

The Economy of Nature

Fifth Edition

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Pathways of Elements in the Ecosystem

Energy transformation and element cycling are intimately linked

Ecosystems may be modeled as a series of linked compartments

Water provides a physical model of element cycling in the ecosystem

The carbon cycle is closely tied to the flux of energy through the biosphere

Nitrogen assumes many oxidation states in its cycling through ecosystems

The phosphorus cycle is uncomplicated chemically

Sulfur exists in many oxidized and reduced forms

Microorganisms assume diverse roles in element cycles



Should you be worried about the change in carbon dioxide concentration in the earth's atmosphere? Combustion of fossil fuels and burning of forests to clear land for

agriculture has increased the atmospheric concentration of CO_2 from 280 to 360 parts per million during the past century. Most of the change has been produced in recent decades, and projections show this trend increasing. The projected increases could bring about dramatic changes in climate through global warming, perhaps on the order of what we experience during extreme El Niño events. Such a scenario may disrupt agriculture and displace some of the human population. But major worries also include a rise in sea level due to melting ice caps and expansion of the surface waters of the oceans as they warm. These changes could flood vast coastal areas, causing economic disaster and rearranging human geography.

Yet the earth has witnessed far greater changes in atmospheric carbon dioxide concentrations in the past. Before the Industrial Revolution, CO_2 concentrations probably were as low as they have ever been in the geologic history of the earth. There is an important difference, however, between the present and the past. CO_2 levels are changing much more rapidly than they ever have before. Carbon and other chemical elements cycle continually through the ecosystem. The routes they take are determined by the particular chemical transformations in which each element participates. Organisms—including humans—move elements through their cycles within the ecosystem whenever they carry out energy transformations. This chapter shows how physical, chemical, and biological processes result in the cycling of elements within ecosystems. We shall see that many aspects of element cycling make sense only when one understands that chemical transformations and energy transformations go hand in hand.

Chemical elements, unlike energy, remain within the ecosystem, where they continually cycle between organisms and the physical environment. Materials used to form biological compounds originate in rocks of the earth's crust or in the earth's atmosphere, but within the ecosystem they are reused over and over by plants, animals, and microbes before being lost in sediments, streams, and groundwater or escaping to the atmosphere as gases. Though all the energy assimilated by green plants is "new" energy received from outside the ecosystem, most nutritive materials taken up by plants have been used before. Ammonia absorbed from the soil by roots might have been leached out of decaying leaves on the forest floor that same day. The carbon dioxide assimilated by a green plant might have been produced recently by animal, plant, or microbial respiration.



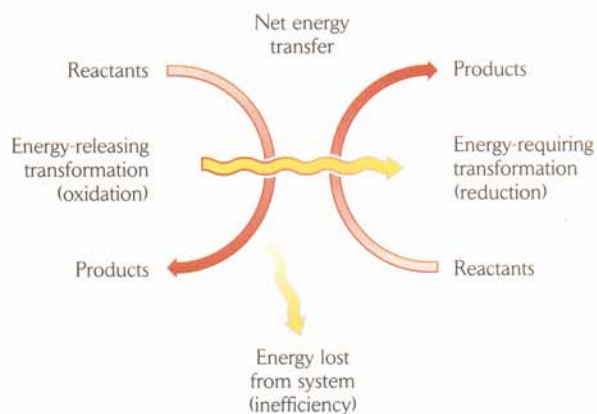
Energy transformation and element cycling are intimately linked

Organisms help to move elements through their cycles within the ecosystem whenever they make the chemical transformations needed to carry out their life processes. Transformations that incorporate inorganic forms of elements into the molecules of plants, animals, and microbes are referred to as **assimilatory** processes. One example of an assimilatory transformation of an element is photosynthesis, in which plants use energy to change an inorganic form of carbon (carbon dioxide) into the organic form of carbon found in carbohydrates. In the overall cycling of carbon, photosynthesis is balanced by respiration, a complementary **dissimilatory** process that involves the transformation of organic carbon back to an inorganic form, accompanied by release of energy.

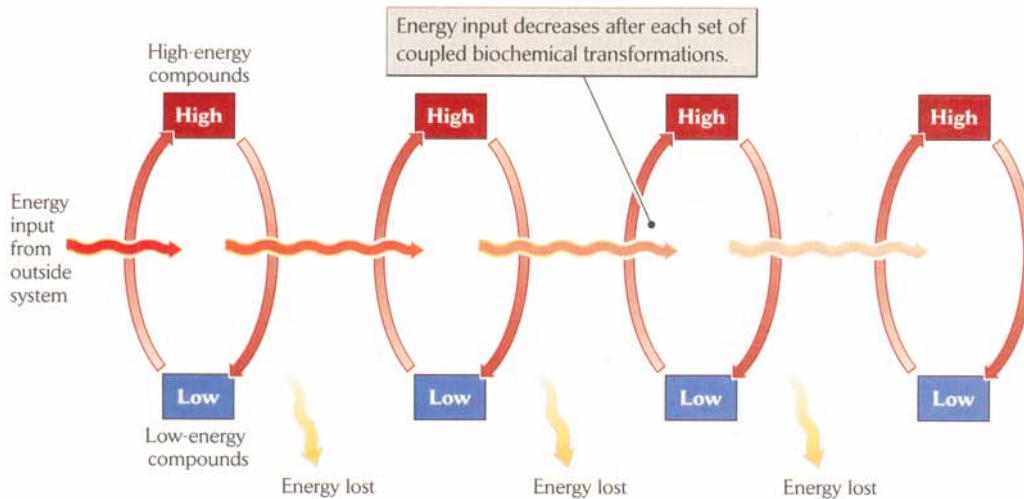
Not all transformations of elements in the ecosystem are biologically mediated, nor do all involve the net assimilation or release of useful quantities of energy. Many chemical reactions take place in the air, soil, and water. Some of these, such as the weathering of bedrock, release certain elements (potassium, phosphorus, and silicon, for example) from compounds in rock and make them available to the ecosystem. Lightning storms produce small amounts of reduced nitrogen (ammonia, NH_3) from molecular nitrogen (N_2) and water vapor (H_2O) in the atmosphere, which plants and microbes can assimilate. Such reactions may have been involved in the origin of life itself. Other physical and chemical processes, such as sedimentation of calcium carbonate in the oceans, remove elements from circulation and incorporate them into rocks in the earth's crust, where they may remain untouched for eons.

Most biological energy transformations are associated with the biochemical oxidation and reduction of carbon, oxygen, nitrogen, and sulfur. As we saw in Chapter 2, an atom is oxidized when it gives up electrons, and it is reduced when it accepts electrons. In a sense, the electrons carry with them a portion of the energy content of an atom. In biological transformations, an energy-releasing oxidation is paired with an energy-requiring reduction, and energy shifts from the reactants in one transformation to the products in the other (■ **Figure 7.1**). Such coupled transformations are possible only when the oxidation side releases at least as much energy as the reduction side requires. The energy changes associated with various transformations vary widely depending on the compounds involved and the number of electrons exchanged. It is in the nature of the physical world that the energies of the two transformations rarely match. Energy supplied by an oxidation reaction in excess of that required by a coupled reduction reaction cannot be used, and is lost in the form of heat. These imbalances account for the thermodynamic inefficiency of life processes.

A typical coupling of transformations might involve the oxidation of carbon in a carbohydrate (glucose, for example), which releases energy, and the reduction of nitrate-nitrogen to amino-nitrogen (which forms the building blocks of proteins), which requires energy. This, like many biochemical transformations, ties an energy-releasing transformation to the assimilation of an element—nitrogen, in this case—required for growth and reproduction. In animals, such biochemical transformations are also used to maintain the cellular environment and to effect movement. Some of these transformations involve many



■ **Figure 7.1** The coupling of energy-releasing and energy-requiring transformations is the basis of energy flow in ecosystems.



■ **Figure 7.2** Energy flows through biochemical pathways. As energy flows through an ecosystem, elements alternate between assimilatory and dissimilatory transformations, thus going through cycles.

intermediate steps of the type shown in Figure 7.1, linked together into a biochemical pathway (■ **Figure 7.2**). Plants accomplish the initial input of energy into the ecosystem by an assimilatory reduction of carbon in which light, rather than a coupled dissimilatory process, serves as the source of energy. A portion of that energy escapes biological systems with each subsequent transformation. The cycling of elements between the living and nonliving parts of the ecosystem is thus connected to energy flow by the coupling of the dissimilatory part of one cycle to the assimilatory part of another.



Ecosystems may be modeled as a series of linked compartments

With each biochemical transformation, one or more elements are changed from one form to another. Each form of an element within an ecosystem may be thought of as a separate compartment, like a room of a house, into and out of which atoms move as physical and biological processes transform them. The entire ecosystem may be thought of as a set of compartments among which elements are cycled (■ **Figure 7.3**). For example, photosynthesis moves carbon from the inorganic carbon compartment to that containing organic forms of carbon (assimilation); respiration returns it to the inorganic compartment (dissimilation). Such **compartment models** of ecosystems can be organized hierarchically, having subcompartments within compartments.

The inorganic carbon compartment includes carbon dioxide both in the atmosphere and dissolved in water, carbonate and bicarbonate ions dissolved in water, and calcium carbonate, mostly as a precipitate in the water column and in sediments. The organic carbon compartment also has many subcompartments: autotrophs, animals, microorganisms, and detritus. As organisms feed on others, they move carbon among these subcompartments.

