1 Fuels and the global carbon cycle

Fuels are substances that are burned to produce energy. In many practical situations, it can be advantageous first to carry out one or more processing steps on a fuel before it is burned. This might be done to improve the yield of the fuel from its source, to improve the performance of the fuel during combustion, or to mitigate potential environmental problems resulting from using the fuel. Examples include processes to enhance the yield of gasoline from petroleum, to improve gasoline performance in engines, and to convert solid coal into cleaner gaseous or liquid fuels. Some fuels, particularly natural gas and petroleum, also serve as important feedstocks for the organic chemical industry, for producing a host of useful materials. So, fuels can be used in at least three different ways: burned directly to release thermal energy; chemically transformed to cleaner or more convenient fuel forms; or converted to non-fuel chemicals or materials. These uses might appear quite different at first sight, but all have in common the making and breaking of chemical bonds and transformation of molecular structures. The ways in which we use fuels, and their behavior during conversion or utilization processes, necessarily depend on their chemical composition and molecular structure.

The world is now in a transition state between an energy economy that, in most nations, has an overwhelming dependence on petroleum, natural gas, and coal, to a new energy economy that will be based heavily on alternative, renewable sources of energy, including fuels derived from plants. This book covers both. The dominant focus is on wood, ethanol, and biodiesel among the plant-derived fuels, and on coal, petroleum, and natural gas as traditional fuels. If we were to assemble a collection of examples of each, at first sight they would appear to be wildly different. Natural gas, a transparent, colorless gas, commonly contains more than ninety percent of a single compound, methane, at least as delivered to the user. Ethanol, a transparent, volatile, low-viscosity liquid, is a single compound. Petroleum is a solution of several thousand individual compounds. Depending on its source, the color, viscosity, and odor can be very variable. Biodiesel, a lightly colored, moderate viscosity liquid, contains only perhaps a half-dozen individual compounds. Wood, a heterogeneous solid, is usually of light color, but varies in density, hardness, and color, depending on its source. Coals usually are black or brown heterogeneous solids of ill-defined and variable macromolecular structure.

Despite these apparent differences, there are two very important points of commonality. First, all of these fuels occur directly in nature or are made from materials that occur in nature. The second point becomes apparent when we consider the chemical compositions of representative samples, see Table 1.1.

Table 1.1 Chemical compositions, in weight percent, of representative samples of the major fuels covered in this book. The data for wood and coal do not include moisture that might be present in these materials, or ash-forming inorganic constituents.

	Carbon	*Hydrogen*	*Oxygen*	*Nitrogen*	*Sulfur*
Biodiesel	76	13	11	0	0
Coal, bituminous	83	5	8	1	3
Ethanol	52	13	35	0	0
Natural gas	76	24	0	0	0
Petroleum	84	12	1	1	2
Wood, pine	49	6	45	0	0

