

CARBON IN THE GEOBIOSPHERE  
— EARTH'S OUTER SHELL —

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# Carbon in the Geobiosphere — Earth's Outer Shell —

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## Preface

What is the importance of carbon on Earth? Why at this time devote a book to its discussion? Carbon is essential in all biological processes and in a great variety of mineral and inorganic processes near the Earth's surface. Carbon is the chemical element that is the main building block of living organic matter, and no evidence has been found so far of the existence of non-carbon-bearing life forms. Carbon in the atmosphere and waters is critically important to plants that make their organic matter from carbon dioxide and water and produce oxygen in the presence of light and the nutrients nitrogen, phosphorus, and bioessential trace elements, in a process known as photosynthesis. In the absence of light, where life exists below the Earth's surface and in the deep ocean, carbon dioxide is also involved in the production of organic matter. In addition, carbon dioxide in the atmosphere acts as a greenhouse gas that helps maintain temperatures suitable to life and life processes as we know them and an equable climate. Furthermore, carbon dioxide dissolved in rain water makes an acidic solution which, when falling on land, leads to the weathering of minerals and rocks, erosion of land, and transport of dissolved and particulate materials to the ocean.

We chose for the title of this book *Carbon in the Geobiosphere* to convey the view that the naturally occurring inorganic and organic forms of carbon and, in particular, carbon dioxide always played an environmentally important role within that part of the planet Earth that is the home to all living organisms, collectively known as the biosphere. Most of the plants and animals in the biosphere inhabit the region of the Earth's surface that is affected by processes occurring beneath as well as above it. As the book focuses on the integrated, interactive system of the atmosphere, oceans, continental waters, living biota, soils, minerals and organic matter in sediments, and near-surface and deeper interior, we use the term *Outer Shell of the Earth* as extending from the surface to the base of the lithosphere, at a mean depth of  $-150$  km, and to about  $+30$  km above the surface, a layer that contains most of the mass of the atmosphere. This shell comprises the geobiosphere with the lower atmosphere, continental, subsurface, and oceanic waters, the biosphere, and the sedimentary and crystalline lithosphere that contain carbon or react chemically with its species in the gaseous phase and natural waters. Among all the organisms, from bacteria to plants and animals, the humans have so far been the strongest and fastest agents of environmental change that affects the geobiosphere. The human species as a geologic agent modifies the Earth's surface environment not only through emissions of gases from the burning of fossil fuels, but also through numerous industrial and agricultural activities that lead to changes in the Earth's vegetation cover, the atmosphere, the quality of soils and groundwaters, concentration of various metals in the geobiosphere, changes in the water regime of rivers and lakes, and a variety of chemical and biological changes that are broadly known as pollution. Such human-induced changes affect the cycles of carbon and other nutrient elements linked to it that are of fundamental importance to life on Earth.

A great deal of attention has been paid in recent years to issues associated with the accumulation of carbon dioxide in the atmosphere, sources of emissions of the gas to the atmosphere and its removal processes, and the future time course of accumulation under different scenarios of growth of the human population and its use of fossil fuels, forest materials, and other natural resources. Human concerns about global warming have become a part of everyday discourse on how increasing carbon dioxide levels might affect the future climate of the world and what are the possible environmental, social, and economic implications of climatic change for human societies worldwide and for different nations of the world. This attention has led to a strong growth and diversification in scientific research and literature on the history and present situation regarding carbon dioxide in the Earth's atmosphere, and a search for reliable indicators in the geological record of past atmospheric carbon dioxide concentrations.

The issues of carbon dioxide in the atmosphere and its potential effects on the global climate represent changes that are gradual but concern all of humankind. Thus it is understandable that responses to the carbon dioxide accumulation in the atmosphere and its future consequences are, and will be, driven to a large extent in the near future by economic, social, and political considerations of societies in different regions of the world. However, for humans to be informed about the basic environmental issue of global warming, it takes considerably more insight into the functioning of the planet Earth than can be gained from reading the popular press, or from other news media, to understand why and how the concentration of carbon dioxide in the atmosphere—that is a relatively very small reservoir of carbon on a global scale—has been changing in the course of Earth's history, and what were and will be the consequences of such changes. The time scale of anthropogenic emissions of carbon dioxide from the increasing consumption of wood and natural biomass, coal, oil, and natural hydrocarbon gases includes less than three centuries of the present industrial age. The effects of these emissions on the chemical composition of the atmosphere and other processes taking place on the Earth's surface can be measured against the longer-term changes that have been occurring in the atmosphere, and the water, soils, rocks, and biota exposed to it.