The movement of elements within and between compartments often involves energy. Photosynthesis adds energy to carbon, which we may think of as lifting the element to the second floor of a house. In descending the respiration “staircase,” carbon releases this stored chemical energy, which an organism can then use for other purposes.

Elements cycle rapidly among some compartments of ecosystems and much more slowly among others. The movement of an element between living organisms and inorganic forms occurs over periods ranging from a few minutes to the life spans of organisms or their subsequent existence as organic detritus. We saw in the last chapter that some organic matter in some terrestrial environments has an average residence time on the order of centuries. Both organic and inorganic forms of elements occasionally leave rapid circulation within ecosystems for compartments that are not readily accessible to transforming agents. For example, coal, oil, and peat contain vast quantities of organic carbon that has been removed from circulation in ecosystems, often for many millions of years. Inorganic carbon is removed from circulation in aquatic ecosystems by precipitation of calcium carbonate, which forms thick layers of

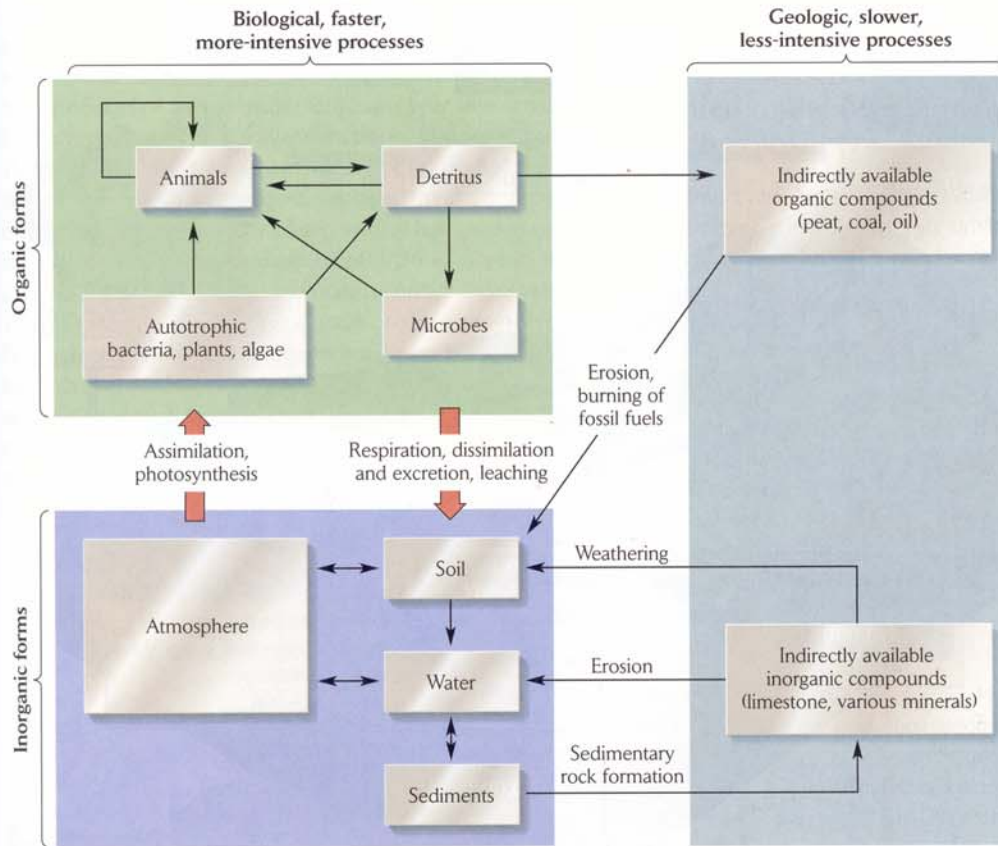


Figure 7.3 A generalized compartment model of the cycling of elements within ecosystems. Within each compartment, we can recognize subcompartments; for example, the compartment that represents available organic forms of nutrients is further subdivided into compartments occupied by autotrophs, animals, detritus, and microbes.

marine sediments that may eventually turn to limestone. These forms of carbon are returned to the rapidly cycling compartments of the ecosystem only by the slow geologic processes of volcanism, uplift, and erosion.



Water provides a physical model of element cycling in the ecosystem

Water is involved chemically in photosynthesis, but it is evaporation, transpiration, and precipitation that drive most movement of water through terrestrial ecosystems (Figure 7.4). These physical processes nonetheless couple the movement of water to transformations of energy. Thus, the global hydrologic cycle illustrates many basic features of the cycles of elements.

Light energy absorbed by water performs the work of evaporation. Water vapor has a potential energy, which is the energy of separation of individual water molecules from each other. When atmospheric water vapor condenses to form clouds, water molecules aggregate, and the potential energy in water vapor is released as heat, which eventually escapes the earth as long-wave radiation. From a thermodynamic standpoint, evaporation and condensation resemble photosynthesis and respiration.

Water in the biosphere totals about 1.4 billion cubic kilometers, or $1,400,000 \times 10^{18}$ g. It's hard to get a feeling for such a large number. 10^{18} g of water is a billion times a billion, or a quadrillion, grams. Each cubic meter contains 10^6 g, or 1,000 kg (a metric ton, T) of water, and so 10^{18} g is a trillion (10^{12}) metric tons—that is, a teraton (TT). Numbers on the order of 10^{18} generally are reserved for astronomy and the Federal budget, but we'll use

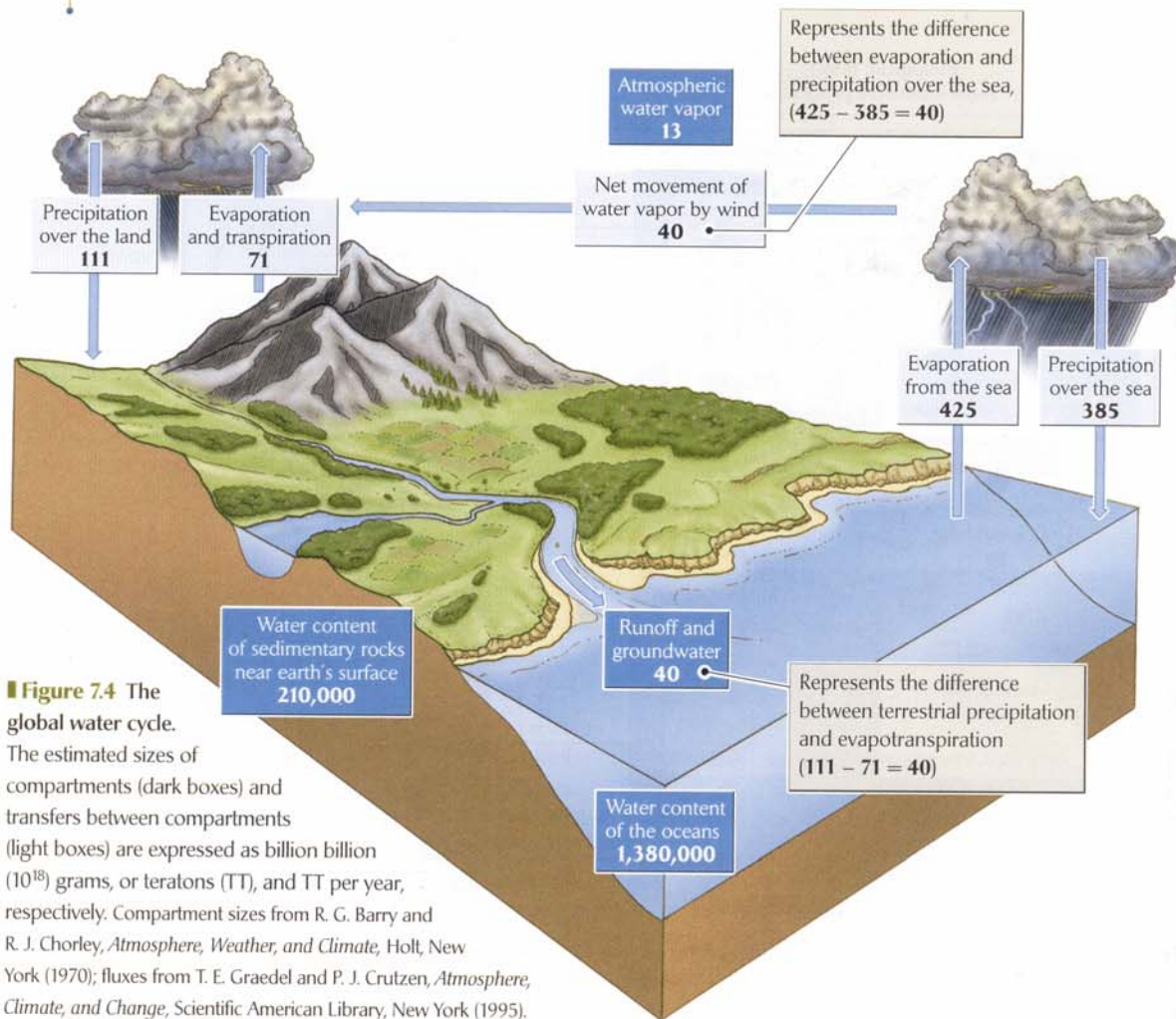


Figure 7.4 The global water cycle.

The estimated sizes of compartments (dark boxes) and transfers between compartments (light boxes) are expressed as billion billion (10^{18}) grams, or teratons (TT), and TT per year, respectively. Compartment sizes from R. G. Barry and R. J. Chorley, *Atmosphere, Weather, and Climate*, Holt, New York (1970); fluxes from T. E. Graedel and P. J. Crutzen, *Atmosphere, Climate, and Change*, Scientific American Library, New York (1995).

teratons here as a unit of global water to keep the number of zeros to a minimum.

