In this chapter, we will look at some representative global biogeochemical cycles and their role in climate. The elements whose cycles are discussed are intimately connected through the organic processes of photosynthesis and respiration and/or decay. These elements are carbon (C), nitrogen (N), sulfur (S), oxygen (O), and—for completeness, because it is an important biological nutrient—phosphorus (P). We will begin with a discussion of gases whose production or consumption on the earth’s surface is accomplished by biological reactions (biogenic gases) and the possible effects of these gases on the earth’s climate. To set the stage, the greenhouse effect is discussed briefly here.

Greenhouse gases, which are all naturally biogenic in origin, allow incoming shortwave solar radiation to pass through the atmosphere to the earth’s surface, but when part of that radiation (about 45%) is reradiated back toward space as heat (infrared radiation), the gases absorb it and thus retain it in the atmosphere. This is the greenhouse effect. We can thank the natural greenhouse effect for the earth’s equable climate. Without it, the planet would be about 33°C cooler than its mean global temperature of 15°C, that is, –18°C. (See the Global Change Instruction Module The Sun-Earth System, by John Streete.)

There can be, however, too much of a good thing. In recent years, the concentrations of these gases in the atmosphere have been rising because of fossil fuel combustion, biomass burning, rice paddy cultivation, and other human activities. This buildup may absorb increased amounts of outgoing infrared radiation, leading to an enhanced greenhouse effect and global warming.

It is interesting and informative to put this present-day worry in the context of public and scientific concern about climate during the 1950s and 1960s. Between about 1940 and 1970, global mean temperatures remained nearly constant, or even declined slightly. There was considerable discussion and concern in the scientific literature and in public forums about global cooling and perhaps another ice age. Much of the discussion below in the context of global warming is applicable to a scenario of global cooling as well. The difference is that in a global cooling, many of the feedbacks mentioned would act in the opposite direction and would probably have different magnitudes of change.

**The Biogenic Gases and Climate**

It is very likely that during the next century the earth’s climate will change due to natural causes. Changes in the amount of solar radiation received by the planet, in the circulation of the atmosphere and the oceans, and in volcanism can affect climate on this time scale. On the longer time scale, if left to its own recourse, the planet will most likely enter another ice age about 10,000–30,000 years from now.

On the other hand, human-induced climate change during the next century is also very likely. The flywheel of population growth and fossil fuel burning is turning rapidly and will be difficult to slow in this time. The global population is growing at a rate of 1.5% per year, a doubling time of 45 years. This rate of growth implies a population of about 10 billion by 2050. All these people will require energy to sustain themselves and to develop their industries, farms, and cities. Most scenarios of future global energy use project a continuous heavy reliance on fossil fuel into the 21st century. Continued fossil fuel burning will result in continued emissions of CO$_2$, methane (CH$_4$), and nitrous oxide (N$_2$O) to the atmosphere. These greenhouse gases will be accompanied by emissions of trace metals, non-methane hydrocarbons (NMHCs), oxides of sulfur (SO$_x$), and the most reactive oxides of nitrogen (NO and NO$_2$, collectively known as NO$_x$).
The latter three groups of chemical compounds react with other chemical components of the climate system, particularly the hydroxyl radical (OH*). Also, SOx and NOx are the principal constituents in acid deposition, and NOx and NMHCs are involved in the formation of ozone (O3), another greenhouse gas, in the troposphere. The unchecked accumulation of these gases in the atmosphere could lead to an uncomfortably warm planet.

The burning of fossil fuels and the burning of forests and other biomass are the principal human-induced, or anthropogenic, emissions of most biogenic gases to the earth’s atmosphere. Also, fossil fuel burning and changes in land use (such as deforestation) are responsible for many of the global environmental problems the people of the world face today. Fossil fuel burning alone accounts for perhaps 80% of sulfur dioxide (SO2) emissions from the land surface to the atmosphere, 50% of carbon monoxide, 50% of NOx, 20% of methane, 20% of NMHCs, 5% of ammonia, and 4% of nitrous oxide. It is also responsible for 70–90% of anthropogenic CO2 emissions to the atmosphere. This amount is equivalent to about 10% of the natural CO2 emissions from respiration and decay.