In considering the geobiosphere and the Earth's outer shell, we provide in Chapter 1 of this book an overview of its structure at scales ranging from the Earth's dimensions to the atomic dimensions of the constituents of the atmosphere, water, and crustal rocks, and also give an outline of the global carbon cycle, its major reservoirs, and the fluxes between them. Because of the importance of fossil fuels to our technological society, the occurrences of these forms of carbon are also reviewed in the chapter. It is emphasized that the global cycles of carbon and many other elements are driven by biological and inorganic geochemical processes. The term biogeochemical cycle that describes the environmental reservoirs and flows of materials between them reflects the joint role of these processes in the environment.

The long period of about 600 million years since the formation of the Earth to the first records of life is addressed in Chapter 2. The primordial atmosphere of the Earth was largely a product of degassing of the Earth's interior, its chemical composition was very different from that of the present-day atmosphere, and its temperature and pressure were likely to have been considerably higher early in Earth's history. We consider in Chapter 2 the early stages of the chemical composition of ocean water that was to a large

extent controlled by dissolution of hydrogen chloride, carbon dioxide, and hydrogen sulfide into the hydrosphere and its subsequent reactions with the early lithosphere of the Earth. We also address the question of the occurrence of the gases methane ( $\text{CH}_4$ ), as a chemically reduced form of carbon, and its oxidized form, carbon dioxide ( $\text{CO}_2$ ). The formation of living organic matter by chemical synthesis and, later, by photosynthesis signals the end of the prebiotic stage of Earth's history, and a discussion of the basic chemical reactions that lead to the formation of organic matter concludes this chapter.

In Chapter 3 we address the fundamentals of the thermal energy balance between the incoming solar radiation and the Earth's surface, and the greenhouse effect of the atmosphere that is responsible for a warmer Earth's surface than it would be without the atmosphere. We also point out that the term "greenhouse effect" is something of a misnomer, despite its well-rooted and widely accepted usage everywhere. As a reminder of the historical background, we discuss an early treatment of the greenhouse warming of the Earth's atmosphere by Milutin Milankovitch in 1920–1930, and conclude the chapter with a summary of the recent evidence of the radiation forcing and temperature increase projected for the 21st century, the so-called enhanced greenhouse effect.

The chemical and mineralogical properties of the three common carbonate minerals of calcite, aragonite, and dolomite are discussed in Chapter 4. The chapter describes the mineral characteristics of pure and magnesium-containing calcites, pure and strontium-containing aragonites, and dolomites with slightly variable calcium and magnesium content. The chapter also discusses the essentials of the solid solution theory, and the theoretical and experimental treatment of the dissolution and precipitation rates of these minerals at the conditions approximating those of the Earth's outer shell. Because much of the present mass of limestone in the sedimentary record was formed by marine organisms as skeletal parts and shells, the biogenic and non-biogenic occurrences of these minerals, as well as the relevance of this information to other processes on Earth, are also briefly discussed in this chapter.

The behavior of inorganic carbon as  $\text{CO}_2$  and other carbonate ionic species in fresh and ocean waters is treated in Chapter 5. We discuss the implications of the fact that in modern times, part of the  $\text{CO}_2$  from industrial and land-use emissions to the atmosphere accumulated in the ocean. We provide calculations for the average thickness of the surface ocean layer that absorbed this  $\text{CO}_2$ , showing its dependence on how the carbonate equilibria respond to changing environmental conditions and turbulent mixing and water transport in the ocean. We also consider the implications of the fact that the rate of calcite dissolution is related to the degree of carbonate mineral saturation and that although surface seawater is everywhere supersaturated with respect to calcite, calcite dissolves at depth in the oceans because of decreasing saturation state due to increasing internal  $P_{\text{CO}_2}$  and pressure with depth. Considering the extensive research activity behind the issue of possible storage of industrial  $\text{CO}_2$  as liquefied gas in the deep ocean, we discuss in this chapter the properties of the  $\text{CO}_2$  liquid and hydrate phases in the environment of ocean water. We also show that because  $\text{CO}_2$  forms in the precipitation and storage of mineral  $\text{CaCO}_3$ , it is a possible source of emission of  $\text{CO}_2$  gas to the atmosphere from ocean water, where the outward directed flux might be in part counteracted by biological primary production and storage of organic carbon in sediments.