More than 97% of the water in the biosphere resides in the oceans. Other reservoirs of water include ice caps and glaciers (29,000 TT), underground aquifers (8,000 TT), lakes and rivers (100 TT), soil moisture (100 TT), water vapor in the atmosphere (13 TT), and all the water in living organisms (1 TT). Each of these may be regarded as a separate compartment in a compartment model of water in the biosphere.

Over land surfaces, precipitation (111 TT per yr, which is 22% of the global total) exceeds evaporation and transpiration (71 TT per yr; 16% of the global total). Over the oceans, evaporation exceeds precipitation by a similar amount. Much of the water that evaporates from the surface of the oceans is carried by winds to the continents, where it is captured as precipitation by the land. This net flow of atmospheric water vapor from ocean to land

(40 TT per yr) is balanced by runoff from the land by way of rivers back into ocean basins.

Evaporation determines how fast water moves through the biosphere. The absorption of radiant energy by liquid water to create water vapor couples an energy source to the hydrologic cycle. We can calculate the energy that drives the global hydrologic cycle by multiplying the total weight of water evaporated (456 TT per yr) by the energy required to evaporate 1 g of water (2.24 kJ). The product, approximately 10^{21} kJ per yr (about 32 billion megawatts), represents about one-fourth of the total energy of the sun's radiation striking the earth. Condensation of water vapor to form precipitation releases the same amount of energy as heat. Evaporation and precipitation are closely linked because the atmosphere has a limited capacity to hold water vapor; any increase in the evaporation of water into the atmosphere creates an excess of vapor and causes an equal increase in precipitation.

The amount of water vapor in the atmosphere at any one time corresponds to an average of about 2.5 cm of water spread evenly over the surface of the earth. An average of 65 cm of rain or snow falls each year (the water flux), which is 26 times the average amount of water vapor. Thus the steady-state content of water in the atmosphere—the atmospheric compartment—replaces itself 26 times each year on average. (Conversely, water has an average residence time in the atmosphere of 1/26 of a year, or 2 weeks.) Soils, rivers, lakes, and oceans contain more than 100,000 times as much water as exists in the atmosphere. Fluxes through both compartments are the same, however, because evaporation balances precipitation. Thus the average residence time of water in its liquid form at the earth's surface (about 2,800 years) is about 100,000 times longer than its residence time in the atmosphere.



The carbon cycle is closely tied to the flux of energy through the biosphere

The carbon cycle resembles the hydrologic cycle in that energy from the sun provides its driving force. The carbon cycle is much more complex, however, owing to the various chemical reactions of carbon. Three classes of processes cause carbon to cycle through aquatic and terrestrial ecosystems (■ Figure 7.5): (1) assimilatory and dissimilatory reactions of carbon, primarily in photosynthesis and respiration, (2) exchange of carbon dioxide between the atmosphere and the oceans, and (3) sedimentation of carbonates.

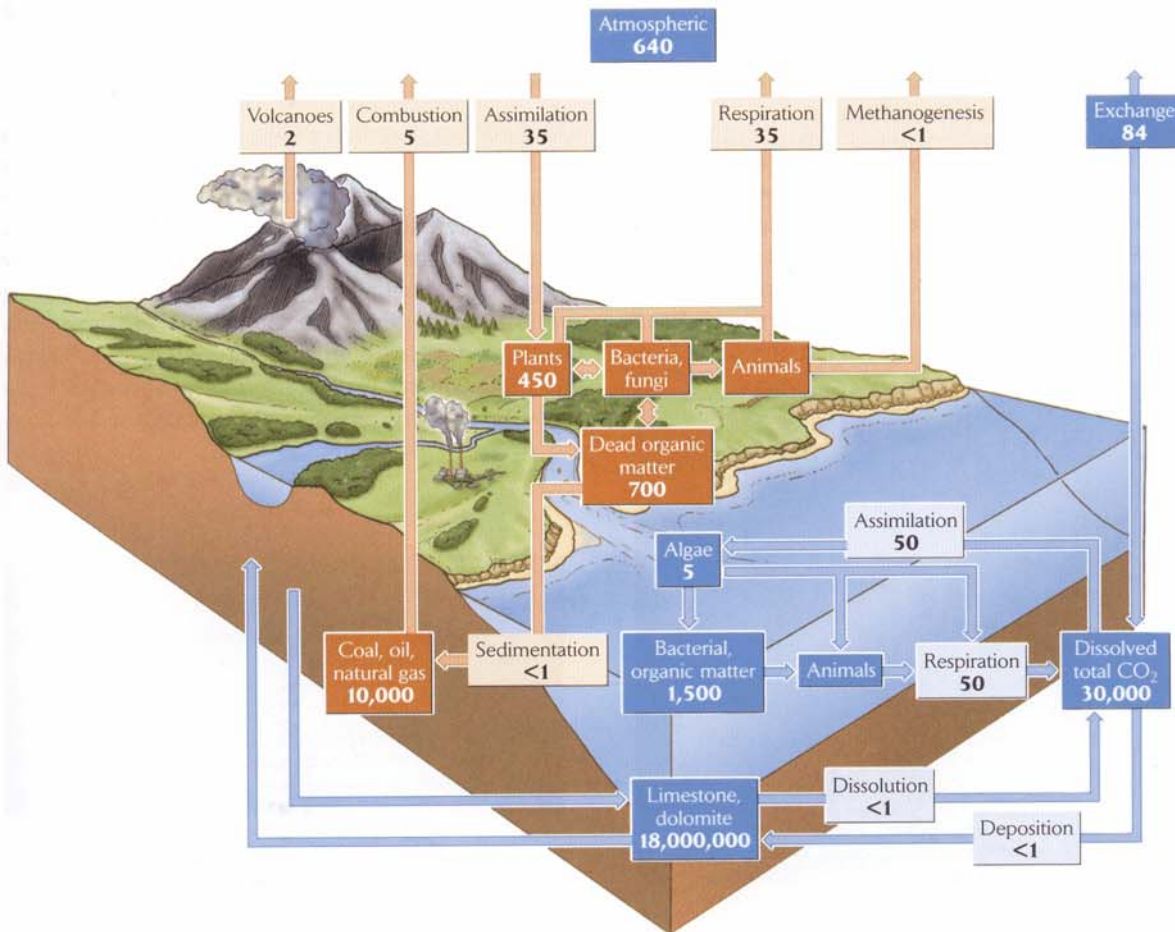


Figure 7.5 The global carbon cycle. The sizes of compartments and transfers between compartments are in billions of metric tons (10^{15} g), or gigatons (GT), and GT per year. After T. Fenchel and T. H. Blackburn, *Bacteria and Mineral Cycling*, Academic Press, New York (1979); W. D. Grant and P. E. Long, *Environmental Microbiology*, Wiley, New York (1981).

Photosynthesis and respiration

Photosynthesis and respiration are the major energy-transforming reactions of life. Approximately 85 billion metric tons (85×10^{15} g) of carbon enter into such reactions worldwide each year. (We will refer to a billion metric tons as a gigaton, using the symbol GT). During photosynthesis, carbon gains electrons and is reduced (■ Figure 7.6). This gain of electrons is accompanied by a gain in chemical energy. An equivalent amount of energy is released by respiration, which results in a loss of electrons and a loss of chemical energy.

Although it is difficult to estimate the total carbon in organic matter within the biosphere, it probably adds up to something like 2,650 GT, including both living organisms and organic detritus and sediments. Thus, considering that 85 GT of carbon are assimilated by photosynthesis each year, the average residence time of carbon in biological molecules is approximately 2,650 GT divided by 85 GT per yr, which equals 31 years.

Ocean–atmosphere exchange

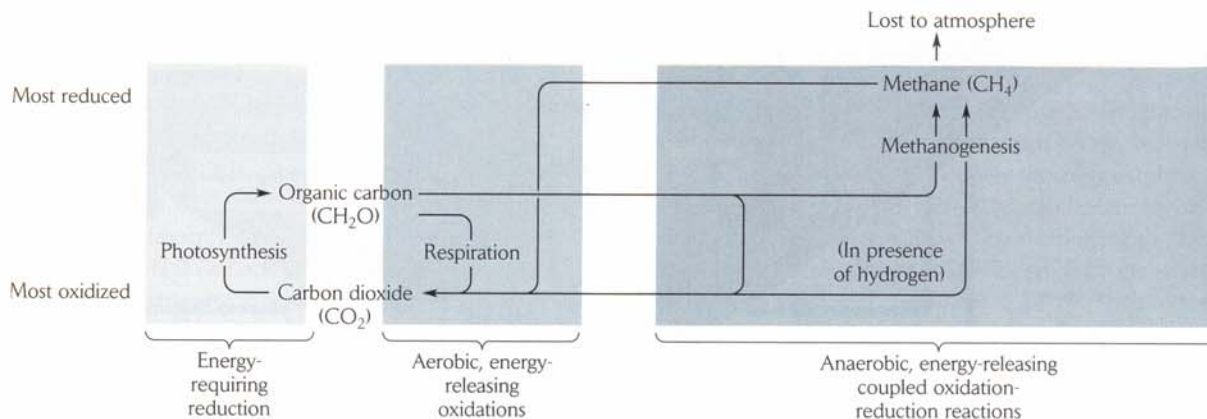
The second class of carbon cycling processes involves the physical exchange of carbon dioxide between the atmosphere and oceans, lakes, and streams. Carbon dioxide dissolves readily in water; indeed, the oceans contain about 50 times as much CO_2 as the atmosphere. Exchange across the air–water boundary links the carbon cycles of terrestrial and aquatic ecosystems. In fact, the ocean is an important sink for the carbon dioxide produced by the burning of fossil fuels. As the CO_2 content of the atmo-

sphere increases, the rate of solution of CO_2 in the ocean increases, thereby reducing the rate of increase of CO_2 in the atmosphere below what it would be in the absence of air–water interchange.

