sediments become part of new mountain ranges. On a civilizational timescale, mineral cycles thus appear only as one-way oceanward flows, with human activities enhancing some of these fluxes, most notably the oceanward flow of phosphorus used as crop fertilizer.

The Water Cycle

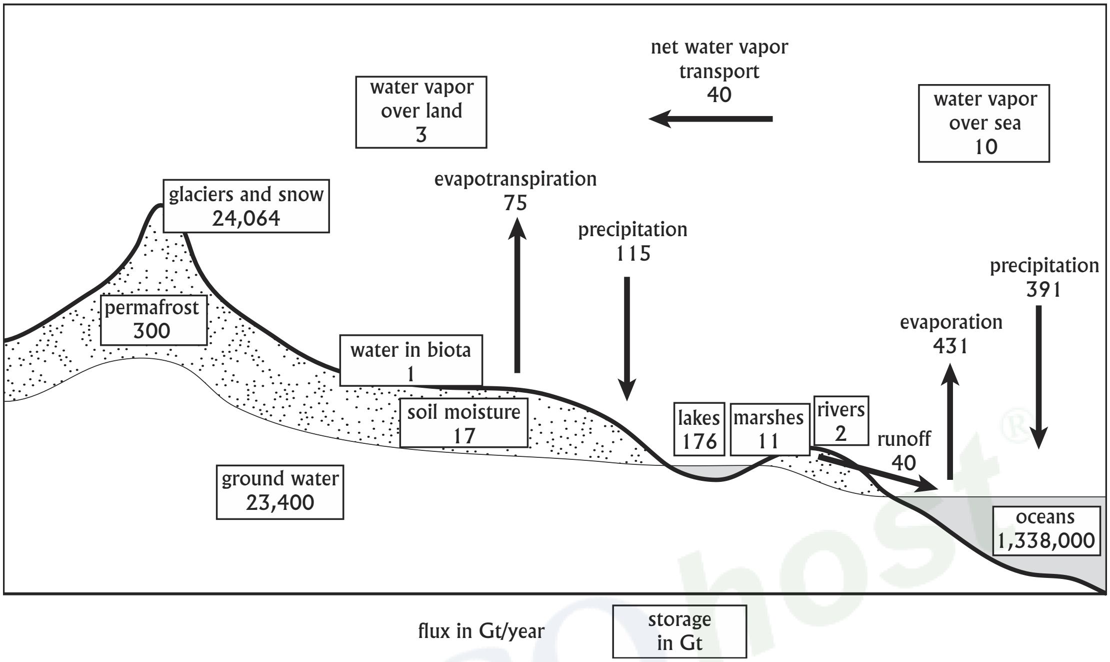
Water is indispensable for life because it makes up most of the living biomass and because it is an essential metabolic input. Very few organisms are less than 60% water, and many fresh tissues are more than 90% water, with 99% in phytoplankton. Water is also the dominant donor of hydrogen in photosynthesis and the irreplaceable carrier of nutrients and metabolic products. Consequently, it is fortunate that the water molecule is too heavy to escape the Earth's gravity, and hence the only instances when significant volumes of water have ever left the planet were in the aftermath of major extraterrestrial impacts that took place more than 3.8 Ga ago. Today only a very small mass of water is constantly being destroyed in the upper atmosphere through photodissociation. Water from hot springs and water vapor in volcanic eruptions is made up largely of recycled flows, and juvenile water arriving from deeper layers of the crust totals only about 100 Mt/year, an entirely negligible amount.

The water cycle is the biosphere's most rapid and the most massive circulation, driven overwhelmingly by evaporation and condensation (fig. 5.1). Human activities have changed some local and even regional water balances drastically, and pronounced anthropogenic global warming would accelerate water's global cycle. But the only man-made additions to water's circulating mass are globally negligible withdrawals from ancient aquifers and water formation during some chemical syntheses and combustion of fossil fuels. Biomass combustion, no matter whether it is in natural forest and grassland fires or through deliberate burning during deforestation or for household or industrial uses, is obviously a form of accelerated water recycling.

In contrast, combustion of fossil fuels is a source of new water formed by the oxidation of hydrogen. Hydrogen accounts for less than 5% of the dry mass in coals, 11–14% in crude oils, and 25% in natural gas. Its complete oxidation is now producing annually about 9 Gt of water, a negligible amount (less than 0.002%) of annual precipitation. Moisture evaporated from coals and peats adds less than 500 Mt of water a year. Consequently, both the total volume of the Earth's water and its division among the major reservoirs on the Phanerozoic Earth can be considered constant on a time scale of 10^3 years. On longer time scales the periodic ebb and flow of glaciations, including some extreme ice ages, obviously shift a great deal of water among oceans and glaciers and permanent snow.

The Ocean

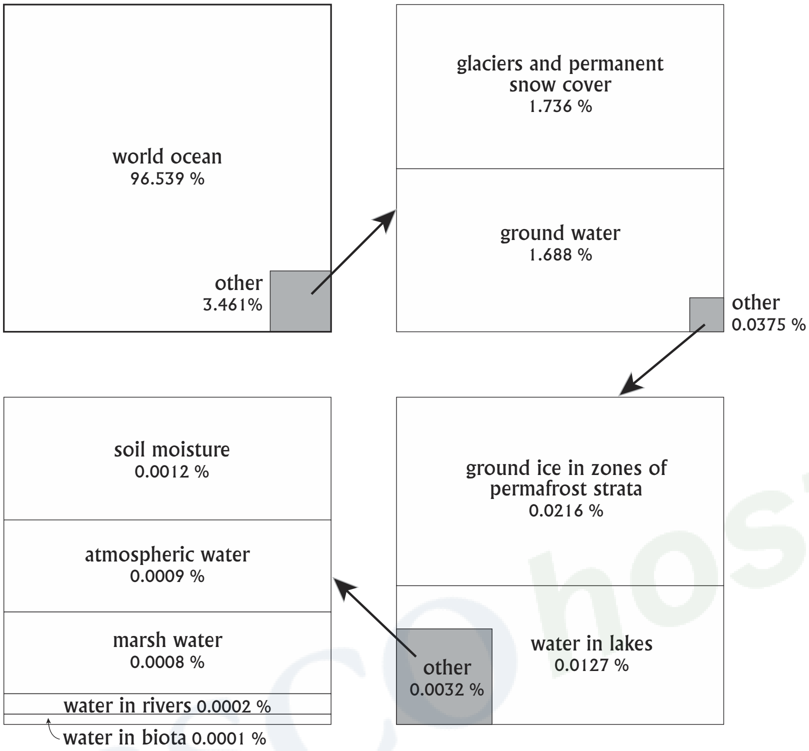
Just over 70% of the Earth is covered by the ocean, to an average depth of 3.8 km: hence *Aqua,* rather than *Terra,* would be the planet's more appropriate name. The dominance of the ocean in the global water cycle is overwhelming: it stores 96.5% of the Earth's water, it is the source of about 86% of all evaporation, and it receives 78% of all precipitation (fig. 5.2). But the ocean's enormous importance for the biosphere rests more on the extraordinary properties of water than on its enormous area. As already noted (in chapter 4), water has both very high specific heat and heat capacity. Because of its intermolecular hydrogen bonds, it also has an unusually high boiling point; its very high heat of vaporization makes it an ideal transporter of latent heat; and its relatively low viscosity makes it an out-



5.1 Annual global flows of the Earth's water cycle; the totals (in Gt/year) are from Oki (1999).

standing carrier of heat in countless eddies and currents (Denny 1993). Its high boiling point also allows for the existence of very hot aquatic ecosystems (see chapter 7). Its high heat of vaporization helps retain plant and soil moisture in hot environments, and its fairly low viscosity makes it an excellent medium for swimming. Water is sufficiently buoyant without being an impediment to a relatively fast movement: yellow-fin tuna (*Thunnus albacares*) can go as fast as 21 m/s in 10- to 20-second bursts (Walters and Fierstine 1964).

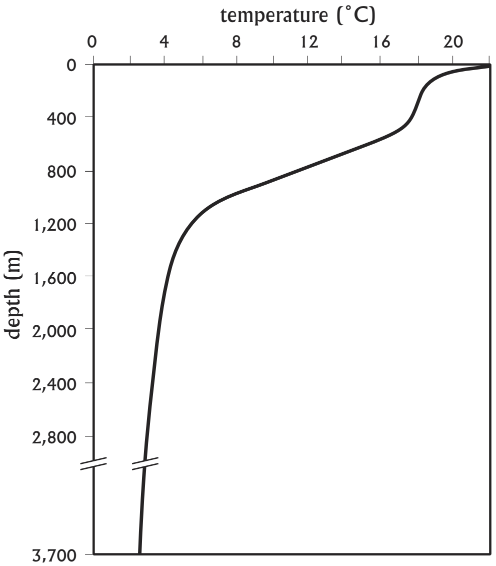
Because of the ocean's great average depth, air-sea interactions cannot directly affect the entire water column. Water is densest at about 4 °C, and hence the deep ocean, with a temperature stable near that point, is isolated from the atmosphere by the mixed layer, a relatively shallow column agitated by winds and waves and experiencing both daily and seasonal temperature fluctuations (fig. 5.3). And because of water's extraordinarily high heat of vaporization—about 2.45 kJ/g, although the rate is temperature-dependent, and the exact formula (giving results in J/g) is $2{,}475 - 2.26T$—evaporation transports not just large volumes of water but also huge quanta of thermal energy. Vaporization of 1 mm/day requires inputs of between 28 and 29 W/m^2, and solar radiation averages that much annually even in high-latitudes seas, up to 70° N in the Atlantic and to about 60° S in the Antarctic Ocean. The global mean



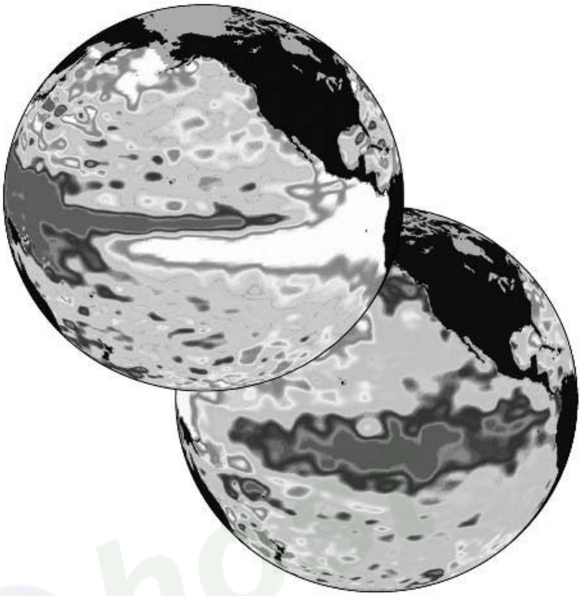
5.2 Nested comparisons of global water reservoirs show the overwhelming dominance of ocean storage and the insignificant, but vital, water content of the biomass. Based on data in Oki (1999).

flux of close to 90 W/m^2 translates into an average daily evaporation of around 3 mm, or an annual total of 1.1 m.

Evaporation of seawater is also affected by the ocean's overturning circulation, a vertical heat exchange whereby cold, dense water sinks near the poles and is replaced by warmer poleward flow from low latitudes (Toggweiler 1994). Macdonald and Wunsch (1996) concluded that there are two nearly independent overturning cells, one connecting the Atlantic Ocean to other basins through the Southern Ocean, and the other connecting the Indian and Pacific basins through the Indonesian archipelago. Complex pathways of Pacific water flowing into the Indian Ocean in the Indonesian seas were traced only recently: the throughflow is dominated by low-salinity water moving through the Makassar and Lombok Straits and more salty water going through the Banda Sea (Gordon and Fine 1996). The World Ocean Circulation Experiment (WOCE), currently under way with the participation of nearly thirty countries, will greatly expand our understanding of the phenomenon. Ganachaud and Wunsch



5.3 The normal temperature profile of ocean water shows a rapid decline from surface maxima to a nearly constant value around 3–4 °C below 2,000 m (Smil 1999d).



