CHAPTER 3

How the Cycles Work

A nitrogen atom in a large beech tree may persist for centuries in following the same circumscribed wanderings, making a spring journey from the trunk to a new leaf and a late summer trip from a senescing leaf back to the trunk. Or, if it escapes from a decaying leaf and makes its way into the ocean's surface waters, it may be caught up in a more frantic circuit of production, consumption, and decay that prevents its irretrievable sinking into the abyss—absorbed into a short-lived phytoplanktonic cell, then perhaps digested by an avidly feeding zooplankton, and finally released by rapid decomposer assaults, only to be absorbed again by phytoplankton.

In contrast, a carbon atom in a bog-dwelling plant may disappear into newly forming peat and not reenter the biosphere for millennia. Or, if it escapes that fate through being eaten by a deer and one day, long after the deer's death, ends up washed into the ocean, it may become trapped in a shell, sink to the ocean floor, and be buried for tens of millions of years before tectonic uplift reexposes it to erosion. Much like the dolls within dolls in the Russian *matrioshka* doll, every cycle hides nested subcycles, and, depending on the subcycle in which an individual atom lands, its fate can range from frantic recirculation to protracted isolation.

Our understanding of this immense complexity is uneven at best. We know to within one part per billion, or even one part per trillion, the quantities of several atmospheric trace gases containing one of the doubly mobile elements, most notably those of methane, carbon monoxide, nitrous oxide, and carbonyl sulfide. But the numbers we put to, say, the amount of lignin annually decomposed in the litter of boreal forests or the volume of sulfur compounds emitted from tropical swamps could be off by up to an order of magnitude.

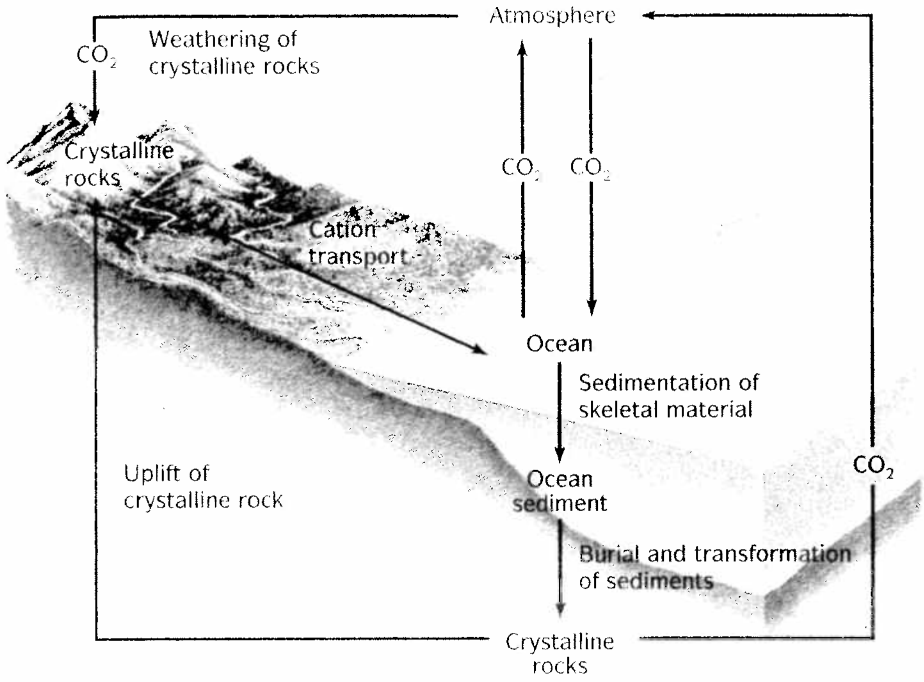
Any realistic discussion of biospheric cycles will be plagued by this often exasperating mixture of confident understanding and persistent uncertainty. Nevertheless, our overall grasp of biospheric cycles is good enough for us to appreciate their linked complexities and be concerned about the long-term consequences of our interventions in their flows and stores. This chapter will focus on what we know about the natural dynamics of the three cycles, detailing their workings in the absence of human interference. While these interventions have not changed the basic dynamics described in these pages, they have affected, often enormously so, the rates of many fluxes and the size of some storages. The three chapters following this one will deal with the rise and consequences of this unprecedented change.

The Geochemical Carbon Cycle

Living organisms take part in two concurrent grand biogeochemical carbon cycles, one a very slow journey into the planet and back, the other an intricate web of relatively rapid exchanges within the biosphere, on the Earth's surface. The first cycle, operating on timescales of tens to hundreds of millions of years, is governed by immense but ponderous geotectonic forces. Although living organisms take part in a few critical links in this cycle, they are not its dominant controllers, and the cycle existed billions of years before any terrestrial plants and animals did. In fact, this first cycle played a critical role in the evolution of life, as a look at our closest planetary neighbors suggests.

The atmospheres of Venus and Mars are, respectively, 96 percent and 95.3 percent CO_2, and they contain only around 3 percent N_2. CO_2 is a strong absorber of longwave radiation, a highly significant property in light of what happens to much of the sunlight reaching the planet. Recall that the Earth absorbs solar energy and reradiates it back toward space as heat. The atmosphere keeps the planet warm by preventing all that heat from escaping into space at once: it acts like the glass of a greenhouse, letting through the light but retaining temporarily part of the heat emanating from the ground. In scientific terms, the atmosphere is highly (though not perfectly) transparent to incoming (shortwave) solar radiation, but it is a strong absorber of certain wavelengths of the outgoing (longwave) infrared spectrum produced by the reradiation of absorbed sunlight.

CO_2 has a broad absorption band between 12.5 and 16.6 micrometers (or millionths of a meter, μm), which coincides with the Earth's peak heat emission. The gas also has several minor absorption bands below 5 μm (the ones around 2.7 and 4.3 μm are relatively more important). Consequently, a Mars-like terrestrial atmosphere would create a very strong greenhouse effect: CO_2 absorbing, and



The geochemical carbon cycle is controlled by slow geomorphic and geotectonic processes, including the burial and transformation of sediments, the eventual uplift of crystalline rocks, and their subsequent weathering.

reradiating, the outgoing heat would push average surface temperatures above 200 °C, too hot for even the most heat-tolerant bacteria.

Some 4 billion years ago, CO_2 concentrations above the primordial ocean-covered Earth were comparable to those on Mars today—three orders of magnitude higher than in the Earth's present-day atmosphere. The enhanced greenhouse effect produced by these high CO_2 levels prevented the Earth from freezing during that time, when the solar luminosity was about 30 percent below what it is now.

As the Sun subsequently grew brighter and its energy output became greater, atmospheric CO_2 levels had to decline by several orders of magnitude in order to keep the Earth's temperature relatively constant, and especially to keep it well below the point at which proteins denature (they begin disintegrating as their temperature rises above 45 °C). The carbon leaving the atmosphere would have had to move into a new reservoir, and that reservoir turned out to be the Earth's crust. This transfer was accomplished by the processes of evaporation and weathering.

A more luminous Sun evaporates more water, and the evaporated water dissolves more CO_2 in the troposphere, a process that results in the formation of carbonic acid (H_2CO_3), the primary chemical agent responsible for the weathering of calcium silicate rocks. As the carbonic acid reacts with the calcium silicate in exposed rock surfaces, two ions are released, the calcium ion (Ca^{2+}) and the bicarbonate (HCO_3^-) ion. Streams transport the ions to the ocean, where they react to produce sediment-forming carbonates, CO_2, and water.

The carbonate sediments are tied to the interlocking system of huge tectonic plates that form the Earth's surface, and whose slow movement shapes the Earth's gross features. When two plates collide head on, one plate dives below the other, taking its burden of carbonate and other sediments far below the surface. There the carbonates react with silica, releasing CO_2 that is returned to the biosphere by degassing along spreading ridges and in volcanic eruptions; the re-created calcium silicate rocks are eventually reexposed to weathering by tectonic uplift. This cycling proceeds at a slow, geotectonic pace measured in no less than tens of millions of years, but the rates at which CO_2 is removed from the air may change rather rapidly. Should the surface temperature drop and the weathering of silicates slow down, the emitted gas would gradually accumulate and lead to subsequent warming.

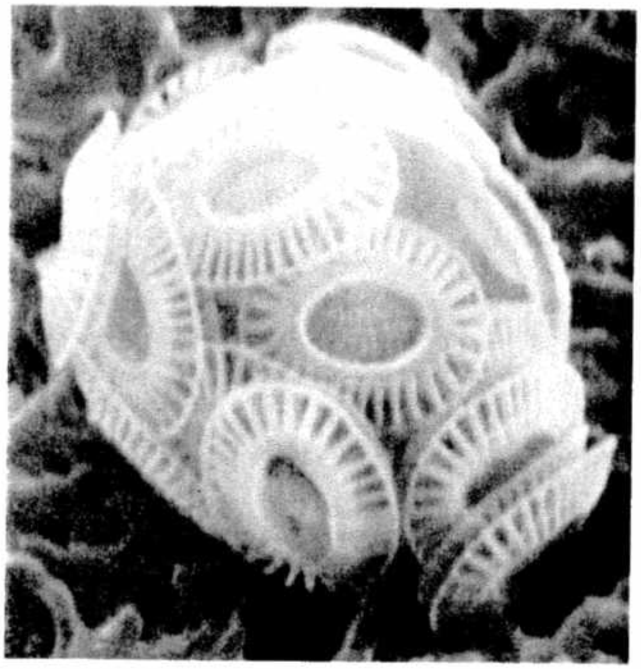
Conversely, should the surface temperature increase, the higher rates of evaporation would lead to accelerated weathering and a faster removal of atmospheric CO_2—but not a faster return of the gas from the geotectonic cycle. With the intensified removal of atmospheric CO_2, more outgoing radiation would escape immediately into space, and the planet would cool slightly. These feedback effects would have compensated for the brightening of the Sun as well as for any extraordinary volcanic activity, precluding any possibility of either runaway greenhouses or runaway icehouses.

During the past 25 years a number of American geochemists and atmospheric chemists—most notably Robert Garrels, Paul Hays, James Kasting, Fred Mackenzie, Manfred Schidlowski, and James Walker—have worked to elaborate the details of these long-term feedbacks to which the planet owes the relative constancy of its climate. This dynamic stability (or homeostasis), achieved through the slow cycling of carbon, clearly predates the emergence of life—but living organisms came to intensify this geochemical cycle in three ways.

Life Arrives

The Earth's oceans first appeared some 4 billion years ago, and the earliest living organisms, bacteria, made their appearance a few hundred million years later. Both in the early lifeless ocean, and in waters containing bacteria as the only form of life, the formation of carbonates could proceed only after the two constituent ions reached critical concentrations in the seawater. Only the emergence of shell-forming organisms, almost 600 million years ago, greatly accelerated the rate of carbonate sedimentation. At their death, these organisms leave behind shells made of calcium carbonate ($CaCO_3$). These shells sink to the bottom and accumulate as the minerals aragonite or calcite, mostly in shallow waters on reefs, banks, and continental shelves, but also in deeper seas.

The remarkably shaped and patterned shells of molluscs are a minor constituent of this sedimentary rain. Its main suppliers are a variety of planktonic



Coccoliths cover the surface of a coccolithophorid, species *Emiliania huxleyi* magnified about 10,000 times. These oval discs are made up of radial arrays of calcite crystals, whose growth is controlled by polysaccharides formed inside the algal cell.

creatures, above all coccolithophorids and foraminiferans. Coccolithophorids begin their life as tiny golden swimming algae, then change into resting forms covered with overlapping disclike microstructures called coccoliths, made of calcite. Foraminiferans grow inside pore-studded shells called tests, made mostly of tightly cemented $CaCO_3$. These organisms have pseudopods that they extend through the test pores and use for both swimming and capturing their prey. The massive, mountain-building remains of foraminiferans date to more than 200 million years ago (Egyptian pyramids are built with limestone replete with foraminiferan shells); the remains of coccoliths date back as far as 100 million years.

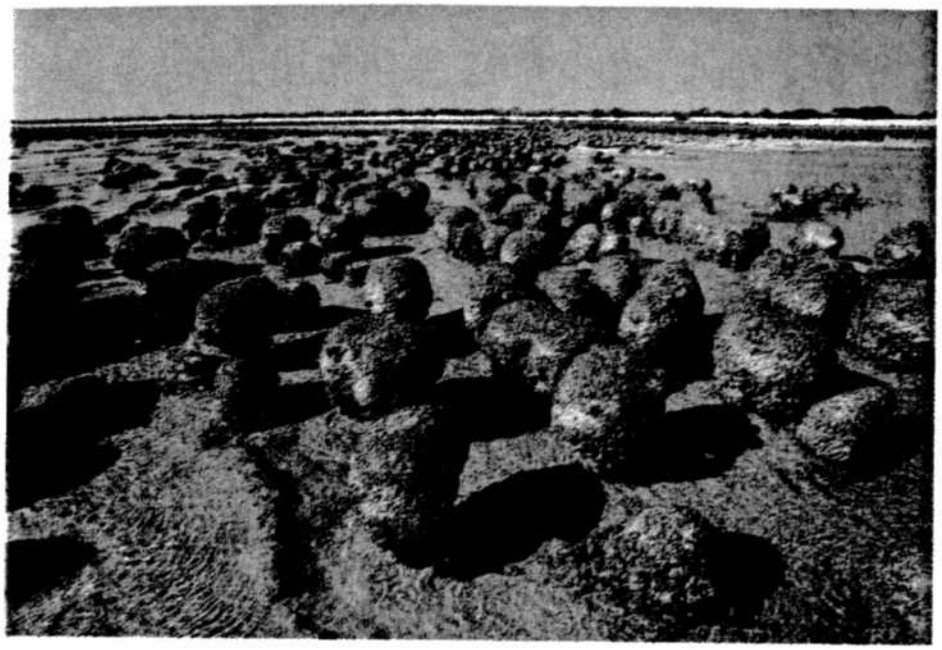
Life had an even more important effect on carbon's oceanic flows, for photosynthesis provided an additional means of sequestering the element in marine sediments. Some small proportion of dead phytomass would join these sediments after sinking to the ocean floor, removing carbon from the biosphere for many millions of years. By far the most persuasive evidence of this impact comes from examining carbon's isotopic record. Carbon has two stable isotopes, the less abundant ^{13}C and the dominant ^{12}C, and variations in the $^{13}C/^{12}C$ ratio tell us something of the origin of the carbon in sediments. These variations are expressed as $\delta^{13}C$, the difference between the ratio of the two stable isotopes in a tested sample and their ratio in a standard carbonate (taken from a mollusc shell in a South Carolina Cretaceous sediment). This difference is given as a deviation from the constant value in ‰ (per thousand) rather than per hundred.