Of the total carbon in the atmosphere in the form of carbon dioxide (640 GT), approximately 35 GT is assimilated by land plants, and 84 GT dissolves in the ocean and other surface waters, each year. Respiration and the escape of dissolved carbon dioxide from water to the atmosphere replace these amounts. Overall, the average residence time of carbon in the atmosphere is about 5 years. Because of this short residence time, the amount of carbon dioxide in the atmosphere is very sensitive to the rate of CO_2 production, increasing very nearly in parallel with the burning of fossil fuels. By 1990, combustion of fossil fuels contributed about 6 GT of carbon annually, equivalent to almost 1% of the total atmospheric carbon dioxide and a sixth of the total assimilation of carbon by land plants.

Precipitation of carbonates

The third class of carbon cycling processes occurs only in aquatic systems. It involves the dissolution of carbonate compounds in water and their precipitation (deposition) as sediments, particularly limestone and dolomite. On a global scale, dissolution and precipitation approximately balance each other, although certain conditions favoring precipitation have led to the deposition of extensive layers of calcium carbonate sediments in the past. Dissolution and deposition in aquatic systems occur about 100 times more slowly than assimilation and dissimilation by biolog-



■ **Figure 7.6** Schematic diagram of transformations of compounds in the carbon cycle. Most of the carbon in the biosphere cycles between organic forms and carbon dioxide. Methane is produced only by certain archaeobacteria under anaerobic conditions.



Figure 7.7 Most of the earth's carbon is in sedimentary rocks. These sedimentary deposits of limestone in the mountains of southern Texas represent calcium carbonate precipitated out of solution in the shallow seas that once covered the area. Photo by Gerald & Buff Corsi/Visuals Unlimited.

ical systems. Thus, the exchange between sediments and the water column is relatively unimportant to the short-term cycling of carbon in the ecosystem. Locally and over long periods, however, it can assume much greater importance; in fact, most of the ecosystem's carbon is locked up in sedimentary rocks (■ Figure 7.7).

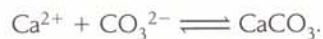
As we saw in Chapter 2, when carbon dioxide dissolves in water, it forms carbonic acid,



which readily dissociates into hydrogen, bicarbonate, and carbonate ions:



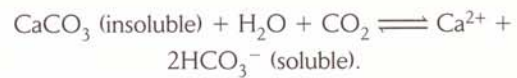
Calcium, when present, also equilibrates with the carbonate ions to form calcium carbonate:



Calcium carbonate has low solubility under most conditions, and readily precipitates out of the water column to form sediments. This sedimentation effectively removes carbon from aquatic ecosystems, but the rate of removal is less than 1% of the annual cycling of carbon in these

ecosystems, and this amount is added back by input from rivers, which are naturally somewhat acid and tend to dissolve limestone (carbonate) sediments.

Dissolution and dissociation may be affected locally by the activities of organisms. In the marine system, under approximately neutral pH conditions, carbonate and bicarbonate are in chemical equilibrium:



Uptake of CO_2 for photosynthesis by aquatic algae and plants shifts the equilibrium to the left, resulting in the formation and precipitation of calcium carbonate. Many algae excrete this calcium carbonate to the surrounding water, but reef-building algae and coralline algae incorporate it into their hard body structures (■ Figure 7.8). In the system as a whole, when photosynthesis exceeds respiration (as it does during algal blooms), calcium tends to precipitate out of the system.

Changes in the carbon cycle over time

Geologists can estimate the amounts of carbon removed from the atmosphere by burial of organic matter and precipitation of carbonates in marine sediments, as well as when these sediments were formed. From this information, they

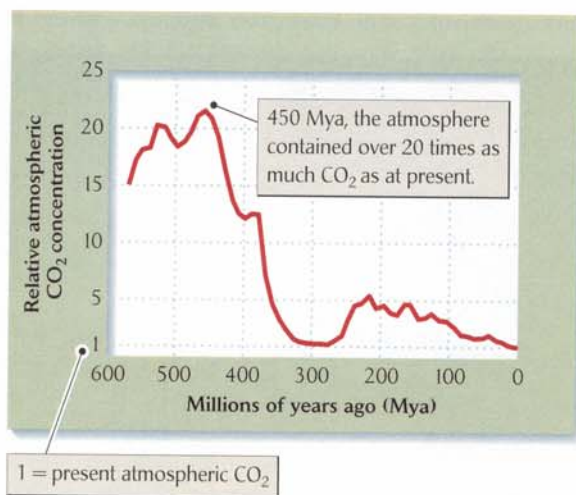


Figure 7.8 The "skeleton" of coralline algae is made of calcium carbonate. This is precipitated in conjunction with the uptake of dissolved carbon dioxide during photosynthesis. Photo by L. Newman & A. Flowers/Photo Researchers.

can estimate the original concentration of carbon dioxide in the atmosphere and its change over time (■ Figure 7.9).

These estimates indicate that during the early part of the Paleozoic era, roughly 550–400 million years ago (Mya), the atmosphere held 15 to 20 times more carbon dioxide than at present. This amount decreased precipitately early in the Devonian period, nearly 400 Mya, dipping to nearly its present levels by 300 Mya. This decline was initiated by a sharp increase in the rate of weathering of terrestrial environments following the development of forests on land, and by the deposition of the vast accumulations of organic sediments that make up most of the earth's coal beds. Toward the end of the Paleozoic era, at about 250 Mya, CO₂ concentration in the atmosphere again increased, to nearly five times its present level, remained high for approximately 100 million years through the early Mesozoic, and has been declining steadily ever since.

The early Paleozoic and early Mesozoic eras were truly greenhouse times. Average temperatures throughout the earth were hot, and tropical life flourished even at high latitudes. Declining CO₂ in the Devonian set the stage for cooler climates and extensive glaciations at the end of the Mesozoic era, much like those the earth has experienced during the past million years. The current increase in atmospheric CO₂, troubling as it is, will not return the earth to the hothouse conditions of former times, at least not any



■ **Figure 7.9** Concentrations of carbon dioxide in the atmosphere have decreased since the beginning of the Paleozoic era. Values are expressed in multiples of the concentration (approximately 300 parts per million) at the beginning of the Industrial Revolution. After R. A. Berner, *Science* 276:544–546 (1997).

time soon. Most of the “geologic” carbon taken from the earth’s primitive atmosphere is bound up in limestone sediments. This carbon is returned to the atmosphere very slowly as limestone is subducted below the edges of continental plates, carbonates are turned to carbon dioxide under intense heat and pressure deep in the earth, and carbon dioxide is finally outgassed in volcanic eruptions.

ECOLOGISTS IN THE FIELD

What caused the precipitate decline in atmospheric carbon dioxide during the Devonian?



Why did concentrations of carbon dioxide in the atmosphere decline precipitately over a period of 50 million years during the Devonian period (409–363 Mya)? How can we infer events in the biosphere that occurred so long ago? Were ecological changes in ancient ecosystems involved? Geologist Gregory Retallack of the University of Oregon used several lines of evidence to provide a plausible explanation for this change. Retallack studied fossilized soils (paleosols) formed during the Devonian period in what is now Antarctica. (At that time, the climate there was warm, and vegetation flourished.) By comparing paleosols with modern soils, it is possible to interpret many processes occurring in soils in the past and their consequences for the biosphere.

The beginning of the Devonian was marked by two striking changes (■ Figure 7.10). One was a change in soil chemistry, indicated by a marked increase in clay content. The other was a dramatic increase in the density and depth of plant roots. The middle of the Devonian witnessed a striking increase in the diameter of trunks, stems, roots, and rhizomes of plants, indicating the development of the first forests on earth. These changes were followed at the end of the Devonian and beginning of the Carboniferous by the appearance of thick peat deposits, which later turned into coal.

The level of atmospheric CO₂ itself may be estimated by the ratio of ¹³C to ¹²C carbon isotopes in soil carbonates. Carbon dioxide in soil comes both from atmospheric sources directly and from respiration of soil organisms. The ¹³C/¹²C ratio indicates the relative amounts of atmospheric carbon compared with respired CO₂. With some assumptions about the production of CO₂ in soil, one can estimate the concentration of CO₂ in the atmosphere.