5.4 The dramatic contrast of the cool surface sea temperature in the equatorial Pacific waters during an El Niño event (white wedge on October 28, 1997) and the warm waters of a La Niña episode (dark area on February 27, 1999). The images, from the U.S.-French TOPEX/POSEIDON mission, are available at <http://www.jpl.nasa.gov/elnino>

(2000) used WOCE data to calculate a water and heat flow of, respectively, 505 Gt/year and 1.3 PW between the subtropical (latitude of southern Florida) and North Atlantic and virtually identical rates between the Pacific and Indian Oceans through the Indonesian straits.

Water sinking proceeds in restricted currents, including giant ocean cataracts. The most voluminous of these plunges southward about 3.5 km between Iceland and Greenland, carrying 25 times the flow of the Amazon (Whitehead 1989). In contrast, wind-driven upwelling of deep, cold, nutrient-laden waters goes on along the low-latitude western shores of the Americas, Africa, and India as well as in the Western Pacific equatorial zone, and it is marked by high rates of photosynthesis in what would be otherwise fairly barren surface waters. Even relatively minor changes in ocean surface temperature can have pronounced consequences. This phenomenon is best illustrated by far-flung effects of oscillations between El Niño, a periodic westward expansion of warm surface waters beginning off the coast of South America and by early winter often extending all along the Equator to join warm water off Australasia, and La Niña, a large, wind-driven area of cool water off the South American coast (fig. 5.4).

All but about 10% of water evaporated from the ocean is precipitated back onto sea surfaces. Evaporation exceeds precipitation in the Atlantic and Indian Oceans; the reverse is true in the Arctic Ocean, and the Pacific flows are nearly balanced. Irregular patterns of oceanic evaporation (maxima up to 3 m/year) and precipitation (maxima up to 5 m/yr) require substantial compensating flows from the regions with excess rainfall in order to maintain sea level (Schmitt 1999). The North Pacific, particularly its eastern tropical part, is the largest surplus region (and hence its water is less salty), whereas evaporation dominates the Atlantic waters.

Ocean evaporation produces both constant gentle fluxes of water and latent heat as well as some of the most violent atmospheric flows in seasonal cyclones (American hurricanes, Asian typhoons). The process is also responsible for the Asian monsoon, the planet's most spectacular mechanism for transferring heat absorbed by warm tropical oceans to dry land (Webster 1981). Some of the world's most productive and most diverse ecosystems, as well as nearly half of humanity, are directly affected by this immense seasonal pulse generated by intense heating of equatorial waters.

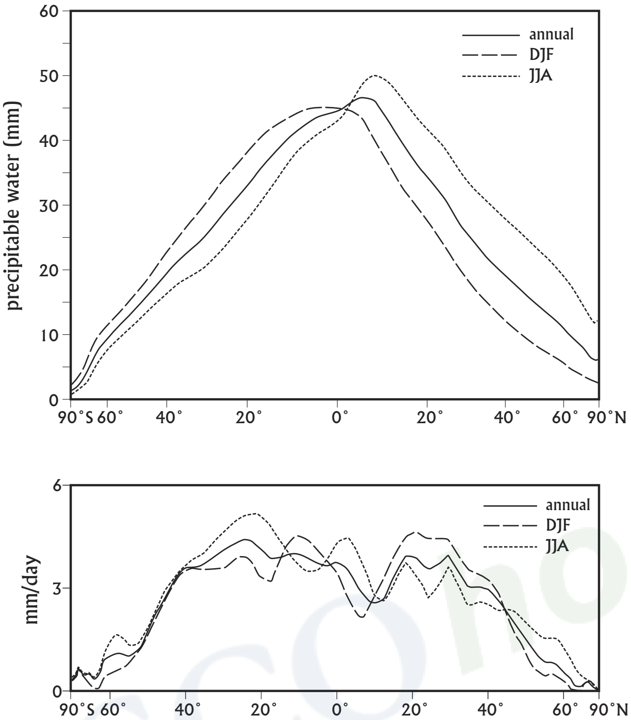
In the long run oceanic evaporation, and hence the intensity of the global water cycle, is also influenced by the mean sea level: during the last glacial maximum, 18,000 years ago, that level was 85–130 m lower than it is now (CLIMAP 1976). Measurements with an altimeter on the US-French TOPEX/POSEIDON satellite indicate a recent global mean sea level change of almost 4 mm a year, and most of this increase is a short-term variation unrelated to the expected rise caused by global warming and the resulting thermal expansion of water (Nerem 1995).

Other Reservoirs and Global Fluxes

Only two distinctly secondary reservoirs—glaciers and permanent snow, and groundwater—claim more than 1% (roughly 1.7%) each of the Earth's water stores. The tiny remainder of less than 0.04% is stored mostly in ground ice in permafrost strata of soils (0.02%) and in lake waters (0.01%), with the next largest reservoir, soil moisture, being an order of magnitude smaller (0.001%) and with all biomass containing a mere 0.0001% of the total (Oki 1999; fig. 5.2). But such comparisons do not convey the qualitative importance of various water reservoirs, and atmospheric water is perhaps the best illustration of this fact. Water aloft is a mere 0.0009% of the global presence; it makes up only about 0.3% of the atmosphere by mass and 0.5% by volume, and its average residence time is just 10–14 days, yet it suffices to cover some 60% of the planet with clouds at all times, greatly modifying the amount of solar radiation reaching the ground. In addition, as described in chapter 4, water is also by far the most important absorber of outgoing IR radiation, and its high heat capacity and release of latent heat on condensation are critical determinants of the planet's thermal regime.

The net transfer of ocean-derived water vapor to the continents supplies about one-third of terrestrial precipitation. The remainder comes from evaporation from nonvegetated surfaces and from evapotranspiration, the evaporation of water through stomata of leaves. Naturally, dense forests with rich canopies are best at "pumping" water for photosynthesis, and in the process they can increase the latent heat flux by an order of magnitude compared to barren surfaces. Because of its strong absorption of outgoing IR as well as its interaction with aerosols, tropospheric water vapor is a key determinant of the Earth's climate, but global observations of water vapor at higher levels (5–10 km above the surface) have been scarce. Consequently, it is helpful that Price (2000) demonstrated that lightning activity is a good proxy for convection and thus could be used to monitor water vapor concentrations in the upper atmosphere.

Rising air parcels are cooled (dry ones adiabatically, at a rate of 10 °C/km), and rain or snow begin when water drops or ice crystals making up the clouds grow to form



5.5 Meridional profiles of zonal mean precipitable water and evaporation. Based on data in Oki (1999).
Notes: DJF = December, January, February; JJA = June, July, August.

particles of sufficient size to fall as precipitation. These processes take place mostly in the lower two-thirds of the troposphere, but massive thunderclouds penetrate the entire troposphere and can be often seen in space imagery as protruding above the tropopause. Roughly three-fifths of all continental precipitation is evaporated, one-tenth returns to oceans as diffused surface and underground runoff, and just short of one-third is carried by rivers (fig. 5.1). With a mean continental elevation of about 850 m, this implies an annual conversion of some 400 EJ of potential energy to the kinetic energy of flowing water, which is the principal agent of geomorphic denudation shaping the Earth's surfaces.

A global graph of the latitudinal distribution of evapotranspiration shows a weakly bimodal distribution, whereas precipitable water has a clear equatorial peak; the difference between precipitation and evaporation forms a wavy pattern with the maximum surplus at the Equator, secondary maxima almost symmetrically at near 50° N and S, and pronounced minima in the subtropics (fig. 5.5). The equatorial maximum is associated with convective cloud systems, whereas the secondary maxima are the result of extratropical cyclones and midlatitude convection (Jonas 1999). Notable departures from these latitudinal regularities are caused by irregular distribution of continental masses and by major mountain ranges whose orographic uplift results in record rainfalls (extremes in Assam and Hawai'i). Global gridded fields of monthly precipitation patterns can now be constructed based on five different sources of gauge and satellite observations (Xie and Arkin 1996). Because the biosphere's primary productivity is so highly dependent on water supply, these precipitation patterns clearly prefigure the intensity of photosynthesis.

Surface runoff returns the precipitated water to the oceans rather rapidly: average residence times of fresh water range from just two weeks in river channels and weeks to months in soil to years in lakes and swamps. Annual river runoff ranges typically between 200 and 300 mm, but it is as high as 800 mm for Amazonian South America and as low as 25 mm for Australia. Not surprisingly, the Amazon alone carries about 16% of the planet's river water, and the world's five most voluminous streams (the Amazon, Ganges-Brahmaputra, Congo, Orinoco, and Yangzi) carry 27% of all river runoff (Shiklomanov 1999).

In contrast to the rapid surface runoff, water may spend many thousands of years in deep aquifers. Perhaps as much as two-thirds of all fresh water on the Earth is contained in underground reservoirs, which annually cycle an equivalent of some 30% of the total runoff to maintain stable river flows (Ambroggi 1977). Submarine groundwater discharge (SGWD), the direct flow of water into the sea through porous rocks and sediments, appears to be a much larger flux of the global water cycle than previously estimated. Moore (1996) found large enrichment of groundwater-borne ^{226}Ra in brackish waters along the coast of the southeastern United States and concluded that this influx was equivalent to about 40% of the river water flow during the study period, whereas previous estimates of global SGWD ranged from just 0.01% to 10% of runoff (Church 1996). An important consequence of this finding is the need to revise upward estimates of terrestrial fluxes of dissolved materials to coastal waters.

Cycles of Doubly Mobile Elements

The level of high mobility of carbon, nitrogen, and sulfur makes these three elements fairly readily available in spite of their relative biospheric scarcity. Their cycles are complex both in terms of the number of major reservoirs, fluxes, and compounds involved in the cycling processes and in temporal terms as well. Every one of these grand biospheric cycles hides numerous nested subcycles whose fluxes operate on time scales ranging from minutes to millions of years, as the elements may move rapidly among ephemeral reservoirs or be sequestered (assimilated, immobilized) for extended periods of time. Rapid cycling of nutrients in shallow waters is a common example of the first kind of transfers, whereas massive withdrawals of carbon into extensive carbonate deposits illustrate the slow cycling.

And the three cycles are not just essential for the biosphere; they are also fundamentally its creations. Although abiotic transfers and reactions are important in all of them, key fluxes of these cycles would be impossible without living organisms. Rapid cycling of carbon and all essential macro- and micronutrients depends on prompt degradation of dead biomass and the return of elements from complex organic molecules to much simpler inorganic compounds that can be reused in autotrophic production. On land this recycling returns 98–99.8% of all elements incorporated in dead biomass; in the ocean the remineralization puts back 85–90% of carbon and nutrients, with the remainder lost to sediments. Multistep mineralization processes involving archaea, bacteria, protists, and invertebrates cannot be accomplished in any other way—nor could, to give just two examples, nitrogen fixation under ambient conditions or dissimilatory reduction of sulfates.

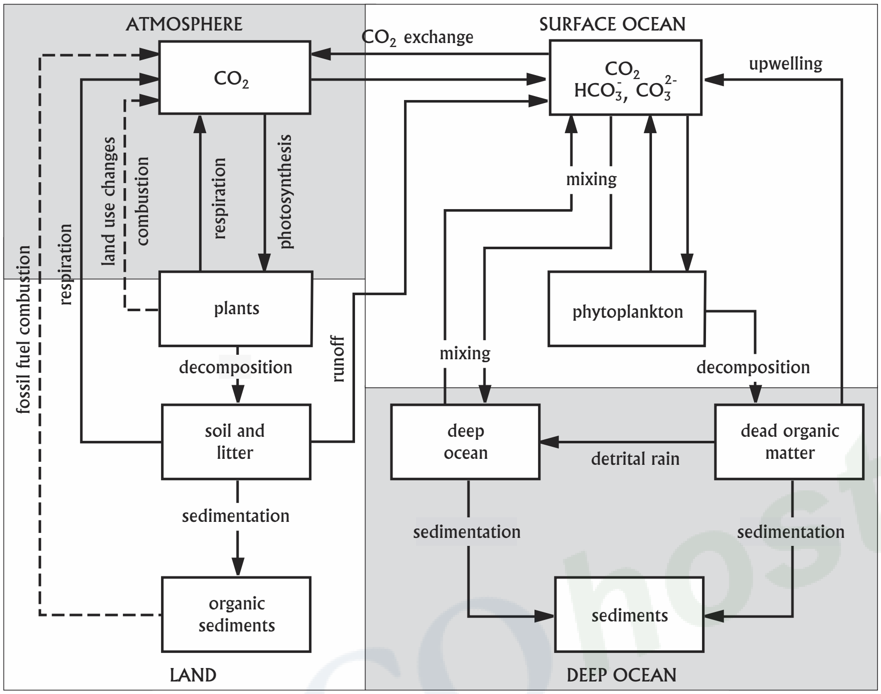
Unfortunately, the easy mobility of these three elements—the result of many of their volatile and highly water-soluble compounds—also means that human interference in these cycles has become evident on the global level, above all as rising atmospheric concentrations of CO_2, CH_4, and N_2O. Such interference has, as in the case of acid deposition of sulfates and nitrates, major impacts on large regional or continental scales. Environmental problems arising from these changes—potentially rapid global warming, widespread acidification of soils and waters, growing eutrophication of aquatic and terrestrial ecosystems—have been receiving a great deal of research attention in the last decade (Turner et al. 1990; Schlesinger 1991; Butcher et al. 1992; Wollast et al. 1993; Mackenzie and Mackenzie 1995; Agren and Bosatta 1998; Smil 2000a). I will comment on these perils in the closing chapter.