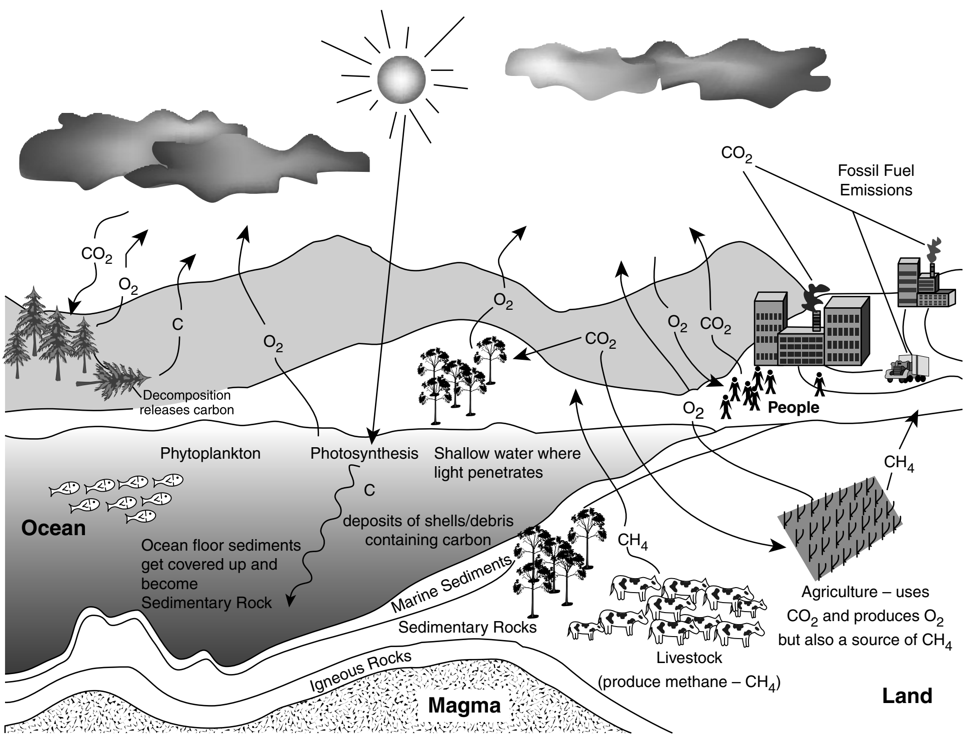

Figure 1.1 The global carbon cycle, one of the major developments in the earth sciences, allows us to account for the distribution of carbon among the atmosphere, biosphere, and geosphere, and account for the interchange of carbon.

In every case the predominant element, on a mass basis, is carbon. These two points establish a starting place for a study of the chemistry of fuels: the transformations of carbon in natural processes. We will see also that all of these have something else in common – they represent stored solar energy.

The transformations of carbon in nature are conveniently summarized in a diagram of the global carbon cycle, see Figure 1.1.

The global carbon cycle establishes the fluxes of carbon among various sources that introduce carbon into the total environment, and among sinks, which remove or

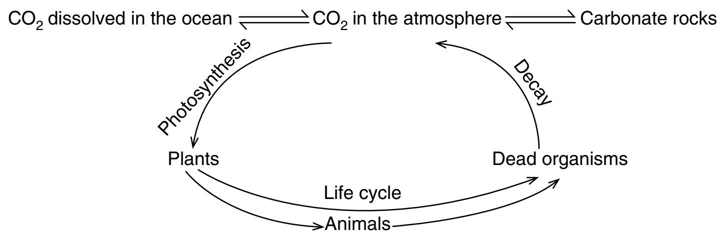

Figure 1.2 This simplified sketch of the global carbon cycle focuses on processes of particular interest in fuel chemistry. Atmospheric carbon dioxide is incorporated into plants by photosynthesis. The life cycle of living organisms terminates in decay, which returns the carbon to the atmosphere as CO_2.

sequester carbon. An understanding of the directions of flow and annual fluxes among the sources and sinks has become especially important in recent decades, with increasing concern and focus on atmospheric carbon dioxide concentration and its consequence for global climate change. The world can be thought of as consisting of: the atmosphere; the hydrosphere, dominated by the global ocean; the lithosphere, the crust and upper mantle of solid Earth; and the biosphere, living organisms on, and in, Earth. For the purpose of fuel chemistry, Figure 1.1 can be simplified to the cyclic process of Figure 1.2.

Two equilibria of atmospheric carbon dioxide with natural systems will henceforth be neglected: incorporation of carbon dioxide into carbonate rocks and its release when these rocks are transformed or destroyed; and dissolution of carbon dioxide into the ocean, or its coming back out of solution. Both processes have great importance in the global carbon cycle, but neither has a significant role in formation and use of fuels.

In principle one can start at any point in a cycle and work through it, eventually to return to the start. For this simplified global carbon cycle (Figure 1.2), the atmosphere makes the most convenient starting point. A single compound, carbon dioxide, represents 99.5% of the carbon in the atmosphere (though CO_2 itself is a minor component of the atmosphere, about 0.035% by volume). Green plants remove carbon dioxide from the atmosphere by the process of photosynthesis. The energy in sunlight drives photosynthesis, hence the prefix “photo.” (Chapter 2 discusses the chemical details of photosynthesis.) Arguably, photosynthesis is the most important chemical reaction on the planet. Though some life forms do not depend in some way on photosynthesis [end note A], the majority certainly do. Almost all living organisms either use photosynthesis directly or, like us, rely on other organisms that are capable of photosynthesis. Our food consists of plants, or of parts of animals that themselves ate plants. Direct use of plants (e.g. wood) or plant-derived substances (e.g. ethanol and biodiesel) as fuels means that we utilize the solar energy accumulated in the plants during their growth.