Why did the earth lose its greenhouse atmosphere during the Devonian? Retallack surmised that the increase in terrestrial vegetation, particularly the penetration of soil by fine roots, would have dramatically increased the rate of weathering of soil, thus increasing its clay content. Roots and

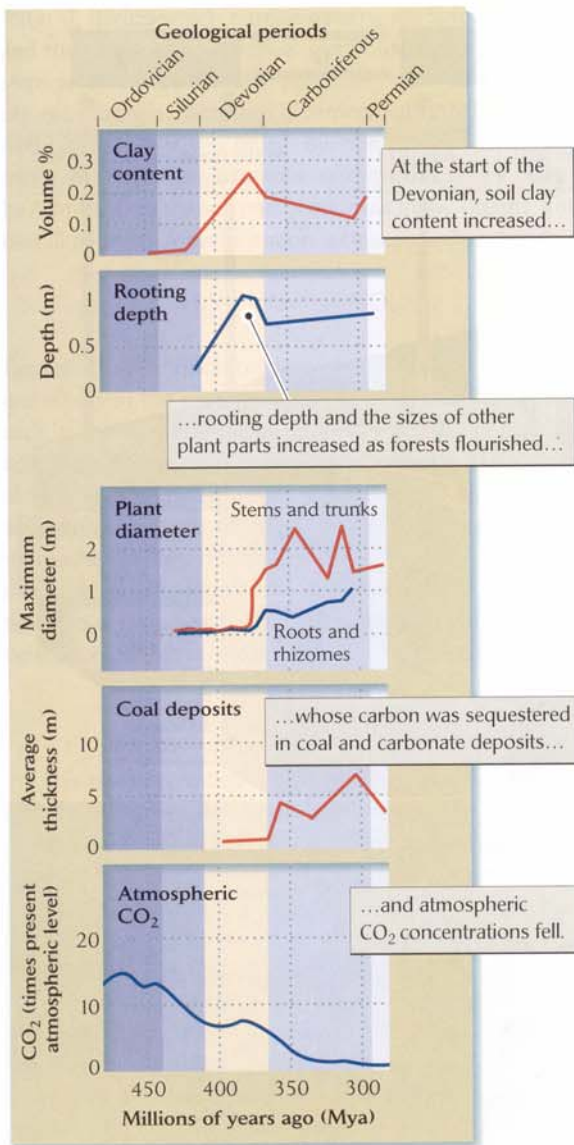


Figure 7.10 Fossil soils reveal changes in the biosphere. The features of paleosols during the middle of the Paleozoic era reveal increases in terrestrial vegetation and progressive weathering of soils accompanied by sequestration of atmospheric carbon dioxide in carbonate precipitates. After G. J. Retallack, *Science* 276:583–585 (1997).

their associated microflora secrete organic acids to mobilize soil minerals; decomposition of organic matter also forms acids, which speed the breakdown of minerals. Roots hold clay particles in the soil and therefore enhance the soil's water-holding capacity, which further helps chemical weathering. This enhanced weathering would have caused tremen-

dous amounts of calcium and magnesium to be washed out of soil wherever terrestrial vegetation had developed. As solubilized calcium and magnesium ions entered the oceans, they formed insoluble compounds with the abundant bicarbonate ions there and precipitated out of the water as sediments. As bicarbonate was withdrawn from the oceans, it was replaced by carbon dioxide diffusing in from the atmosphere. Thus, as vegetation promoted weathering, new sedimentary rock was formed, partly from constituents of old continental crust and partly from the missing atmospheric carbon dioxide.



Nitrogen assumes many oxidation states in its cycling through ecosystems

The ultimate source of nitrogen for life is molecular nitrogen (N_2) in the atmosphere. This form of nitrogen dissolves to some extent in water, but is absent from native rock. Lightning discharges convert some molecular nitrogen to forms, such as ammonia, that plants can use, but most enters the biological pathways of the nitrogen cycle (■ Figure 7.11) through its assimilation by certain microorganisms in a process referred to as **nitrogen fixation**. Although this pathway ($N_2 \rightarrow NH_3$) constitutes only a small fraction of the earth's annual nitrogen flux, most biologically cycled nitrogen can be traced back to nitrogen fixation. Once in the biological realm, nitrogen follows pathways more complicated than those of carbon because more oxidized and reduced forms are possible for nitrogen atoms.

Ammonification

Let's begin with the reduced (organic) nitrogen found in proteins. Plants obtain nitrogen from the soil, either as ammonia or as nitrate, which they must then reduce to an organic form. From this point, the first step in the nitrogen cycle is **ammonification**. Ammonification involves the breaking down of proteins into their component amino acids by hydrolysis and the oxidation of the carbon in those amino acids. This results in the production of ammonia (NH_3). Ammonification is carried out by all organisms. Although carbon is oxidized, releasing energy, the nitrogen atom itself is not oxidized, and so its energy potential does not change during ammonification.

Nitrification and denitrification

Nitrification involves the oxidation of nitrogen, first from ammonia to nitrite (NO_2^-), then from nitrite to nitrate

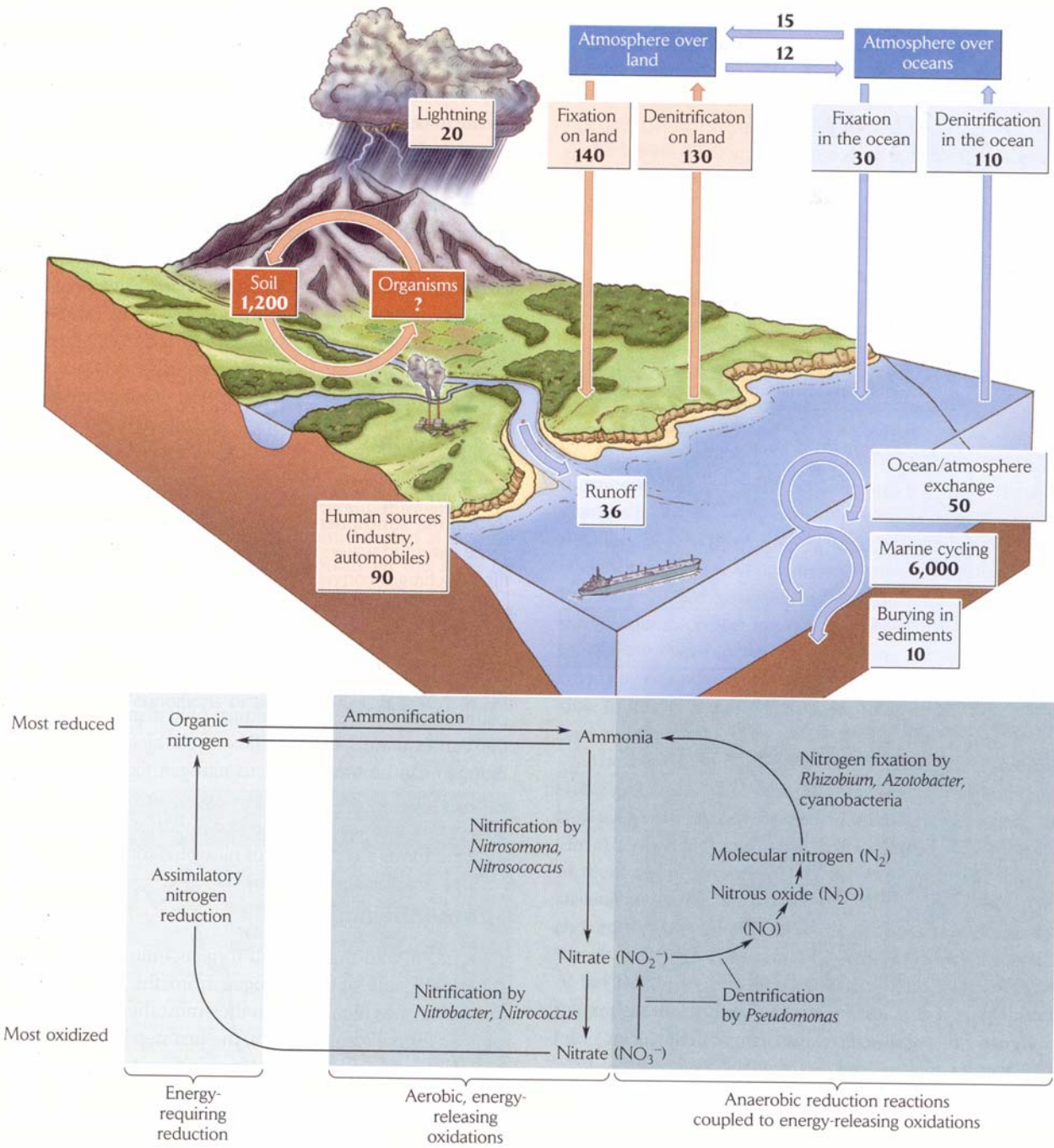
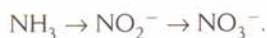


Figure 7.11 Schematic diagram of transformations of compounds in the nitrogen cycle. The most reduced state of the nitrogen atom has the highest chemical energy potential.

(NO_3^-), during which nitrogen atoms are stripped of six, and then two more, of their electrons. These oxidation steps release much of the potential chemical energy of organic nitrogen. Each step is carried out only by specialized bacteria: $\text{NH}_3 \rightarrow \text{NO}_2^-$ by *Nitrosomonas* in the soil and by *Nitrosococcus* in marine systems; $\text{NO}_2^- \rightarrow \text{NO}_3^-$ by *Nitrobacter* in the soil and *Nitrococcus* in the oceans. The overall pathway for nitrification is thus



Because both nitrification steps are oxidations, they can occur only in the presence of a powerful oxidizing agent, such as molecular oxygen, that can act as an electron acceptor. However, in waterlogged, anaerobic soils and sediments and in oxygen-depleted bottom waters, nitrate and nitrite are more oxidized than the surrounding environment, and they themselves can act as electron acceptors (oxidizers). Under these conditions, reduction reactions are thermodynamically favorable, and nitrogen may be reduced to nitric oxide (NO):



This reaction, called **denitrification**, is accomplished by bacteria such as *Pseudomonas denitrificans*. Denitrification is important for breaking down organic matter in oxygen-depleted soils and sediments, but it also results in the loss

of nitrogen from soils because some nitric oxide escapes as a gas. Additional chemical reactions under anaerobic, reducing conditions in soils and water can produce molecular nitrogen,



with the consequent loss of nitrogen from general biological circulation.