The Carbon Cycle

Water aside, the circulation of carbon is undoubtedly the biosphere's pivotal mass flow, as it has to assure the availability of tens of billions of tons of the element needed annually by plants; hence it is also the best studied of all elemental cycles (Dobrovolsky 1994; Smil 2000a; Wigley and Schimel 2000; Falkowski et al. 2000; fig. 5.6). Atmospheric CO_2 is the only source of CO_2 required for photosynthesis—land plants tap it directly, and aquatic plants use it after it has been dissolved in water—but its reservoir is by far the smallest presence among the element's principal biospheric storages. With about 280 ppm of CO_2 in the preindustrial atmosphere, the airborne carbon amounted to almost exactly 600 Gt, a mass that terrestrial and aquatic photosynthesis would have sequestered in new phytomass in just four or five years!

In reality, carbon assimilated by plants returns—part of it rather rapidly, the other part only after 10^2–10^3 years—to the atmosphere through soil respiration and wildfires. The best proof that past rates of carbon recycling were closely balanced with photosynthesis soil is the total mass of organic carbon stored in the lithosphere: some 15 Pt of carbon are locked mostly in kerogens, transformed remains of buried biomass found mostly in calcareous and oil shales. Assuming that nearly all of this mass was accumulated during the past 550 Ma, since the beginning of the Cambrian, only about 0.03% of newly formed phytomass had to be sequestered every year to arrive at the total. The accumulation rate was particularly high after the appearance of first forests (about 370 Ma during the Devonian) and before the emergence of the first large herbivores (about 250 Ma ago) and colonial herbivorous insects, whose grazing limited the amount of biomass that could be buried. The late emergence of lignin digestion by fungi may have been another important contributing factor (Robinson 1996).

The continuous transfer of a tiny fraction of assimilated carbon from soils to sediments remains the principal terrestrial bridge between the element's rapid and slow cycles, and it has also been responsible for the accumulation of free oxygen in the atmosphere. Only some 3% of all O_2 produced by photosynthesis in excess of respiration remains airborne, however, as the bulk of it is consumed by the oxidation of reduced iron compounds that produced massive banded iron formations. These deposits, the principal source of the world's iron ore, contain about 2×10^{22} g of O_2, or 20 times the present atmospheric level of the gas (see also chapter 2). Only a minuscule part of all sequestered



5.6 Principal reservoirs and flows of the biospheric carbon cycle (Smil 2000a).

organic carbon, about 6 Tt, or on the order of 0.04%, is present in traditional fossil fuels (coals and liquid and gaseous hydrocarbons) and only a small part this resource will eventually be recovered. But conversion of more accessible and higher-quality fuels has built the first high-energy civilization in human history and is largely responsible for extensive anthropogenic interference in the biospheric carbon cycle, whose most worrisome outcome may be a relatively rapid rate of global climate change. I will return to this challenge in the closing chapter.

Compared to the atmospheric reservoir of some 600 Gt C, preagricultural ecosystems may have stored nearly twice as much carbon in phytomass (about 1,100 Gt C; see chapter 7), and more than twice as much of it in soils, where it was, and is, overwhelmingly bound in organic matter. Soils now store on the order of 1,500 Gt C, with the storage density going up with higher precipitation and lower temperature and the peak deposit rates in tundra peats (Schlesinger et al. 2000). Soil respiration (oxidation of organic soil matter by microbial and invertebrate decomposers) may result in very rapid biospheric carbon cycling, but the average residence time of carbon in the long-lived humus pool is on the order of 1,200 years. Raich and Potter (1995) estimated annual soil respiration of microbes, fungi, roots, and invertebrates at 77 Gt C/year. Soil respiration is thus higher than our best estimates of net primary productivity (NPP), because it also includes CO_2 evolved by roots and mycorrhizae.

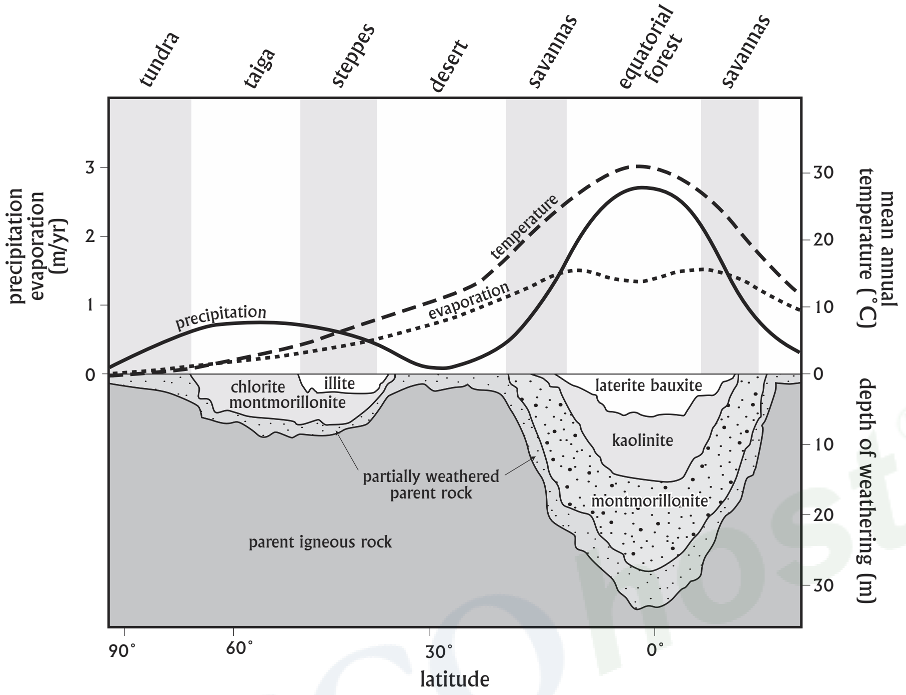
If, as used to be generally assumed, average rates of soil respiration increase with temperature, then global warming should lead to accelerated release of CO_2 from soils. A survey of decomposition in forest mineral soils on five continents, however, found that the rates of CO_2 release were remarkably constant across a global-scale gradient of mean annual temperatures (Giardina and Ryan 2000). Ambient temperature thus appears to be less of a limiting factor for microbial activity than previously believed, and future changes in ambient temperature may have little impact on soil respiration (Grace and Rayment 2000). But these findings cannot exclude the possibility of an eventual positive feedback between temperature and soil respiration resulting in a relatively sudden pulse of CO_2 injected into the atmosphere (Cox et al. 2000).

Standing ocean phytomass is only a tiny fraction, no more than 0.5%, of the terrestrial total. But because of the rapid turnover of phytoplankton, marine photosynthesis assimilates annually almost as much carbon as do land plants, turning parts of the ocean into major carbon sinks during the months of highest productivity. Respiration by zooplankton and other oceanic herbivores returns more than nine-tenths of this assimilated carbon to surface waters to be reused by phytoplankton or to equilibrate with CO_2 in the overlying atmosphere. The rest of the assimilated carbon sinks, with interruptions caused by feeding throughout the water column, to the ocean bottom.

Biomass thus acts as a pump, drawing atmospheric CO_2 into the ocean's depths, and diatoms (about 1,000 species of single-celled algae with silica cell walls and shapes ranging from flat discs to slender rods) make a particularly large contribution to this particle rain from the surface layer (Smetacek 2000). The annual burial rate is on the order of 100 Mt C, or less than 0.3% of all carbon assimilated by phytoplankton. The eastern equatorial Pacific accounts for 20–50% of oceanic net phytoplankton productivity and is also the site of the greatest CO_2 from the ocean to the atmosphere. (Loubere 2000). In the long run the region's high NPP is not governed by aeolian flux of growth-limiting iron or by wind-driven changes in the upwelling rate, but by changes in ocean circulation and the chemical composition of the upwelled water.

Although carbon's slow circulation is overwhelmingly a matter of inorganic reactions, it has important organic components. The process begins with the weathering of silicate rocks (calcium silicate [$CaSiO_3$] is used as a proxy for common Ca and Mg silicates, which are major constituents of the Earth's crust; their principal constituent minerals are plagioclase, biotite, pyroxenes, olivine, and amphiboles) driven by the water cycle and consuming CO_2 from the atmosphere (fig. 5.7; Garrels and Mackenzie 1971; appendix D). In vegetated areas this weathering is accelerated by interactions with the rapid, biota-driven carbon cycling as roots and microbes release CO_2 into soils, where it combines with water and attacks silicates (Schwartzman 1999). The resulting ions and dissolved silica are gradually transported to the ocean, which contains roughly 37 Tt of dissolved inorganic carbon, about 95% of it in highly soluble bicarbonate ions, HCO_3^-, and nearly 98% of it dissolved in dark intermediate and deep waters with temperatures at 2–4 °C.

Inorganic precipitation of carbonates proceeds only after the two constituent ions have reached critical concentrations in the seawater, but the process of carbonate sedimentation is greatly accelerated by marine biomineralizers, which use calcium carbonate ($CaCO_3$) to build their



5.7 Weathering of silicate rocks in different environments is affected primarily by precipitation, evaporation, and temperature. Based on Hay (1998).

shells. These and other marine organisms also contribute organic carbon to marine sediments. As noted in chapter 4, the remarkably constant bipartition of sedimented carbon between organic and inorganic compounds—their ratio has been close to one to five for almost four billion years—makes it clear that biota have had a critical role in the element's cycle throughout the biosphere's evolution.

Loose sediments are slowly converted to compact carbonates and hard quartz. $CaCO_3$, as calcite or aragonite, is most abundant, and $CaMg(CO_3)_2$ (dolomite) is the third most common carbonate mineral; $MgCO_3$ (magnesite) and $FeCO_3$ (siderite) are much less common. The eventual fate of these sediments is determined by the large-scale processes of global plate tectonics: they are either pushed up in plate collisions to form mountain ranges or subducted into the mantle as they ride on relatively rapidly moving oceanic plates. The eventual metamorphosis of subducted sediments (by reactions with silica) re-creates silicate rocks that are re-exposed by tectonic uplift, and CO_2 is degassed along the spreading ridges and in volcanic eruptions. In any case, the sediments will reappear after 10^7–10^8 years to be weathered once more.