Plants proceed through their life cycles and eventually die, or might be eaten by animals that, in turn, live through their life cycles and die [B]. The convenient euphemism “organic matter” denotes the accumulated remains of dead plants and animals. Eventually, organic matter decays, usually as a result of action of aerobic bacteria, releasing its carbon back to the atmosphere as carbon dioxide and closing the carbon cycle. The decay process is responsible for the fact that dead organisms disappear from the environment [C]. On a walk in a forest, for example, we do not wade hip-deep in the

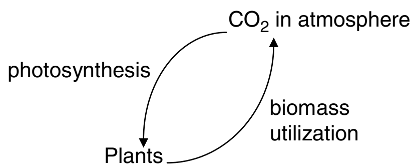

Figure 1.3 Use of biofuels represents a "short-circuit" in the global carbon cycle. CO_2 produced by burning biofuels is removed from the atmosphere by photosynthesis when the next crop of biomass is grown. In principle there should be no long-term net increase in atmospheric concentrations of CO_2.

accumulated fallen leaves from decades' worth of autumns – leaves from years past are gone because they have decayed.

Photosynthesis converts atmospheric carbon dioxide to glucose [D]:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2.$$

Glucose is an example of a simple sugar. Its molecular formula could be rewritten as $C_6(H_2O)_6$ as if it were some sort of compound of carbon and water. The apparent compositional relationship of sugars to a hydrated form of carbon gives the name of this class of compounds – carbohydrates. These sugars play an important role in the biochemistry of plants, acting as an energy source and chemical starting material for the biosynthesis of many other compounds involved in the life processes of the plant. Although the net equation for photosynthesis appears to be fairly simple, the chemistry of photosynthesis is vastly more complicated than implied by this simple equation. Unraveling the chemistry of photosynthesis produced at least one Nobel Prize in chemistry. Oxygen is also a product of photosynthesis. The evolution of photosynthetic organisms about three billion years ago allowed oxygen to accumulate in the atmosphere; that in turn made possible the development of life forms that utilize oxygen (including us).

Any organism can consist of hundreds, thousands, possibly tens of thousands of individual chemical components. Decay of accumulated organic matter involves the oxidation reactions of these thousands of compounds. For simplicity, though, consider the oxidative decay of glucose:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O.$$

It can be seen by inspection that an attempt to sum the photosynthesis and decay reactions would result in all terms canceling, i.e. no net output, and the cycle is indeed closed,

$$\cancel{6\,CO_2} + \cancel{6\,H_2O} \rightarrow \cancel{C_6H_{12}O_6} + \cancel{6\,O_2},$$
$$\underline{\cancel{C_6H_{12}O_6} + \cancel{6\,O_2} \rightarrow \cancel{6\,CO_2} + \cancel{6\,H_2O}},$$
$$\text{net} = 0.$$

At some point very early in human evolution, roughly a million years ago, our ancestor *Homo erectus* learned to burn plants as a source of heat for comfort and for cooking, and likely too in the early development of smelting metals and firing pottery. Grasses and wood were probably the earliest fuels of choice. Sometimes it can be more useful to take only portions of plants, such as the oils used for energy storage in seeds or nuts, for conversion to fuels. Regardless, organisms harvested for use as energy sources represent biomass energy. Fuels made from components of such organisms can be called biofuels. Use of biofuels represents a "short circuit" of the global carbon cycle, see Figure 1.3.

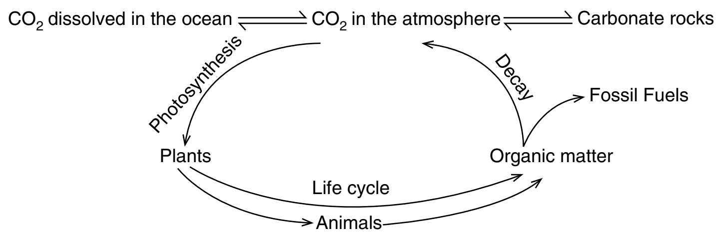

Figure 1.4 Formation of fossil fuels is a “detour” in the global carbon cycle. About one percent of accumulated organic matter does not decay, but is preserved in the Earth, where a succession of biochemical and geochemical processes transforms the organic matter to fossil fuels.