Denitrification may be a major cause of low availability of nitrogen in marine systems. When organic remains of plants and animals sink to the depths of the oceans, their oxidation by bacteria in deep waters and bottom sediments often is accomplished anaerobically using nitrate as an oxidizer. This results in the conversion of nitrate and nitrite to the dissolved gases NO and N_2 , which cannot be used by algae.

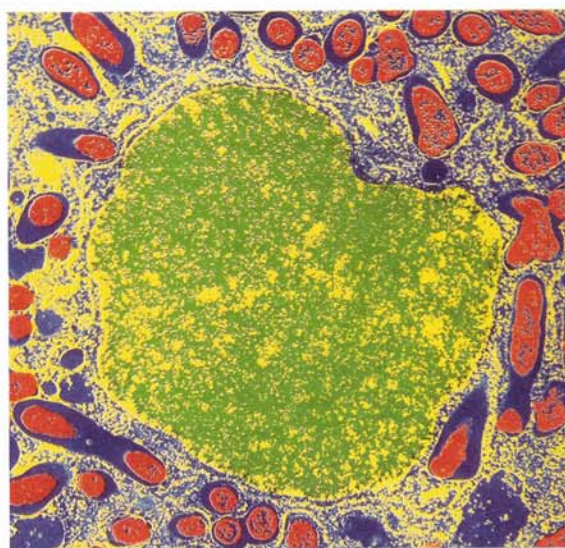
Nitrogen fixation

The loss of readily available nitrogen to ecosystems by denitrification is offset by nitrogen fixation. This assimilatory reduction of nitrogen is accomplished by bacteria such as *Azotobacter*, which is a free-living species; *Rhizobium*, which occurs in symbiotic association with the roots of some legumes (members of the pea family) and other plants (■ Figure 7.12); and cyanobacteria. The enzyme responsible for nitrogen fixation by these microorganisms—

(a)



(b)



■ **Figure 7.12** Some bacteria carry out nitrogen fixation. The nodules on the roots of soybeans (left) harbor symbiotic nitrogen-fixing bacteria, as shown in red in the false-color transmission electron micrograph (right). Photo (a) courtesy of Thomas R. Sinclair; photo (b) by Dr. Jeremy Burgess/Science Photo Library/Photo Researchers.

nitrogenase—is inactivated by oxygen and works efficiently only under extremely low oxygen concentrations. This explains why *Azotobacter* bacteria, living freely in the soil, exhibit only a small fraction of the nitrogen-fixing capacity of *Rhizobium* bacteria, which are sequestered in the relatively anoxic cores of root nodules. In these nodules, root cells infected by *Rhizobium* form membrane-bounded structures called symbiosomes, within which the bacteria are maintained. Oxygen within a symbiosome is maintained at a very low level so as not to interfere with the activity of nitrogenase. This level of oxygen would limit respiration of plant root cells severely, but is suitable for respiration by *Rhizobium*. Although symbiosomes contain little free oxygen, they do have an abundant supply bound to a special kind of hemoglobin. This so-called leghemoglobin has a high affinity for oxygen and therefore keeps the concentration of free oxygen very low while providing a continuous supply for respiration.

Nitrogen fixation proceeds by reducing nitrogen and therefore requires energy, though no more than the conversion of an equivalent amount of nitrate to ammonia by plants. The reduction of one atom of molecular nitrogen to ammonia requires approximately the amount of energy released by the oxidation of an atom of organic carbon to carbon dioxide. Nitrogen-fixing microorganisms obtain the energy and reducing power they need to reduce N_2 to NH_3 by oxidizing sugars or other organic compounds. Free-living bacteria must obtain these resources by metabolizing organic detritus in the soil, sediments, or water column. More abundant supplies of energy are available to the *Rhizobium* bacteria that enter into symbiotic relationships with plants, which provide them with malate, a four-carbon carbohydrate produced as an end product of glycolysis.

On a global scale, nitrogen fixation approximately balances the production of N_2 by denitrification. These fluxes amount to about 2% of the total cycling of nitrogen through the ecosystem. On a local scale, nitrogen fixation can assume much greater importance, especially in nitrogen-poor habitats. When land is first exposed to colonization by plants—as, for example, are areas left bare by receding glaciers or newly formed lava flows—species with nitrogen-fixing capabilities dominate the colonizing vegetation.



The phosphorus cycle is uncomplicated chemically

Ecologists have studied the role of phosphorus in ecosystems intensively because organisms require this element at a rela-

tively high level (though only about one-tenth that of nitrogen). Phosphorus is a major constituent of nucleic acids, cell membranes, energy transfer systems, bones, and teeth. Phosphorus is thought to limit plant productivity in many aquatic habitats. Influxes of phosphorus into rivers and lakes in the form of sewage and runoff from fertilized agricultural lands can artificially stimulate production in aquatic habitats, which can upset natural ecosystem balances and alter the quality of aquatic habitats. Pollution by phosphorus-containing detergents was a major contributor to this problem until phosphorus-free alternative detergents were developed.

The phosphorus cycle (■ Figure 7.13) has fewer steps than the nitrogen cycle because, except in a very few microbial transformations, phosphorus does not undergo oxidation–reduction reactions in its cycling through the ecosystem. Plants assimilate phosphorus as phosphate ions (PO_4^{3-}) directly from soil or water and incorporate it directly into various organic compounds. Animals eliminate excess phosphorus in their diets by excreting phosphate salts in urine; phosphatizing bacteria also convert phosphorus in detritus to phosphate ions. Phosphorus does not enter the atmosphere in any form other than dust, so the phosphorus cycle involves only soil and aquatic compartments of the ecosystem.

Acidity greatly affects the availability of phosphorus to plants. In acidic soils, phosphorus binds tightly to clay particles and forms relatively insoluble compounds with iron and aluminum. In basic soils, it forms other insoluble compounds—for example, with calcium. When both calcium and iron or aluminum are present under aerobic conditions, the highest concentration of dissolved phosphate—that is, the greatest availability of phosphorus—occurs at a pH of between 6 and 7.

In well-oxygenated aquatic systems, phosphorus readily forms insoluble compounds with iron or calcium and precipitates out of the water column. Thus, marine and freshwater sediments act as a phosphorus sink, continually removing precipitated phosphorus from rapid circulation in the ecosystem. Phosphorus compounds readily dissolve and enter the water column only in oxygen-depleted aquatic sediments and bottom waters. Under such conditions, iron tends to form soluble sulfides rather than insoluble phosphate compounds.



Sulfur exists in many oxidized and reduced forms

Sulfur is part of two amino acids—cysteine and methionine—and is therefore required by plants and animals. But the

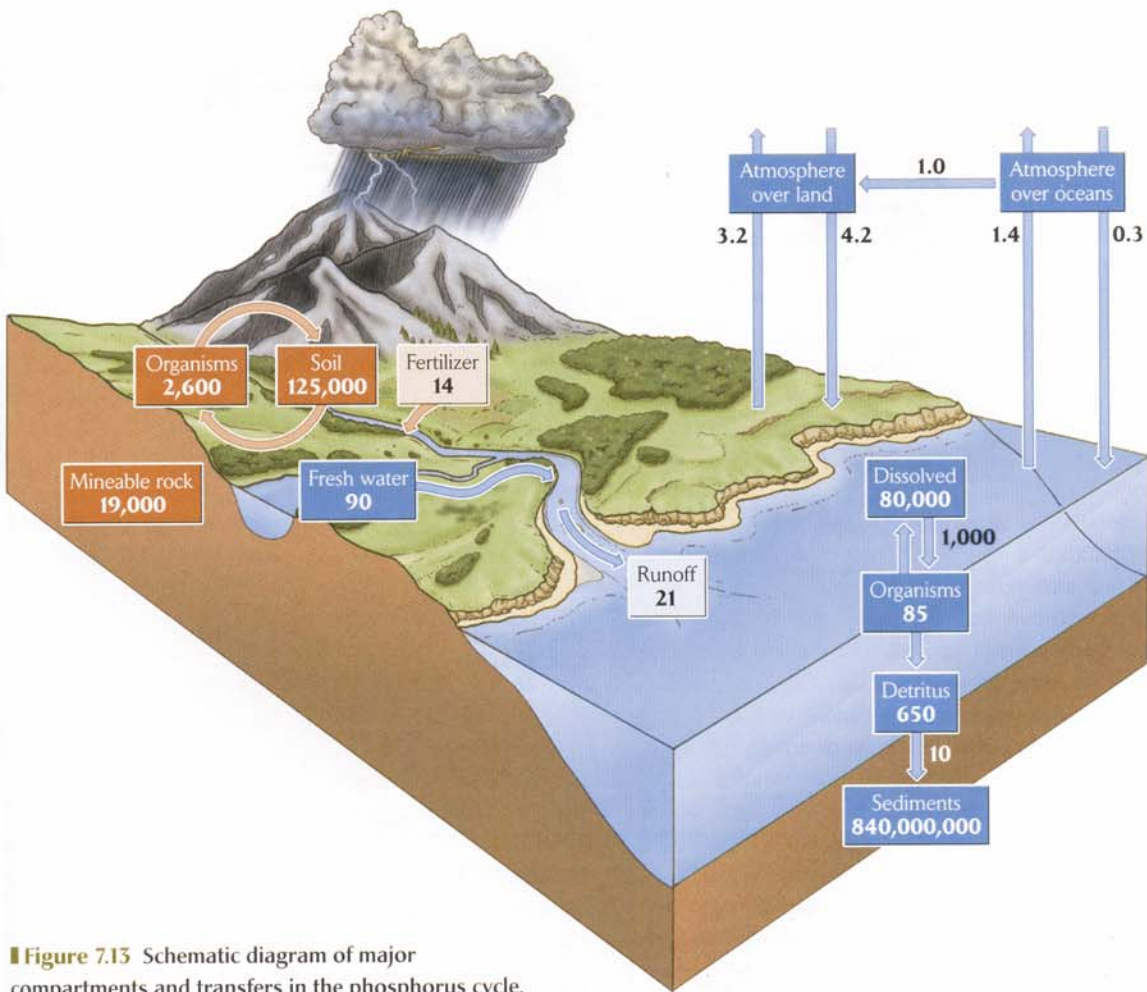


Figure 7.13 Schematic diagram of major compartments and transfers in the phosphorus cycle.