Photosynthesizers—be they ancient bacteria or modern plants—prefer to take up ^{12}C, so the $\delta^{13}C$ value of their tissues is low, typically between -20 and -30. In contrast, the $\delta^{13}C$ value of marine carbonates formed inorganically from reacting calcium and bicarbonate ions is mostly between 0 and $+4$ relative to the dissolved carbonate. These distinct isotope ratios are largely preserved in sediments, so we can trace the origins of ancient photosynthesizers in graphitized organic matter found in some of the world's oldest known rocks, such as the banded iron formations of the Isua suite in southern Greenland. These deposits, laid down almost 4 billion years ago, were created when sediments became trapped within layers of bacterial growth. The oldest distinctly preserved forms of these early photosynthetic bacteria are fossil stromatolites dated to about 3.5 billion years ago.

At roughly that time a quantitative leap took place in photosynthetic CO_2 reduction as some bacteria switched away from oxidizing H_2 or H_2S in order to obtain electrons needed for the process and began splitting water instead. Water splitting requires more energy than the oxidation of H_2 or H_2S, but because the compound is nearly ubiquitous in the biosphere, photosynthesizers that used it could diffuse to many new environments and produce much larger amounts of phytomass.

Ever since that time the relative contribution of organic carbon to near-surface sediments, when measured as a long-term mean, appears to have been remarkably constant. No matter how far back we look, close to one-fifth of the carbon in these sediments has come from organic matter. This fact leaves no doubt that on evolutionary timescales biota have played a far from negligible role in the element's cycling.

The same temperature-driven feedbacks that regulate the silicate-carbonate cycle also affect the rates of photosynthesis and the burial of organic matter. Higher surface temperatures boost rates of photosynthesis, and lower temperatures reduce them. But the relative constancy of the organic carbon share in sediments across a long time span means that these temperature changes had a limited effect on overall phytomass production. This constancy is usually explained by the availability of phosphorus. One atom of phosphorus is needed for every 106 carbon atoms in phytoplanktonic biomass, and the limited supply of the slowly



Stromatolites are fossil colonies of bacterial growth, some older than 3.5 billion years, that have been lithified—that is, compressed and cemented together by mineral compounds. In this image they are exposed by a high tide in Hamlin Pool, western Australia.

cycled element restricts the range of photosynthetic productivity.

There is yet another way in which living organisms intensify carbon's cycling. Ever since vascular plants appeared about 450 million years ago, terrestrial biota have helped to accelerate the weathering of silicate minerals. Roots, through respiration, and litter, through decomposition, release CO_2 into the soils, and plants provide organic matter for the formation of humic acids. Both of these compounds react with silicate minerals and incorporate carbon into HCO_3^-, which may eventually make its way into the ocean. But this carbon flux is relatively minor: current global total of atmospheric CO_2 consumed annually in chemical weathering, estimated from the river flux of bicarbonates, is less than 500 Mt C, only a small fraction of the net photosynthetic uptake.

During the Carboniferous and Permian periods between 350 and 250 million years ago, intensive erosion produced huge deltas and swamps, and the plant matter buried in these swamps became the source of most of the world's coal deposits. There is little doubt that this massive burial of organic matter intensified the decline of atmospheric CO_2. But photosynthesis has not been the key regulator of atmospheric CO_2—a fact that is not surprising since its performance is too often limited by the availability of water and nutrients.

On the other hand, we have no doubt that photosynthesis was overwhelmingly responsible for the oxygen in our atmosphere. More precisely, we owe the creation of an oxygen atmosphere to the imbalance of photosynthetic and decomposition rates caused by the burial of some phytomass beyond the reach of decomposers. The buried biomass could not be reoxidized, and so the O_2 released during its synthesis remained in the atmosphere. The atmosphere's oxygen level began rising rather abruptly about 2.1 billion years ago, but it did not come close to the present concentration of roughly 20 percent until about 500 million years ago.

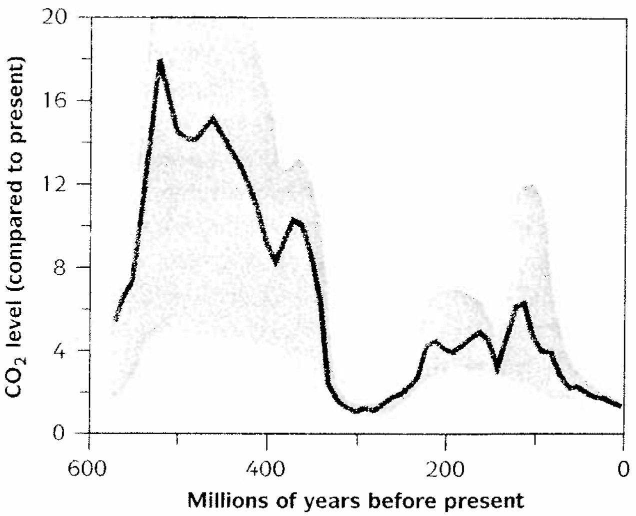
The rising levels of O_2 in the troposphere eventually resulted in the accumulation of ozone (O_3) in the stratosphere. The triatomic molecules of this gas absorb virtually all incoming solar radiation with wavelengths shorter than 295 nanometers (nm), shielding the biosphere from the damaging effects of ultraviolet radiation. The reduction of CO_2 by photosynthesis thus created the protected conditions in which complex forms of life could evolve—and helped to produce a unique atmosphere dominated by a roughly 4:1 mixture of N_2 and O_2.

Atmospheric CO_2 levels have fluctuated throughout the Earth's history. Their course can be reconstructed only with considerable margins of uncertainty, a reality well illustrated by a model built by Robert Berner, an American geochemist. This model calculates CO_2 levels during the past 570 million years and it takes into account both the geochemical feedbacks described earlier in this chapter and the effects of life.

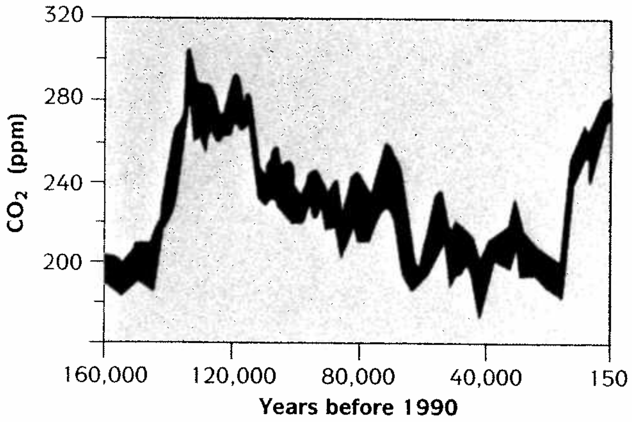
For example, there can be little doubt that the widespread distribution of vascular land plants, dating to some 350 million years ago, accelerated the decline of atmospheric CO_2 through the massive burial of organic matter that created abundant coal deposits. This drastic lowering of the greenhouse effect opened the way for the most extensive and longest glaciation of the last half billion years. Afterward, the atmospheric CO_2 underwent another pronounced rise during the Cretaceous period, mainly because intensified geotectonic activity caused the release of the gas to the atmosphere. This rise was followed by yet another decline, as tectonic activity waned and weathering accelerated, speeding the removal of CO_2.

Our data become accurate only for the past 420,000 years, thanks to the analyses of air bubbles from ice cores retrieved in Antarctica and Greenland. Throughout that period atmospheric CO_2 levels did not fall below 180 ppm, and they never rose above 300 ppm during interglacial periods. And during the time between the rise of the first high civilizations (5000 to 6000 years ago) and the beginning of the fossil fuel era, atmospheric CO_2 levels fluctuated within an even narrower range, never departing from 250 to 290 ppm.

CO_2 is not the only gas absorbing infrared radiation—in fact, it does not even account for most of the biosphere's greenhouse warming. Water vapor is the biosphere's dominant greenhouse gas; it mostly absorbs terrestrial radiation having wavelengths between 2.4 and 3 μm and between 5 and 7 μm. Before industrialization raised CO_2 levels, water vapor's total atmospheric mass was about six times the mass of CO_2. Methane (CH_4) and nitrous oxide (N_2O) are two minor natural contributors. But because both gases are more effective absorbers than CO_2, their relative global warming potential is considerably higher. Over a relatively short period of 20



The most likely value (solid line) and the range of possible extremes of CO_2 concentrations during the past 600 million years.



During the 160,000 years before the year 1850, CO_2 concentrations fluctuated between 180 and 300 ppm. The uneven band marks the extremes recorded by analyzing air bubbles from the Vostok ice core in Antarctica.

years, every CH_4 molecule is about 60 times, and every N_2O molecule about 270 times, more effective as a greenhouse gas than CO_2. Over a period of 100 years the two values change to, respectively, about 20 and 310.

Greenhouse gases reradiate the energy they absorb, also as heat. This thermal energy is the most important source of the heat warming oceans and continents, and the fluctuating concentrations of water vapor are its largest source: even an isolated passing cloud can boost the rate of downward heat radiation momentarily. At its current atmospheric levels, CO_2 contributes less than a quarter of this downward flux of thermal energy. The cycling of heat between the ground and the atmosphere delays the return of infrared radiation to space, and it keeps the Earth's average surface temperature at around 15 °C, about 33 °C warmer than if the absorbed incoming sunlight were reradiated directly into space.

Although water vapor is now responsible for almost two-thirds of the warming generated by greenhouse gases, water could not have maintained the planet's relatively stable temperatures during the billions of years of evolution. Unlike CO_2, water vapor amplifies, rather than counteracts, departures from the average surface temperature: its evaporation declines with cooling and rises with warming. In addition, changes in soil moisture do little to alter rates of chemical weathering, while higher, biota-induced CO_2 levels in soil accelerate the conversion of the crust's silicates into sedimentary carbonates.

By maintaining a relatively invariant climate, long-term carbon cycling provided an inestimable service that made possible the evolution of life—but the much more rapid cycling of CO_2 between the atmosphere and the ocean, and the atmosphere and plants, is a matter of more immediate human interest. Over thousands of years feedback effects may counteract any conceivable increases of atmospheric CO_2, but that is of little comfort to a civilization facing a climatic change whose duration would surpass its life span.

Carbon in the Ocean

The ocean is the biosphere's largest reservoir of carbon. The roughly 37,000 Gt of inorganic carbon dissolved in its vast volume dwarfs the almost exactly 600 Gt C present in the preindustrial atmosphere. But the huge size of this reservoir does not mean that the ocean can simply absorb almost any conceivable amount of additional CO_2 that enters the atmosphere, maintaining a relatively stable climate. CO_2 is being exchanged constantly across the vast interface between the ocean and the atmosphere, but the exchange is conditioned by many factors and it is subject to a major bottleneck.

The flow of CO_2 between the atmosphere and the surface ocean may be greater in one direction or the other, depending on the complex interaction of many variables, including temperatures, pressures, photosynthetic productivity, respiration, and decay rates. The interchange of CO_2 between the air and the ocean eliminates the difference in flow quite rapidly. The pressure of the gas in the lower troposphere and the pressure of the gas in the mixed ocean—the shallow layer agitated by winds—reach equilibrium within just one year. Assuming a near-perfect equilibrium, the preindustrial exchange of CO_2 between the atmosphere and the ocean moved annually about 75 Gt C in each direction.

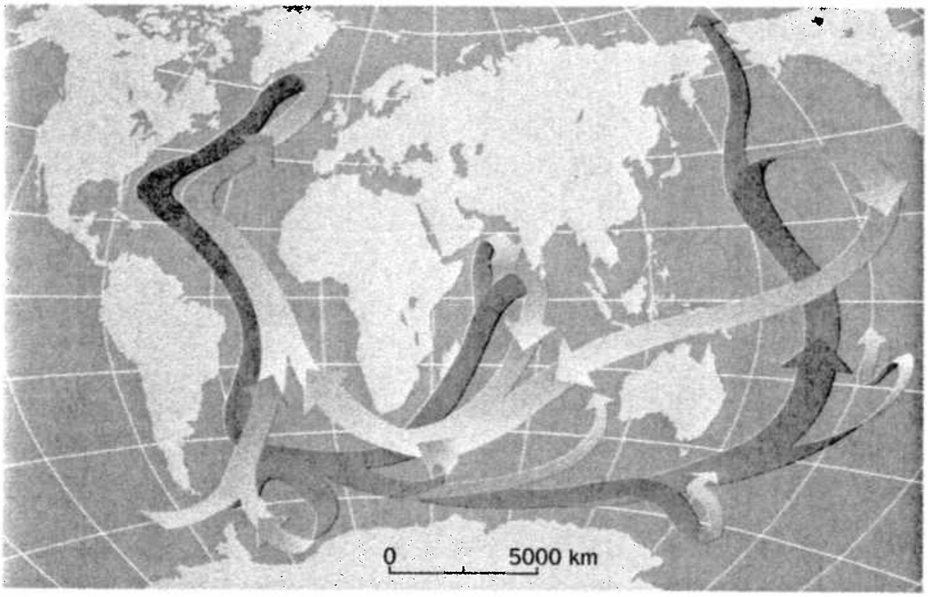
Less than one percent of this mass was, and is, stored in the ocean as gaseous CO_2. As the gas dissolves, it forms aqueous CO_2 and H_2CO_3, which is ionized to H^+ and the bicarbonate ion (HCO_3^-). This latter ion, in turn, gives rise to H^+ and the carbonate ion (CO_3^{2-}). The two ions account, respectively, for about 95 and 3 percent of the ocean's huge inorganic carbon mass. CO_2's reaction with CO_3^{2-} and H_2O, producing HCO_3^-, provides the major sink for atmospheric CO_2—but it also accounts for most of the ocean's surprisingly limited chemical capacity to absorb additional amounts of the gas.

To preserve thermodynamic equilibrium, the ratio of HCO_3^- concentration to CO_3^{2-} and CO_2 concentrations must remain constant. Because the concentration of HCO_3^- is so large, its fractional change in response to higher CO_2 inputs will be quite small, and the rise in CO_2 will have to be compensated by a relatively large decline in CO_3^{2-}. Naturally, the diminishing amount of CO_3^{2-} will limit the reaction that transfers CO_2 to the huge HCO_3^{2-} pool, and the ocean's capacity to absorb additional CO_2 will decrease as the amount of CO_2 entering the seawater increases. Detailed calculations show that the increase in the total dissolved inorganic carbon is only about one-tenth the increase in the partial pressure of CO_2 in surface seawater.

In addition, an important physical obstacle limits the ocean's capacity to absorb speedily large amounts of CO_2. Nearly 98 percent of the ocean is far beyond the reach of solar radiation, and its temperature remains stable, mostly between 2 and 4 °C. These heavy and stable cold waters are capped by the warmer waters of the mixed layer, which extend no more than 50 to 100 m below the surface. While CO_2 exchange between the atmosphere and the mixed layer is relatively speedy, a complete water exchange between the mixed layer and the deep ocean takes at least 500 years, and as many as a thousand. This slow exchange restricts the access of atmospheric CO_2 to the vast pool of water below the mixed layer.