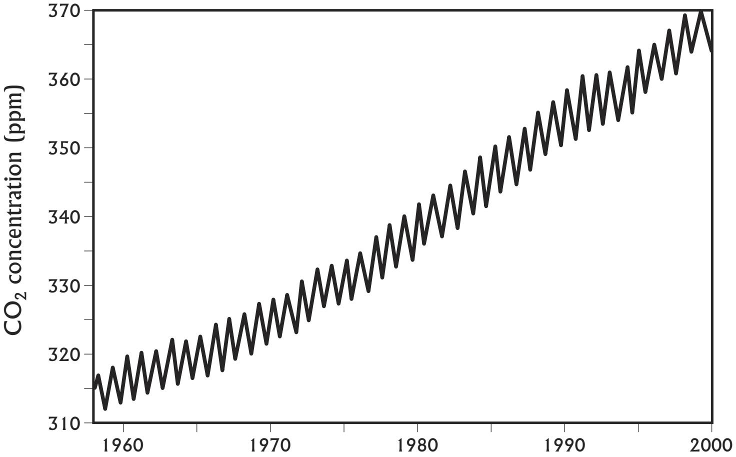
This cycling of oceanic sediments, and the attendant return of carbon as CO_2, cannot be accelerated by any atmospheric or biospheric influences, but the rates of CO_2 removal from the air may change rather rapidly. Lower tropospheric temperatures and decreased rates of silicate weathering would lead to gradual accumulation of emitted CO_2—and to subsequent warming. Increased temperatures would result in higher rates of evaporation and hence in a faster dissolution of CO_2; the resulting carbonic acid (H_2CO_3), the primary chemical agent of weathering the silicate rocks, would remove more Ca^{2+} and HCO_3^- to be transported by streams to the ocean, where they form carbonate sediments. At the same time, the return of CO_2 from the grand geotectonic cycle would remain unchanged, and the planet would gradually cool.

The loss of atmospheric CO_2 accelerates during the periods of mountain building and greater limestone deposition brought by intensified weathering. Raymo et al. (1988) suggested that the uplift of the Himalayas led to a reduced greenhouse gas effect because of an increased sequestration of CO_2 in what is the planet's most intensive region of denudation, but this proposal has been strongly challenged (Schwartzman 1999). Most notably, without a balancing source of CO_2, all of the gas would have been removed from the atmosphere/ocean pool in a relatively short period of time. Rates of CO_2 release are related above all to sea floor generation. This slow carbon cycle—feedbacks involving CO_2 consumed by weathering and the gas released from metamorphism and magmatism—controls the Earth's temperature on time scales exceeding 1 Ma (Walker et al. 1981; Berner et al. 1983). These feedbacks prevented complete ocean freeze-up even when the early biosphere received 30% less radiation (compared to current levels) from the faint young Sun.

As noted in chapter 4, only approximate reconstructions of CO_2 levels are possible for more distant periods, but air bubbles from Antarctic and Greenland ice cores (the largest one is 3,623 m deep) make it possible to trace CO_2 levels with high accuracy for the past 420,000 years (Petit et al. 1999). During that time CO_2 levels have stayed between 180 and 300 ppm, and during the 5,000 years preceding 1850, they fluctuated only between 250–290 ppm (Petit et al. 1999; fig. 4.10). Their post-1850 rise will be described in chapter 9.

The plant- and microbe-dominated fast cycle also generates pronounced daily and seasonal cycles of atmospheric CO_2 levels. The latter undulation is essentially the biosphere's breath, a globally integrated annual cycle of respiration and photosynthesis. Its inhalations and exhalations are particularly pronounced in the Northern Hemisphere, where most of the terrestrial phytomass is located: CO_2 minima are in August, during maximum carbon storage by forests and grasslands, and maxima in January, when much of the vegetation is either leafless or dormant (fig. 5.8). Both of these cycles have been altered by human actions. Whereas the traditional burning of phytomass fuels (wood, charcoal, crop residues) was essentially just an accelerated form of recycling carbon that was stored in plants for months to decades, combustion of fossil fuels has been emitting increasing amounts of carbon that has been sequestered for 10^6–10^8 years, and an additional net release of carbon comes from the conversion of natural ecosystems (mainly from tropical deforestation) to agricultural, industrial and urban uses (for details, see chapter 9).

Before turning to the nitrogen cycle, I must note that a substantial portion of buried organic carbon is involved in a methane subcycle: it is returned to the atmosphere by anaerobic methanogenic archaea, then oxidized in a stepwise process to CO_2 (Warneck 2000). By far the largest mass of CH_4 generated by microbial decomposition is stored beneath the sea floor in methane hydrates (a combination of ice and the gas). A massive release of this gas,



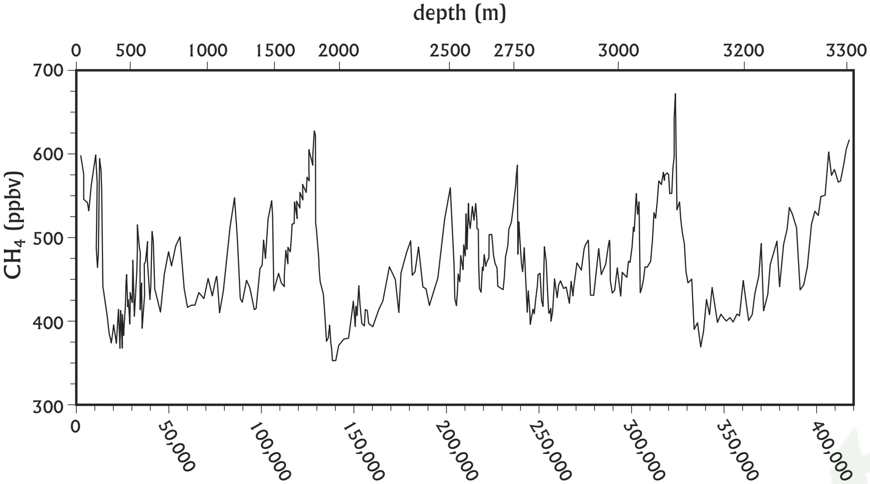
5.8 The biospheric breath is clearly discernible in seasonal fluctuations of CO_2 concentrations monitored at Mauna Loa. Monthly data available at <http://cdiac.esd.ornl.gov/trends/co2/nocm-ml.htm>

followed by its oxidation to CO_2, may have led to the sudden warming experienced 55 Ma ago and associated with the rise of mammals to terrestrial dominance (Katz et al. 1999).

But even noncatastrophic CH_4 oxidation does not perfectly match natural methanogenesis, and the gas released from wetlands, wild ruminants, and wildfires is present in trace amounts in the atmosphere. Air bubbles in polar ice show levels between 300 and 700 ppb during the past 100,000 years, with narrow oscillations around about 700 ppb during the last preindustrial centuries (Etheridge et al. 1998; fig. 5.9). Although low in absolute terms (three orders of magnitude below CO_2 levels), such concentrations are almost infinitely higher than would be their thermodynamic equilibrium value in the Earth's oxygen-rich atmosphere, and they are possible only because methanogenesis is constantly outpacing oxidation. But as with CO_2, current sources of CH_4 exceed its sinks because of human actions ranging from natural gas losses in pipelines to more extensive rice cultivation and growing cattle numbers. At almost 1800 ppb the atmospheric level of CH_4 is now more than twice as high as it was in 1850. And because CH_4 is, over a period of 100 years, an approximately 20 times more potent absorber of outgoing IR than is CO_2, it has become the second most important anthropogenic contributor to the tropospheric warming (Watson et al. 1996).

The Nitrogen Cycle

Although the biosphere is bathed in nitrogen—the gas makes up almost 80% of the atmosphere by volume—the element is not readily available in forms assimilable by organisms. And although biota need the element in only

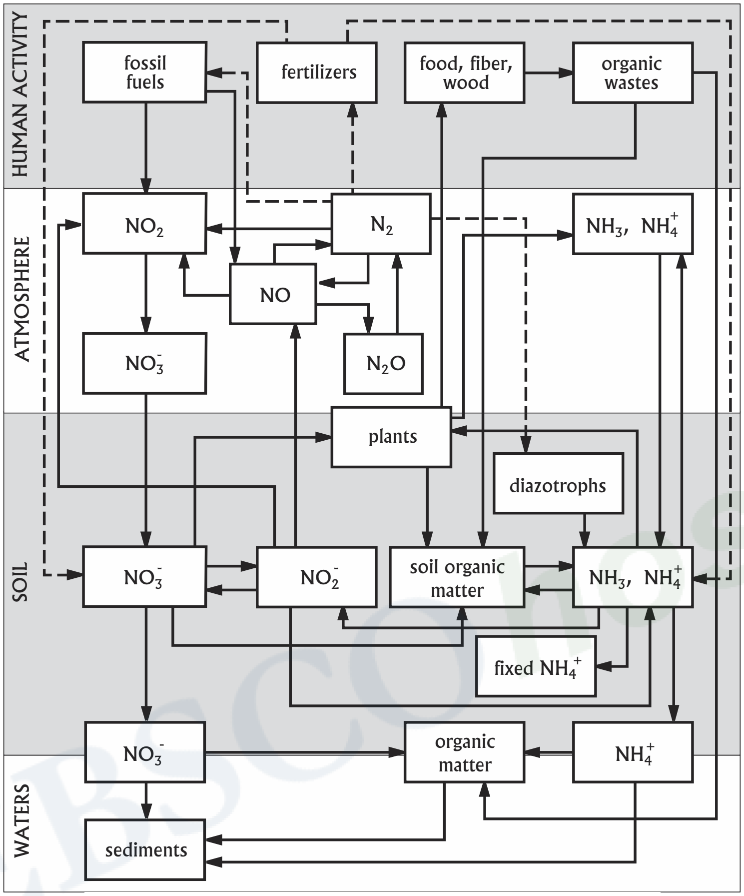


5.9 Methane concentrations derived from ice cores and from recent tropospheric measurements. Based on Petit et al. (1999) and U.S. Environmental Protection Agency (2001).

small quantities, its scarcity is often the most important factor limiting photosynthesis and compromising heterotrophic growth. These paradoxes are explained by nitrogen's atmospheric presence as a nonreactive N_2 molecule held by one of the strongest known triple bonds (–945 kJ/mol) and by a shortage of natural processes that can split it and incorporate the atomic N into reactive compounds. But the relative inertness of N_2 is not entirely unwelcome: a more reactive molecule combining with oxygen might lead to constant nitrate rains and an acid ocean.

Not surprisingly, none of the three principal polymeric constituents of phytomass—cellulose, hemicellulose, and lignin—contains any nitrogen, but life cannot exist without it. The element must be present in every living cell in the nucleotides of nucleic acids (DNA and RNA), which store and process all genetic information; in amino acids, which make up all proteins; and in enzymes, which control life's metabolism; and nitrogen is also a part of chlorophyll, whose excitation by light energizes all photosynthesis.

Nitrogen's biospheric cycle also stands apart from the circulations of the other two doubly mobile elements because its three key fluxes—fixation, ammonification, and nitrification and denitrification—are nearly completely dominated by bacteria (fig. 5.10). Nitrogen fixation, the conversion of unreactive N_2 to reactive compounds, can be abiotic, but it requires the high-energy discharge in lightning to sever the N_2 molecule, and the element then forms nitrogen oxides (NO and NO_2), which are eventually converted to nitrates. In contrast, biofixation, moving N_2 to NH_3, takes place at atmospheric temperatures and pressures and fixes two orders of magnitude more N than lightning, but it is performed only by about 100 bacterial genera

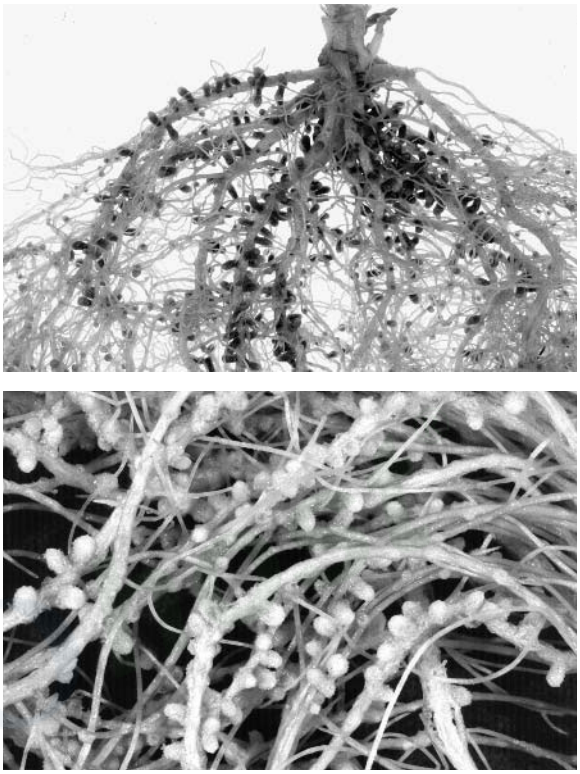


5.10 Principal reservoirs and flows of the biospheric nitrogen cycle (Smil 2000a).

that posses nitrogenase. This specialized enzyme that can cleave N_2, acquired during the almost anoxic conditions of the early Archean by copying a short-chained ferredoxin, was essential for Archean microbes, but biofixation is costly in energy terms, and no eukaryotes resort to it.