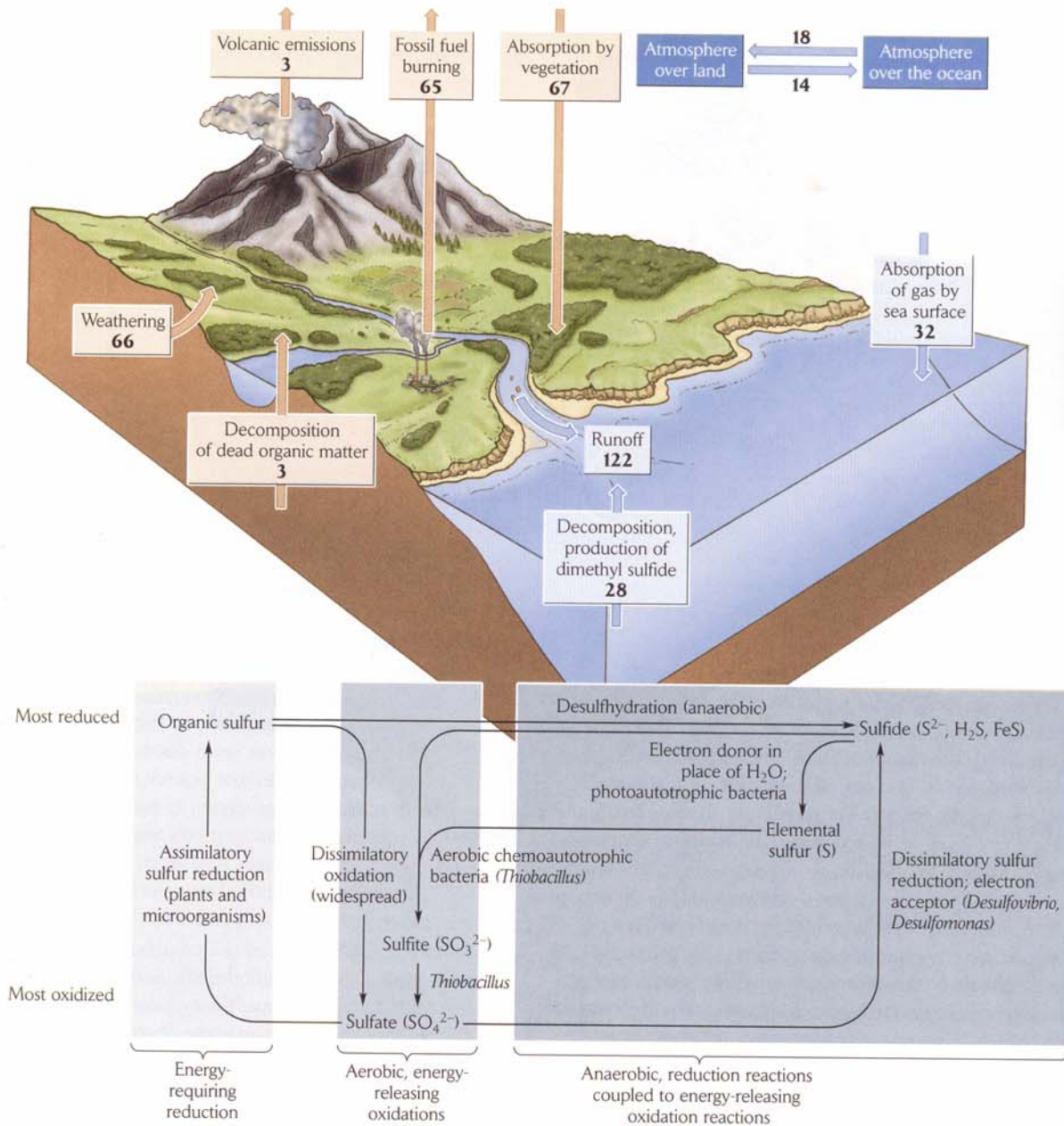
importance of sulfur in the ecosystem goes far beyond this role. Like nitrogen, sulfur exists in many reduced and oxidized forms, and so it follows complex chemical pathways and affects the cycling of other elements (■ Figure 7.14).

The most oxidized form of sulfur is sulfate (SO_4^{2-}); the most reduced forms are hydrogen sulfide (H_2S) and organic forms of sulfur, such as those found in amino acids. Under aerobic conditions, energy-requiring assimilatory sulfur reduction by organisms ($\text{SO}_4^{2-} \rightarrow \text{organic S}$) balances the oxidation of organic sulfur back to sulfate, which occurs either directly or with sulfite (SO_3^{2-}) as an intermediate step. This oxidation occurs when animals excrete excess dietary organic sulfur and when microorganisms decompose plant and animal detritus.

Under anaerobic conditions, such as those in waterlogged sediments, sulfate, like nitrate, may function as an oxidizer. In such reducing environments, the bacteria *Desul-*

fovibrio and *Desulfomonas* can use energetically favorable sulfate reduction to oxidize organic carbon. The coupling of these reactions makes some energy available to the organisms. The reduced sulfur may then be used by photosynthetic bacteria to assimilate carbon by pathways analogous to photosynthesis in green plants. In these reactions, sulfur takes the place of the oxygen atom in water as an electron donor. As a result, elemental sulfur (S) accumulates unless the sediments are exposed to aeration or oxygenated water, at which point sulfur may be further oxidized by aerobic chemoautotrophic bacteria, such as *Thiobacillus*, to sulfite and sulfate.

The fate of reduced sulfur produced under anaerobic conditions depends on the availability of positive ions. Frequently, hydrogen sulfide (H_2S) forms; it escapes from shallow sediments and mucky soils as a gas having the characteristic smell of rotten eggs. Anaerobic conditions



■ **Figure 7.14** Schematic diagram of transformations of compounds in the sulfur cycle.

generally favor the reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}), which can combine with sulfide ions to form iron sulfide (FeS). For this reason, sulfides are commonly associated with coal and oil deposits. When these materials are exposed to the atmosphere in mine wastes

or burned for energy, the reduced sulfur oxidizes (with the help of *Thiobacillus* bacteria in mine wastes) to sulfate. This oxidized sulfur combines with water to produce sulfuric acid (H_2SO_4), which leads to acid rain and acid mine drainage (■ **Figure 7.15**).



Figure 7.15 Streams draining from the refuse of coal mines may be extremely acid. Mine spoils in Tioga County, Pennsylvania. Photo by Tim McCabe, courtesy of the U.S. Department of Agriculture, Soil Conservation Service.



Microorganisms assume diverse roles in element cycles

As you may have noticed, many of the transformations discussed in this chapter are accomplished mainly or entirely by bacteria. In fact, were it not for the activities of such microorganisms, many element cycles would be altered drastically and the productivity of the ecosystem much reduced. For example, without the capacity of some microbes to use nitrogen, sulfur, and iron as electron acceptors, little decomposition would occur in anaerobic organic sediments, and their resulting accumulation would reduce the amount of inorganic carbon in the ecosystem. Without nitrogen-fixing bacteria, denitrification under anaerobic conditions would slowly deplete ecosystems of available nitrogen and reduce biological productivity proportionally.

Many of the transformations carried out by microorganisms, such as metabolism of sugars and other organic molecules, are accomplished in similar ways by plants and animals. The bacteria and cyanobacteria are distinguished physiologically by the ability of many species to metabolize substrates under anaerobic conditions and to use substrates other than organic carbon as energy sources.

Every organism needs, above all, a source of carbon for building organic structures and a source of energy to fuel the life processes. As pointed out earlier in this book, we can distinguish organisms in terms of their sources of

carbon. Heterotrophs obtain carbon in reduced (organic) form by consuming other organisms or organic detritus. All animals and fungi, and many bacteria, are heterotrophs. Autotrophs assimilate carbon as carbon dioxide and expend energy to reduce it to an organic form. **Photoautotrophs** use sunlight as their source of energy for this reaction (photosynthesis). All green plants and algae are photoautotrophs, as are cyanobacteria, which use H_2O as an electron donor (reducing agent) and are aerobic; and purple and green bacteria, which have light-absorbing pigments different from those of green plants, use H_2S or organic compounds as electron donors, and are anaerobic.