The bulk of the flow between the two layers is driven by the gargantuan, conveyor-like circulation connecting all oceans. Atlantic surface waters, flowing northward from the tropics, cool and sink when they reach sub-Arctic latitudes. After sinking, the waters become part of a huge, deep, southward counterflow reaching all the way to the Antarctic. From there, cold, dense flows of deep waters extend far northward into the Indian and Pacific Oceans, and they are balanced by a shallow return flow forming a long loop extending from the northern Pacific past Hawai'i, through the Indonesian archipelago, and past the east coast of Madagascar. Cold deep water does not form in the northern Pacific where abundant rains make surface waters less salty, and hence less dense and less prone to sinking, than those of the northern Atlantic.

Water rises from the deep ocean relatively rapidly only in areas of vigorous upwelling. This phenomenon is caused by strong winds, prevailing or seasonal, that push away the surface waters, which are replaced by the upwelling of cold deep water, bringing nutrients to the surface, where they support massive phytoplankton blooms. This process is particularly vigorous in the central and eastern equatorial Pacific, where it supports at least one-quarter, and possibly as much as one-half, of all oceanic plankton production. These CO_2-rich



A simplified drawing of the grand oceanic conveyor. The most recent research shows that the warm-water route south of Africa is weak and intermittent, splitting the global circulation into two large-scale cells.

equatorial waters are also the largest oceanic source of the gas.

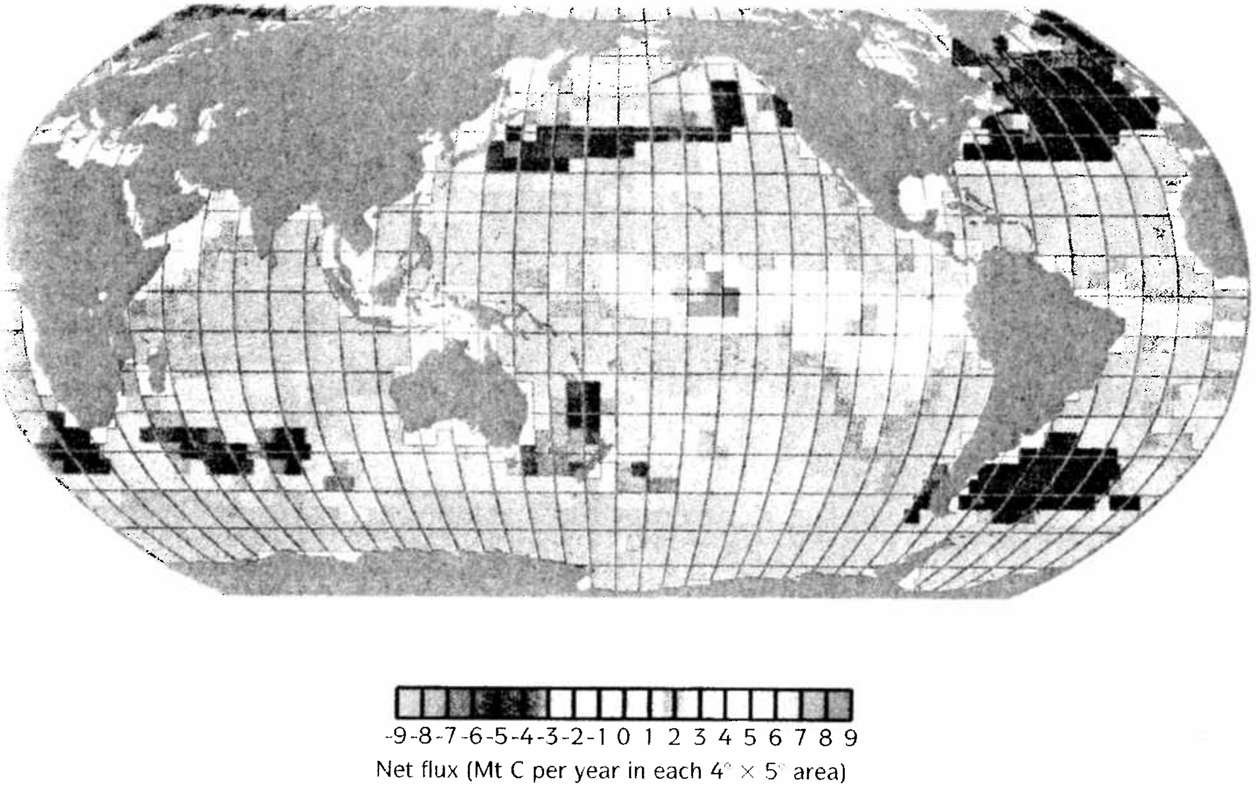
A world with a lifeless ocean would have a much higher atmospheric level of CO_2. As water welled up toward the surface from the deep ocean, it would warm and become supersaturated with CO_2. Unable to retain so much of the gas, the near-surface waters would release CO_2 to the atmosphere. Not all the excess CO_2 in surface waters would be forced into the atmosphere: some would be precipitated in the form of $CaCO_3$, reducing the total dissolved carbon. The ocean would continue releasing CO_2 until the deep-sea pool of carbon had reached equilibrium with the atmospheric reservoir. In that new steady state, achieved after several thousand years, there would be about three times as much CO_2 in the atmosphere as there is now.

Marine life prevents such a huge shift by constantly removing carbon from the near-surface layer. The tiny organisms making up the phytoplankton consume huge quantities of carbon in photosynthesis. Much of this carbon remains in the mixed layer, cycling among the various organisms. Part of it is transferred into deeper waters through carbonate precipitation and detrital sinking.

Due to their short life span (just days to weeks) and quick growth, phytoplankton species can assimilate more carbon than their relatively small standing biomass would lead one to suspect. Although their total biomass is equal to no more than about half a percent of the continental phytomass, these microscopic organisms, capable of doubling their mass in just days, withdraw annually at least half as much carbon from the mixed ocean layer as land plants take up every year from the atmosphere. In general, circumpolar oceans are major CO_2 sinks during the summer months, when photosynthesis continues for more than 18 hours a day. In subtropical latitudes, the relatively feeble photosynthesis makes little difference to the ocean's carbon storage.

Respiration by zooplankton, and by other heterotrophs, returns at least 90 percent of the assimilated carbon to the near-surface waters, from which the gas can either escape to the atmosphere or be reused by phytoplankton. Carbon in the remaining dead biomass settles to the deeper ocean. Dead plankton in this particulate marine snow sink slowly (typically no more than about 100 m a day), while the carcasses of fish, shrimps, and decapods can descend from 50 to 500 m in one hour. As this detrital rain falls through the mesopelagic zone (between 200 and 2000 m), some nine-tenths of it is either eaten by zooplankton and fish or slowly decomposed by bacteria, and its carbon returns to the ocean's deeper waters as HCO_3^- and CO_3^{2-}. In reversing the photosynthetic process, this settling, oxidation, and decay increase the ocean's total carbon.

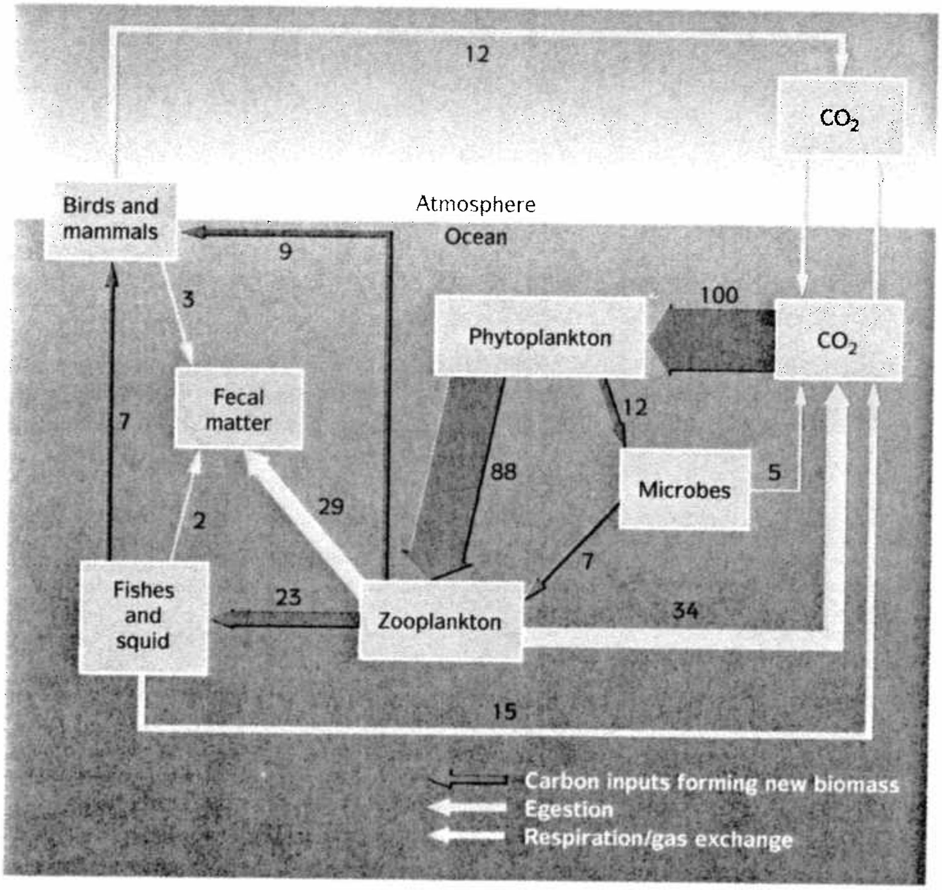
Marine life thus forms a kind of living pump that removes carbon, as well as nutrients, from the



Taro Takahashi and his colleagues at Columbia University constructed this global map of air-sea CO_2 exchange, using 250,000 measurements, gathered over 30 years, of the partial pressure of CO_2 in surface ocean water and in the overlying air. They concluded that in 1990 the global ocean took up between 0.8 and 1.4 Gt C. Thanks to intensive photosynthesis, the higher-latitude waters in both hemispheres are major CO_2 sinks, while upwelling makes the tropical areas the largest CO_2 sources.

mixed layer and transfers the element into deep waters, from which it can return to the atmosphere only after many decades or even centuries. Most likely, between 5 and 10 Gt C sink into the deep ocean annually, but extreme estimates have ranged from as low as 4 Gt C to as much as 20 Gt C. Were this continuous biotic transfer to cease, atmospheric CO_2 concentrations would rise, eventually surpassing 400 ppm, 40 to 50 percent higher than the preindustrial mean of 280 ppm.

But this great phytoplanktonic pump has a major leak. In summer the highly productive circumpolar oceans, above all in Antarctic waters, teem with birds and mammals feeding on fish, squid, and the larger zooplankton, especially krill and copepods. Through respiration, these top predators may return to the atmosphere as much as one-quarter of all carbon assimilated through photosynthesis, reducing the amount available for sedimentation. In global terms, only about one percent of the carbon assimilated by phytoplankton makes it through the mesopelagic zone into the deep sea, and less than half this relatively tiny organic input, merely some 200 Mt C a year, is sequestered in sediments.



The respiration of birds and mammals is responsible for a substantial carbon "leak" in a great phytoplanktonic pump operating in Antarctic waters. In the depicted case, about one-eighth of all assimilated carbon is respired by these top predators. All values are shown as shares of the total carbon assimilated by phytoplankton.

The remains of marine organisms form mineral deposits on the sea floor only in relatively shallow waters, for the debris sinking in the open ocean will not make it beyond intermediate depths. The higher pressure and lower temperatures of deep waters increase the solubility of $CaCO_3$, and the compound dissolves into Ca^{2+} and HCO_3^- ions that remain in solution, from which they can be eventually taken up again by shellmakers. The compound can accumulate only at depths at which the supply rate surpasses the dissolution rate.

Dissolution in the deep sea destroys more than four-fifths of all precipitated $CaCO_3$, leaving large areas of the deepest ocean, mostly in the Pacific, without any $CaCO_3$ deposits. Without this dissolution the continuing sedimentation would soon create huge carbon deficits in the ocean, and, because of the constant exchange of gas between the air and ocean, it would lead inevitably to much lower atmospheric CO_2 levels.

Oceans can eventually absorb any plausible natural additions of CO_2, but, everything else being equal, the bottleneck created by the slow exchange of surface and deep waters inevitably leads to a temporary rise in atmospheric concentrations. Consequently, those basically stationary CO_2 levels of the preindustrial atmosphere—which varied less than 20 ppm around the 280 ppm mean during the eight centuries preceding the year 1800—tell us that no major natural event disturbed CO_2 cycling during the past millennium.

The Cycling of Continental Carbon

The exchange of carbon between the atmosphere and continents was overwhelmingly dependent on photosynthesis in preagricultural times, and remains so today. (The carbon consumed in weathering, for example, is less than 1/200 of the photosynthetic uptake on land.) Although the total mass of carbon in marine sediments is about 50 percent larger than the mass of the element in terrestrial plants and soils, the bulk of the marine carbon is effectively isolated from the biosphere. In contrast, plants, as well as most of the soil carbon, participate in constant exchanges with the atmosphere. Consequently, changes in the extent and type of vegetation cover have significant, and long-lasting, effects on the levels of atmospheric CO_2.

On land the reduction of CO_2 is carried on by unknown numbers of bacterial genera, and by no less than 300,000 species of plants. In preagricultural times, all of these photosynthesizers took up annually almost four times as much carbon per square meter as ocean organisms. Although plants and bacteria produced annually only about twice as much new biomass per year as did phytoplankton, land ecosystems stored nearly 200 times as much phytomass. The large and diverse repository of organic compounds in this phytomass has provided nutrition for heterotrophs, as well countless niches for the evolution of an unknown number of these species (at least millions, but possibly tens of millions), including our own.

Yet as a means of converting one form of energy (electromagnetic radiation) to another (chemical bonds), photosynthesis is rather inefficient. Over the course of a year less than half a percent of the incoming solar radiation is transformed into new living tissue. Of course, much of this radiation is at wavelengths that photosynthetic pigments do not respond to. These pigments are excited only by energy carried by wavelengths between 400 and 700 nm. This photosynthetically active radiation (PAR) amounts to half the total solar flux. Still, even when we consider only these usable wavelengths, we find that terrestrial photosynthesis converts a bit less than 2 percent of the PAR.

The biosphere's most important reduction process is also a very inefficient user of water. C_4 species lose at least 450 to 600 molecules of H_2O for every molecule of CO_2 that they absorb, and the ratio is commonly two, and even three, times higher for C_3 plants. Consequently, water, rather than light, is the most common limiting factor in the conversion. Shortages of macronutrients, especially of nitrogen and phosphorus, are also common. The combination of these natural factors puts a clear limit on the rate at which the terrestrial biosphere can take up atmospheric carbon.

Plants spend their days in photosynthesis and undo a part of that work at night when they respire, as they must to grow new tissues and maintain old ones. The situation is actually worse for C_3 plants, the vast majority of photosynthesizing species, since they carry on the process of respiration in daylight as well. This largely wasteful photorespiration is virtually absent in C_4 plants. Respiration returns to the atmosphere about half the more than 100 Gt of carbon assimilated yearly by terrestrial plants and bacteria, leaving behind at least 50 to 60 Gt of carbon in new phytomass.