Most of the focus on biomass energy and biofuels is on plants or plant-derived materials. In part, this is because of the vastly greater mass of plant material available, compared to animals. However, in the developing world, animal dung has been, and still is, dried and used as fuel; animal fat, lard, offers a superb replacement for petroleum-derived fuel oils. Two major considerations drive the current interest in biofuels: First, in principle, biofuels are renewable. For instance, a crop of soybeans harvested this year for production of biodiesel fuel could be re-grown next year to produce more biodiesel, and again the year after that, and on and on. Second, again in principle, biofuels have no net impact on atmospheric carbon dioxide; i.e. they are said to be CO_2-neutral. The amount of CO_2 released by burning a biofuel would be absorbed from the atmosphere during the growth of next year’s crop. Both considerations can be challenged in practice. Concerns can be raised about prospects of soil depletion and about the danger of long-term reliance on monocultures. Over the whole life cycle of a biofuel, petroleum and natural gas would probably be used in farming and transportation of the biomass, and in its processing. Despite these concerns, biofuels enjoy both increasing public interest and increasing use.

Currently, though, the mainstay of the energy economy in industrialized nations is energy from coal, petroleum, and natural gas. In the United States, about half of the electricity used is produced in generating plants that burn coal. All of the coke used as fuel and reducing agent in iron-making blast furnaces is made from coal. Natural gas dominates for home heating, except in all-electric homes, and is growing in importance in electricity generation. About 98% of the transportation energy comes from petroleum products. Oil sands, especially those in Canada, are rapidly increasing in importance. Nothing in Figure 1.2, however, accounts for the world’s enormous deposits of coal, petroleum, natural gas, oil sands, and oil shales. Multiple lines of evidence, especially for coals and petroleum, show that they derived from once-living organisms. This evidence is discussed in Chapter 8. Because these substances derive from organisms, commonly they are referred to as fossil fuels, from the definition of a fossil as being a remnant of past life preserved in the Earth’s crust. Fossil fuels occur because the decay process is not perfectly effective. Some 98–99% of accumulated organic matter indeed decays as indicated in Figure 1.2. The remaining small fraction is preserved against decay, and, over geological time, turns into the materials that we recognize today as the fossil fuels. Formation of fossil fuels can be considered as a detour in the global carbon cycle, see Figure 1.4.

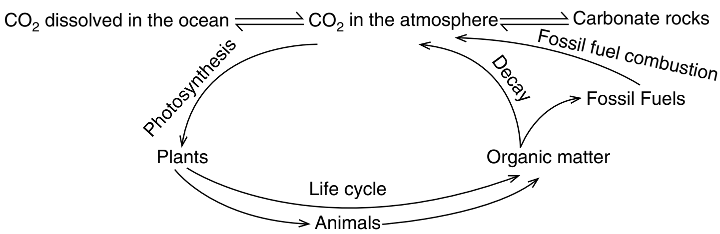

Figure 1.5 Combustion of fossil fuels completes the cycle, releasing the carbon stored in the fuels into the atmosphere as CO_2.

Thus the origin of the vast deposits of fossil fuels on which we depend so much for our energy economy lies in the fact that a seemingly simple reaction – decay – goes "only" 98–99% to completion. Since the fossil fuels derive from once-living plants that had accumulated energy from sunlight, fossil fuels themselves represent a reservoir of stored solar energy.

However, Figure 1.4 is not complete. Even if <1% of the carbon proceeded through the detour to fossil fuels, running the cycle enough times eventually would result in all the carbon being locked up in fossil fuels. The missing link in Figure 1.4 is the eventual fate of the fossil fuels: they are extracted from the Earth and burned.

Burning fossil fuels (Figure 1.5) inevitably liberates carbon dioxide. Combustion of methane, the dominant ingredient of natural gas, provides an example:

$$CH_4 + 2\,O_2 \rightarrow 2\,H_2O + CO_2.$$

For the global carbon cycle to be at steady state, the rates of removing CO_2 from the atmosphere and adding it to the atmosphere must be equal. The important step for CO_2 removal is photosynthesis. CO_2 returns to the atmosphere from burning biomass or biofuels, decay of organic matter, and burning fossil fuels. When the flux of carbon dioxide into the atmosphere exceeds the flux of carbon into the sinks, concentration of CO_2 in the atmosphere necessarily must increase. A wealth of solid evidence shows that atmospheric CO_2 has been increasing for some time, Figure 1.6 being an example. Carbon fluxes from the sources are indeed outrunning fluxes back into the sinks.

