Chapter 5).

Some organisms, such as diatoms (Figure 8-8a), radiolarians (Figure 8-8d), and sponges, remove dissolved silica from seawater. They convert it into solid (opaline) silica as the structural part of their skeletons. Other organisms, such as foraminifera (Figure 8-8c), coccolithophorids (Figure 8-8b), corals, and shellfish, produce solid CaCO_3 in forming their shells and skeletons. Although these minerals can form *abiotically* (without the aid of organisms), most of the CaCO_3 precipitated from the ocean today is formed by such organisms.

These carbonate-producing marine organisms remove Ca^{2+} and HCO_3^- from seawater and precipitate CaCO_3 as a shell or skeleton. The overall chemical reaction is essentially the reverse of the carbonate weathering reaction:

Carbonate precipitation:

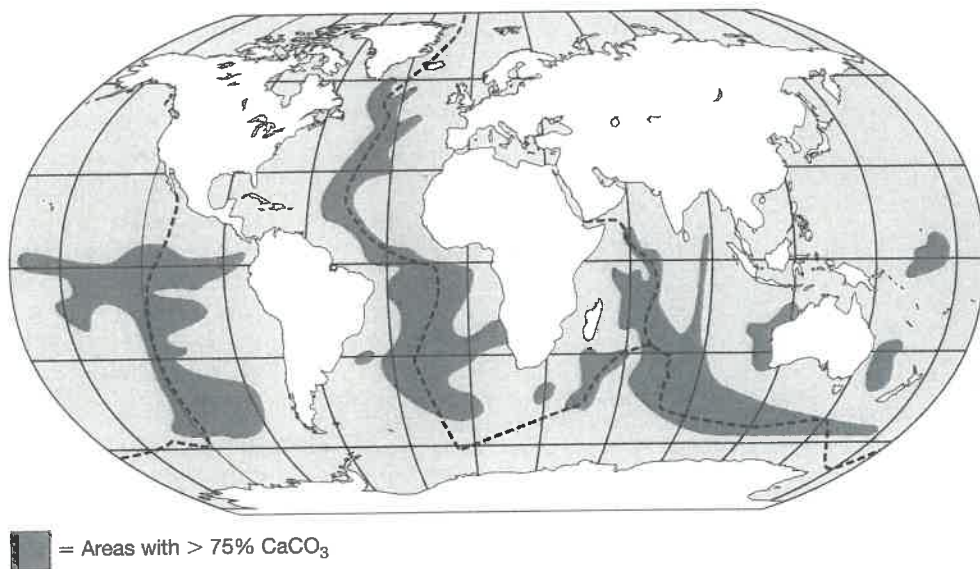


Calcium carbonate producers cause a shift in the ocean's carbon chemistry. By precipitating CaCO_3 shells or skeletons, they enhance H_2CO_3 (and, because of the equilibrium in reaction 1, dissolved CO_2) concentrations and reduce HCO_3^- concentrations, as well as pH. By increasing the concentration of dissolved CO_2 in surface waters, carbonate-producing organisms produce a CO_2 gradient between the oceans and the atmosphere. This gradient promotes the diffusion of CO_2 from the oceans to the atmosphere.

Some carbonate producers (e.g., coccolithophorids) are also phytoplankton. They photosynthesize organic matter, which tends to drive the dissolved carbon system in the opposite direction, toward lower CO_2 concentrations; hence these microorganisms have opposing effects on atmospheric CO_2 concentrations. However, the majority of phytoplankton do not produce carbonate skeletons. Thus, the overall effect of biological production in the surface ocean is in favor of reduced CO_2 concentrations: On average, the ratio of organic matter to carbonate mineral production for plankton is about 4:1.

When plankton die, their shells or skeletons sink through the water column but are less subject to destruction during the trip to the seafloor than is their organic debris. In regions where the total water depth is less than 4 km or so, carbonate particles accumulate more or less intact on the seafloor. These waters are said to be *saturated* with respect to CaCO_3 . This shallower-water deposition of planktonic debris is part of the material that eventually becomes limestone. Other limestones form in very shallow

FIGURE 8-15 The distribution of CaCO_3 -rich sediments on the seafloor. The pattern closely matches the areas of higher topography (shallower water) along the mid-ocean ridge system. (Source: W. S. Broecker and T.-H. Peng, *Tracers in the sea*, New York: Eldigio Press, Columbia University, 1982, p. 59.)



tropical waters, where reefs and other carbonate-producing organisms live on the seafloor. Deeper waters, however, have higher concentrations of dissolved CO_2 (carbonic acid), due to the decomposition of organic matter (Box Figure 8-1). As a result, these waters are corrosive to CaCO_3 ; they are said to be *undersaturated* with respect to CaCO_3 . Carbonate particles (mostly shells and skeletons of planktonic organisms) settling through these corrosive waters dissolve slowly, and if the water is very deep, they dissolve completely. The depth below which they are completely dissolved is called the *carbonate compensation depth* (CCD). Below this depth, carbonate materials do not accumulate on the seafloor. Thus, the deep-ocean basins are devoid of the cover of plankton-derived carbonate sediments that occupy the shallower parts of the ocean, for example, along the mid-ocean ridges (Figure 8-15). Interestingly, carbonate sediments deposited on mid-ocean ridges are carried slowly to depths below the CCD as the seafloor spreads away from the ridge, cools, and subsides (see Chapter 7). If it weren't for a protective layer of sediments deposited above these carbonate sediments, they would dissolve as they were carried below the CCD by seafloor spreading.