As mentioned previously, C, N, P, and S, besides O and hydrogen (H), are the principal elements that make up living matter. The biogeochemical cycles of these elements are intimately coupled through biological productivity and respiration and/or decay. Ecosystems take energy from their surrounding environment. The net result is production of organic matter, more disorder on the planet (increased entropy), and waste. The waste may act as a pollutant. The biogenic gases of carbon, nitrogen, and sulfur are a consequence of this entropy production. Their fluxes maintain the earth’s atmosphere in a state of disequilibrium.

The natural sources of these biogenic gases are processes at the earth’s surface or chemical reactions in the atmosphere. The processes by which biogenic gases and other components cycle through the coupled C-N-P-S-O system, although in some environments operating close to equilibrium, are principally controlled by the rates at which the processes operate.

During the last half century, scientists have tended to specialize. Consequently, most global environmental systems have been little studied or studied only in a piecemeal fashion. Only recently has attention been paid to the coupled earth-surface system of atmosphere, hydroosphere, biosphere, cryosphere, and shallow lithosphere. Basic information on global reservoir sizes and fluxes (e.g., biological productivity) is lacking or is only partly known. An example of this lack of data is the estimates of tropical forest biomass, which vary by a factor of 2 or 3 for Amazonia alone.

It is very unlikely that the anthropogenic fluxes of gases to the atmosphere will substantially decline as we enter the 21st century. Population growth and our global reliance on fossil fuels as an energy source make such a scenario highly improbable. Thus, continued global environmental change is a virtual inevitability. It is likely that, by the middle of the next century, the atmospheric concentration of CO2 will be double what it was before the Industrial Revolution (to date, it has increased about 30%), and concentrations of other greenhouse gases will also increase. Such a change in the composition of the atmosphere portends a strong probability of climate change.

**Historical Framework**

It is worthwhile considering at this stage how the earth’s biogeochemical cycles and climate system functioned prior to human interference. It is impossible to consider the functioning of all the biogeochemical cycles of concern because of space limitations. Only the global biogeochemical cycles of carbon and oxygen are used as examples in this section. We will end with a brief summary of environmental conditions just prior to major human interference in the biogeochemical cycles and climate system.

**Carbon**

Carbon composes approximately 50% of all living tissues. In the form of carbon dioxide, it is necessary for plants to grow. Carbon dioxide also helps to sustain an equable climate on earth. The concentration of carbon dioxide in the
The atmosphere has varied during the geologic past, but has remained within limits that permit life to exist on earth. Carbon dioxide is cycled throughout the spheres of earth on different time scales. We can refer to these scales as short-, medium-, and long-term. Figures 3 and 4 illustrate the processes involved in these time scales.

**The short-term carbon cycle**

Photosynthesis is part of the short-term carbon cycle (on the order of years). We can look at the short-term cycling of carbon as carbon dioxide by beginning with the producers of organic carbon, the plants. Carbon in the form of atmospheric carbon dioxide is removed from the air by plants. This removal occurs both on land—for example, in forests and grasslands—and in water—for example, in lakes, rivers, and the surface waters of the oceans. The primary producers, the photosynthetic phytoplankton and benthic plants in the oceans and plants on the terrestrial surface, transform inorganic carbon as carbon dioxide into organic carbon within their tissues. Light and nutrients, like phosphate and nitrate, are necessary for this reaction to occur. Some of the energy from the light is used in the growth of plants, and some remains stored in the tissues of plants as carbohydrates.