With over 1000 Gt C stored in plants, phytomass carbon in preagricultural tissues must have had an average lifetime of about 20 years. Its storage in the plant came to an end when some herbivore, whether a small ant or a huge elephant, ingested the nutritious phytomass and oxidized it to gain energy for its growth, or when the plant died and its tissues were decomposed by bacteria, fungi, and soil invertebrates. In either case, heterotrophic respiration eventually returned the remainder of the fixed carbon to the atmosphere. Only a tiny fraction of new phytomass was not eventually recycled, and this was the fraction that entered terrestrial or marine sediments.

Residence times of carbon in phytomass vary widely. A carbon atom trapped in lignin in the trunk of a long-lived tree may take hundreds or even thousands of years to complete a single cycle, while the carbon of a leaf decaying rapidly in a warm and humid rain forest may complete a cycle within a few weeks or months.

The relatively constant levels of preindustrial atmospheric CO_2 might suggest that a near equilibrium existed between photosynthetic uptake of carbon on the one hand and its release in respiration on the other hand—but this was true only as a long-term average on a global scale. Few ecosystems are in such balance over the short term. When grasslands are rapidly shooting up after the onset of seasonal rains, they will be major net importers of carbon; their low respiration losses (below 20 percent) will translate into high net productivities. When the same communities burst into flames after prolonged drought, they will suddenly become massive exporters of carbon.

Such imbalances are common even in mature forests, one of the stablest of ecosystems. Recurrent forest fires cause huge phytomass losses, as do, in some parts of the world, major hurricanes. Catastrophic windthrows, heavy snowfall, and pest outbreaks can also be very damaging. David Raup, an evolutionary biologist at the University of Chicago, concludes that it is probable that in some parts of New England no forest tree has ever lived its full natural span.

Old-growth stands of huge conifers found on rainy slopes in the Pacific Northwest are one of the few ecosystems that get enough respite between major disturbances to reach maximum possible phytomass. In these stands virtually all the carbon taken in is respired, and changes in the standing phytomass are hardly measurable from year to year.

The two fates of a piece of phytomass—to be consumed by a herbivore or left to die and be recycled by decomposers—seem to be about equally likely. If its fate is the latter, it may first end up as a piece of litter on the forest floor. How long the carbon stays in dead biomass depends on how quickly the litter is decomposed.

Walks in old-growth temperate forests are cushioned by mats of springy, absorbent foliage and by bark, cone, and twig litter—while the floors of many tropical forests may be covered with only a smattering of leaves. The difference can be traced to the ratio of carbon to nitrogen in litter and to temperature. The carbon/nitrogen ratio is lower in the tropics, resulting in easier digestibility of dead phytomass, and the temperature is higher (year-round maxima above 20 °C in the equatorial zone). As a result, tropical plant litter degrades up to four times faster than the litter in temperate and boreal forests. Plant litter thus forms continuous and fairly thick layers in ecosystems with low rates of organic decay—and it may be discontinuous and very thin in both arid subtropical and moist tropical settings.

Organic matter in soil contains between 1200 and 1800 Gt C, or at least twice as much as all the plants growing on the world's land masses. More than nine-tenths of this soil carbon is in dead biomass derived through the activity of microorganisms and soil invertebrates that decompose leafy and woody litter and roots. The rest is made up largely of living roots, bacteria, fungi, and soil invertebrates. In chemical terms, soil organic matter is a complex mixture of acids (humic, amino, and fatty), carbohydrates, and aromatic carbon compounds; some of them are readily decomposable, others persist for centuries.

Cold and wet soils can store carbon in greater quantities than warm and dry soils. Thus, how much CO_2 is emitted from soils by decomposition of biomass has little to do with the magnitude of organic carbon stored in soil, and far more to do with soil temperature and precipitation, the two key variables controlling organic decay. The range of recent estimates giving the annual global carbon flux from soils is fairly narrow, between 50 and 77 Gt C, and at least a quarter of the total flow is derived from the respiration of live roots. These rates imply that roughly 10 percent of the preindustrial atmospheric CO_2 would have passed through soils every year, and that the average residence time of the element in soils was on the order of 30 years. Specific estimates for major ecosystems, made by American biologists James Raich and William Schlesinger, show extremes of just 10 years for tropical grasslands, and 500 years for tundra and peaty wetlands.

The abundant litter on the floor of a Sierra Nevada forest in California (left) contrasts with the sparse sprinkling of leaves in an upland tropical rain forest in Queensland, Australia (right).

Earthworms and Termites

The bacteria and fungi dominating phytomass decomposition could not perform their tasks so well did not other organisms—especially earthworms and termites—help to process these remains. Although so unlike each other, earthworms and termites are both diligent processors of the surface litter: they drag it below the surface, feed on the debris, reduce it to smaller particles, and metabolize it, or at least partially solubilize it. The litter becomes mixed with soil during its passage through their guts, and the undigested portion is returned to the soil in copious casts. As they process litter, both earthworms and termites have considerable help from microbes that they harbor in their guts. These bacteria and protozoa help to decompose many breakdown-resistant macromolecules and provide digestible metabolites for their hosts.

A hectare in a rich temperate meadow may contain hundreds of kilograms of earthworms, and in aggregate the organisms swallow, digest, and pass on enormous amounts of organic debris mixed with soil. The bacteria ingested with litter may increase in number a thousandfold as they pass through an earthworm's gut, and microbial activity in casts may remain higher than in the surrounding soil for up to 50 days. Not surprisingly, experiments have shown CO_2 emissions from the soil to increase substantially in the presence of earthworms. No appraisal of earthworms' importance is more eloquent than a closing sentence from Charles Darwin's last, and so little known, book, *The Formation of Vegetable Mould through the Action of Worms*. In this book, published in 1881, a year before his death, Darwin wrote: "It may be doubted whether there are many other animals which have played so important a part in the history of the world, as have these lowly organized creatures."

Termites are among those few exceptions: on the global scale, their contribution to litter decomposition is even greater. At its highest, the mass of termites per hectare is of the same order of magnitude as the mass of earthworms, but the biosphere's nearly 250 quadrillion termites process between one-third and two-fifths of all phytomass in their tropical and subtropical habitats—accounting for perhaps as much as one-quarter of all terrestrial primary productivity! These estimates suggest that termite respiration returns annually at least 12 Gt C to the atmosphere, although not all of it comes from surface litter. Termites feed not only on plant litter, alone or mixed with soil, but also on fresh grass and sound woody tissues.

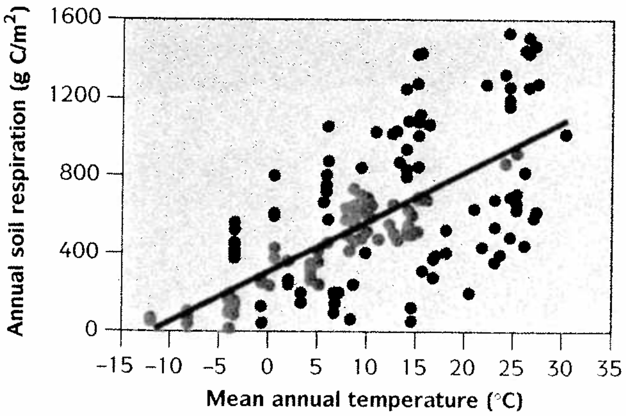
They do so largely in symbiosis with microorganisms, in an arrangement similar to ruminant digestion. Flagellated protozoa live in the hindgut of lower termites, bacteria inside the hindgut of the higher termites. Some species have evolved a more elaborate, extracorporeal, scheme for breaking down phytomass: they cut leaves, drag them into special chambers, and use them as a substrate for the cultivation of fungi whose tips they eat (attine ants practice the same remarkable way of feeding). But while termites can partially degrade lignin, only white-rot fungi can decompose it completely. Many termite species thus eat wood only after it has been attacked and degraded by fungi.

Debris-feeding termites rework tropical soils no less thoroughly than earthworms rework temperate soils. In areas where the litter density is low, some termite species may have to swallow tens of thousands of kilograms of soil per hectare every year in order to get enough cellulose. Their concentrated respiration produces very high levels of CO_2 in their nests: commonly 2 to 4 percent, and up to 15 percent, of the air in a termite's nest is CO_2, up to three orders of magnitude above the ambient level.

Termite mounds dotting a grassland near the Gulf of Carpentaria in northwestern Queensland, Australia.

Carbon may remain in the ground much longer if it becomes part of the tiny organic fraction that is buried in sediments, a process that is fastest in mires, bogs, and marshes. There the absence of oxygen hinders rapid decay, and the undecomposed tissues amass to form peats. Their subsequent exposure to high temperatures and pressures can eventually (after up to hundreds of million years) transform them into coals, whose best grades (anthracites) are virtually pure carbon. This process of sedimentation is the principal terrestrial bridge between the element's rapid and slow cycles.

Sedimentation removes only a small fraction of assimilated carbon, but the process may be more important than previously thought. In Russia alone, according to a recent reappraisal, the area covered by peatlands is about twice as large as earlier estimates, and contains no less than 215 Gt C. Consequently, global peat stores containing at least 400 Gt C are likely, and carbon continues to accumulate in this youngest of fossil fuels at a rate of more than 100, and perhaps even more than 200, Mt a year. In contrast, we have recently been extracting fossil fuels at the rate of about 6 Gt C a year.



Higher mean annual temperatures promote organic decay, and hence a higher soil respiration. Departures from the fitted trend are relatively large—but the general relationship is unmistakable.

Accumulations of kerogens contain more than 10,000,000 Gt of carbon, while global resources of traditional fossil fuels are most likely in excess of 6000 Gt C. Because of the excessive cost of extracting many deep or low-grade deposits, our fossil-fueled civilization will eventually recover only a small part of these coals and hydrocarbons,

Most carbon stored in the Earth's crust is in carbonate rocks. Limestones are by far the most abundant carbonates; the calcite and aragonite that make up these rocks have identical composition ($CaCO_3$) but different crystal structure. These often beautifully colored and patterned rocks are commonly used as building stones. Dolomite, $CaMg(CO_3)_2$, is the third most common carbonate mineral; most people have heard of it because of the eponymous range of the Italian Alps (Dolomiti) famous for its jagged peaks and difficult climbs.

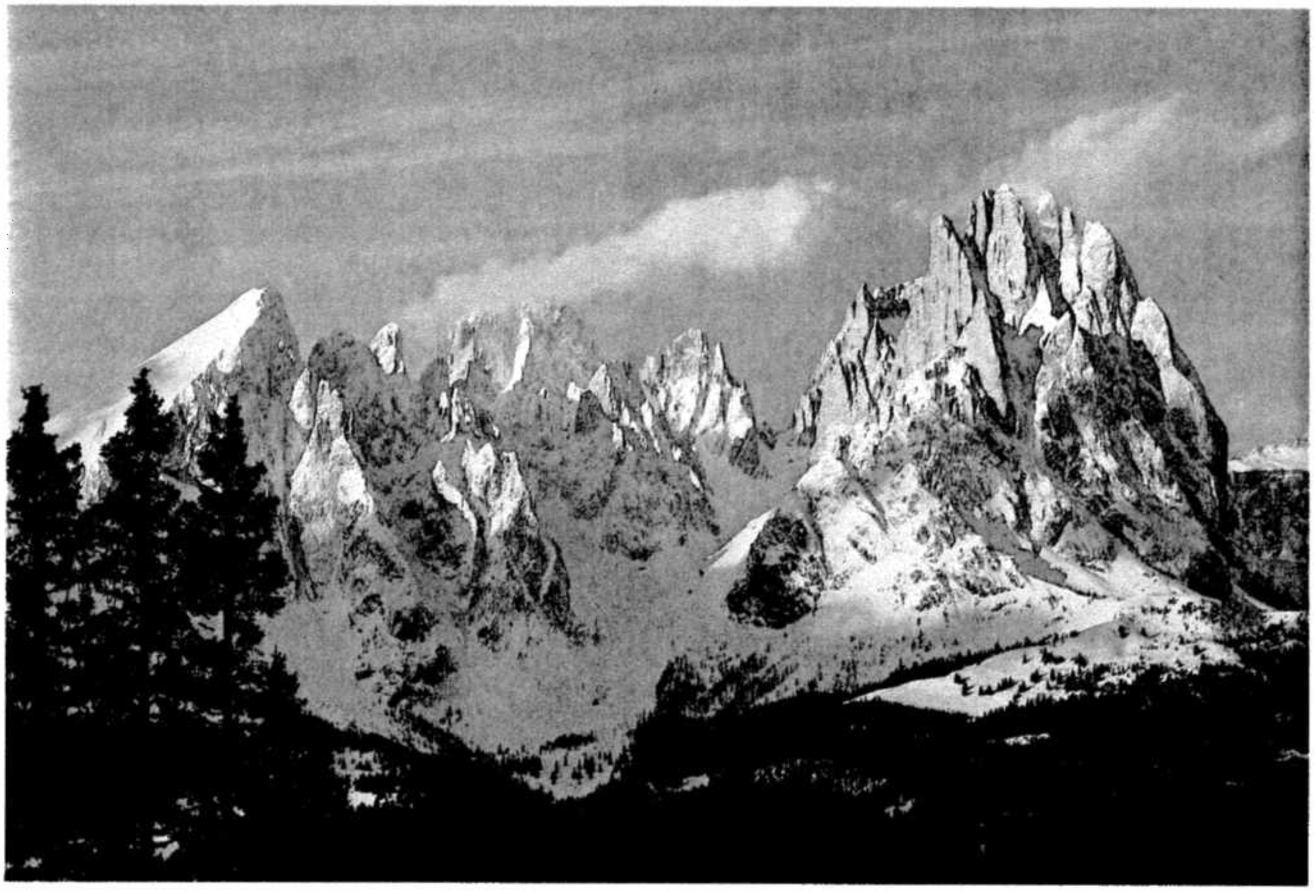
Weathering of these carbonates withdraws CO_2 both from the atmosphere and from soils, and rivers carry these weathered materials mostly as dissolved and particulate inorganic carbon. Only about half of all carbon entering streams from terrestrial ecosystems reaches the ocean; the rest is respired by aquatic heterotrophs or deposited on floodplains.

CO_2 flows dominate the biospheric carbon cycle, but the gas is not the only carbon compound found in the atmosphere: methane (CH_4) and carbon monoxide (CO) are always present in trace quantities. We can track prehistoric concentrations of CH_4 by measuring its levels in the air trapped in polar ice. These samples show that the CH_4 level fluctuated mostly between 400 and 700 ppb during the past 420,000 years, while its level during the few centuries before the year 1800 oscillated fairly narrowly around 800 ppb. While these concentrations are three orders of magnitude below CO_2 levels, they are almost infinitely higher than we would expect them to be in the Earth's O_2-rich atmosphere, where CH_4 oxidizes rapidly. This enormous disparity could not exist if bacterial generation of the gas did not constantly outpace the rapid oxidation.

The peatlands of northern Minnesota, dotted with islands of black spruce trees. Carbon stored in this and similar ecosystems escapes the rapid biospheric cycling and may eventually become fossilized.