Diazotrophs (microbial fixers) can be free-living species, endophytes, or symbionts (Broughton and Puhler 1986; Smil 2000a). Free-living diazotrophs, including such common soil bacteria as *Azotobacter* and *Clostridium,* usually fix less than 0.5 kg N/ha per year, but cyanobacteria can add substantial amounts of nitrogen both to soils and surface waters. *Anabaena, Nostoc,* and *Calothrix* are by far the most important genera of cyanobacteria, enriching soils by as much as 20–30 kg N/ha per year. To protect the O_2-intolerant nitrogenase, they fix nitrogen in special heterocysts formed at regular intervals along their filaments. Common anaerobic fixers, such as *Oscillatoria* and *Plectonema,* do not need heterocysts. Colonial filamentous *Trichodesmium* was seen as the dominant oceanic diazotroph ever since its N-fixing ability was discovered in 1961, but new research indicates that unicellular cyanobacterial nanoplankton may be a significant source of reactive nitrogen (Zehr et al. 2001).

Endophytic diazotrophs (*Gluconacetobacter, Herbaspirillum*) live inside plant roots, stems, and leaves and can fix at least 50 kg N/ha annually; their presence explains high yields of unfertilized sugar cane and other tropical grasses (Boddey et al. 1995).



5.11 Roots of a pea (*Pisum sativum*) plant with numerous nodules containing *Rhizobium* bacteria. Images courtesy of Bert Luit, Department of Plant Science, University of Manitoba, Winnipeg.

Some nitrogen-fixing organisms live in association with plants: *Frankia,* an actinomycete genus, forms nodules on roots of some 170 plants, including alder (*Alnus*) and *Myrica,* species common in bogs and on eroded slopes; *Anabaena* is associated with a water fern, *Azolla,* and *Beijerinckia* with sugar cane. But by far the most productive diazotrophs belong to just six genera of rhizobial bacteria: *Rhizobium, Bradyrhizobium, Sinorhizobium, Mesorhizobium, Azorhizobium,* and *Allorhizobium* (Spaink 2000). These chemoheterotrophs have the unique capacity to induce the formation of root nodules and are symbiotic solely with plants of Leguminoseae family, both large tropical trees and small temperate-climate annuals (fig. 5.11). These symbionts are concentrated in distinct root nodules, and they obtain carbohydrates in a rather energy-expensive exchange for their fixed nitrogen, which they supply in the form of ammonia or alanine: the typical cost is between 3 and 6 g C/g N fixed. Depending on the site and season, there may be anywhere between 10^0–10^6 rhizobia per gram of soil.

Not surprisingly, natural biofixation has strong positive relationships with evapotranspiration and NPP (for details on the latter, see chapter 7). Rhizobia can add annually more than 500 kg N/ha with such highly productive cover legumes as alfalfa, but more typical fixation rates in forests and grasslands are well below 100 kg N/ha. Because of large natural variability of biofixation rates observed in individual leguminous plants and in legume-rich ecosystems, it is difficult to offer a tightly constrained estimate of global biofixation. The most comprehensive recent evaluation of natural terrestrial biofixation, dominated by the contribution of tropical forests, ended up with a rather wide range of 100–290 Mt N, with 150–190 Mt N per year being the most likely value (Cleveland et al. 1999). This means that without any recycling, biofixation would exhaust the atmospheric reservoir of N_2 (3.9 Pt) in about twenty million years.

Plants can use the ammonia produced by diazotrophs as a source for nitrogen but prefer to assimilate the much more soluble nitrate. As previously explained (in chapter 3), the conversion of NH_3 to NO_3 is strictly microbial; nitrifying bacteria are common in both soils and waters, and the process is fairly rapid, particularly in warm and well-aerated soils. Assimilated nitrogen is embedded mostly in the amino acids that form plant proteins. Heterotrophs must ingest preformed amino acids in feed and food to synthesize their proteins. After plants and heterotrophs die, enzymatic decomposition (ammonification) moves nitrogen from dead biomass to NH_3, which is again oxidized by nitrifiers. Finally, denitrification returns the element from NO_3^- via NO_2^- to atmospheric N_2. This closing arm of the nitrogen cycle is also almost entirely microbial (abiotic denitrification, when soil organic matter reacts with nitrites, is of minor importance). But unlike nitrification, which depends on just a few bacterial genera, many common aerobic bacteria — including *Pseudomonas, Bacillus,* and *Alcaligenes,* whose enzymes use successively more reduced nitrogen compounds as electron acceptors — can perform denitrification.

Because not all of these bacteria have the requisite reductases for carrying the process all the way to N_2, denitrification also produces appreciable amounts of nitric oxide (NO) and N_2O. N_2O is unreactive in the troposphere, but in the stratosphere it reacts with O^* and produces NO, whose release sets off the catalytic destruction cycle of O_3. This sequence, whose discovery by Crutzen (1970) was rewarded with the 1995 Nobel Prize in chemistry, is the most important natural cause of O_3 decomposition — and the reason for concerns about the long-term effects of increasing N_2O emissions from intensifying fertilization. In addition, N_2O is also a greenhouse gas considerably more potent than CO_2. Denitrification proceeds faster in soils with high levels of nitrate, organic matter, and moisture levels and low levels of O_2, and in fairly high temperatures, but its natural rates range over two orders of magnitude. Not surprisingly, global estimates of denitrification have more than a threefold range.

There are also many leaks, detours, and backtrackings along this main cyclical route from fixation to denitrification. Volatilization from soils, plants, and heterotrophic wastes adds NH_3 to the atmosphere, and the gas is rather rapidly redeposited in dry form or in precipitation. Both nitrification and denitrification release NO_x and N_2O. NO_x nitrogen is soon redeposited, mostly after oxidation to NO_3. In contrast, N_2O is basically inert in the troposphere, but as noted above, it is a powerful greenhouse gas. Highly soluble nitrates leak readily into ground and surface waters, and both organic and inorganic nitrogen in soils is moved to waters by soil erosion.

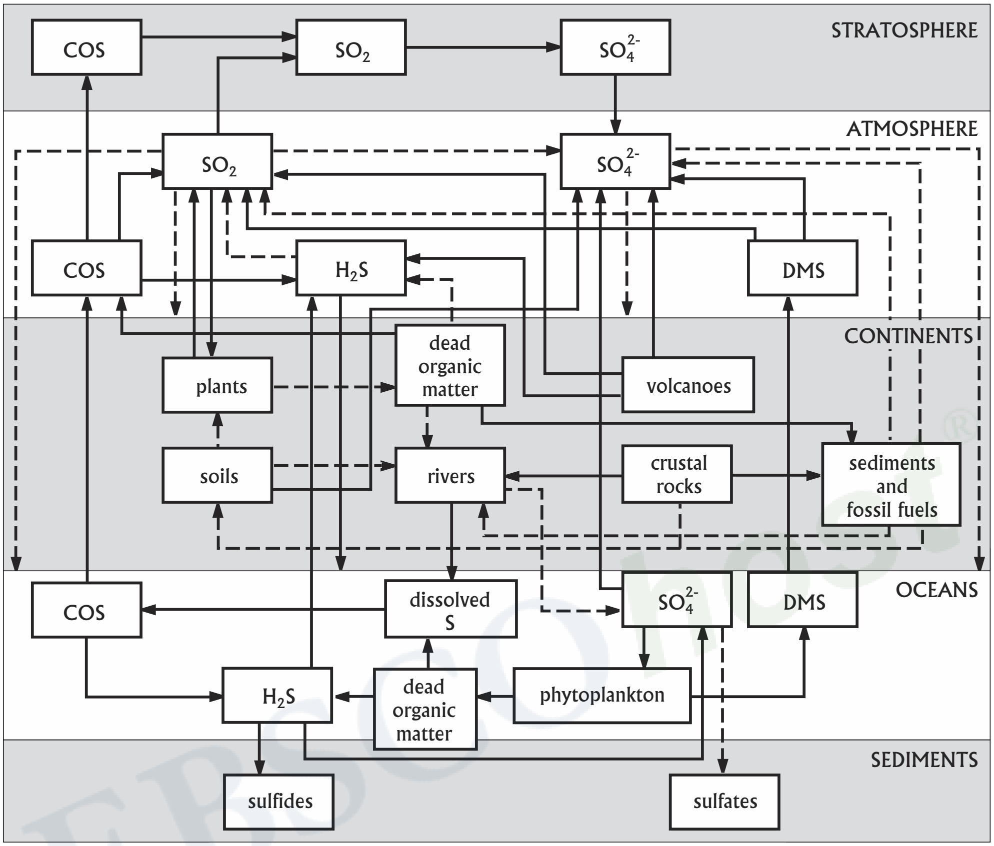
Compared to the huge amounts of atmospheric storage—besides the dominant N_2, there are also traces of NO, NO_2, N_2O, NO_3^-, and NH_3—other biospheric nitrogen reservoirs are small. Because most of the Earth's phytomass is composed of nitrogen-poor polymers (see chapter 6), the amount of the element stored in preagricultural vegetation added up to no more than 10 Gt. Soils contain about 100 Gt N, mostly in long- and short-lived humus. Average values for larger areas are not very meaningful, as nitrogen content varies by more than an order of magnitude among various soil types—ranging from less than 1,000 kg N/ha in poor glacial soils to well over 10,000 kg N/ha in excellent chernozems—and by a considerable margin even within a single field. The uncontaminated waters of the preindustrial era stored very little nitrogen: ammonia is not very soluble, and nitrate concentrations in preindustrial streams were very low (less than 0.1 mg NO_3-N/L), and even today clean rivers generally carry less than 1 mg N/L. Today's levels of aquatic nitrogen, as well as many other biospheric reservoirs and flows, have been much affected by the growing human interference in the element's cycle (chapter 9).

The Sulfur Cycle

Sulfur's critical role in life (as noted in chapter 2) is to keep proteins three-dimensional. Only two of the twenty amino acids providing building blocks for proteins (methionine and cysteine) have sulfur in their molecules, but when amino acids form polypeptide chains, disulfide bridges link them to maintain their complex folded structure, which is necessary for engaging proteins in biochemical reactions. Photosynthesis incorporates roughly one atom of sulfur for every 1,000 atoms of carbon. The initial uptake is in the form of soil sulfate, which is then reduced intracellularly to H_2S and incorporated mostly in cysteine and methionine. Nonprotein sulfur is in biotin (vitamin H), thiamine (vitamin B_1), glutathione, and coenzyme A. Phytomass contains between 0.08 and 0.5% S, which means that terrestrial ecosystems now assimilate annually about 150 Mt S, and standing phytomass contains less than 500 Mt S.

Degradation of sulfur-containing organic compounds by many common bacteria (*Pseudomonas, Escherichia*) and fungi (*Aspergillus, Streptomyces*) promptly returns most of the assimilated sulfur to soils. Organic sulfur, nearly equally split between amino acids and nonprotein compounds, accounts for more than 90% of total soil stores which, with carbon-to-sulfur ratios of 60 to 130, amount to about 15 Gt S; most of the rest is in highly soluble sulfates. The rapid sulfur cycle, consisting of assimilatory reduction of sulfate by plants, decomposition, mineralization, and plant uptake, has no major leak through which the element can be moved to a more persistent reservoir (fig. 5.12).

In contrast, dissimilatory bacterial sulfate reduction, which generates H_2S as well as more complex compounds including $(CH_3)_2S$ (methyl sulfide), COS (carbonyl sulfide) and CS_2 (carbon disulfide), has moved large masses of sulfur into long-term mineral stores. The process is carried on by thiopneuts, more than a dozen bacterial genera that reduce sulfate (or elemental sulfur) in a way analogical to denitrification. *Desulfutomaculum* and *Desulfovibrio* are particularly common in tidal and marine sediments, which combine an anoxic environment with abundant carbon substrate for metabolism. The reduction takes place in the topmost mud layers, with the required sulfate coming from the interstitial water. The portion of H_2S that does



5.12 Principal reservoirs and flows of the biospheric sulfur cycle (Smil 2000a).

not escape into the water and the atmosphere diffuses within the mud and reduces the oxidized ferric ion (Fe^{3+}) to the ferrous ion (Fe^{2+}). Further reactions of Fe^{2+} with H_2S produce first FeS (frequently imparting black pigmentation to tidal muds) and then FeS_2 (pyrite).