Plants remove about 100 billion tons of carbon as carbon dioxide from the global atmosphere each year, which is about 14% of the atmosphere’s total carbon. Most, but not all, of the carbon dioxide taken from the atmosphere during photosynthesis is returned to the atmosphere during respiration and decay. The annual
removal rate of atmospheric carbon dioxide in photosynthesis is slightly larger on land than in the ocean.

After photosynthesis, carbon may next be transferred to a consumer organism if the plant is eaten for food. The carbon stored in the tissue of the plant enters an animal’s body and is used as energy or stored for growth. Land animals, such as cows and deer, are the primary consumer organisms. Aquatic plants are eaten by zooplankton (small sea animals) and larger animals. When an animal breathes, some of this carbon that was
taken up from plants is released from the animal’s body as carbon dioxide gas.

Besides the carbon stored above ground in living and dead vegetation, there is carbon below ground in the root systems of terrestrial plants. When the plants die, some of this carbon may be released as carbon dioxide or methane gas to the air trapped in the soil, or it may accumulate in the soil itself as dead organic material. This dead organic matter may be ingested by consumer organisms, such as insects and worms living in the soil.

Some of the organic carbon generated in land environments is weathered and eroded, and the organic debris is transported by streams to the ocean. In the ocean, some of this debris, along with the organic detritus of dead marine plants and animals, settles to the ocean floor and accumulates in the sediments. However, some of the debris is respired in the ocean to carbon dioxide. This carbon dioxide may leave the ocean and be transported over the continents, where it is used again in the production of land plants.

The long-term carbon cycle

The long-term carbon cycle (on the order of tens to a hundred million years) requires that we consider the earth’s history over the last 600 million years or so—the period covered by the fossil record. Figure 5 defines the terms and intervals of geologic time.

The long-term cycling of carbon (Figures 3 and 4) involves interconnections between the cycling of the minerals calcium carbonate (CaCO$_3$) and calcium silicate (CaSiO$_3$). This series of processes dates back to the beginning of plate tectonics. This cycling includes not only the land and ocean reservoirs but also that of limestone rocks. Limestone rocks are mainly composed of calcium carbonate and are the fossilized skeletal remains of marine organisms or, less commonly, inorganic chemical precipitates of calcium carbonate. Limestones are great storage containers for carbon. Most of the carbon near the earth’s surface is found in these rocks or in fossil organic matter in sedimentary rocks. Weathering and erosion of the earth’s surface result in the leaching of dissolved calcium, carbon, and silica (SiO$_2$) from limestones and rocks containing calcium silicate.

The dissolved substances produced by weathering are transported to the ocean by rivers. As discussed in on p. 9, they are then used to form the inorganic skeletons of benthic organisms and plankton, which are composed of calcium carbonate and silica. During formation of the calcium carbonate skeletons, the carbon dioxide derived from the weathering of limestone is returned to the atmosphere.

When marine animals and plants die, their remains settle toward the seafloor, taking the carbon stored in their bodies with them. En route, their organic matter is decomposed by bacteria, just as on land. Some shells may dissolve. Thus, animal and plant organic and skeletal matter is turned back into dissolved carbon dioxide, nutrients, calcium, and silica in the ocean. This carbon dioxide is stored in the deeper waters of the
oceans for hundreds to a thousand or so years before being returned to the atmosphere when the deep water moves upward (upwelling), usually because of divergent movements of surface water.

Some of the animal and plant plankton sinks to the bottom, where the carbon in the organic matter and shells escapes degradation and becomes part of the sediment. As the seafloor spreads through plate tectonics, the sediments containing the remains of marine plants and animals are carried along to subduction zones, where they are transported down into the earth’s mantle. At the severe pressures and high temperatures in the subduction zones, organic matter is decomposed and calcium carbonate reacts with the silica found in the subducted rocks to form rocks containing calcium silicate.

During this metamorphism, carbon dioxide is released and makes its way into the atmosphere in volcanic eruptions and via hot-spring discharges. Once in the atmosphere, it can then combine with rainwater. The rainwater falls on the land surface and seeps down into the soils, where it picks up more carbon dioxide from decaying vegetation. This water, enriched in carbon dioxide, weathers and dissolves the compounds of calcium and silica found in rocks of the continents. The cycle begins again.