CO concentrations in the troposphere are also three (and even four) orders of magnitude below the levels of CO_2: well below 100 ppb in remote marine atmospheres, and around 250 ppb for the mean in the northern hemisphere. The concentrations of the two gases are linked because of the principal way in which CH_4 is removed—it is oxidized in two steps to yield CO. In turn, CO is oxidized to CO_2, returning the element to its largest atmospheric reservoir. This oxidation takes place so fast that tropospheric CO has a lifetime as short as 10 days and no longer than a few months.

Surprisingly high concentrations of CO have been observed above undisturbed tropical rain forest, up to 400 ppb. The chemist Paul Crutzen of the Max Planck Institute for Chemistry has ascribed these concentrations to the photochemical oxidation of hydrocarbons emanating from the resins and oils of tropical trees. Another major source of tropospheric CO in the tropics is the combustion of phytomass. Satellites have repeatedly detected CO-rich plumes above parts of Africa, Asia, and Latin America far from any industrial or urban sources of the gas.



Carbonate sediments form some of the most spectacular high mountain ranges, including the picturesque Sassolungo group in the Italian Dolomites.

Methane, the simplest of all organic molecules in the atmosphere, is generated largely by anaerobic decomposition of biomass in environments ranging from the bottoms of lakes to waterlogged soils. Methane-producing microbes are strict anaerobes belonging to Archaea, a group phylogenetically distinct from bacteria. Methanoarchaea produce about 400 Mt CH_4 a year, mostly from the northern hemisphere's boreal peat bogs and temperate swamps. The enteric metabolism of herbivores—especially of large ruminant species and termites—and incomplete combustion of phytomass in forest and grassland fires are the other major natural sources of CH_4.

A substantial share of CH_4 from methanogenic fermentation is oxidized in waters above the anoxic muds even before the gas can escape into the air. Similarly, methanogens in deep anoxic forest soils release the gas, and oxidizers in the surface layer consume it. In aggregate, the annual atmospheric throughput of preindustrial CH_4 emissions made up only a small fraction of the biospheric carbon cycle, most likely no more than 300 Mt C from CH_4 a year compared to some 175 Gt of C from CO_2.

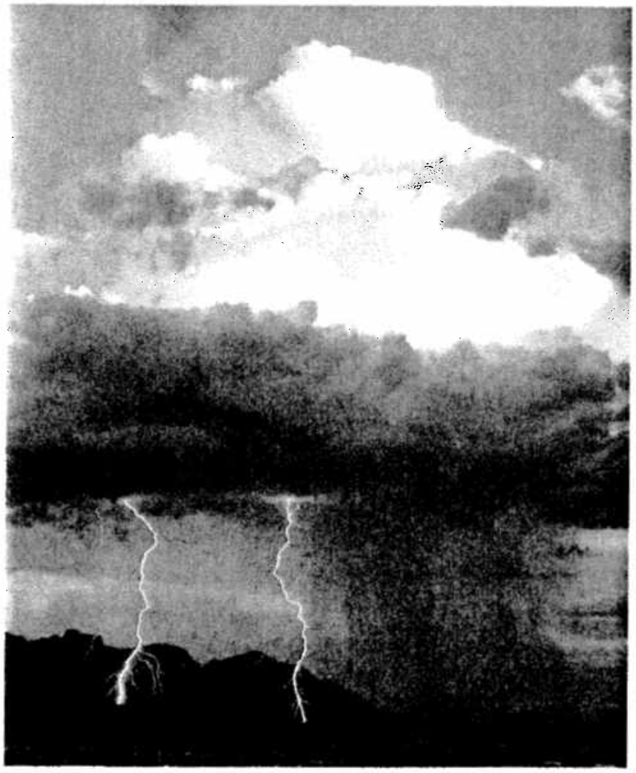
Fixing Nitrogen: From Lightning to Microbes

Studying nitrogen's biospheric fluxes is difficult: none of them can be easily monitored, and only one of them—uptake by plants—can be calculated with satisfactory accuracy. Although there is plenty of nitrogen in the Earth's crust—at least 3×10^{16} t of it—the bulk of the element is locked in igneous rocks, hard and slow to weather, and mostly well beyond the reach of biospheric flows. Only the weathering of nitrogen-rich sediments, constituting just around one percent of the element's crustal stores, releases significant quantities of reactive nitrogen. Living organisms, then, must get their nitrogen overwhelmingly from the atmosphere's vast stores of unreactive N_2.

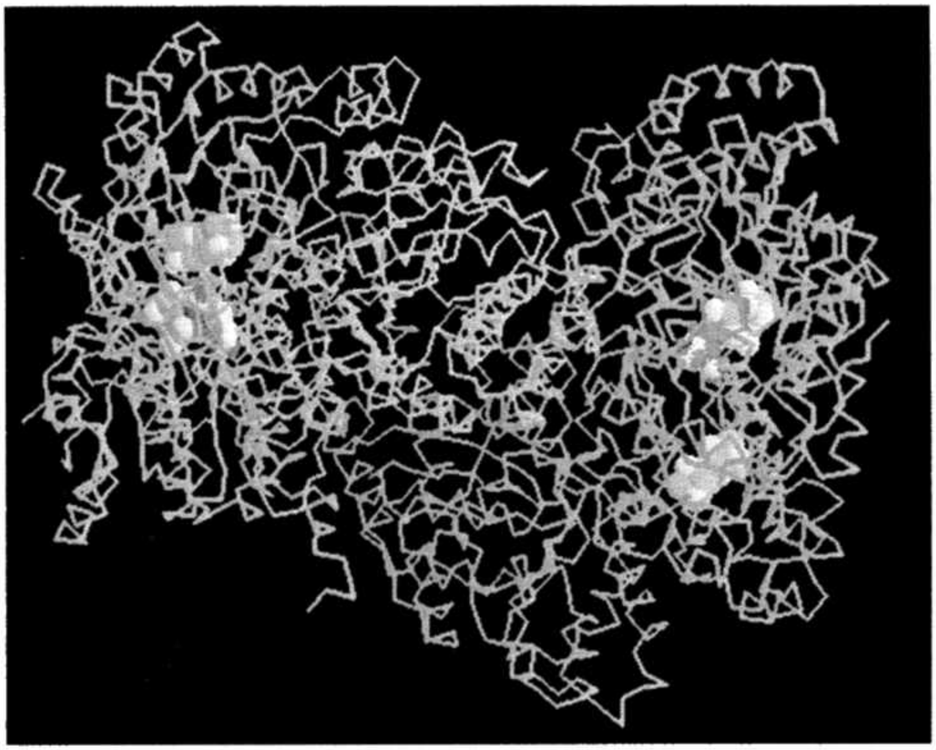
Before plants and animals can make use of N_2, the element must first be "fixed"—that is, incorporated into reactive compounds. Dinitrogen's strong triple bond must be broken, and the atoms incorporated into either nitrogen oxides or ammonia. Because nitric oxide, NO, and nitrogen dioxide, NO_2, are usually generated together and because NO is readily oxidized to NO_2, the two nitrogen oxides are commonly designated as NO_x. Falling meteorites and lightning, two common but ephemeral atmospheric phenomena, create the high temperatures and pressures needed to break N_2. Although shock waves generated by falling meteorites contribute a small fraction of a percent of all fixed nitrogen, lightning may be the largest natural source of NO_x.

Most powerful lightning strokes originate in cumulonimbus clouds, which develop with the highest frequency in the tropics and moist subtropics. There these clouds reach the greatest heights, often growing to the very top of the troposphere or even protruding into the lower stratosphere. The power of a lightning stroke goes up with the fifth power of the cloud size (so that doubling the cloud increases the total power 30-fold), and this property explains why the lightning originating in the huge clouds of the tropics is the most powerful. The visible flash accounts for just 0.2 to 2 percent of the lightning's energy. The bulk of the discharge goes into heating and compressing the surrounding atmosphere, just what is needed to dissociate the N_2 along the bolt's path. Yet estimates of how much NO_x is produced per stroke differ so much that we are not certain if lightning is only a marginal contributor of reactive nitrogen, or one of its largest global sources.

Nitrogen oxides are also created when chemical reactions transform stratospheric N_2O in a process destroying O_3. Another nitrogen compound, ammonia, enters the atmosphere from the volatilization of



Double lightning strikes the foothills of Tucson, Arizona. Generation of NO_x by lightning is a major source of fixed nitrogen in all regions where storms are frequent—but our estimates of the global total are highly uncertain.



The structure of the MoFe protein of the nitrogenase enzyme of *Azotobacter vinelandii*. The site where the molecule binds and reduces N_2 is shown most clearly as the cluster of spheres (atoms) inside the green subunit on the right, and the molybdenum atom is colored pink.

organic wastes. NH_3 escapes in especially large quantities from ecosystems with high concentrations of large herbivores, such as African savannas, and from naturally alkaline soils. Once formed, NO_x and NH_3, and its cation NH_4^+, are washed out of the atmosphere by precipitation or they may gradually settle to the ground in dry weather—but the few kilograms deposited per hectare annually by these means cannot satisfy the requirements of highly productive ecosystems. Life instead depends on the ability of a surprisingly small group of living organisms to fix N_2 into usable form.

Only certain bacteria have the special ability to reduce N_2 to NH_3. They fix nitrogen in much less spectacular fashion than lightning—at ambient temperature and at a normal atmospheric pressure—but in a no less remarkable manner. In order to sever the extraordinarily strong N_2 bond, they all rely on nitrogenases, a rather uniform group of enzymes made up of two protein molecules, the larger one containing atoms of molybdenum and iron and the smaller one just iron.

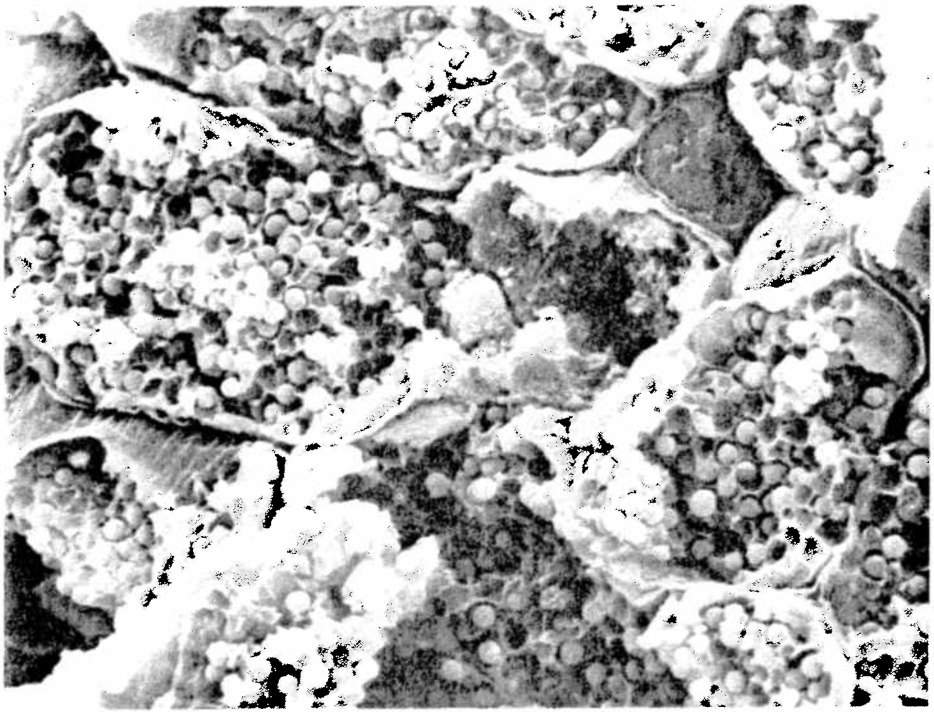
Bacteria of the genus *Rhizobium*, hidden in root nodules, carry out most of this dinitrogen scission. These bacteria secrete unique compounds that trigger the formation of nodules on curled root hairs. For nodules to form on specific leguminous plants, particular rhizobial strains must be present in the soil. Because nitrogenase tolerates no more than a fleeting exposure to O_2, bacteria form an oxygen barrier in the nodule tissue, and they carry the oxygen needed for the respiration of nitrogen-fixing organelles in molecules of leghemoglobin, a protein whose high affinity for O_2 prevents the gas from reaching and inactivating nitrogenase.

Many environmental conditions set limits to the rate of bacterial nitrogen fixation. Biofixation is slowed in acid soils or at high temperatures. Since rhizobia require carbon from their host, their performance is also limited by the plant's photosynthetic rate. And an abundance of inorganic nitrogen in soil usually suppresses the rate of fixation. Not surprisingly, fixation rates in natural ecosystems vary widely, from just a few kilograms per hectare in arid grasslands to over 100 kg N/ha in *Acacia* savannas or in stands of such tropical woody legumes as *Leucaena*.

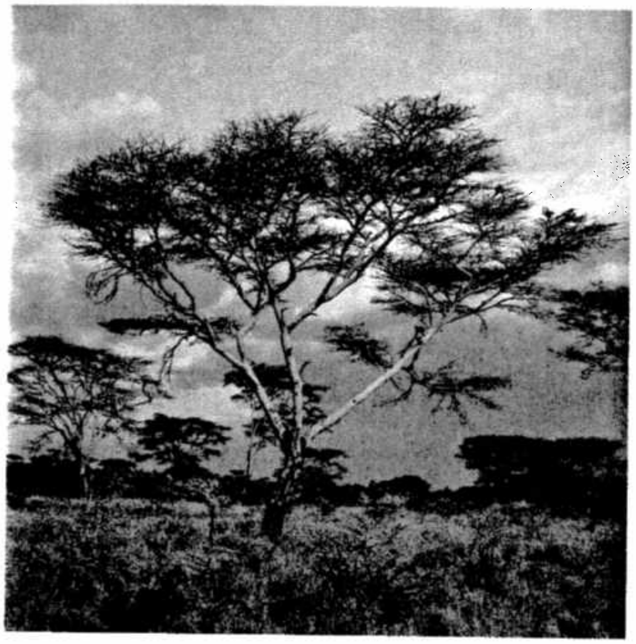
Symbiotic fixation carried out by bacteria other than *Rhizobium* makes a secondary contribution on the biospheric scale, but it is of great importance in some plant communities. The cyanobacteria that live in symbiosis with fungi in lichens are by far the largest source of fixed nitrogen in the Arctic. *Frankia*, the most productive nitrogen fixer among symbiotic actinobacteria, is responsible for the luxuriant growth of red alder stands in the Pacific Northwest.

Among free-living nitrogen fixers, only cyanobacteria provide substantial amounts of the element. Some 60 genera of cyanobacteria are responsible for these contributions, with *Anabaena*, *Nostoc*, and *Calothrix* by far the most important. They fix nitrogen in special cells (heterocysts), formed at regular intervals along their filaments: the multilayered envelope surrounding heterocysts reduces gas diffusion and prevents O_2 damage to nitrogenase.