Summary of the Inorganic Carbon Cycle

In the past few sections, we have discussed several processes that affect the transfer of inorganic carbon. These processes can be combined into a mass-flow diagram for the inorganic carbon cycle (Figure 8-16). The free exchange of CO_2 between the atmosphere and the oceans tends to keep the atmosphere near equilibrium with surface waters. During chemical weathering, CO_2 dissolved in rain and soil waters becomes converted to HCO_3^- (neutralized), which is carried to the oceans. There organisms combine it with Ca^{2+} in precipitating CaCO_3 shells or skeletons. Some of the CaCO_3 dissolves in the water

column and on the seafloor. The rest is buried beneath the seafloor, becoming part of the limestone reservoir. When tectonic uplift occurs after millions of years, the limestones become exposed at Earth's surface. There they undergo chemical weathering, and the cycle continues.

Net Removal of CO_2 from the Ocean and Atmosphere

We can combine the equations that we presented in previous sections for carbonate and silicate weathering and for CaCO_3 precipitation to determine the net effects of these processes on the chemistry of the oceans and on the composition of the atmosphere. To do this, we simply add the equations by adding the left-hand sides of both equations, adding the right-hand sides of both, and then canceling out terms that appear on both sides of the resulting equation—exactly as we would in adding two algebraic expressions. The net effect of CaCO_3 weathering on land and CaCO_3 precipitation in the ocean is zero, because the two processes balance each other:

Carbonate weathering:



Carbonate precipitation:



Net result: 0

The weathering equation is the reverse of the precipitation equation.

The situation is different for the weathering of calcium silicate minerals on land. First of all, calcium-silicate minerals do not reform under Earth surface conditions. Thus, the calcium liberated during silicate weathering ultimately leaves the ocean as CaCO_3 . Second, recall from the silicate weathering equation that two molecules of H_2CO_3 are needed to dissolve silicate minerals, whereas only one

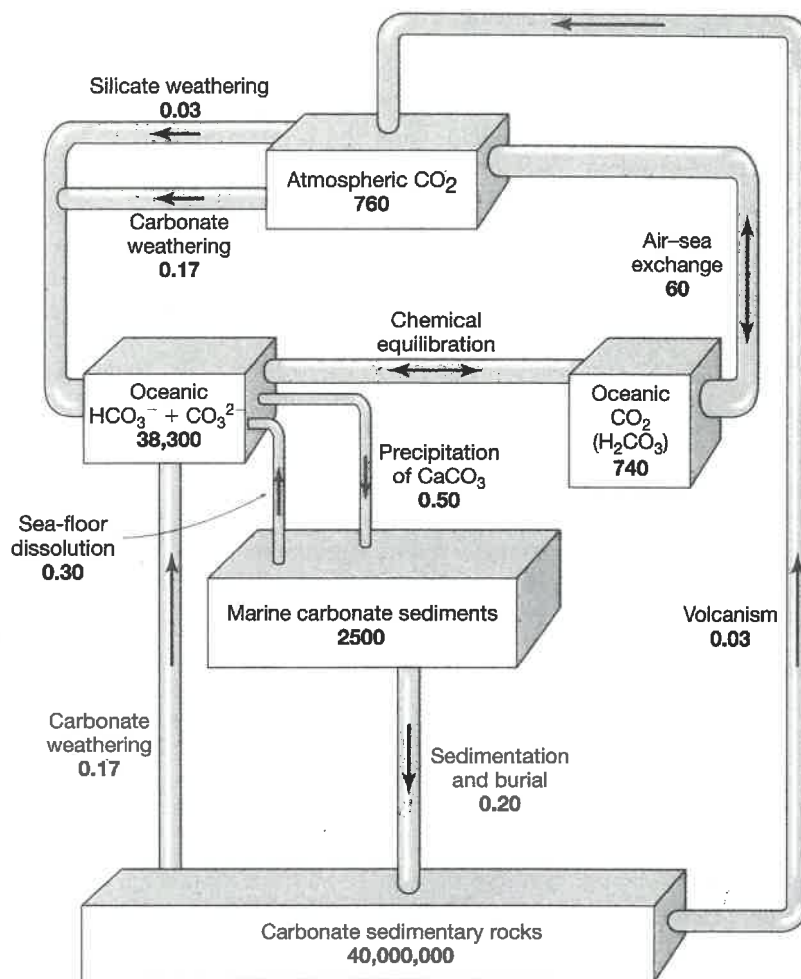
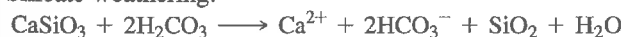


FIGURE 8-16 The global inorganic carbon cycle. Reservoir sizes in Gt(C), fluxes in Gt(C)/yr.

H₂CO₃ molecule is liberated when carbonate-bearing organisms precipitate their shells or skeletons. Thus:

Silicate weathering:



Carbonate precipitation:



Ocean-atmosphere CO₂ exchange:



Net result:



(The SiO₂ liberated during silicate weathering is utilized by diatoms and radiolaria in skeleton production.) So, the combined processes of silicate weathering on land and carbonate precipitation in the sea lead to a net conversion of atmospheric CO₂ to solid CaCO₃. This process serves as a net outflow of CO₂ from the atmospheric reservoir, analogous to the net outflow of photosynthetically produced organic carbon that leaks out of the organic carbon cycle due to sedimentary burial.