This series of processes has been active for at least 600 million years, since the advent of the first organisms that made shells (and were therefore the first to leave fossils). The processes were important even earlier in earth’s history, when calcium carbonate was deposited in the ocean by inorganic processes.

Figure 6. Model calculation of atmospheric carbon dioxide during the last 600 million years. The horizontal axis shows time in millions of years before the present (top) and geological time period (bottom). The left vertical axis shows the number of times today’s C level that existed in the atmosphere of the time; the right vertical axis shows the amount of CO$_2$ in the atmosphere. For example, 500 million years ago there was about 14 times as much CO$_2$ in the atmosphere as there is today, with a total amount of about 37 x 10$^{18}$ grams (after Berner, 1991).
Atmospheric CO₂ levels of the past

One outcome of changes in the rates of processes in the long-term biogeochemical cycling of carbon is that atmospheric carbon dioxide has varied in a quasicyclic fashion during the last 600 million years of earth’s history. Robert A. Berner of Yale University and colleagues have developed models of the carbon cycle to calculate these variations. Figure 6 shows the results of one such calculation.

Periods of high atmospheric carbon dioxide levels are the result mainly of intense plate tectonic activity, with increased metamorphism of limestone and release of carbon dioxide to the atmosphere from volcanoes. These high carbon dioxide periods are often referred to as hothouses or greenhouses. They are also periods of relatively high sea level; for example, in the Cretaceous and Cambrian periods, much of what would become the present continent of North America was covered by water. This flooding of the continental landscapes was due principally to the large size and volume of the midocean ridges, caused by intense plate tectonic activity. The increase in ridge volume led to the displacement of ocean water onto the continents of the time.

Periods with lower atmospheric carbon dioxide levels, such as the Carboniferous through Triassic and much of the Cenozoic, are the outcome of less intense plate tectonic activity and increased removal of carbon dioxide from the atmosphere by weathering. These intervals, which include the present era, are extended cool periods (ice houses) in the climatic history of the earth. They are also times of relatively low sea level due to a decrease in the volume of the midocean ridges.

Biological and other factors also play a role in regulating atmospheric carbon dioxide levels over the long term. For example, the lowering of atmospheric CO₂ from the high levels of the mid-Paleozoic era, about 400 million years ago, was not simply the result of the waning intensity of plate tectonic processes. It followed the evolution of land plants, which withdrew CO₂ from the atmosphere by photosynthesis. Similarly, the lowering after the Cretaceous period, about 100 million years ago, followed the appearance of flowering plants, which resulted in an increase in weathering rates and withdrawal of CO₂ from the atmosphere.

The important point is that atmospheric CO₂ has varied by a factor of perhaps more than ten during the last 600 million years of the earth’s history. This variation certainly has had climatic implications, because CO₂ is an important greenhouse gas. In fact, for much of the last 600 million years, the planet had a different atmospheric composition and a more equable climate than that of today.

The medium-term carbon cycle

Medium-term cycling of carbon dioxide (millions to tens of millions of years) involves organic matter in sediments; coal, oil, and gas; and atmospheric oxygen (Figures 3 and 4). It commences, as does the short-term cycling, with the removal of carbon dioxide from the atmosphere by its incorporation into plants and the accumulation of the dead plant and animal carbon in sedimentary organic matter (the dead and fossilized remains of plants and animals). When dispersed throughout a sedimentary rock, this organic matter is termed kerogen. Shales are very fine-grained sedimentary rocks that are often rich in kerogen. Coal, oil, and gas deposits are also the altered remains of the soft tissues of plants and animals which have accumulated in a geographically restricted area.