The isotopic fractionation of the two stable isotopes of carbon,  $^{13}\text{C}$  and  $^{12}\text{C}$ , is treated in Chapter 6. The equilibrium fractionation is discussed for the inorganic system of gaseous  $\text{CO}_2$ , aqueous carbonate species, and mineral  $\text{CaCO}_3$  at the environmental conditions of the Earth's surface. The non-equilibrium or kinetic fractionation occurs in the photosynthetic production of organic matter and other biologically mediated reactions. The  $^{13}\text{C}/^{12}\text{C}$  fractionation is considered the first evidence for the occurrence of life on the early Earth, and it is also an indicator of the origin of various organic and mineral substances. In addition, the geologically established long-term record of the isotopically fractionated carbon in limestones and sedimentary organic matter provides bounds on the origin and evolution of the biosphere and the history of oxygen accumulation in the atmosphere.

Chapters 7 through 9 deal with three important parts of the global carbon cycle. First, in Chapter 7 we discuss the storage of carbon in sediments and the recycling that returns it to the atmosphere, biosphere, and ocean, as well as the sedimentary history of carbonate rocks that constitute about 80% of the mass of sedimentary carbon. The carbonate sedimentary record, its mineral composition, and isotopic ratios of  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  provide a picture of long-term trends of evolution of ocean water and atmosphere that is supplemented by the isotopic evidence of strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) in limestones, sulfur ( $^{34}\text{S}/^{32}\text{S}$ ) in the sulfate minerals of evaporitic rocks, and the chemical composition of fluid inclusions in  $\text{NaCl}$  crystals in evaporites. This chapter also begins to address the evolving carbon cycle since Hadean time. Next, Chapter 8 focuses on the dissolution of sedimentary and crustal rocks in mineral reactions with acidic,  $\text{CO}_2$ -containing atmospheric precipitation and groundwaters. This process is the first step in the transport of dissolved and particulate materials from land to the ocean by the release due to weathering of the main constituents of river waters. The weathering rates of the individual rock types that produce the global average river water, relative stabilities of rock-forming minerals, and consumption of  $\text{CO}_2$  in weathering are also discussed in this chapter, where we emphasize the importance of the  $\text{CO}_2$  flux in weathering in the global carbon cycle. The third part, addressed in Chapter 9, is the processes in the oceanic coastal margin that corresponds roughly to an area equivalent to about 8% of the ocean surface area. In this region there occurs at present a significant delivery of dissolved and particulate materials, an important part of oceanic primary production, storage of land-derived carbon, and calcium carbonate sequestration. The important processes in this relatively small area of the global coastal ocean are the remineralization of organic matter produced *in situ* and transported from land, the production of  $\text{CaCO}_3$  minerals of different solubilities (calcite, aragonite, and magnesian calcites of variable magnesium content), and the changes in biological production and calcification that are expected due to the rising atmospheric  $\text{CO}_2$  concentration that lowers the degree of saturation of ocean water with respect to the different carbonate minerals ("ocean acidification"). Combinations of these factors and physical mixing of the water masses determine the role of the coastal ocean as either a source or sink of atmospheric  $\text{CO}_2$ .

Building on the preceding chapters, Chapter 10 presents the major aspects of the evolving carbon cycle since geologically distant to more recent time. The chapter starts with the earliest Eon of the Earth's history, the Hadean, and ends in the Pleistocene and Holocene Epochs, and the time of the last glacial to interglacial transition. This

chapter draws on the simple picture of the carbon cycle that began in Chapter 1 and the primordial Earth, discussed in Chapter 2, expands it from the material given in the succeeding chapters, and presents our thoughts on the main driving mechanisms of the carbon cycle and the evolution of the ocean-atmosphere-biosphere-sediment system through geologic time.