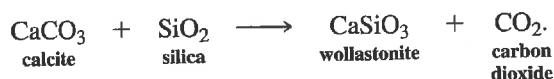
Like the leak in the organic carbon cycle, the rate of conversion of atmospheric CO₂ to limestone by silicate

weathering and CaCO₃ deposition is quite small: about 0.03 Gton(C)/yr. Nevertheless, if left unbalanced, this flux would apparently deplete the atmosphere of carbon in about 20,000 years. Actually, this number is misleading, because we have not accounted for the fact that the various oceanic reservoirs hold more than 50 times more carbon than the atmospheric reservoirs hold (see Figure 8-3). A reduction in atmospheric CO₂ creates a concentration gradient between the atmosphere and the oceans. As a consequence, CO₂ diffuses from the oceans to the atmosphere until the gradient is removed. Thus, the depletion time would be more like a million years, the time it would take for all the oceans' inorganic carbon to diffuse into the atmosphere and react with silicate rocks. Although this characteristic response time is significantly longer than the calculated 20,000 years, it is still short in terms of changes in atmospheric composition and climate over geologic time scales of many millions of years. On such time scales, then, there must be a return flux of CO₂ to the atmosphere and oceans to offset this outflow. This balance, which is in essence the long-term inorganic carbon cycle, has come to be known as the *carbonate-silicate geochemical cycle*.

THE CARBONATE-SILICATE GEOCHEMICAL CYCLE

After inorganic carbon is involved in chemical weathering and carbonate mineral precipitation and is removed by sedimentary burial, plate tectonics provides the needed return flux of CO_2 in the form of metamorphic and volcanic CO_2 inputs to the atmosphere. Mantle-derived CO_2 is released to the ocean-atmosphere system at mid-ocean ridges and along convergent margins (Figure 8-17). This carbon is derived from the mantle and so is, in a sense, "new."

At convergent plate margins (deep-sea trenches), some of the sediments resting on the downgoing slab are subducted along with the plate (see Chapter 7). The plate and its sediment cover are carried to depths as great as hundreds of kilometers within the mantle, where high temperatures and pressures promote chemical reactions that transform the sediments into metamorphic rock. Among these reactions is the reaction between sedimentary carbonate minerals and silica-rich sediments that forms silicate minerals and releases CO_2 :



This process is termed **carbonate metamorphism**. As before, we use the mineral wollastonite to represent the more complex silicate minerals that are typically generated by this process.

If sufficiently high temperatures are reached at depth during carbonate metamorphism, magmas are generated. These magmas may erupt in volcanoes at the surface, releasing CO_2 to the atmosphere. The CO_2 in these volcanoes probably includes some mantle-derived CO_2 and some CO_2 from the subducted crust and sediments, but scientists do not yet know the relative proportions of these two sources. Under metamorphic conditions the CO_2 produced can migrate as a fluid toward the surface. Although a substantial fraction of it reacts with minerals along the way, some CO_2 is released through springs and seeps to the atmosphere.

Together, silicate weathering, carbonate precipitation, and ocean-atmosphere exchange are the reverse of carbonate metamorphism. (Compare the equation for the net result of these processes, given in the previous section, with the carbonate metamorphism equation.) Without a fairly close balance between the inflows and outflows of carbon, the supply of this important greenhouse gas to the atmosphere and ocean would, on geological time scales, quickly be depleted. Earth would soon become a frozen ball of ice.

That may have been the fate of Mars, which appears to once have had flowing water on its surface and, perhaps, a CO_2 -rich atmosphere with a stronger greenhouse effect. In contrast, on Earth the release of CO_2 after carbonate metamorphism and volcanism has essentially balanced the consumption of CO_2 during silicate weathering over the history of the planet. What has ensured this balance? We cannot call on simple chemical equilibrium, because the reactions involved are representative of a whole host of processes rather than a single chemical reaction. Rather, we must look for feedback loops that, according to the amount of CO_2 in the atmosphere, adjust the rates of CO_2 input by volcanism or of CO_2 removal by silicate weathering and thereby keep the reservoir at steady state.

Long-Term Feedbacks in the Carbonate-Silicate Cycle

Because it is driven largely by heat flow from Earth's interior, the rate of volcanism is probably not very sensitive either to the amount of CO_2 in the atmosphere or to the climate of Earth's surface. In contrast, many climatic factors affect the rate of chemical weathering. The regulation of atmospheric CO_2 on long time scales (millions of years) likely is the consequence of the feedback between climate and rates of silicate weathering. The climatic factors that help regulate the chemical weathering rates of silicate rocks include the following:

- **Temperature:** rates of reactions, including chemical weathering, tend to increase as temperature increases.

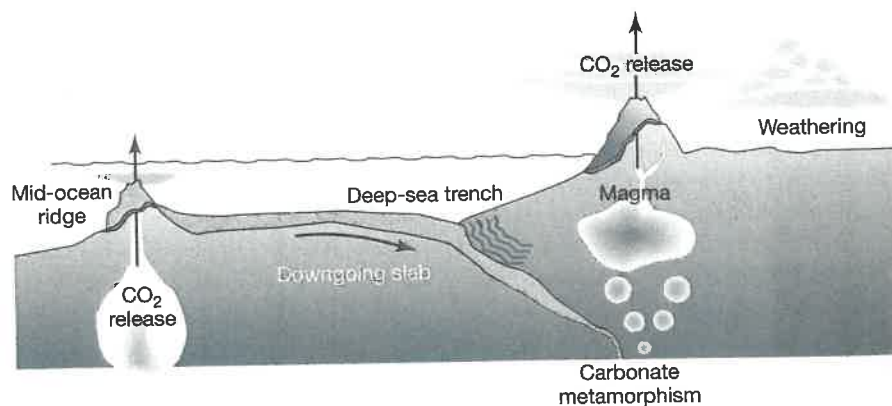


FIGURE 8-17 Pictorial representation of the carbonate-silicate geochemical cycle.