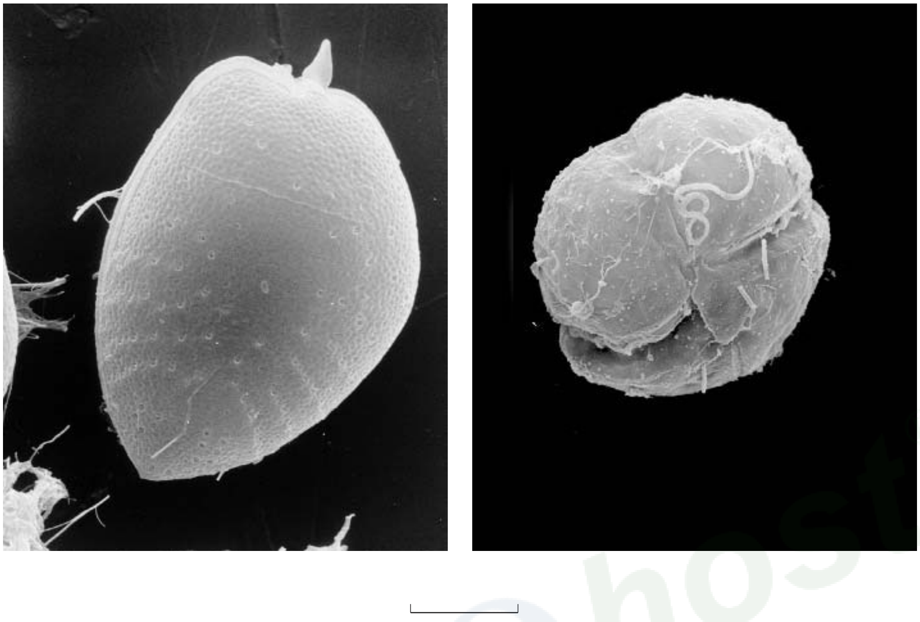
Together with the formation of stromatolites (see chapter 2), this conversion is one of the two oldest biogenic processes of mineral formation, as the precursors of today's thiopneuts were among the earliest organisms. Ohmoto et al. (1993) described a pyrite deposit in South Africa's Barberton Greenstone Belt that was formed unmistakably by bacterial reduction of seawater sulfate about 3.4 Ga ago. Shen et al. (2001) found unequivocal evidence of microscopic sulfides in approximately 3.47-Ga-old barites from North Pole, Australia. And sulfate reduction remains at the core of long-term cycling of the element: best estimates of current marine FeS_2 formation indicate sequestration of at least 40 Mt S per year, but the actual flux may be much higher. The other process that has sequestered large amounts of oceanic sulfur is abiotic: episodic evaporation of seawater in shallow basins in arid climates precipitates carbonates first, and sulfates (mostly $CaSO_4 \cdot 2H_2O$) form only once the water volume is reduced by 80%.

Major natural sources of sulfur entering the biosphere include both nonvolatile and volatile compounds originating in sea spray, wind erosion, volcanoes, and a variety of biogenic emissions (Bates et al. 1992). Sea salt sulfates, lofted into the air primarily not by spectacularly breaking waves, but by incessant microbursts of countless bubbles at the ocean's surface, are by far the largest natural input of sulfur into the atmosphere. SO_4^{2-} is, after Cl^-, the second most abundant ion in seawater, but most of its huge mass (about 1.3 Pt) is beyond the reach of the near-surface turbulence. Global annual estimates of the annual sulfate flux have ranged from a mere 44 Mt to 315 Mt, with 140–180 Mt being the most likely input. In any case, only about a tenth of this mass settles on the continents; gravitation promptly returns the rest to the ocean.

Volcanic emissions are, on average, a relatively large source of sulfur compounds, mainly of SO_2, but their contributions are highly variable. For example, Mount St. Helens' spectacular plume and mud flows of May 18, 1980, contained no more than about 1,000 t S (Decker and Decker 1981). In contrast, the largest stratospheric cloud of SO_2 ever measured, emitted by Mount Pinatubo's eruption in June 1991, carried at least 17 Mt of the gas, or nearly 9 Mt S (Kress 1997). Reconstructions of total sulfur emissions based on sulfate deposits in Antarctic ice indicate that the 1815 Tambora eruption, the largest in modern history, spewed out as much as 50 Mt S.

Recent long-term annual global emission means, made up of quiescent degassing and explosive ejections originating mostly in the East Pacific arc between Kamchatka and Indonesia, add up to 14 ± 6 Mt S (Graf et al. 1997). Submarine volcanism, concentrated along the spreading zones of midocean ridges, is a source of identical magnitude, but we do not know what share of that flux enters the atmosphere. After reaching the stratosphere, sulfur-containing dust from volcanic emissions may contribute to global cooling not primarily, as originally thought, because it blocks the incoming radiation, but because atmospheric reactions produce sulfuric acid (H_2SO_4) aerosols, which are very efficient in back-scattering and absorbing incident radiation and have longer residence times than dust particles. Moreover, studies of polar ice cores show that these aerosols are dispersed globally, and hence it may be the sulfur emitted in an eruption rather than the total amount of dust that determines the degree of posteruption cooling. Estimates of sulfur in airborne dust, mainly desert gypsum ($CaSO_4 \cdot 2H_2O$) are also highly uncertain, ranging from 8 to 20 Mt S per year, with most of this burden promptly redeposited downwind. On the other hand, as already noted, major dust storms can carry considerable masses of particulate matter across continents or oceans, but some particulate matter crosses the oceans constantly.

Biogenic emissions of sulfur come from the decomposition of biomass by a variety of specialized bacteria that use the energy liberated by oxidation or reduction of elemental sulfur or sulfur compounds, including H_2S from the decomposition of cysteine and dimethyl sulfide (DMS), CH_2SH (methyl mercaptan), and $(C_3H_7)_2S$ (propyl sulfide) from the transformation of methionine. Terrestrial emissions come mostly from aquatic ecosystems, river and lake muds, and hot springs. Biogenic sulfur gases include H_2S (the dominant product from wetlands, lakes, and

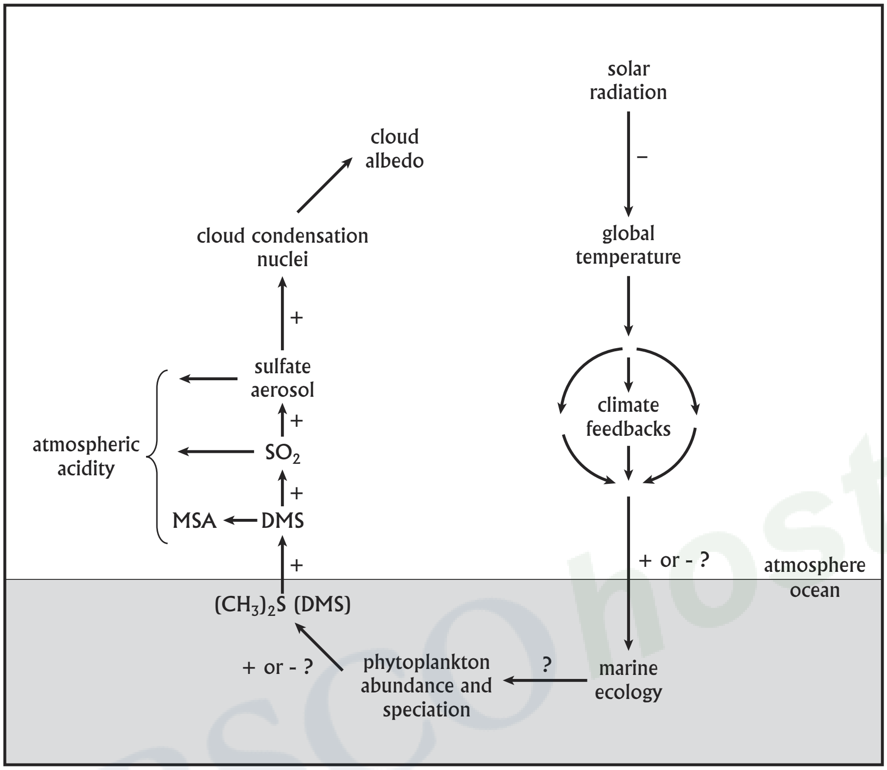


5.13 Two species of dinoflagellates, an armored cell of *Prorocentrum micans* and an unarmored *Gymnodinium mikimoti*. Both images courtesy of E.G. Vrieling and J. Zagers, Rijksuniversiteit Groningen.

anoxic soils), DMS (CH_3SCH_3), methyl mercaptan, and propyl sulfide. Terrestrial emissions peak during summer and are generally most intensive in the tropics; their total flux, about 14 Mt S per year, is small compared to the biogenic sulfur flux from the ocean.

H_2S was once assumed also to be the most important biogenic gas released from the ocean to the atmosphere, but we now know that DMS makes up at least four-fifths, if not nine-tenths, of that flux. The gas comes, via dimethylsulfonium propionate, from the decomposition of methionine in marine plants. Prymnesiophytes (brown algae) and coccolithophorids and dinoflagellates (fig. 5.13) are especially prolific producers. Global DMS flux is now estimated between 16–22 Mt S/year, with summer peaks produced in oceans at latitudes 50–65 °S and 50–75 °N (Bates et al. 1992). Products of its oxidation are either methanesulfonic acid (CH_3SO_3H, MSA) or SO_2 which is fairly rapidly oxidized to sulfate. As the MSA is not produced in any other way, its presence is an unambiguous indicator of biogenic sulfur emissions.

A possible feedback loop was postulated between DMS generation and received solar radiation (Lovelock et al. 1972; Charlson et al. 1987): more DMS would produce more condensation nuclei thus increasing cloud albedo,



5.14 The mechanism proposed by Charlson et al. (1987) to explain the effect of DMS emissions on climate contains several uncertain links. Based on Watson and Liss (1998). *Note:* MSA = methanesulfonic acid

and the reduced radiation would lower planktonic photosynthesis, generating fewer condensation nuclei and letting in more insolation (fig. 5.14). This postulate of a homeostatic control of the Earth's climate by the biosphere was used for some time as an argument for the existence of Lovelock's planetary superorganism, a self-regulating Gaia (see chapter 9), but the magnitude, and indeed the very direction, of the feedback remains questionable (Watson and Liss 1998). In any case, the DMS hypothesis stimulated a great deal of research into interactions between ocean biota and the atmosphere.

In contrast to those produced by the carbon and nitrogen cycles, sulfur compounds have no long-lasting presence in the atmosphere. Primordial SO_2 and H_2S degassed into the Archean atmosphere were rapidly oxidized and deposited on continents and oceans. Sulfates became a permanent ingredient of ocean water, from which they were gradually incorporated into sediments or bacterially reduced to metal sulfides. Once the atmosphere became sufficiently O_2-rich, all reduced gaseous sulfur compounds were rapidly oxidized to sulfates. The residence time of SO_2 in humid air may be just a few minutes, and the global mean is only about a day; H_2S does not stay much longer, and marine DMS remains aloft up to three days, but commonly it takes less than 10 hours before it reacts with OH radical.

Consequently, the global burden of these gases, and of sulfates generated by their oxidation, staying in the lowermost troposphere usually no longer than three to four days, is low, only about 5–6 Mt S. This is five orders of magnitude less than the atmospheric CO_2 and nine orders of magnitude behind nitrogen's huge atmospheric stores. Carbonyl sulfide (COS), produced directly by sulfur-reducing bacteria, by photochemical reactions with dissolved organic matter in the ocean, by biomass burning, and by atmospheric oxidation of carbon disulfide (CS_2), has the highest background levels. At around 500 ppt, they are an order of magnitude above the levels of either H_2S or SO_2, but the atmospheric throughput of these two gases, as well as that of DMS, is much higher.