In recent decades, multiple, independent observations from geology, meteorology, and biology show that profound changes are occurring on the planet. These observations include partial melting of the polar ice caps, shrinkage of glaciers, increasing desertification, spreading of tropical diseases, and setting of new records for high temperatures and for frequency of severe storms. All of these observations are consistent with the notion that our planet is warming.

The principal source of warmth on Earth is incoming radiation from the sun. To maintain a heat balance, heat is radiated from Earth back into space, largely as infrared radiation. Carbon dioxide is one of a number of gases, others including water vapor, methane, nitrous oxide, and chlorofluorocarbons, that trap infrared. Increasing atmospheric CO_2 concentration acts to retain more heat, by reducing the amount of infrared energy radiated back to space [E]. Hence increasing CO_2 links with increasing warming. While global temperatures and atmospheric CO_2 concentrations appeared to have cycled up and down a long way back into Earth's history – long before humans even evolved – a profound piece of circumstantial evidence connected with the present

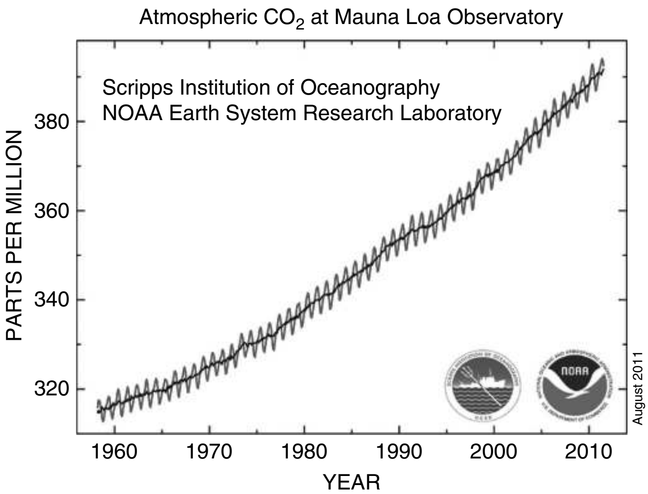

Figure 1.6 The concentration of carbon dioxide in the atmosphere has been rising for many years. The present scientific consensus is that the steadily increasing use of fossil fuels worldwide is a major (but not the only) contribution to this increased CO_2 concentration.

warming cycle is that the increase in atmospheric CO_2 over the past several centuries began at about the same time as the Industrial Revolution, which marked the beginning of large-scale use of fossil fuels. It took millions of years to form fossil fuels. We have been burning them on a large, and ever-increasing, scale only for about 250 years. Thus the rate of CO_2 addition to the atmosphere currently outstrips the rate of CO_2 removal.

Buttressing this circumstantial evidence [F], recent years have seen further evidence added for a link between increased atmospheric carbon dioxide and human use of fossil fuels. Certainly, anthropogenic CO_2 emissions from fossil fuel combustion are not the sole cause of global warming. Nevertheless, connections between global warming, atmospheric CO_2, and fossil fuel use confront us with several energy policy options. One, of course, is to do nothing. At the other end of the spectrum lies the argument that we must stop using fossil fuels *right now*.

History teaches us that some 60 to 70 years are needed for one fuel to replace another as the dominant energy source. In 1830, renewable fuels (mainly wood) dominated worldwide primary energy sources, accounting for more than 90% of total energy. Coal made up most of the rest. By 1900, the contribution from wood had dropped, and that of coal had increased, to a point at which both energy sources were accounting for nearly 50% of world energy use, with a very small contribution from petroleum. Coal dominated the world energy scene until 1965, when coal and petroleum each contributed about 30%, with natural gas and renewables about 15% each. Since 1965 petroleum has dominated the world energy scene. Perhaps at the end of another 70 year cycle, sometime around 2035, we will witness a resurgence of renewable energy sources, not just biomass, but also solar, wind, and other forms that do not involve combustion.

It is likely that we are now somewhere in the "transition state" between an energy economy heavily dominated by fossil fuels and a new one based on alternative energy sources. Plants, or fuels derived from plants, will contribute to the alternative energy mix. We need to understand the chemistry of these biofuels, but also to recognize that fossil fuels will be with us for decades to come, so we should be concerned with their conversion to clean, efficient fuel forms. Furthermore, we should recognize that, at the end of the transition, fossil fuels will be important sources of graphite, activated carbon, and other carbon-based materials.