- Net rainfall: weathering requires water as a medium both for the dissolution of minerals and for the transport of the dissolved material to the oceans, and thus weathering rates rise as precipitation increases.

These environmental factors are responsive to atmospheric CO_2 levels. Recall from Chapter 3 that, as a result of the greenhouse effect, global temperatures rise as the atmospheric content of CO_2 increases and that rates of evaporation increase with increasing temperature. We know from Chapter 4 that water that evaporates from the ocean must fall as precipitation. For these reasons, we would expect that a warmer world would be a wetter world: Net precipitation should increase as temperature increases. Thus, the silicate weathering rate should increase as the atmospheric CO_2 level rises. Figure 8-18 shows a feedback loop for these processes. On the other side of the feedback loop, increased silicate weathering rates tend to reduce atmospheric CO_2 levels because silicate weathering uses up carbonic acid.

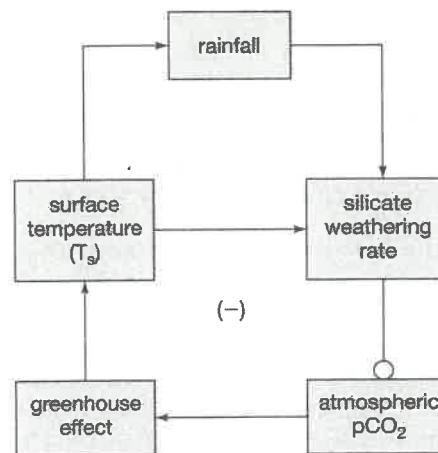


FIGURE 8-18 Systems diagram showing the negative feedback loop that results from the climate dependence of silicate–mineral chemical weathering and its effect on atmospheric CO_2 . This feedback loop is thought to be the major factor regulating atmospheric CO_2 concentrations and climate on long time scales.

A CLOSER LOOK

Biological Enhancement of Chemical Weathering

A particularly active and controversial area of geological research centers on the extent to which terrestrial biota may enhance rates of chemical dissolution of minerals exposed at Earth's surface. Several factors are involved, including the following:

- Microbial decomposition and respiration by plant roots in soils generate large amounts of carbon dioxide. The CO_2 concentration in soils is generally 10 to 100 times that in the atmosphere.
- Microbial decomposition also releases organic acids that cause mineral dissolution. By increasing weathering rates, these biological processes enhance the release rate of essential mineral nutrients to the biota.
- Plant root development leads to the stabilization of soils on steep slopes, where erosion would otherwise strip soils away. This process creates a more stable weathering environment where mineral dissolution can take place for longer times before erosion takes place.
- Roots penetrating through fractured rock tend to enlarge the fractures, causing further disintegration of the rock and allowing water and soil acids to penetrate deeper into the rock.

Field experiments to test the hypothesis of biological enhancement of chemical weathering span environments that have huge contrasts in climate (Iceland and Hawaii) but similar types of exposed rocks (basalts). In Iceland, scientists have found that streams draining areas of plant cover have significantly higher dissolved ion concentrations than do those draining areas of bare rock.

In Hawaii, scientists are looking at rock surfaces covered with lichens (Box Figure 8-3) and comparing them with bare surface exposures. Underneath the lichen there generally is a

thin layer of material that is leached of the more soluble elements; bare surfaces have no such layer. These leached layers appear to be the result of mineral dissolution aided by the production of organic acids, although some scientists argue that the leached layers actually are wind-blown dust trapped by the lichens. Further research is needed to resolve this controversy.

Calculations of the extent of biological enhancement from various field studies are somewhat wide-ranging but indicate that biological activity accelerates rates of chemical weathering by at least a factor of 2. Some lichens studies have concluded that that factor is several hundred times. In any case, biological processes are very important components of the feedback loop that regulates global chemical weathering rates, and thus atmospheric CO_2 levels, on geological time scales.



BOX FIGURE 8-3 [See color section] The lichen *Xanthoria parietina* and other lichens on a seashore rock, England. (Source: Dr. Morley Read/Shutterstock.)

The overall feedback loop, as shown in Figure 8-18, is negative. The feedback tends to stabilize Earth's climate against perturbations, as we will see later.

LINKS BETWEEN THE ORGANIC AND INORGANIC CARBON CYCLE

Although we have differentiated between the terrestrial and marine organic carbon cycles and between the organic and inorganic carbon cycles, all these cycles are inextricably linked as parts of the global carbon cycle. Changes that occur on land rapidly affect the oceans through the transport of carbon and nutrients by rivers and through variations in atmospheric CO₂. Changes in the recycling of organic matter affect atmospheric and oceanic CO₂ and in turn the whole of the carbon cycle. Thus, the cycle divisions we have made are artificial, but they help us represent a complicated system in simple terms.

PHOSPHORUS AND NITROGEN CYCLES

Our focus in this chapter and throughout the book is on the carbon cycle because of its paramount importance to the functioning of the Earth system. However, most elements on the periodic table are recycled along with carbon on a variety of time scales. Rocks exposed to weathering contain a host of elements that are carried by rivers to the ocean, taken up by marine organisms or scavenged onto settling particles, removed to sediments and sedimentary rocks, and entrained in the rock cycle.