Coal is derived mainly from terrestrial plant material, which is often deposited in swampy environments. The plant material is altered when the swamp sediments are buried. If buried deep enough, the dead plant material may be substantially changed because of the increased temperatures and pressures at depth. Different types of coal are formed by varying conditions of temperature and pressure. Anthracite—a hard, dense, black coal—is formed by alteration of plant material at a relatively high temperature and pressure. Bituminous, brown coal is formed under less intense conditions. Peat, used as a fuel in some parts of the world, is little-altered plant material that has not been buried deeply. It is high in carbon. Peat is an important component of tundra areas in the Northern Hemisphere.

Oil and gas represent highly altered organic matter, principally the altered remains of marine
phytoplankton that were deposited on the seafloor. During burial, these organic materials are broken down at elevated temperature and pressure, forming oil and gas. The oil and gas may migrate hundreds of miles in the subsurface before coming to rest in large accumulations in the voids of rocks. Often, oil and gas are formed in shales; but as temperature and pressure increase with depth, they move to more coarse-grained rocks like sandstones and limestones. It is in these latter rocks, dating from the Cretaceous and Cenozoic periods, that the great oil and gas reserves of the world are found, like those of the Persian Gulf.

These deposits of coal, oil, and gas come from organic carbon that has escaped respiration and decay. Thus, they represent carbon dioxide that has been removed from the atmosphere. The same is true of the kerogen dispersed as fine-grained materials in the sedimentary rocks. Because these materials were buried, the oxygen that would have been used in their decay has remained in the atmosphere. Eventually, however, the carbon in these deposits and in kerogen is recycled into the atmosphere, returning carbon dioxide to that reservoir and removing oxygen. This happens when these fossil fuel deposits and kerogen are uplifted by plate tectonic forces after millions of years of burial and exposed to the atmosphere. When this occurs, the oxygen that previously accumulated in the atmosphere reacts with the coal, oil, gas, and kerogen. The reaction involves the decay of these organic materials in the presence of oxygen (equation 5). This results in the removal of oxygen from the atmosphere and the return of carbon dioxide to the atmosphere. The ongoing dynamic cycle is complete.

Fossil fuel is a nonrenewable energy source, because coal, oil, and gas deposits take millions of years and specific environmental conditions to form. The mining of these deposits brings these materials back to the surface much more rapidly than natural processes do. The stored energy from the long-dead organisms is released in the form of heat when the coal, oil, and gas are burned. This fossil fuel energy keeps us warm, powers our cars, and moves the machinery of industry. It is also a main cause of environmental pollution, because a byproduct of fossil fuel burning is the release of gases and particulate materials into the environment. Climatic change is an important potential global environmental effect of the release of carbon dioxide and other gases to the atmosphere by combustion.

In summary, carbon is found in all four major surface spheres of the earth. In the ecosphere, it is essential to every life form, occurring in all organic matter. In the atmosphere, it is found as the gases carbon dioxide, methane, and several other compounds. It occurs as carbon dioxide dissolved in lakes, rivers, and oceans in the hydrosphere. In the earth’s crust—part of the lithosphere—it is found as calcium carbonate originally deposited on the seafloor, as kerogen dispersed in rocks, and as deposits of coal, oil, and gas. It is because carbon is stored in the large sedimentary reservoirs of limestone and fossil organic carbon, and not in the atmosphere, that life on earth is possible. If all this carbon were stored in the atmosphere, there would be about 30 times the existing amount of CO₂. The result would be a substantial heating of the atmosphere because of the increased absorption of the long-wave infrared radiation emitted from the surface of the earth. The greenhouse effect would be very strong, and our planet would probably have a temperature like that of Venus: 460°C!