Short residence times limit long-distance atmospheric transport to a few hundred kilometers for SO_2 and H_2S, and between 1,000 and 2,000 km for sulfates: as a result, atmospheric sulfur does not have a true global cycle as does atmospheric carbon. Most of it (about 80%) is removed by wet deposition; the remainder is dry-deposited, and SO_2 is absorbed directly by soils and plants. Preindustrial rates of atmospheric deposition added to more than a few kilograms of sulfur per hectare of terrestrial ecosystems. Since 1850 human actions have also made a significant difference in the global sulfur cycle, with anthropogenic emissions coming largely from the combustion of fossil fuels and the smelting of color metals. I will examine these anthropogenic interferences in some detail in the book's last chapter.

Cycles of Mineral Elements

The grand and ponderous sedimentary-tectonic cycle begins with weathering of the Earth's surfaces, a mixture of physical and chemical processes that is also strongly influenced by vegetation. Physical changes in these surfaces are due largely to frost action (differential expansion of mineral grains by freezing and thawing of water in tiny rock crevices), pressure, thermal stresses, and crystal growth. Chemical reactions, involving dissolution, hydrolysis, carbonation, and oxidation and promoted by higher temperatures and water, break rocks down to soluble ions and insoluble residues. Silicate weathering releases dissolved silica (SiO_2), Ca^{2+}, Na^+, K^+, and Mg^+, dissolution of carbonates yields Ca^{2+} and bicarbonate (HCO_3^-) ions, and sulfide weathering produces H_2SO_4, which causes additional silicate weathering. Plants speed up weathering both by the mechanical action of penetrating roots and by introducing respired CO_2 into soils.

On the average, weathering strips less than 0.1 mm from the Earth's crust every year, with extremes ranging from just 1 μm in lowlands to nearly 10 mm in parts of the Himalayas (Selby 1985). Weathered material is removed by water, ice, and wind erosion. Rivers carry the bulk of the mass, in ionic solutions and as suspended matter, and their transport capacities are governed primarily by water flow, gradient, and sediment load itself. Most of the eroded material is temporarily deposited in river valleys and lowlands, and the sediment reaching the ocean, estimated at 9–10 Gt per year during the preagricultural era, is perhaps only a tenth of all annually eroded material. Human activities have markedly increased the rate of soil erosion, above all through deforestation and careless crop cultivation, but in many regions the construction of dams during the twentieth century actually reduced the transport of sediments to the ocean (Hay 1998).

Holeman's (1968) subsequently much cited estimate put sediment transport in the world's rivers at 18.3 Gt per year, and the latest detailed account by Milliman and Syvitski (1992) is little changed at 20 Gt per year. Glacial transport is difficult to estimate, but it may be as low as 1–2 Gt per year, and highly variable wind erosion carries away most likely between 0.5 and 1.0 Gt per year. The total (natural and anthropogenic) annual rate of denudation may be thus on the order of 25 Gt, implying the removal of about 0.17 kg of weathered material per square meter of the Earth's surface. If this eroded material had a composition corresponding to the average makeup of the crust, it would contain about 7 Gt Si, 1.25 Gt Fe, 900 Mt Ca, and 20 Mt P.

An annual sedimentation rate of 25 Gt would denude the continents to the sea level in less than 15 Ma, but tectonic forces keep rejuvenating the Earth's surfaces. Marine sediments can reenter the biosphere in a number of ways. They can reemerge, either still unconsolidated or after they have undergone dehydration, lithification, and metamorphosis, after a simple coastline regression or because of a tectonic uplift during a new mountain-building period. Or they can be carried by a subducting oceanic plate deeper into the mantle, where they are reconstituted into new igneous rocks creating a young spreading ocean ridge or vigorous magmatic hot spots. The transit between a subducting trench and a spreading ridge can take just 10^7 years, and a typical supercontinental cycle takes on the order of 10^8 years (for more on the process, see chapter 4).

Among the scores of mineral elements whose cycling we observe on the civilizational time scale merely as an oceanward flux of eroded sediments, four stand out: phosphorus, because of its fundamental role in metabolism and because of its frequently limiting role in plant growth; calcium and silicon, because of their relatively large uptakes by biota; and iron, because of its controlling effect on marine productivity.

Phosphorus

Phosphorus is rare in the biosphere: in mass terms it does not rank among the first ten elements either on land or in water. Although it is, besides nitrogen and potassium, one of the three macronutrients needed by all plants for vigorous growth, it is entirely absent in cellulose, lignin, and proteins. Phosphorus averages a mere 0.025% in the above-ground forest phytomass, and the biosphere's entire above-ground phytomass stores no more than 500 Mt P. But neither proteins nor carbohydrate polymers can be made without phosphorus. Phosphodiester bonds link mononucleotide units forming long chains of DNA and RNA, synthesis of all complex molecules of life is powered by energy released by the phosphate bond reversibly moving between ADP and ATP, and no life would be possible without at least one atom of phosphorus per molecule of adenosine (Deevey 1970).

The element is relatively abundant in vertebrate bodies, because bones and teeth are composite materials comprised mostly of the phosphorus-rich ceramic constituent: hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, containing 18.5% P and making up almost 60% of bone and 70% of teeth (Marieb 1998). The global anthropomass contains approximately 2.5 Mt P, the reservoir less than half as massive as that of the anthropomass nitrogen (Smil 1999b). Unlike other micronutrients (Ca, Fe, I, Mg, Zn), P is almost never in short dietary supply, with dairy foods, meat, and cereals being its main sources. Crustal apatites—$Ca_{10}(PO_4)_6X_2$, with X being F in fluorapatite, OH in hydroxyapatite, or Cl in chlorapatite—store most of the element. Soluble phosphates are released by the weathering of these apatites: with an average lithosperic content of 0.1% P and a mean global denudation rate of around 750 kg/ha (Froehlich et al. 1982), about 10 Mt P are released annually. Soils store about 40 Gt P, with no more than 15% of this total bound in organic matter.

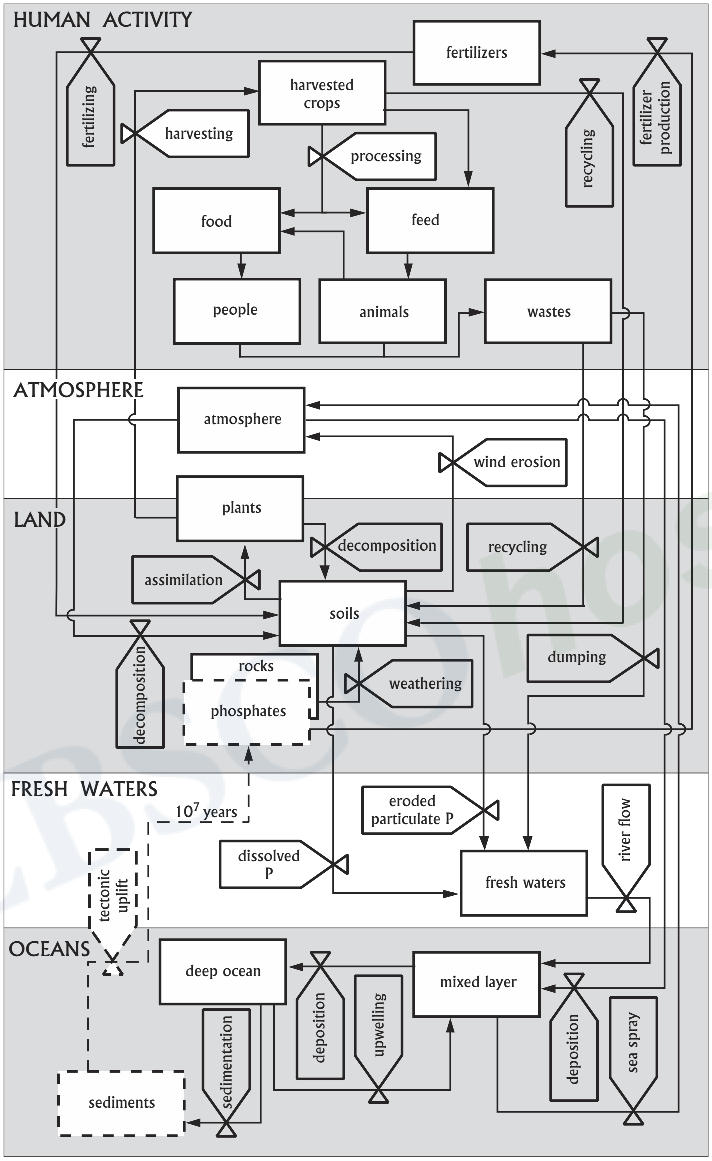
Unfortunately, these phosphates are usually rapidly immobilized by reactions with aluminum and calcium into insoluble forms (Khasawneh et al. 1980). As a result, only a tiny fraction of phosphorus present in soils is available to plants as a dissolved oxy-anion (PO_3^{-4}), and the element is commonly the growth-limiting nutrient in terrestrial ecosystems in general and in tropical soils in particular. This forces plants to absorb the element from very dilute solutions and concentrate it up to 1,000-fold. The average land phytomass carbon-to-phosphorus mass ratio of around 700 to 1 implies annual assimilation of close to 100 Mt P. The marine phytomass stores only some 75 Mt P, but because of its rapid turnover, it absorbs about 1 Gt P annually from surface water, a flux an order of magnitude higher than in terrestrial photosynthesis.

Rapid recycling of the element released by the decomposition of biomass is essential in both terrestrial and aquatic ecosystems, with turnover times of just 10^{-2} to 10^{0} years in either case. As with carbon, nitrogen, and sulfur, biota are essential in this process. Decomposition of dead biomass, solubilization of otherwise unavailable soil phosphates by several species of bacteria, and enhancement of the release of phosphorus from soil apatites by oxalic acid produced by mycorrhizal fungi are especially critical during later stages of soil development, when primary minerals have weathered away (Smil 2000c). This cycling must be highly efficient. As there is neither any biotic mobilization of the element (akin to nitrogen fixation) nor any substantial input from atmospheric deposition, the nutrient inevitably lost from the rapid soil-plant cycling can be naturally replaced only by slow weathering of phosphorus-bearing rocks (fig. 5.15). Shortages of phosphorus in terrestrial ecosystems are thus common.

The nutrient's scarcity is usually even greater in aquatic ecosystems. Only in shallow waters can phosphates circulate easily between sediments and aquatic biota; in deep oceans phosphorus is relatively abundant only in regions of vigorous upwelling, and dissolved phosphorus is often nearly undetectable in surface waters of the open ocean (Jahnke 1992). Scarcity of the nutrient is a key factor limiting photosynthesis in many freshwater bodies, and external phosphorus inputs control longer-term primary production in the global ocean (Tyrrell 1999). But as with all mineral cycles, the long-term phosphorus cycle is not dominated by biota; moreover, the element's transfers within the biosphere are greatly limited, because it does not form any long-lived gaseous compounds. As a result, its atmospheric reservoir is negligible, its flows have no airborne link from ocean to land, and particulate phosphorus that sinks into marine sediments—the rate of phosphorus burial in ocean sediments may have recently added over 30 Mt P/year (Smil 2000c)—becomes available to terrestrial biota only after the tectonic cycle introduces new crystalline rock into the biosphere (Guidry et al. 2000). As with the three doubly mobile cycles, there has been considerable human interference in biospheric phosphorus flows (see chapter 9).

Calcium

Calcium has both structural and dynamic roles in biota. As noted in the previous section, hydroxyapatite is the dominant constituent of bones and teeth, and myriads of aquatic invertebrates, protists, and autotrophs build their support structures from bioprecipitated $CaCO_3$, the compound also used by reptiles and birds to build



5.15 Principal reservoirs and flows of the biospheric phosphorus cycle (Smil 2000c).

their eggs. Calcium's most important functional involvements are in excitation-contraction coupling in skeletal and heart muscles, in neurotransmission at synapses, in intracellular signaling, and in mitotic cell division. In plants the element is in salts of pectic acid, which make up most of the central lamella that binds adjacent cells. Its adequate supply boosts the availability of phosphorus and micronutrients and helps increase the rate of biofixation; most of the element taken up by perennials is recycled in leaf fall.