Two elements are of particular interest: nitrogen (N) and phosphorus (P). These two elements are required by all living organisms for the synthesis of such essential compounds as proteins and ATP (adenosine triphosphate, an important molecule in metabolism). Organisms have evolved special enzymes and metabolic pathways to facilitate the extraction of these nutrient elements from otherwise unavailable forms (e.g., *alkaline phosphatase* to release P from organic compounds, and *nitrogenase* to convert N₂ to nutrient ammonia), thus speeding the recycling of the elements. Let's take a more detailed look at the cycling of these two elements and consider how they together control the productivity of the biosphere.

The Phosphorus Cycle

Cycle of P

I put some P into the sea
the biomass did swell
But settling down soon overcame
and P went down toward Hell

From purgatory soon released
it moved up to the land
To make a perfect rose for thee
to carry in thy hand
But roses wilt and die you know
then P falls on the ground
Gobbled up as ferric P
a nasty brown compound
The world is moral still you know
and Nature's wheels do grind
Put ferric P into the sea
and a rose someday you'll find

Robert M. Garrels

This poem, by the pioneering geochemist Robert Garrels (deceased), describes a life cycle for a P atom (Figure 8-19) that is quite similar to that described for C previously. Phosphorus is a rock-derived nutrient, meaning that its largest repository is in Earth's interior, where it is found in igneous, metamorphic, and sedimentary rocks. It is liberated from these rocks through chemical weathering, and becomes available to terrestrial vegetation in soils. Being quite soluble, phosphorus is leached from soils and carried by rivers and groundwater to the ocean as phosphate ions, PO₄³⁻.

Where rivers discharge to the ocean, productivity is often enhanced by the delivery of nutrients, including P. Productivity is also high in regions of upwelling because deep water is also nutrient-rich. In most other areas, the surface ocean is poor in nutrients because of aggressive uptake by plankton or attachment onto settling mineral particles, especially those containing oxidized iron minerals (the "ferric P" of Garrels's poem). These nutrients are then transferred to the deep ocean by the biological and "iron" pumps. A very small fraction of the P settling with the biological pump is transferred to the seafloor and is buried with the sediments; the rest is released to the deep ocean when the organic matter decomposes.

Over tens of thousands of years, the burial flux of phosphorus must balance the riverine input. How this balance is achieved remains the subject of active research, but it must involve a coupling between the burial rate and the amount of P in the ocean (Figure 8-20). If the P input from rivers were to exceed the P output to sediments, P would accumulate in the ocean. Higher P concentrations of upwelling deep waters would stimulate biological productivity, and the flux of organic detritus to the seafloor would increase. Much of this material would be recycled, but a fraction would escape decomposition and be buried. Hence, the phosphate content of the ocean would eventually stabilize, but at a higher concentration than before the increase in riverine delivery of P.

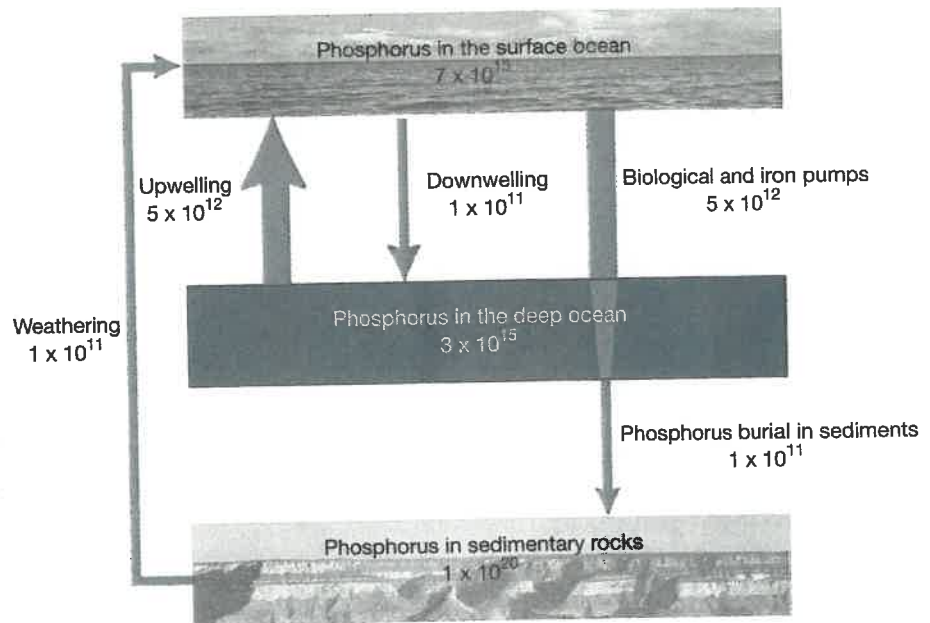


FIGURE 8-19 The global marine phosphorus cycle. Reservoir sizes in moles, fluxes in moles/yr.

The Nitrogen Cycle

This feedback mechanism regulating the phosphorus content of the oceans depends on the response of marine biological productivity and biological pumping to an increase in the phosphate supply. But other nutrients, especially nitrogen, are also required by organisms. Might N become limiting to biological productivity as P availability increases? If so, which element is really controlling productivity? Carbon itself is highly abundant in seawater, and unlikely to become limiting. But nitrogen does show the characteristics of a limiting nutrient: because of biological uptake, surface waters are as strongly depleted in N as they are in P (see Box Figure 8-1 and Figure 8-21). The nitrogen cycle, however, differs from the phosphorus cycle in one key attribute: the supply of N to the ocean

does not come primarily from the weathering of rocks and transport by rivers.