While rhizobia carry out most nitrogen fixation on land, cyanobacteria are the primary nitrogen fixers in the ocean. Away from shore, many species are free floaters, often at concentrations high enough to lend the water a distinct color, while others live as symbionts inside diatoms, single-celled organisms distinguished by their beautifully patterned shells of



A scanning electron micrograph of almost perfectly spherical *Rhizobium* bacteria inside opened root nodules of clover.



Acacia trees in the Serengeti grassland of Tanzania. Hundreds of species of this large genus, ranging from herbs to gigantic trees, host rhizobia whose fixation of nitrogen enriches soils in often very dry environments. Some species have stunning flowers, others are known for their dangerous thorns.

crystallized silica. Closer in, cyanobacteria can form extensive mats on coral reefs, and they abound in the dense roots of salt-water marshes. Whether the diazotrophs in the ocean approach the fixation rate on the continents, though, is a matter of debate. Some global estimates put the total terrestrial fixation considerably above the oceanic level; others see the two as being of the same order of magnitude. Published estimates for the two fluxes range, respectively, from 100 to 170 and from 10 to 130 Mt N a year.

Microbial nitrogen fixation poses a number of puzzles. Why is there so little nitrogenase in the biosphere—the total mass of this unique enzyme may be less than a dozen kilograms—and why is it present only in bacteria, and even then in a relatively limited number of genera? The enzyme is clearly not an evolutionary latecomer: cyanobacteria are among the oldest autotrophs, and their fossils have been reliably dated to more than 3 billion years ago. Why do no higher plants have even a rudimentary capacity to fix their own nitrogen without bacterial help? Why are leguminous species so often excluded, or only weakly represented, in mature ecosystems?

The best answers to these questions lie mainly in the relatively high energy requirements of nitrogen fixation, and in its specific limitations. A bacterial nitrogen fixer must consume at least 8 to 12 g of glucose, or roughly 3 to 5 g C, for every gram of nitrogen reduced from N_2. This relatively high energy expenditure was unavoidable for bacteria in the early biosphere when there was no alternative way to obtain fixed nitrogen, and it pays off in the early stages of ecosystemic succession, when nonleguminous plants have a hard time securing enough nitrogen in soils low in organic matter. But leguminous species are largely absent in mature plant formations, where nonfixers can acquire nitrogen at less cost by producing more roots to scavenge for soil nitrate.

Because of the special micronutrient needs of nitrogen fixers, their performance is often limited by the lack of necessary trace elements, most notably molybdenum on land and iron in the ocean. And both terrestrial and aquatic nitrogen fixers have a consistently higher need for phosphorus than do nonfixing species. Moreover, the energy needed for fixation may not be available where light is insufficient, most commonly in the forest understory and in turbid or deep waters.

Nitrogen in the Environment

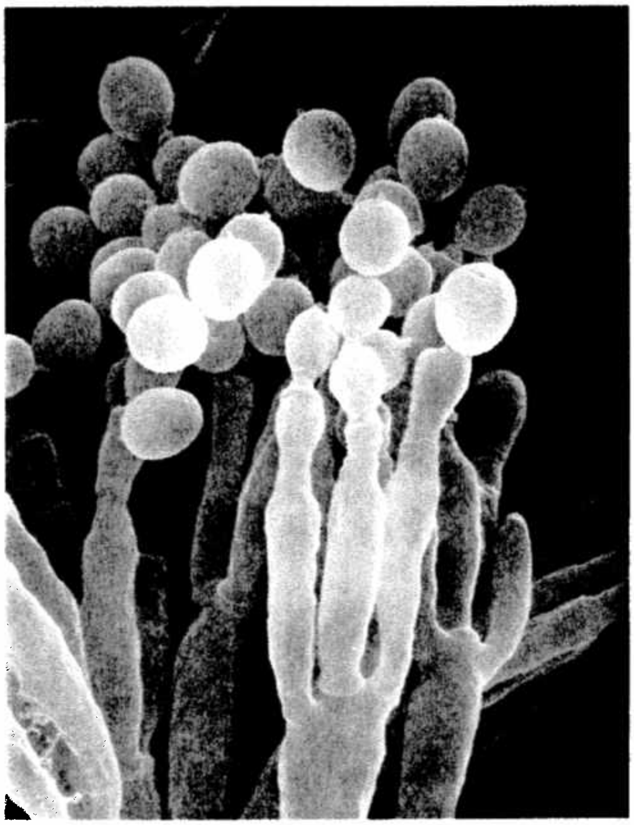
Nitrogen is commonly *the* nutrient limiting the productivity of terrestrial ecosystems, although the precise level of the shortfall is usually hard to determine. The element is scarce above all in many grasslands and boreal forests, but also in the montane—but not in the more extensive lowland—forests of the tropics. Nitrogen is in short supply so often not only because diazotrophs find it difficult to secure the rare nutrients they need but also because the element is easily lost from natural ecosystems through the leaching of highly soluble nitrates and the volatilization of ammonia. Nor can decomposers easily make up the deficiency through rapid recycling: nitrogen is released only slowly from carbon-bonded compounds in the decomposing biomass. Its slow release retards the growth of new, protein-rich decomposer biomass, further delaying the recycling of the assimilated plant nitrogen.

The element's low concentrations in water also limit the productivity of many aquatic species. These nutrient shortages favor the nitrogen-fixing cyanobacteria: some of these species are so common in some nutrient-poor waters that they may account for the largest share of phytomass production among the phytoplankton.

Nitrogen that has been transferred to soils—whether through weathering, atmospheric deposition, or the death of living organisms—becomes subject to complex and relatively rapid cycling. The bulk of the nutrient may keep circulating indefinitely within a small volume of soil, although some amount, and often a very large one, is lost to waters and to the atmosphere. Most estimates of the nitrogen stored in the world's soils are approximations derived from C/N ratios. They range over an order of magnitude, but the most detailed global survey based on direct measurements confirmed the more conservative values by arriving at a total of 95 Gt N.

More than nine-tenths of the nitrogen in soil is bound in organic matter, dead and living. This is not surprising, considering the abundance of soil microorganisms. Beneath every square meter of temperate grassland there are up to 10^{14} bacteria, billions of fungi, and millions of algal cells. Protozoa may be counted in the hundreds of millions per square meter, nematodes in the tens of millions, and earthworms commonly in the hundreds. The total biomass in a hectare's worth of soil may easily reach several tonnes, and most of its species are so short-lived that nitrogen will be constantly moved between the organic and the mineral pool.

Organic nitrogen begins its transformation to inorganic forms with the decomposition of nitrogen-containing macromolecules by enzymes that break them apart into smaller subunits. The newly liberated amino acids, nucleic acids, and amino sugars next release their nitrogen as NH_3 through the



Penicillium chrysogenum, a fungus widely distributed in the soils of temperate forests, grasslands, and fields, is an important ammonifier, as well as the best-known producer of penicillin.

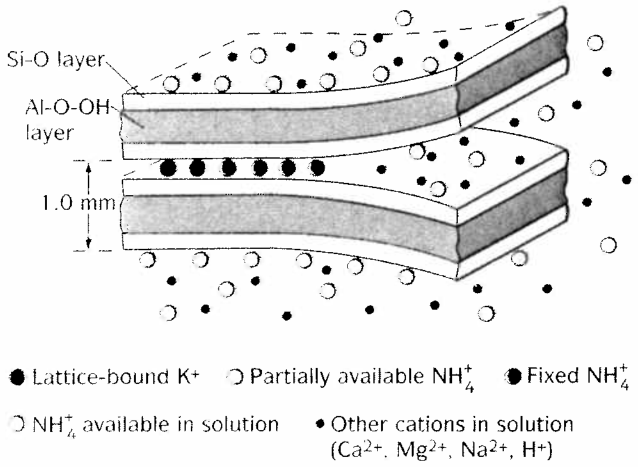
Large herbivores—such as this herd of wildebeest *(Connochaetes taurinus)* in South Africa–are important recyclers of nitrogen in grasslands.

action of such ubiquitous bacteria as *Pseudomonas, Bacillus,* and *Clostridium,* as well as funguslike actinobacteria (most commonly *Streptomyces,* an important source of antibiotics) and fungi (including *Penicillium,* the first, and still very important, source of antibacterial drugs).

All these microorganisms typically manage to release per year only around one percent of the total organic nitrogen stored in the soil, equivalent to a mass of the element amounting to between 20 and 60 kg/ha. Nitrogen may remain in the litter under boreal conifers for more than two centuries—but it may reside less than a decade under temperate deciduous trees. Most of the nitrogen assimilated by plants returns to soils in plant litter—but where grazers are abundant they can recycle more nitrogen in their metabolic waste than the litter fall. The herds of elk in Yellowstone National Park contribute yearly almost five times the nitrogen that comes from plant litter fall.

Except in highly alkaline soils, NH_3 is readily transformed to the NH_4^+ cation. In soils where carbon is abundant, much of this NH_4^+, as well as NO_3^-, will be eagerly taken up by soil microorganisms, which temporarily "immobilize" the assimilated nitrogen in their tissues by making it unavailable to plants. Bacteria thus carry out two opposing processes: they mineralize nitrogen, releasing the element for plant use, and they immobilize it, putting it beyond the plant's reach. The two processes proceed concurrently, and depending on which process is dominant, the presence of mineral nitrogen in the form of NO_3^- and NH_3 will either increase or decline.

Where carbon is in short supply, bacteria and fungi cannot grow quickly enough to immobilize much nitrogen, and one of two common processes disposes of the available NH_4^+. The cation will either be quickly transformed, through nitrification, into the highly mobile anion NO_3^-, or be removed from rapid circulation altogether through its incorporation into clay minerals. *Nitrosomonas,* the oxidizers of NH_3, and *Nitrobacter,* the oxidizers of NO_2^-, perform most of the conversions to nitrates on land, and the bacteria *Nitrosococcus* and *Nitrococcus* carry out the same task in the ocean. The process slows down with decreasing temperatures, and on land it is inhibited in acid, poorly aerated, and very wet soils.

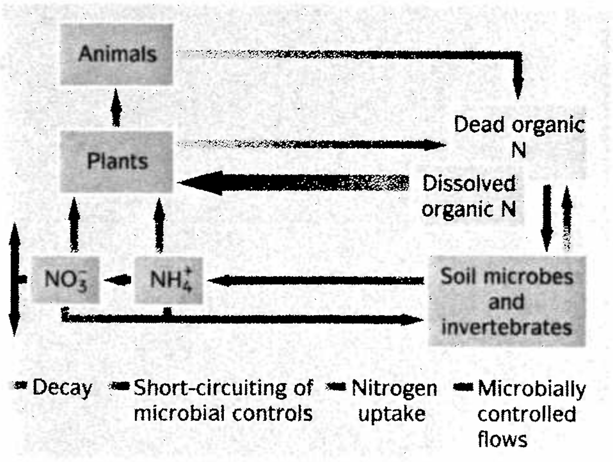


The binding of ammonia in clays. When NH_4^+ cations are caught between the lattice layers of vermiculite or illite, they become trapped and unavailable for plants.

Nitrates produced by nitrifying bacteria are highly water-soluble and hence do not accumulate in soils. Plants absorb them readily through their roots and convert them into NH_3, which they use to produce amino acids for proteins in a process called assimilatory nitrate reduction. In addition, more than 30 bacterial genera use nitrates as the oxygen source for their respiration; these bacteria convert nitrates to NO_2^-, and eventually to N_2, in the process of denitrification (or dissimilatory nitrate reduction). Some fermentative bacteria in carbon-rich soils also reduce nitrates to NH_3. Precipitation washes nitrates, or the soil containing them, into streams, or it carries them into groundwaters. The NO_3^- ion is so mobile, and the soil content of nitrates so variable, that it makes little sense to quote average NO_3^- values even for small areas.

A peculiar property of some soil minerals explains why substantial shares of NH_4^+ become bound into complexes that resist both inorganic breakdown and bacterial attack. Several clay minerals, above all vermiculite and illite, take the form of crystal lattices composed of individual sheets. When the voids on exposed surfaces between the expandable sheets are filled by NH_4^+, the lattice layers contract and trap the cation in the crystal so it can no longer participate in the rapid internal cycling. In some soils the mineral-bound NH_4^+, accounts for up to 8 percent of all nitrogen in the near-surface layer, and up to 45 percent of the nitrogen in deeper soil. The actual amount of mineral-bound nitrogen thus ranges from just a few kilograms to more than one tonne per hectare.

An even more complex chemical process also acts to sequester nitrogen in long-lived compounds: humus forms when polyphenols (aromatic alcohols) derived from decomposed lignin, or synthesized by



A new link in nitrogen cycle: some plants sidestep mineralization by absorbing dissolved organic nitrogen rather than waiting for bacteria to provide the inorganic compounds that plants usually assimilate.

microorganisms, react with amino acids and produce nitrogen-rich humic and fulvic acids of high molecular weight. These polymers lend yellow to black (mostly brown) colors to soil solutions, and they form complexes with clay minerals that allow humus to resist microbial breakdown. Hence even in well-aerated surface soils humus may retain the incorporated nitrogen for several hundreds, or even thousands, of years.

The complex cycling of soil nitrogen thus offers an atom of the element a variety of fates. The atom can move through a cycle from soil to microorganism to soil in a matter of hours, and from soil to plant to soil in a few months—or it can be caught in an illite lattice for decades or in a humic acid for millennia. An already rich organic soil may gain still more nitrogen from atmospheric deposition and decomposing litter, and it may store many tonnes of nitrogen per hectare—but, at any given time, less than 0.1 percent of this total, or just a few kilograms of nitrogen per hectare, may be available to plants as NO_3^- or NH_4^+.

Plants have a few other sources of nitrogen: their leaves can absorb NH_3 and NO_x from the air, for example, but these sources are usually marginal. There is a growing evidence, however, that plants in some infertile soils, where mineral nitrogen is in short supply, have found a way to bypass the mineralization process: they absorb much of their nitrogen in dissolved organic compounds. The nutrient moves directly to plants from the pool of dead organic matter, and the plant does not have to wait for bacteria to transform nitrogen in organic compounds to ammonia or nitrates.