Notes

[A] The recently discovered *Desulfatomaculum* bacteria provide an example. These remarkable organisms exist by reducing sulfate ions to hydrogen sulfide. They have flourished for several million years at depths to four kilometers in a gold mine near Johannesburg. Organisms able to manufacture their own compounds for use as energy sources are called autotrophs. By far the most familiar autotrophs are the green plants. Microorganisms living near deep-sea vents, where conditions are extremely hostile for ordinary life (such as 400°C, 25 MPa, and pH ≈3), obtain energy by using heat from the vents for oxidizing inorganic sulfides or methane. Organisms that rely entirely on chemical reactions to manufacture their biochemical energy sources are chemoautotrophs. Especially weird are the radiotrophs, fungi found growing inside reactors at Chernobyl, Ukraine, that seem to utilize the energy in radiation to help synthesize needed biochemical energy sources. Organisms that must rely on eating other organisms to obtain a supply of energy are heterotrophs. We are heterotrophs.

[B] Sooner or later, biology catches up to all of us. The expression "Mother Nature bats last," the origin of which has been attributed to numerous individuals, has appeared on bumper stickers for at least a decade. Or, as the American author Damon Runyon (1880–1946) said, "in life, it's 6 to 5 against," meaning the odds are against us.

[C] We will not consider the decay process in detail, because it destroys the raw material (organic matter) needed eventually to produce coal, petroleum, and natural gas. For learning more about the decay process in nature, the book *Life in the Soil* (James B. Nardi, University of Chicago Press) is an excellent place to start.

[D] Note that oxygen is a co-product. The first organisms using water as the source of electrons in photosynthesis – the cyanobacteria – evolved approximately three billion years ago. This development in the history of life allowed O_2 to accumulate in the Earth's atmosphere. Chemically, this converted the atmosphere from a reducing environment to an oxidizing one, with profound implications for the further evolution of life.

[E] While it is common to speak of the greenhouse gases acting to trap infrared radiation, they neither trap all of the radiation nor trap it permanently. Absorption of infrared by a greenhouse gas molecule excites the molecule to a higher vibrational energy state. Energy is released when the molecule returns to its ground state, but the energy is released in all directions, re-radiating a portion of it back to Earth.

[F] Two of the finest minds of the nineteenth century provide contrasting opinions on the validity of circumstantial evidence. Henry David Thoreau tells us that, "Some circumstantial evidence is very strong, as when you find a trout in the milk." But Sherlock Holmes cautions that, "Circumstantial evidence is a very tricky thing. It may seem to point very straight to one thing, but if you shift your point of view a little, you may find it pointing in an equally uncompromising manner to something entirely different."

Recommended reading

Cuff, David J. and Goudie, Andrew S. *The Oxford Companion to Global Change*. Oxford University Press: New York, 2009. This is a very handy one-volume reference book with several hundred short articles, including useful material on the global carbon cycle, biomass and biofuels, and fossil fuels.

McCarthy, Terence. *How on Earth?* Struik Nature: Cape Town, 2009. An introductory book on geology with superb color illustrations. Chapter 3, on the Earth's atmosphere and oceans, is relevant to the material in this chapter.

Richardson, Steven M. and McSween, Harry Y. *Geochemistry: Pathways and Processes*. Prentice-Hall: Englewood Cliffs, NJ, 1989. A book on geochemical principles presented in the context of thermodynamics and kinetics. Chapter 4, on the oceans and atmosphere, and Chapter 6, on weathering of rocks, are useful for understanding the global carbon cycle.

Schobert, Harold H. *Energy and Society*. Taylor and Francis: Washington, 2002. An introductory text surveying various energy technologies and their impacts on society and on the environment. Chapter 34 discusses the global carbon cycle and introduces the concept of biomass energy being a short-circuit in the cycle.

Vernadsky, Vladimir I. *The Biosphere*. Copernicus: New York, 1998. This book was first published in 1926, and provides a remarkable discussion of how living organisms have transformed the planet, including the geochemical cycling of elements and the ways in which organisms utilize geochemical energy. The edition listed here is extensively annotated with explanations and findings through the 1990s.

Williams, R.J.P. and Fraústo da Silva, J.J.R. *The Natural Selection of the Chemical Elements*. Clarendon Press: Oxford, 1996. This book presents aspects of the physical chemistry of distribution of chemical elements between living and non-living systems. Chapter 15 on element cycles includes a discussion of the global carbon cycle; other chapters also contain useful discussions of the partitioning of carbon between various natural systems.