Recall that the atmosphere is dominantly composed of nitrogen gas (N_2 ; Table 3-2). Vigorous gas exchange between the atmosphere and ocean provides a tremendous amount of N_2 to the ocean, but it is unavailable to the biota as a nutrient in this form because the chemical bond between the two nitrogen atoms is very strong; organisms need to have N in a reactive form such as nitrate (NO_3^-) or ammonium (NH_4^+) in order to grow. Marine biologists call the biologically available nitrogen in seawater **fixed nitrogen**. Certain types of planktonic organisms, primarily the cyanobacteria, are able to break this strong bond and “fix” nitrogen using the enzyme nitrogenase. These nitrogen fixers have a competitive edge in waters that are depleted of fixed nitrogen but that have an adequate supply of phosphorus. They photosynthesize and grow, and when they die and decompose the nitrogen they fixed becomes available to other organisms. Thus, N_2 fixers tend to increase the inventory of fixed nitrogen in the ocean by providing nutrient N at rates that greatly exceed the riverine input. Nitrogen is also fixed on land, primarily by bacteria that live in the root systems of plants, and some of this fixed nitrogen makes its way to the ocean as dissolved and particulate nitrogen in rivers.

It is fortunate for marine life that nitrogen fixers are so good at creating fixed nitrogen, because there is an equally efficient mechanism at work converting fixed nitrogen (in its predominant form, nitrate) back to N_2 : **denitrification**. We’ll see in Chapter 9 that in environments

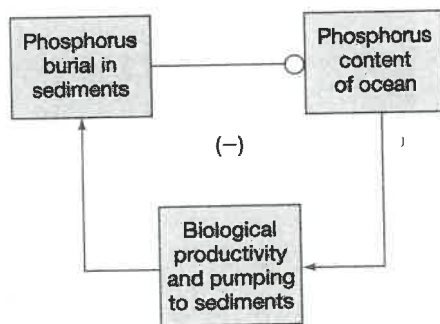


FIGURE 8-20 Negative feedback loop in the marine phosphorus cycle.

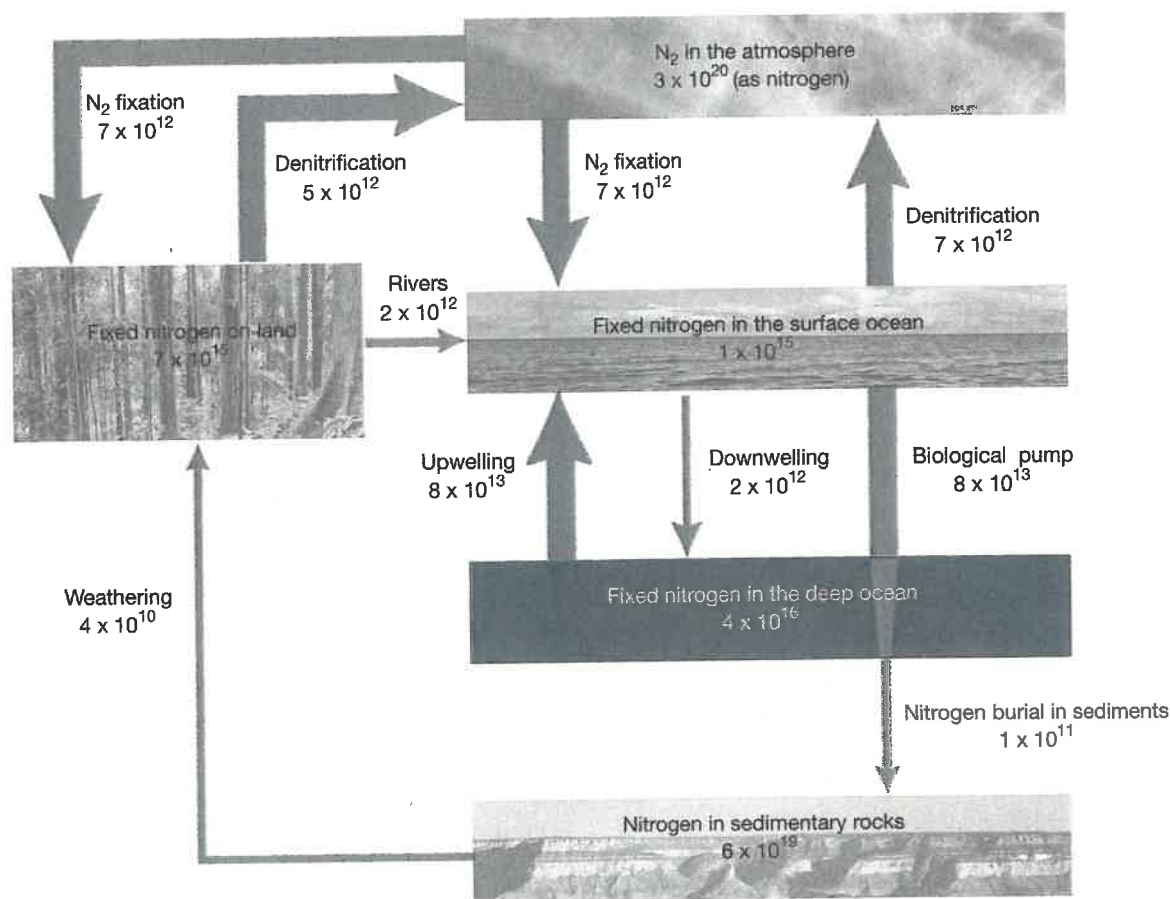


FIGURE 8-21 The global marine nitrogen cycle. Reservoir sizes in moles, fluxes in moles/yr. The cycle is shown as balanced, but there are great uncertainties in the numbers presented, and it is not clear that the modern cycle is balanced. (Source: Eky Chan/Shutterstock (left), Dean Bergmann/iStockphoto (top), Maxim Chupashkin/iStockphoto (center), Liz Leyden/iStockphoto (bottom))