Chemoautotrophs all use CO_2 as a carbon source, but they obtain energy for its reduction by the aerobic oxidation of inorganic substrates: methane (for example, *Methanosomonas* and *Methylomonas*); hydrogen (*Hydrogenomonas* and *Micrococcus*); ammonia (the nitrifying bacteria *Nitrosomonas* and *Nitrosococcus*); nitrite (the nitrifying bacteria *Nitrobacter* and *Nitrococcus*); hydrogen sulfide, sulfur, and sulfite (*Thiobacillus*); or ferrous iron salts (*Ferrobacillus* and *Gallionella*). Chemoautotrophs are almost exclusively bacteria, which apparently are the only organisms that can become so specialized biochemically as to make efficient use of inorganic substrates in this way and efficiently dispose of the waste products of chemoautotrophic metabolism.

The special role of microorganisms in ecosystem function is illustrated nicely by the highly productive communities of marine organisms that develop around deep-sea hydrothermal vents (■ **Figure 7.16**). Scientists from the Woods Hole Oceanographic Institution in Massachusetts first discovered these miniature ecosystems in deep water off the Galápagos archipelago in 1977. Vent communities have since been found to be widely distributed in the ocean basins of the world. The most conspicuous members of the community are giant white-shelled clams and tube worms (pogonophorans) that grow to 3 meters long, but numerous crustaceans, annelids, mollusks, and fish also cluster at great densities around hydrothermal vents. The high productivity of vent communities contrasts strikingly with the desertlike appearance of the surrounding ocean floor.

How do these communities obtain energy? These deep-sea vents occur well below the level of light penetration, and so there can be no photosynthesis. As you might suspect, the productivity of the vent communities is based on the unique qualities of the water issuing from the vents themselves. This water is hot and loaded with a reduced form of sulfur, hydrogen sulfide (H_2S). Where vent water and seawater mix, conditions are ideal for chemoautotrophic



Figure 7.16 Chemoautotrophic sulfur bacteria form the base of the food chain in hydrothermal vent communities. Other vent organisms, such as these tube worms (*Riftia pachyptila*) at a Pacific hydrothermal vent, rely on these bacteria to produce food. Photo by C. Van Dover, courtesy of OAR/National Undersea Research Program (NURP).

sulfur bacteria. These bacteria use oxygen in seawater to oxidize hydrogen sulfide in vent water. In turn, this oxidation provides a source of energy for the assimilatory reduction of inorganic carbon and nitrogen in seawater. All the other members of the vent community feed on these bacteria, which thus form the base of the local food chain. The pogonophoran worms have gone so far as to house symbiotic colonies of the bacteria within the tissues of a specialized organ, the trophosome, providing a protected place to live in return for a share of the carbohydrate and organic nitrogen produced by the bacteria.

In this chapter we have examined the cycling of several important elements from the standpoint of their chemical and biochemical reactions. Elements are cycled through ecosystems primarily because the metabolic activities of organisms result in chemical transformations of elements. The kinds of transformations that predominate depend on the physical and chemical conditions of the system. Each type of habitat presents a different chemical environment, particularly with respect to the presence or absence of oxygen and possible sources of energy. It stands to reason, therefore, that the patterns of element cycling should differ greatly among habitats and ecosystems. In the next chapter, we shall contrast element cycling in aquatic habitats and in terrestrial habitats by focusing on how some of the unique physical features of each of these environments affect the chemical and biochemical transformations involved in organic production and recycling of elements.



Summary

1. Unlike energy, nutrients are retained within ecosystems, where they are cycled between physical and biotic components. The paths that elements follow through ecosystems depend on chemical and biological transformations, which themselves depend on the chemistry of each element, the physical and chemical conditions of the environment, and the ways in which each element is used by various organisms.
2. Movement of energy through ecosystems parallels the paths of several elements, particularly carbon, whose transformations either require or release energy.
3. Energy transformations in biological systems occur primarily in the course of oxidation–reduction reactions. An oxidizer is a substance that readily accepts electrons; a reducer is one that readily donates electrons. Upon being reduced, an atom gains energy along with the electrons it accepts; upon being oxidized, an atom releases energy along with the electrons it gives up.
4. The cycling of each element may be thought of as movement between compartments of ecosystems. The major compartments are living organisms, organic detritus, immediately available inorganic forms, and unavailable organic and inorganic forms, for the most part locked away in sediments.
5. The water cycle, or hydrologic cycle, provides a physical analogy for element cycling in ecosystems. Energy is required to evaporate water because molecules of water vapor have a higher energy content than molecules of liquid water. This energy is released as heat when water vapor condenses in the atmosphere to produce precipitation.
6. All organisms require organic carbon as the primary substance of life. Organic carbon is also the major source of energy for most animals and microorganisms. Carbon shuttles between organic forms and the inorganic compartments of ecosystems by way of photosynthesis and respiration.
7. The carbon cycle involves nonbiological processes such as the dissolution of carbon dioxide in surface waters. Dissolved carbon dioxide enters into a chemical equilibrium with bicarbonate and carbonate ions, which, in the presence of calcium, tend to precipitate and form sediments. Thick accumulations of these marine sediments can become limestone rock.
8. Nitrogen has many reduced and oxidized forms and consequently follows many pathways through ecosys-

tems. Quantitatively, most nitrogen follows the cycle leading from nitrate through organic nitrogen (following assimilation by plants), ammonia, nitrite (following nitrification by bacteria), and then back to nitrate (following further nitrification). The last two steps are accomplished by certain bacteria in the presence of oxygen.

9. Under anaerobic conditions in soils and sediments, certain bacteria can use nitrate in place of oxygen as an oxidizing agent (denitrification): in this process, nitrate leads to nitrite and (eventually) to molecular nitrogen (N_2). This loss of nitrogen from general biological cycling is balanced by nitrogen fixation by some microorganisms.

10. Plants assimilate phosphorus in the form of phosphate ions (PO_4^{3-}). The availability of phosphorus varies with the acidity and oxidation level of the soil or water. The energy potential of the phosphorus atom does not change during its cycling through ecosystems.

11. Sulfur is an important element in anaerobic habitats, where it may serve as an oxidizer in the form of sulfate ions (SO_4^{2-}) or as a reducing agent (for photoautotrophic bacteria) in the forms of elemental sulfur and sulfide.

12. Many elemental transformations, particularly under anaerobic conditions, are accomplished by biochemically specialized microorganisms. These organisms therefore play important roles in the cycling of elements through the ecosystem.

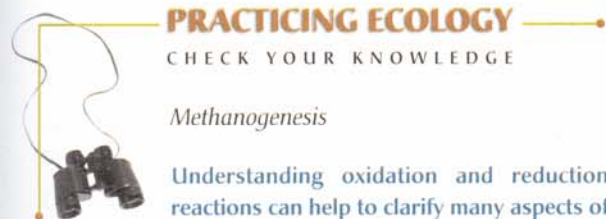
together as a reduction-oxidation (redox) reaction. For the chemical reactions that lead to nutrient transformations in ecosystems, oxidation generally involves oxygen because it readily accepts electrons from other atoms. In contrast, the reduction reaction that is coupled to oxidation usually involves organic forms of carbon because carbon atoms are good at donating electrons during redox reactions.

In some kinds of habitats, such as waterlogged sediments in swamps or marshes, oxygen is not available to serve as a terminal electron acceptor for respiration. Certain kinds of bacteria that live in such sediments (Archaeobacteria) have evolved the ability to use organic carbon to oxidize organic carbon when oxygen is not available. They utilize organic carbon in the form of methanol or acetate as a substrate. Organic carbon acts as an electron acceptor to produce methane (CH_4) and as an electron donor to result in the production of carbon dioxide. The overall reaction is:



The resulting methane is released from the surface of the water and results in the phenomenon known as "swamp gas."

The factors that control methane production have received considerable research attention of late. Methane is an important greenhouse gas that is contributing to the increased absorption of infrared radiation in the atmosphere and global warming. In fact, the heating effectiveness of one molecule of methane is about 25 times that of one carbon dioxide molecule. Moreover, methane production is increasing due to growing numbers of cattle and land conversion to rice paddies (both cattle and the sediments of rice paddies contain methanogenic bacteria). Several factors facilitate the production and release of methane from waterlogged sediments. For example, Grünfeld and Brix (1999) showed that methanogenesis and emission from water is affected by differences in the composition of the sediments, the depth of the water level below the sediments, and the presence of plants that emerge above the water (Table 7.1).



PRACTICING ECOLOGY

CHECK YOUR KNOWLEDGE

Methanogenesis

Understanding oxidation and reduction reactions can help to clarify many aspects of element cycling in ecosystems. Each reduction reaction is coupled to an oxidation reaction; thus they are referred to

Table 7.1 Estimated methane (CH_4) production rate and CH_4 oxidation from treatments that differ in plant cover and water level

	Treatment			
	+	+	+	-
Emergent vegetation	+	+	+	-
Water level	Low	Int	High	High
Methanogenesis (mmol per m^2 per day)	41	55	68	92
CH_4 emission (mean) (mmol per m^2 per day)	22	46	55	85
CH_4 oxidation (% of methanogenesis)	46	20	18	7

CHECK YOUR KNOWLEDGE

1. Of the elements that cycle from the surface of the earth to the atmosphere and back, which is the most important for organisms?
2. From the results presented by Grünfeld and Brix, what is the effect of vegetation cover on methane production, oxidation, and emission?
3. How might a changing climate affect methane production and emission in light of the results presented by Grünfeld and Brix?


**MORE
ON THE
WEB**

4. Read the article "Ruminant Livestock and the Global Environment" from the EPA through *Practicing Ecology on the Web* at <http://www.whfreeman.com/ricklefs>. Why is the cow-calf sector of the beef industry the largest emitter of methane within U.S. livestock industries? How can livestock producers reduce the amount of greenhouse gas emissions coming from their cows?


Suggested Readings

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