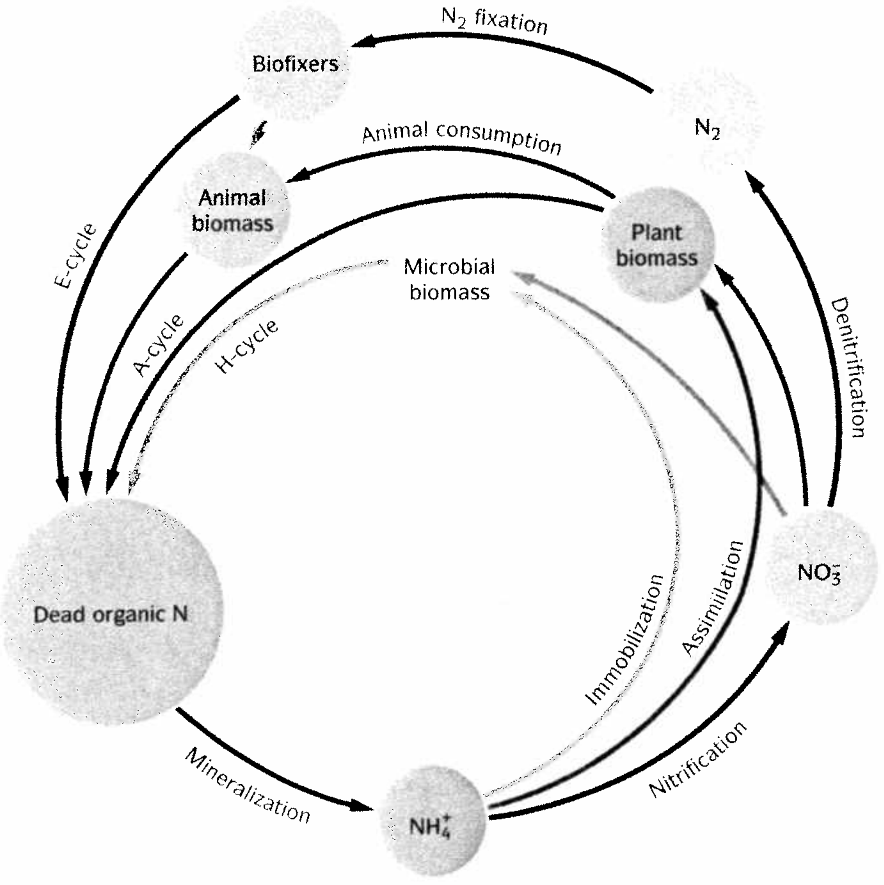
Some plants can even speed up this short-circuiting. Pines growing on infertile soils can strongly influence the release of dissolved detrital organic nitrogen by producing litter with a high content of polyphenols (mainly tannins). Nitrogen in the soil binds to these phenols, and the pines absorb phenols and nitrogen both directly through their roots. These plants have an obvious competitive advantage compared to species using only nitrate or ammonia.

Many plants recover nitrogen still more quickly through effective internal cycling—by not allowing the element to escape when a part of the plant is to die. Northern hardwoods, including sugar maple, American beech, and yellow birch, move nitrogen (as well as phosphorus and potassium) from senescing leaves to stems and roots, where the nutrient is stored until it can be remobilized in the spring. Up to one-third of the nitrogen needed for new phytomass can come from these temporary internal stores.

Whatever their nitrogen sources, virtually all terrestrial ecosystems accumulate nitrogen in the early stages of their evolution, but, in relative terms, and on a global scale, plant life is nitrogen-poor. Cellulose and lignin, the two most abundant structural polymers in the phytomass, contain no nitrogen. Levels of nitrogen are relatively high only in leguminous plants: in these plants, the seeds are between 3 and 6 percent nitrogen, and the leaves and stalks around one percent.

A convenient way to summarize the cycling of nitrogen in terrestrial ecosystems is to partition it into three interdependent subcycles as proposed by the Swedish soil scientist Sven Jansson. In the enveloping "elemental" subcycle, nitrogen is moved by fixation from N_2 to NH_3, assimilated by plants, returned to NH_3 by microbial mineralization, nitrified to NO_3^-, and finally denitrified to N_2O and N_2. In the second, "assimilation" subcycle, nitrogen moves, via mineralization, between dead organic matter and plants. In the third, "heterotrophic" subcycle, microorganisms temporarily immobilize substantial shares of soil nitrogen before returning it to the reservoir of dead organic matter. Mineralized nitrogen is the common starting input, and constant competition among the biota driving the three subcycles determines what shares of the element will end up in new phytomass, in bacterial biomass, or, again, as atmospheric N_2.

Nitrogen's escape from the soil may take the element straight to the atmosphere or, if washed away by rain, through a more circuitous route into the ocean. In forests, dense canopies prevent raindrops from directly hitting the ground, and a thick litter layer protects the soil by soaking up moisture. There, surface runoff and soil erosion may remove



Nitrogen subcycles in soil
After the organic nitrogen is mineralized, an individual atom can be taken along three very different paths. The elemental cycle (the outer ring) takes the atom back a long way through the atmosphere, while the assimilation and heterotrophic cycles can return it rather rapidly to the soil after the decay of biomass.

just a few kilograms of nitrogen per hectare a year, and the losses caused by leaching are similarly small. The runoff losses are far greater in arid grasslands, where erratic seasonal downpours can carry off well over 10 kg N/ha a year. The nitrogen transported by streams, mostly in organic particulate matter or dissolved as nitrates, makes but a minor contribution to the ocean's relatively small nitrogen stores. They are made up overwhelmingly (about 95 percent) of N_2.

Nitrogen returned to the atmosphere by denitrifying bacteria largely rejoins the huge mass (3.9×10^{15} t) of N_2, whose total has remained stable for the past 2 billion years. Not all denitrifiers have the requisite enzymes to carry the process all the way to N_2, and they also release some NO and N_2O. The nitrifying bacteria that convert NH_3 to NO_3^- also release NO and N_2O as an intermediate product in well-aerated soils and in wetlands, as well as in the open ocean. The relative contributions of denitrification and nitrification to global emissions of N_2O remain uncertain, but commonly both processes can be going on simultaneously even in the same bit of soil.

N_2O is best known as the laughing gas in anesthesia, although it is also an ingredient of rocket fuels and canned whipping cream. Because the gas is inert under normal conditions, it has no appreciable biospheric sink, and its molecules are eventually broken apart by the sunlight in the stratosphere. The average length of N_2O's residence time in the atmosphere is about 130 years. Surface ocean waters are supersaturated with N_2O, acting as a major source of the gas.

The same types of bacteria that produce N_2O can also produce considerable amounts of NO, perhaps even more than lightning does (global estimates of microbial NO emissions range from just 4 to about 20 Mt N a year). Surprisingly, this simple molecule also plays incongruously complex roles in the human body, where it acts both as one of the most important neurotransmitters (it controls blood-vessel dilation by signaling the smooth muscle cells to extend) and as a cellular toxin, able to destroy even some cancerous growth, but also sometimes damaging the body's healthy tissues.

Because of its free-radical structure, the gas is much involved in the chains of chemical reactions that take place in the troposphere. Reactions involving NO regulate the levels of $OH\cdot$, the atmosphere's principal oxidizing agent, and are critical for the photochemical production of ozone. In polluted atmospheres, O_3 is lost as it reacts with NO to form NO_2, but it is reformed when the energy of sunlight causes the dioxide to dissociate. The end product of nitric oxides's avid atmospheric reactions is HNO_3, a major contributor to acid rain (but also the reason for the short tropospheric lifetime of the gas).

Flaming savanna fires can volatilize more than 90 percent of all nitrogen in the burning phytomass, releasing NO and NO_2. Intense forest fires can deplete nitrogen stores not only in the litter layer, but also in the uppermost, organic horizon of soil. But the most important nitrogen gas released by wildfires is N_2: Thomas Kuhlbusch of the Max Planck Institute for Chemistry and his colleagues estimate that vegetation fires may transform between one-half to three-fifths of the nitrogen present in the phytomass to molecular nitrogen by the process of pyrodenitrification. These releases could restore one-tenth, or as much as one-half, of all N_2 withdrawn by terrestrial biofixation.

Sulfur in Ocean and Atmosphere

In the early history of the Earth, volcanoes emitted huge volumes of gases, including a great deal of SO_2 and H_2S. These two sulfur gases did not remain in the atmosphere long, for both are highly soluble in water and were removed from the atmosphere during the condensation of the ocean. Once within the ocean, SO_2 participated in a variety of reactions with water that eventually converted the gas to SO_4^{2-}, which became the most abundant sulfur anion in seawater, while the H_2S reacted with iron in the ocean to form sulfides. Eventually, the fate of these two compounds came to be greatly influenced by the appearance of life.

Long before the emergence of an oxygenating atmosphere, bacteria could oxidize elemental sulfur or H_2S during the process of anaerobic photosynthesis, still performed by green or purple sulfur bacteria. These bacteria released sulfates as a by-product of their reduction of CO_2. Sulfates introduced into the ocean during photosynthesis in coastal bacterial mats were gradually incorporated from the seawater into sedimentary rocks or reduced by bacteria to sulfides, as they are still today.

Volcanoes continue to emit sulfur (although at nowhere close to their primordial rates), and the element also makes its way into the atmosphere from sources as diverse as sea spray and the anaerobic decay of biomass. But sulfur's stay in the atmosphere is nearly always brief, precluding any buildup of concentrations in the troposphere. The atmosphere's natural sulfur burden, whether in the form of gases or particulates, amounts to only about 5 to 6 Mt, five orders of magnitude less than the mass of carbon in atmospheric CO_2, and nine orders of magnitude less than nitrogen's huge atmospheric stores.

The gaseous compound carbonyl sulfide (COS), whose ubiquitous presence in the air was discovered only in the mid-1970s, has the highest natural background concentrations of any sulfur compound, entirely because of its relatively long residence time in the atmosphere, where it stays for up to five years. Sulfur-reducing bacteria generate the gas, and biomass burning releases it as well, but it is also produced indirectly by a variety of chemical reactions, some with dissolved organic matter in the ocean. COS will remain in the atmosphere until it reacts with OH· (leading to the production of H_2S) or is split apart by sunlight in the stratosphere. At around 500 ppt, COS levels are an order of magnitude higher than those of H_2S and SO_2—but the atmospheric throughput of these two gases, as well as that of DMS, is much higher.

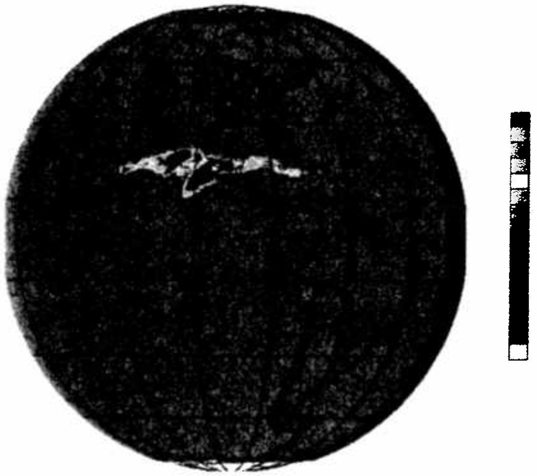
This disparity arises from the usually ephemeral residence times of other forms of sulfur in the planetary boundary layer, the well-mixed part of the troposphere extending roughly one kilometer above the Earth's surface. SO_2 may remain in humid air for just a few minutes before it is oxidized to a sulfate in reactions with H_2O_2 and OH·. Oxidation rates are slower in dry, sunny weather, but they may be speeded up in the presence of various metallic and carbonaceous particles that act as catalysts. Gaseous SO_2 is removed from the atmosphere by precipitation, or absorbed by vegetation and soils. The global mean duration of sulfur dioxide's residence in the atmosphere is just about a day.

Atmospheric H_2S has an equally short residence time, and marine DMS commonly lasts less than 10 hours in the atmosphere before it is removed, also in sulfates, by reacting with OH·. In turn, sulfates in the lowermost troposphere last usually no longer than three or four days. Like other liquid or solid particles, sulfates are washed from the atmosphere in precipitation (wet deposition) or they settle on the ground in dry form (dry deposition). Because sulfur gases leave the atmosphere so quickly, only small fractions of these gases mix into the free troposphere. In preindustrial times, annual rates of deposition totaled about 200 Mt S on the ocean, and no more than 50 Mt S on the land.

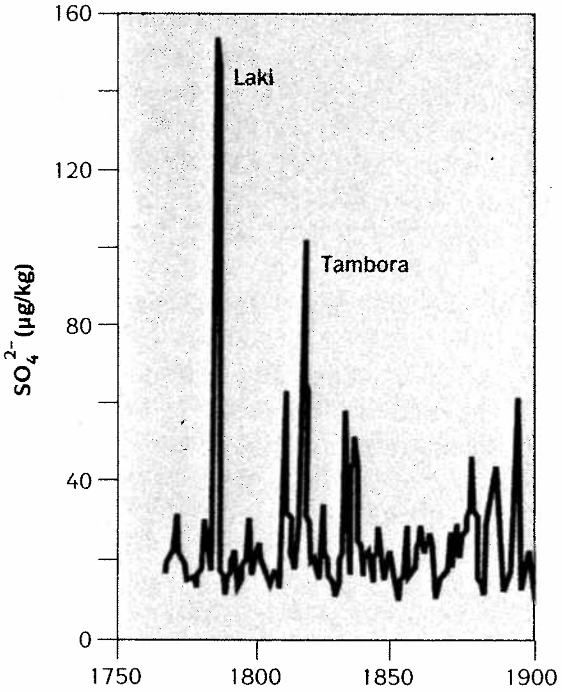
Of all natural sources releasing sulfur into the atmosphere, sea spray makes by far the largest contribution. Most likely it lofts into the air between 140 and 180 Mt of the element a year in the form of dissolved sulfates. The sulfate ion is, after the chloride ion (Cl^-), the second most abundant ion in seawater, although most of its huge mass (about 1.3×10^{15} t) is beyond the reach of near-surface turbulence. At the surface, water droplets containing sulfates are lofted into the air with breaking waves and pounding surf, but most of the airborne sulfate comes from the constant collapsing of countless bubbles at the ocean's surface. These microbursts propel tiny (1 to 20 μm in diameter) drops at air speeds up to 10 m/s. Only about a tenth of the sulfate mass released settles on the continents; gravity promptly pulls the rest back into the ocean.

Volcanic emissions are by far the most spectacular source of atmospheric sulfur. The sulfur content of volcanic plumes has been measured (by direct sampling or, more commonly, by spectroscopic remote sensing) and shows a great deal of variability. The spectacular plume and mud flows loosed by Mt. St. Helens on May 18, 1980, contained no more than about 1000 t S. In contrast, after major explosions during the 1980s plumes rising from Sicily's Monte Etna carried as much as 5000 t SO_2 a day.

Central American volcanoes are also great sulfur producers: even a quiescent cone releasing a steady vapor plume will emit around 100 t SO_2 a day. In 1982 Mexico's El Chichón injected more than 10 Mt of sulfate aerosols into the atmosphere—more than any other eruption of the 1980s. The eruption of Mount Pinatubo in June 1991 released some 12 Mt of sulfuric acid aerosols. For comparison, sulfate deposits in Antarctic ice indicate that the 1815 eruption of Tambora on the Indonesian island of Sumbawa spewed out as much as 50 Mt S.



This satellite image shows the greatest extent of the SO_2 cloud emitted by the eruption of El Chichón in Mexico in spring 1982. This eruption eventually injected about 20 Mt of SO_2 all the way to the stratosphere. The color scale shows concentrations of SO_2, with black being the highest level.



Quantities of sulfate measured in snow (in micrograms per kilogram) dated from 1750 to 1900. Distinct peaks are caused by major volcanic eruptions.