where oxygen is scarce, such as in soils, marine sediments, and low-oxygen marine environments, bacteria use different sources of oxygen to decompose organic matter. One of these sources is the nitrate dissolved in seawater. In regions of low oxygen such as the oxygen minimum zone of the ocean (See the Box “A Closer Look: Oxygen Minimum Zone”), bacteria that can utilize nitrate thrive, converting nitrate to N_2 or the equally biologically unavailable gas nitrous oxide (N_2O), which is also a potent anthropogenic greenhouse gas and involved in the destruction of atmospheric ozone (see Chapters 15 and 17). The N_2 and N_2O they produce can be upwelled to the surface of the ocean and released to the atmosphere. Denitrification thus represents a net loss of fixed nitrogen from the ocean. Nitrogen fixation and denitrification represent the major input and output of fixed nitrogen from the ocean, respectively.

Phosphorus as the Ultimate Limiting Nutrient

Now we can return to the question of whether the proposed mechanism for phosphate regulation (Figure 8-20) is

viable, or whether nitrogen limitation might ultimately disable the coupling between phosphorus content of the ocean and biological productivity. The short answer is that the mechanism works, because the ocean adjusts itself to excesses or shortages of nitrogen through nitrogen fixation and denitrification. Geochemists therefore consider P to be the “ultimate” limiting nutrient. Again, consider the conse-

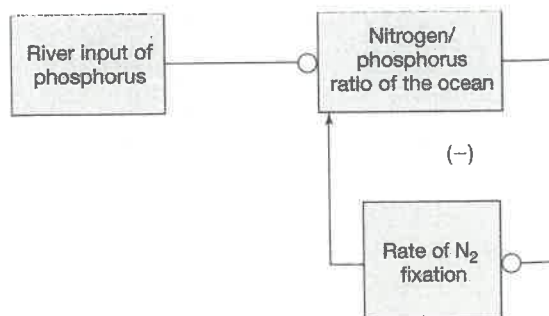


FIGURE 8-22 Feedback loop in the coupled marine phosphorus and nitrogen cycles, proposed to stabilize the N/P ratio of the oceans.

quences of an increase of phosphorus delivery to the ocean (Figure 8-22). The phosphate inventory of the ocean would begin to increase, and thus so would marine productivity. With no increase in the riverine nitrogen input, the fixed nitrogen inventory would fall. The N-P ratio of the ocean would fall below the Redfield ratio (see the section "Nutrient Limitation"). Nitrogen, however, would not become limiting. Upwelling deepwaters would be enriched in P but depleted in N, thus providing a competitive

advantage to nitrogen-fixing phytoplankton. An increase in their numbers would then increase the global rate of nitrogen fixation, thereby restoring the ocean's N-P ratio to the normal Redfield ratio. Global rates of biological productivity and carbon, nitrogen, and phosphorus burial in sediments would all be higher. Thus, even when P input from rivers is relatively high, phosphorus retains its status as the "ultimate" limiting nutrient to biological productivity in the ocean.

Chapter Summary

1. The global carbon cycle involves processes that occur on land and in the oceans and involve both biological and nonbiological chemical reactions.
2. The terrestrial and marine organic carbon cycles operate on a variety of time scales. On the short time scale (tens to hundreds of years),
 - a. carbon dioxide is removed from the atmosphere during photosynthesis on land and returned during respiration and decomposition; methane is released to the atmosphere from soils, where anaerobic metabolism is taking place.
 - b. a small amount of terrestrial organic carbon survives respiration and decomposition and is buried in sedimentary basins on land or is transported to the sea.
 - c. in the oceans, phytoplankton produce organic matter that is consumed by zooplankton and decomposed by aerobic and anaerobic bacteria.
 - d. a small fraction of the organic matter settling through the water column is not decomposed and is instead buried in marine sediments.
3. On longer time scales (millions of years), the organic matter buried in sediments undergoes lithification with the sediments. Most of these sediments are muds, and the rocks formed are shales.
 - a. When concentrations of organic matter are very high in the sediment, fossil fuels may form during burial and lithification.
 - b. The sedimentary rocks may eventually undergo uplift through tectonic processes, exposure, and weathering. During weathering, organic matter undergoes oxidation, producing CO_2 , which escapes to the atmosphere.
4. An inorganic carbon cycle, involving oxidized forms of carbon, is important on both short and long time scales (millions of years).
 - a. Atmospheric CO_2 exchanges with CO_2 dissolved in the surface ocean on a time scale of decades. The uptake of CO_2 is enhanced by reactions among the forms of dissolved inorganic carbon in seawater.
 - b. Atmospheric CO_2 dissolves into rainwater, creating an acidic solution. When the rain falls on the land surface, reactions with carbonate and silicate minerals convert carbonic acid to bicarbonate ion. The bicarbonate ion is carried by rivers to the oceans.
 - c. In the oceans, carbonate-secreting organisms use the bicarbonate ion in the construction of their shells or skeletons. This material may dissolve in transit or it may become part of the sediment that covers the seafloor.
5. The regulation of atmospheric CO_2 on long time scales (millions of years) is the consequence of the feedback between climatic factors and rates of chemical weathering of silicate rocks, as part of the long-term inorganic carbon cycle, referred to as the carbonate-silicate geochemical cycle.
 - a. Any disturbance in the amount of atmospheric CO_2 affects climate through the greenhouse effect. Changes in climate affect silicate weathering rates and thus the rates of CO_2 consumption.
 - b. The overall feedback loop is negative, implying that on long time scales the climate system is stable against a wide range of perturbations.
6. The terrestrial and marine organic carbon cycles, the organic and inorganic carbon cycles, and the carbonate-silicate geochemical cycle are inextricably linked as parts of the global carbon cycle.
 - a. Changes on land are "communicated" rapidly to the oceans by riverine transport of carbon and nutrients and through variations in atmospheric CO_2 .
 - b. Changes in the recycling of organic matter affect atmospheric and oceanic CO_2 and in turn the whole of the carbon cycle.
7. The cycles of phosphorus and nitrogen largely control the biological productivity of the planet on a global scale.
 - a. Weathering provides the input of P to the Earth surface.
 - b. In contrast, the largest supply of nutrient N comes from bacterial nitrogen fixation.
 - c. P thus becomes the "ultimate" limiting nutrient.