**Oxygen**

Oxygen composes 20.9% of the gases of the atmosphere. The cycling of oxygen (Figure 7) is strongly coupled to that of carbon (Figure 4). Oxygen is produced by plants during photosynthesis, when carbon dioxide is consumed. It is removed by respiration and decay, when carbon dioxide is produced. This is a short-term, nearly balanced cycle on land, because the amount of oxygen produced yearly by land plants is about equivalent to the amount they use in the processes of respiration and decay. On average, it takes about a decade for oxygen and carbon dioxide to cycle through living plants. However, a little terrestrial organic matter that has not undergone respiration or decay, such as leaves and trunks of trees and smaller-sized organic debris, leaks from the land to the ocean via rivers. In the ocean, some of this organic detritus escapes destruction and is deposited in the sediments.
In the oceans, phytoplankton produce slightly more oxygen than is consumed during the respiration and decay of marine life. As a result, oxygen is released to the atmosphere. The organic carbon not decayed by this oxygen, along with some of the terrestrial organic detritus mentioned in the preceding paragraph, is deposited on the seafloor and accumulates in the sediments of the ocean. If this accumulation were not counteracted by other processes, and no other factors were to intervene, all the carbon dioxide in the atmosphere would disappear in less than 10,000 years. The oxygen content of the atmosphere would double in less than several million years. Fortunately, the overproduction of oxygen in the oceans is balanced by the weathering of fossil organic carbon and other materials in rocks on land. During this process, carbon dioxide is returned to the atmosphere.

If the burial of organic carbon in sediments were enhanced, oxygen might accumulate in the atmosphere. In fact, it seems to be the case that times of high organic carbon burial in the past gave rise to high atmospheric oxygen levels. Figure 8 is a model calculation of atmospheric oxygen concentration variations during the last 600 million years. Just before the Carboniferous, vascular plants evolved and spread over the continents. Their remains were a new source of organic matter resistant to degradation by atmospheric oxygen. During the Carboniferous and Permian, large quantities of vascular plant organic matter were buried in the vast coastal lowlands and swamps of the time. This material became the coal deposits mined from rocks of Carboniferous and Permian age today. This large accumulation of organic matter gave rise to the high atmospheric oxygen levels of the late Paleozoic. Coal deposits are also important in Cretaceous- and early Cenozoic–age rocks, another time of high atmospheric oxygen concentrations.

**Environmental Conditions Before Human Interference**

From the above discussion, we can conclude that the carbon and oxygen biogeochemical cycles have changed throughout geologic time. These changes have led to changes in atmospheric composition and climate. Just prior to significant human interference in the ecosphere, environmental conditions were also changing naturally because of a variety of factors. These factors include external forcings, such as changes in the orbit of the planet earth and in the flux of solar radiation to the planetary surface, and internal forcings, involving the behavior of the earth’s ocean-atmosphere-land-biota-cryosphere system.

For about 1.6 million years, the earth has experienced a series of cold and icy times known as ice ages or glacial stages. These periods of extensive glaciation of the continents alternated with shorter and warmer periods, interglacial stages like today. During the interglaciations, the great glaciers that covered the continents of Europe and North America to depths of two kilometers or more melted. The glaciers retreated to geographical positions similar to those of the present continental ice sheets of Greenland and Antarctica. As the glaciers waxed and waned...
through the last 2 million years, global temperatures went up and down, as did sea level. The composition of the atmosphere and other environmental conditions changed.

The earth, before extensive human interference in its biogeochemical cycles, was recovering from the climax of the last great glaciation 18,000 years ago. The recovery has not been smooth. There have been times in the past 18,000 years when the planet cooled quickly. Also, there have been periods when the earth was warmer than today. However, during the past several centuries, the global environment has changed substantially and rapidly. Atmospheric trace gas concentrations, matter in runoff, temperature, and other indicators have increased in magnitude. A major reason for all the changes is the impact of human activities on the environment.

Figure 8. Model calculation of atmospheric oxygen during the past 600 million years. The dashed line across the figure shows today’s atmospheric concentration of O₂. The left vertical axis shows the atmospheric O₂ level; the right vertical axis shows O₂ as a percentage of the total atmospheric gases. The horizontal axis shows time in millions of years before the present and geological time period (after Berner and Canfield, 1989).