Only the plumes of exceptionally large eruptions will inject sulfur high into the atmosphere, from where it can be carried by convective air circulation to polar regions. Consequently, sulfates from major eruptions, such as Tambora in 1815, leave behind clear spikes in polar ice. Total volcanic sulfur emissions amount to around 20 Mt S a year over the long term. Submarine volcanoes, concentrated along the spreading zones of midocean ridges, are a source of identical magnitude, but we do not know what portion of their emissions eventually enters the atmosphere.

Analyses of the sulfur in polar ice cores indicate that the amount of the element deposited from the atmosphere varied little between the end of the last ice age and the year 1900, and only large volcanic eruptions caused notable excursions. Even after adding the contributions of all sulfur compounds, during the preindustrial era no more than a few kilograms of sulfur per hectare were deposited on terrestrial ecosystems per year, just a fraction of total sulfur that these ecosystems required.

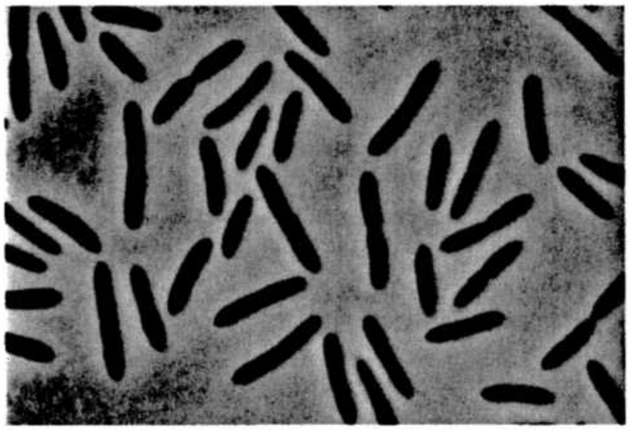
Biogenic Sulfur

Most of the sulfur in the atmosphere comes not from the spectacular eruptions of volcanoes, but from the quiet activity of countless bacteria. Some of these bacteria are the commonplace decomposers of dead biomass, others are one of a variety of specialized organisms that utilize the energy liberated by oxidizing or reducing elemental sulfur or sulfur compounds. Many common bacteria *(Pseudomonas, Escherichia)* and fungi *(Aspergillus, Streptomyces)* degrade sulfur-containing compounds, but in most terrestrial ecosystems their activity is not a particularly large source of sulfur gases. Many herbaceous plants and such leguminous trees as *Acacia* and *Leucaena* emit sulfur gases in small quantities as by-products of normal metabolic activity. Indeed, the emissions from floor litter, soil, and roots around the Central American rain forest tree *Strypinodendron excelsum* are so strong that the plant can be located by its odor. But volatile sulfur fluxes from forests are tiny compared to the emissions from coastal wetlands and the ocean.

Terrestrial ecosystems release a complex mix of biogenic sulfur compounds, including varying shares of COS, DMS, and others, but among all the gases they emit one is dominant, and that gas is H_2S. Its emissions are especially plentiful from coastal and freshwater wetlands, from muddy lake bottoms rich in organic matter, and from anoxic soils. Predictably, dry soils have the lowest total emissions, and warm coastal marshes and mangrove swamps the highest.

Numerous species from more than a dozen genera of bacteria can reduce sulfate (or elemental sulfur), releasing H_2S, in a process analogous to denitrification. *Desulfotomaculum* and *Desulfovibrio* are the two dominant genera of bacteria, called thiopneutes, engaged in this mineralization, which can

A mangrove forest in Australia. The decomposition of biomass in these warm coastal wetlands is a major source of sulfur gases.



Motile, rodlike cells of *Desulfotomaculum acetoxidans* magnified about 3500 times.

take place only in the absence of oxygen. These bacteria are common in tidal and marine sediments, where the decomposition of abundant organic matter consumes the available oxygen, producing a nearly anoxic environment. They tolerate high levels of the H_2S and heavy metals, toxic to many organisms, that commonly accumulate in marine sediments.

These bacteria are primarily responsible for the 15 to 40 Mt of sulfur that, as an increasing number of field measurements suggests, are contained in the emissions given off over land, including wetlands, every year. These emissions appear to be matched in quantity, although not in composition, by those originating in the ocean. For decades H_2S was thought to be the most important biogenic gas carrying sulfur from the ocean to the atmosphere—but during the 1970s investigators measuring the gas in remote marine atmospheres found levels no higher than 50 ppt. After two decades of sampling in far-flung locations, we now know that the gas dimethylsulfide (DMS) makes up at least four-fifths, if not nine-tenths, of the biogenic flux from the ocean.

The gas originates from the decomposition of the amino acid methionine in the remains of marine phytomass. Some brown algae are especially prolific producers, as are coccolithophorids and dinoflagellates. The amount of DMS released into the atmosphere is now put at less than 20 Mt S per year, but the gas does not stay aloft very long. After oxidation by OH· or other free radicals, DMS is converted either to methanesulfonic acid (CH_3SO_3H, MSA) or to SO_2, and the dioxide is fairly rapidly oxidized to sulfate. As MSA is not produced in any other way, its presence in the air is an unambiguous indicator that its sulfur is of biogenic origin. Most of the oxidation products are deposited back into the ocean in just a matter of days.

Compared to the ubiquitous decomposers, there are relatively few bacteria, including *Beggiatoa* and rod-shaped thiobacilli, that oxidize elemental sulfur or sulfide and thiosulfate ($S_2O_3^{2-}$). By producing soluble SO_4^{2-} these bacteria provide a critical service for higher plants needing an accessible form of sulfur for their proteins. They also oxidize H_2S produced by thiopneutes or evolved during biomass decomposition, returning the reduced sulfur to sulfate, the form in which it originally entered living matter. Green and purple sulfur bacteria also use H_2S as the hydrogen donor in their anaerobic photosynthesis.

The reverse reaction—the reduction of sulfate—proceeds along two very different paths, one that keeps sulfur cycling within the biosphere, and another that removes the element for prolonged spells of sedimentary storage. During the first path, the assimilatory reduction, plants reduce sulfate to create the proteins necessary for growth. In mass terms, photosynthesis incorporates about one unit of sulfur for every 1000 units of carbon; in relative terms, various phytomass tissues contain between 0.08 and 0.5 percent sulfur.

Plants obtain the requisite amounts of sulfur predominantly from sulfates in the soil (they can use sulfide, too, and they can also absorb sulfur gases from the atmosphere). They reduce the sulfates to H_2S and incorporate most of it into cysteine and methionine, the two sulfur-containing amino acids. Sulfur is also a constituent of biotin (vitamin H), thiamine (vitamin B_1), and a few other important molecules of life that are not proteins.

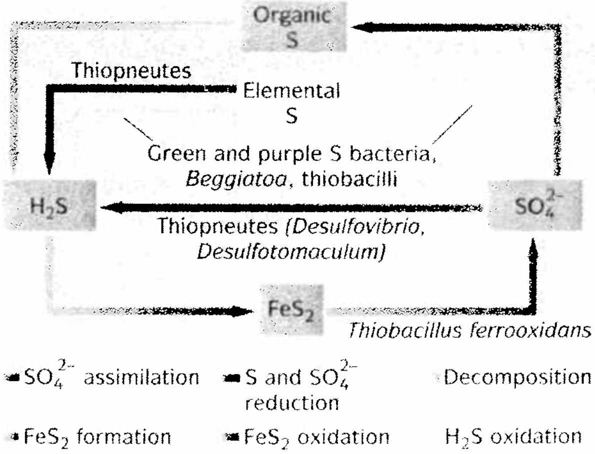
Decomposition returns most of this sulfur to the soil. Organic sulfur, nearly equally split among amino acids and nonprotein compounds, accounts for more than nine-tenths of the total mass of the element in soils; most of the rest is in highly soluble sulfates. The fairly rapid progress of microbial decomposition promotes the efficient recycling of the element within a localized area: plants reduce sulfur, decomposition releases it, mineralization converts it to sulfates, and plants take it up again. This tight cycle has no substantial leak through which the element could be moved to a more persistent reservoir.

In contrast, the importance of the second, dissimilatory, pathway of sulfate reduction is due precisely to the existence of a huge leak diverting large masses of biogenic sulfur into long-term mineral stores. These reductions take place mostly in coastal marine mud at depths ranging from a few millimeters to a few centimeters. There, thiopneute bacteria reduce sulfates to H_2S, as well as a number of more complex compounds, taking most of the required sulfate from the water within the sediments. A large part of the generated H_2S escapes into aerobic mud and water layers, and there it is promptly reoxidized.

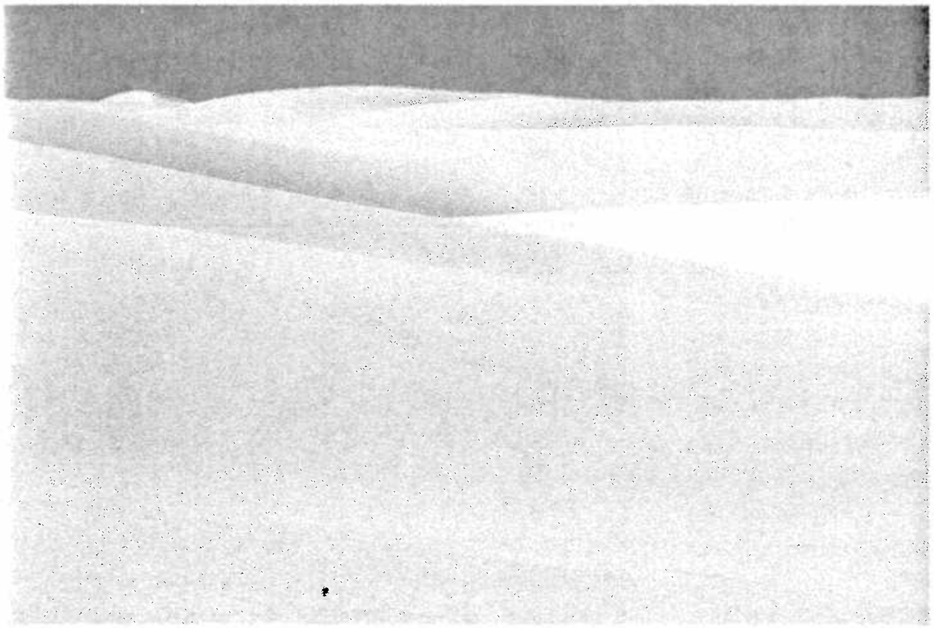
Inside the mud, H_2S can release iron from fine-grained oxides coating sedimentary clays or from other iron-bearing minerals, by reducing the ferric ion (Fe^{3+}) to the ferrous ion (Fe^{2+}). The Fe^{2+} reacts further with H_2S to produce first ferrous sulfide (FeS), whose tiny crystals impart the black pigmentation often seen in tidal muds, and then iron disulfide (FeS_2). The latter mineral, commonly known as pyrite or fool's gold, forms shiny and often fairly large cubic crystals. FeS_2 is a large sink of biospheric sulfur, but not a commercial source of iron: separating so much sulfur from the metal would be too costly.

The conversion of sulfates to sulfides is one of the two oldest biogenic processes of mineral formation, and the precursors of today's thiopneutes appear to be among the earliest organisms that lived on Earth. Through their metabolic activity these bacteria were sequestering substantial quantities of sulfur more than 2.5 billion years ago. And the origin of that process appears to match the age of the oldest known cyanobacterial photosynthesis. In 1993 a Japanese geologist, Hiroshi Ohmoto, and his colleagues described a pyrite deposit in South Africa's Barberton Greenstone belt that bacteria had unmistakably formed through the reduction of seawater sulfate about 3.4 billion years ago.

Researchers can gauge past rates of sulfate reduction by measuring the deviation (in ‰) from the standard ratio of the two most common sulfur isotopes, $^{34}S/^{32}S$. Because their enzymes catalyze reactions with $^{32}SO_4$ faster than reactions with $^{34}SO_4$, sulfate-reducing bacteria cause the seawater to become enriched in ^{34}S. Consequently, a high positive enrichment of seawater during the Cambrian period (590 to 500 million years ago) marks a period of



Several pathways through which bacteria take sulfur, during the cycling of the element in waters and shallow sediments.



Huge gypsum sand dunes in New Mexico's White Sands National Monument, the evaporites of an ancient sea.

high thiopneut productivity. During that period, the amount of FeS_2 formed in marine muds greatly exceeded the amount lost through weathering of exposed continental sulfides. In contrast, when the bulk of the Earth's photosynthesis shifted from the ocean to freshwater swamps during the late Paleozoic and Mesozoic eras (between about 360 and 200 million years ago), the shift brought markedly reduced FeS_2 formation and lowered ^{34}S enrichment.

Volcanic and hydrothermal sources aside, about 95 percent of sulfur's concentrated compounds in the crust are of biogenic origin, products of extensive sulfureta whose existence predates the rise of a highly oxygenated atmosphere. Sulfate reduction remains at the core of the long-term cycling of the element: our best estimates indicate that about 40 Mt S are sequestered yearly as FeS_2, but the actual flux may be substantially higher. Today perhaps the most concentrated biogenic production of elemental sulfur is taking place in the mud flats of the Bay of Bengal, seasonally flooded by high monsoonal tides, where *Beggiatoa* and thiobacilli oxidize H_2S released by sulfate reducers.

The other process that sequesters large amounts of oceanic sulfur needs no help from biota: the evaporation of seawater in shallow basins is a purely inorganic process that takes place in arid climates. As the water evaporates, carbonates precipitate first; sulfate compounds (mostly gypsum, $CaSO_4 \cdot 2H_2O$) form when the volume of water is reduced by 80 percent. The total mass of evaporites in the Earth's crust—dominated by anhydrite ($CaSO_4$)—has been put as low as half of all reduced mineral sulfur, and as high as all pyrites. Sulfate precipitation is a highly episodic process. Only when the action of global tectonics creates extensive shallow lagoons and basins can evaporation sequester massive amounts of sediments. Currently such opportunities are limited, and relatively small amounts of evaporites are being laid down at present.

Sedimentary burial of pyrites and evaporites removes their sulfur beyond the reach of living organisms. Only after undergoing dehydration (converting gypsum to anhydrites), compression and cementing by minerals (most iron sulfides are found in shales and coals), and eventual tectonic uplift or coastline regression, are they reexposed to the biosphere. A new cycle begins with weathering, which now releases annually close to 100 Mt of sulfur from the Earth's crust, about two-thirds from sulfate minerals and the rest from pyrites, to be carried by streams to the ocean.

A complete circuit of the sulfur rock cycle is accomplished only after tens of millions to hundreds of millions of years. We are not sure if the fluxes of the rock sulfur cycle—the element's sequestration in pyrites and evaporites and its eventual return to the ocean via weathering and atmospheric deposition—are closely balanced, or if there are other substantial sulfur sinks.

The sulfur flux was only one of many biospheric flows that changed substantially with the emergence of agriculture. As societies have become increasingly more complex, leading to our high-energy fossil-fueled civilization, their impacts on the three biospheric cycles have become ever greater. Although I will trace these impacts separately for each of the three cycles—looking in every case first at the stages of these expanding interferences and then at the manifold environmental and social consequences—it must be stressed that the changes were commonly concurrent, and often mutually reinforcing.