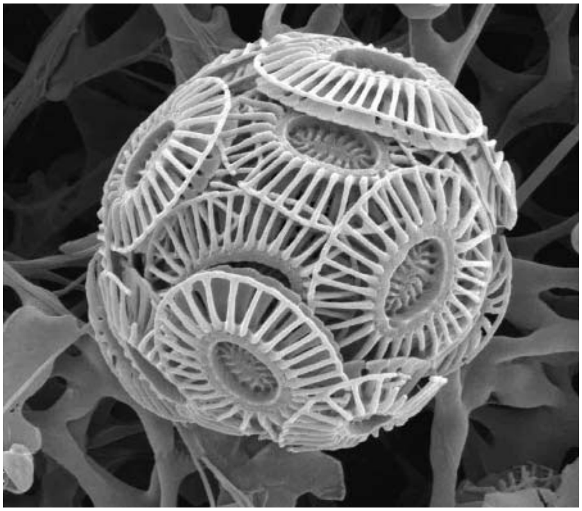
Long-term cycling of calcium is to a high degree coincidental with the slow carbon cycle, and it also entails the hydrothermal exchange in the oceanic crust. Although there are substantial amounts of calcium locked in apatites (see the preceding section) and in gypsum ($CaSO_4$, produced by evaporation in shallow waters in arid climates), the element's largest sedimentary repository is $CaCO_3$ forming limestones, followed by another carbonate, dolomite ($CaMg(CO_3)_2$), which makes up the bulk of dolostones. Garrels and Mackenzie (1971) estimated the total mass of limestones at 350 Pt, with about a quarter of this huge mass deposited during the Precambrian era. The ready solubility of carbonates in slightly acidic precipitation makes Ca^{2+} one of the most abundant cations in river water: about two-thirds of it originates in carbonate weathering, roughly a fifth comes from silicates, and the rest from gypsum.

Deposition of carbonates can take place only in continental shelves and in the shallower parts of the deep ocean containing warmer water. In the colder waters of the deeper layers—below the carbonate compensation depth (CCD), which is about 5000 m at the equator, close to 3000 m in high latitudes—dissolution is greater than precipitation, and no carbonates can accumulate at the ocean's bottom. Most inorganically precipitated carbonates have thus been laid down in shallow waters, as must have been the case with biomineralized calcium, whose producers either are photosynthesizers or feed on these autotrophs. In the early lifeless ocean or in waters containing just prokaryotic organisms, formation of carbonates could proceed only after the two constituent ions reached critical concentrations in the seawater.

Only the emergence of marine biomineralizers using dissolved $CaCO_3$ to make calcite or aragonite shells (differing only in crystal structure) greatly accelerated the rate of calcium sedimentation in the ocean. Reef-building corals are certainly the most spectacular communal biomineralizers, but coccolithophorids, golden motile algae which surround themselves with intricate disclike calcitic microstructures, and foraminiferal tests (pore-studded microshells of protists) are the main contributors to the rain of dead $CaCO_3$ shells on the sea floor (fig. 5.16). Mollusks, often intricately shaped and patterned, are only minor contributors. Where the detritus rain is heavy, the remains of organisms can be buried quickly to form calcium deposits below the CCD. The eventual return of calcium to subaerial weathering through tectonic uplift is abundantly demonstrated by the extensive (and often very thick) layers of limestone and dolomite encountered in all of the world's major mountain ranges.

Silicon

Silicon is best known today as a semiconductor, but to produce it in the purest elemental crystalline form required for microchips takes a great deal of ingenuity and energy. In contrast, in its various oxidized forms—mostly as silica (SiO_2, pure sand) and various silicate minerals—the element is, with 27% of the total, the second most abundant presence (after oxygen) in the Earth's crust. As it is the second element in the carbon group, with four valences forming a variety of polymers—silicates, whose



5.16 The coccolithophore *Emiliania huxleyi,* a unicellular planktonic protist containing chloroplasts and covered by coccoliths formed inside the cell and extruded to form a protective armor. Cretaceous and Tertiary chalks are composed almost exclusively of the remnants of these tiny (diameter less than 0.01 mm) organisms. This and other excellent images of coccolithopores are available at <http://www.soc.soton.ac.uk/SOES/STAFF/tt/eh/pics/>

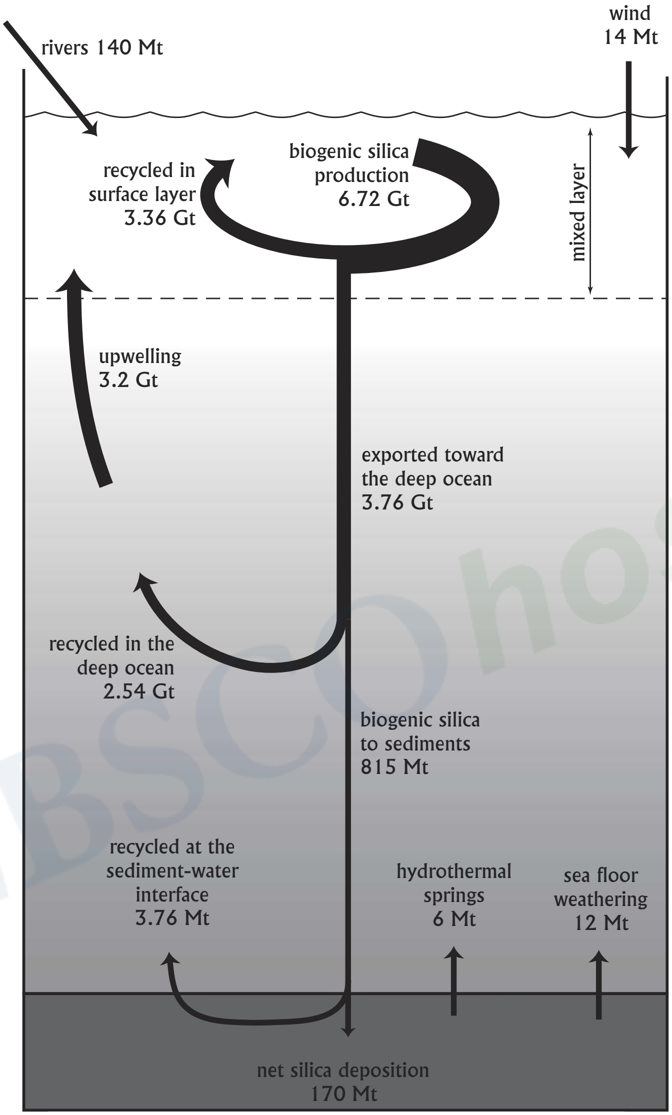
common property is Si atoms at the center of tetrahedrons with O at the corners—it has been suggested that silicon might be the base of noncarbon life, possibly extant deep in the crust (Gold 1999). Although plant physiologists do not class the element as an essential micronutrient, it is absorbed from soil, as H_4SiO_4 (silicic acid), in quantities surpassing several fold those of other minerals, and in some instances even rivaling the uptakes of macronutrients. For example, rice (*Oryza*) takes up about as much silicon as nitrogen in order to stiffen its stems and leaves, which contain as much as 5% silicon (Ponnamperuma 1984). The aggregate annual uptake of the element by the terrestrial phytomass is nearly 500 Mt Si.

Silicon is carried to the ocean mostly in suspended sediments, with dissolved silicic acids amounting to only about 5% of the net flux transported by rivers (fig. 5.17). Silicon is dissolved in the ocean largely as undissociated monomeric silicic acid, with concentrations being very low in surface waters of central ocean gyres and high in the Antarctic ocean as well as in bottom layers almost everywhere. Silicon is assimilated vigorously by a variety of marine organisms, including diatoms, silicoflagellates, and radiolarians, which take up silicic acid from seawater to build their intricate opal (hydrated, amorphous biogenic silica, $SiO_2 \cdot 0.4H_2O$) structures (fig. 5.18). Tréguer et al. (1995) estimated that these organisms' annual silicon uptake amounts to about 7 Gt Si; this silicon dissolves after these organisms die, and about half of it is promptly recycled within the mixed layer. The remainder settles into the deeper ocean, but all but a small share of it is returned to the mixed layer by upwelling, with net coastal and abyssal sediments of biogenic silicon accounting for less than 3% of the annual uptake by biota.

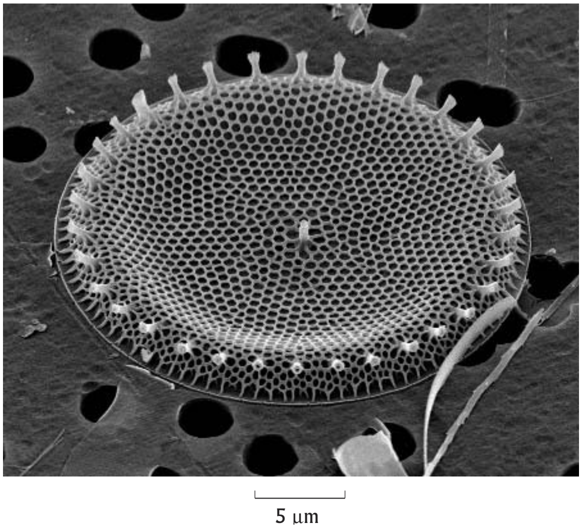
After burial, these deposits are rapidly recrystallized, primarily as chert. Schieber et al. (2000) suggest that quartz silt in mudrocks comes from the siliceous skeletons of marine plankton rather than, as previously believed, from eroded continental sediments.

Iron

Iron's biospheric importance is due to its common presence in the metalloproteins that activate or catalyze just about every essential life process (Butler 1998). Iron is the essential metal in chlorophyll, and it is present both in the cofactor and phosphorus-cluster of nitrogenase. The



5.17 Silicon cycle in the ocean. Based on Tréguer et al. 1995.



5.18 *Thalassiosira aestivalis* is an excellent example of a centric diatom with a near-perfect radial symmetry. Electron microscope image of its SiO_2-impregnated test courtesy of James M. Ehrman, Digital Microscopy Facility, Mount Allison University, Sackville, New Brunswick.

element's importance is magnified because of its insolubility under the neutral pH that prevails in living organisms. Iron's special place in oceanic photosynthesis was pointed out for the first time by Martin and Fitzwater (1988), who demonstrated that, in spite of a relative abundance of macronutrients, phytoplankton growth in the subarctic Pacific is not more vigorous largely because of the scarcity of iron. The element's poor supply also limits phytoplankton productivity in the equatorial Pacific and in the Southern Ocean. Most of the element assimilated by phytoplankton comes from aeolian deposition of poorly soluble dust iron (Fung et al. 2000).

Consequently, it has been suggested that iron enrichment could explain why atmospheric CO_2 levels during the last glacial maximum were 40% lower than today. According to this explanation, additional iron transported to the ocean in dusts blown by stronger winds across drier lands stimulated ocean photosynthesis and hence removed more carbon from the atmosphere in sedimented organic matter. Transfers of iron in surface ocean waters have been assumed to move in tandem with nitrogen flows, and grazing of heterotorphic bacteria and phytoplankton is assumed to balance iron uptake rates (Tortell et al. 1996). In any case, phytoplankton in shallow coastal waters depends primarily on iron in continental-shelf sediments (Johnson et al. 1999), and in deeper waters it is entirely dependent on aeolian deposition.

Iron's controlling role in phytoplankton production was experimentally confirmed during the IronEx II test in 1995, when nearly half a ton of iron was added to 72 km^2 of the ocean west of the Galapagos Islands and its effects were tracked for 18 days (Coale et al. 1996). In a matter of days, the specific growth rate of phytoplankton doubled and its abundance increased more than twenty times, with larger sizes (mostly diatoms) dominant, changes clearly supporting the conclusion about iron's growth-limiting role. In addition, atmospheric levels of DMS increased 3.5-fold during the experiment. Similar results were obtained during a mesoscale iron fertilization experiment in the polar Southern Ocean (61° S), when phytoplankton bloom (mostly due to diatoms) stimulated by iron caused a large drawdown of CO_2 and macronutrients and elevated DMS levels after 13 days (Boyd et al. 2000).

As the IronEx experiment was conducted in waters that are representative of roughly one-fifth of the ocean's surface, where nitrate levels are high but chlorophyll levels, and hence photosynthetic rates, are low, the experiment also led to some unjustified expectations that iron fertilization of seas could significantly counteract a future rise