Key Terms

acid	denitrification	photic zone
anion	fixed nitrogen	photosynthesis
base	inorganic carbon	primary producer
biological pump	limestone	primary productivity
biomass	methanogenesis	Redfield ratio
biosphere	nitrogenase	reduced carbon
carbonate metamorphism	nutrient	residence time
cation	organic carbon	steady state
characteristic response time	oxidized carbon	zooplankton
coal	petroleum	
consumers	pH	

Review Questions

- Which of the following carbon reservoirs has the longest residence time: plants, the oceans, or sedimentary limestone?
- One or more of the following processes involves organic carbon; identify it (them): the precipitation of a calcite skeleton, the exchange of carbon between the oceans and the atmosphere, dissolution at the seafloor, or oxidation during weathering.
- Describe the biological pump.
- Why is plate tectonics critical to the maintenance of an atmosphere-ocean reservoir rich in carbon?
- Limestone (carbonate) weathering does not lead to the net removal of carbon dioxide from the atmosphere. Why not?

Critical-Thinking Problems

- The key to stability is feedback between the reservoir and the fluxes into and/or out of the reservoir. Assume that the rate of outflow from a reservoir depends on the size of the reservoir according to the following relationship: outflow rate = $k \cdot (\text{size of reservoir})$, where k is a constant.
 - A reservoir of water has a volume of 5000 liters, and the rate of outflow at steady state is 25 liters per minute. What is k ? (Give both the numerical value and its units.) What is the residence time? What is the relationship between k and the residence time?
 - The inflow rate is 25 liters per minute. Describe graphically and in words how the reservoir size would change with time, beginning with a reservoir size of zero and continuing until the reservoir reaches steady state.
- Use Figure 8-4 to answer the following questions:
 - During which months is the rate of photosynthesis greatest, relative to the combined rate of respiration and decomposition, and during which months is it smallest? Explain your reasoning. Why aren't these coincident with the minimum and maximum CO_2 levels for the year, respectively?
 - On the basis of your answer to part (a), estimate, for each year, the maximum net rate of photosynthesis and the maximum net rate of respiration/decomposition for each of the three years shown.
 - Are there significant differences in these rates from year to year? If so, propose an explanation for them.
- A giant meteor crashes into Earth, causing devastating environmental changes that kill off all life in the oceans.
 - Describe how the vertical distribution of dissolved oxygen, carbon, and nutrients would respond over the course of the next several thousand years.
 - Would the temperature and salinity of the ocean be affected by the loss of the biological pump? Why or why not?
 - If global warming from CO_2 released to the atmosphere from the meteor impact site caused, instead of the complete loss of marine life, the sudden cessation of thermohaline circulation in the oceans, what would be the effect on the vertical and spatial distribution of dissolved nutrients, carbon, and oxygen in the world's oceans over the next thousand years?
- The atmosphere consists of 78% N_2 , 21% O_2 , 1% Ar, and about 0.036% (360 ppm) CO_2 . What is the mean molecular weight of air? Round your answer to three significant figures, and use the following table of atomic weights:

Element	Atomic Weight
C (Carbon)	12.011
N (Nitrogen)	14.0067
O (Oxygen)	15.9994
Ar (Argon)	39.948

 - The total mass of the atmosphere is about 5×10^{18} kg. How many moles each of air, O_2 , and CO_2 are present in the atmosphere? (Note: Calculate the latter two answers from the first one rather than by computing the masses of O_2 and CO_2 . The values listed in part (a) for the various gases are abundances by volume, not by mass. This fact, and the fact that a mole of any gas takes up the same volume at a given pressure and temperature, mean that you need to work in moles.)

- c. Forests contain about 600 Gton(C) in the form of wood and leaves. Suppose that all the world's forests were to burn down instantaneously. By how much would atmospheric CO_2 increase? By how much would O_2 decrease? Express your answers in percentages. Assume that the

equation for burning is the same as that for respiration (given earlier in this chapter).

5. Explain why lakes and rivers have slightly basic pH values, whereas rainwater (the ultimate source of water for lakes and rivers) is slightly acidic.

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