Chapter 11 discusses the global carbon cycle in the Anthropocene, the period of the industrial age that started about 250 years ago. Because the Anthropocene is very likely to continue into the future, the chapter also considers the last two to three centuries of environmental change in terms of what might lie ahead. The effect of the carbon cycle on climate is only one important aspect of this global change. The human-produced perturbation of the global carbon cycle by the burning of fossil fuels and emissions from land-use has far-reaching effects on the linkages between the carbon cycle and the nutrient nitrogen and phosphorus cycles that are its drivers.

The literature dealing with the past, present, and future of carbon in the geobiosphere and the Earth's outer shell is very extensive. We attempted to cite those publications that bear directly on the ideas, factual material, and data in the diverse topics that we discuss in the book, but even the more than 700 bibliographic entries, from the 1840s to the present, are only an incomplete list. Any errors of omission in the choice and coverage of the subject matter and in the recognition of other authors' contributions in the different fields are entirely ours.

The past and the future are usually studied by means of models of different degrees of complexity. The models are useful to our understanding of the relative magnitude and importance of the different geological, physical, chemical, and biological processes that control the distribution of carbon, and to our ability to describe the past and, at least to some extent, the future. The predictive ability of any model has a great value in forecasting and planning for the future, particularly for the processes that have a human dimension and affect the fabric of human societies. However, these useful features of models encounter serious obstacles because of the often-unforeseen developments in the future that do not conform to the basic assumptions and mechanisms of the models. Therefore our approach in this book is to discuss the fundamental principles of the biogeochemical cycling of carbon and give examples of how they contribute to our understanding of an integrated global picture that has been only recently affected by humans as a geologic agent.

It is our anticipation that this book will serve mainly as a reference text for Earth, ocean, and environmental scientists from various subdisciplines who might be interested in an overview of the carbon cycle and behavior of carbon dioxide, and the effects humans are having on them. Parts of this book have already been used by the authors as material for classroom discussion, so the book might also serve a one-semester course at the upper-undergraduate or graduate level addressing the behavior of the carbon cycle and its human modifications.

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## Picture Credits on the Front Cover

### Top, from left to right:

Mount Erebus, Antarctica, the southernmost volcano on Earth, elevation 3794 m above sea level (77°32'S, 167°17'E), photographed in 1983 by Nelia Dunbar and published in Internet by the National Science Foundation and New Mexico Tech. <http://www.ees.nmt.edu/Geop/mevo/mevomm/imagepages/dunbar/index.html>  
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Earth photographed on 7 December 1972 by the Apollo 17 crew on the way to the Moon. NASA, [http://visibleearth.nasa.gov/view\\_rec.php?id=1597](http://visibleearth.nasa.gov/view_rec.php?id=1597)

Reef limestone of Middle Permian Age, approximately 265 million years ago. El Capitan peak, Guadalupe Mountains, Texas, 2464 m above sea level (31°53'N, 104°51'W). <http://www.utexas.edu/features/archive/2003/graphics/texas5.jpg>  
Photograph and information courtesy of Professor J. Richard Kyle, Department of Geological Sciences, Jackson School of Geosciences, University of Texas, Austin, Tex.

True-color image of a portion of the Great Barrier Reef, off the coast of central Queensland, Australia, north of the Tropic of Capricorn, taken by NASA on 26 August 2000. The width of the reef zone is approximately 200 km. NASA Earth Observatory, [http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img\\_id=4797](http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=4797)

### Center:

Main features of the global carbon cycle at the Earth's surface. Based on Figures 1.4, 5.11, and 10.7.

# Contents

Published Titles in Topics in Geobiology Book Series	ii
Aims & Scope Topics in Geobiology Book Series	v
Preface	vii
Acknowledgements	xiii
Picture Credits	xvii
<b>1 Brief Overview of Carbon on Earth</b>	<b>1</b>
1 An Unusual Look at Earth's Shells	2
2 Global Carbon Cycle	7
3 Fundamental Equation of a Cycle and Carbon Flows	14
4 Carbon in Fossil Fuels	18
5 Feedbacks in the Carbon Cycle	21
<b>2 Earth's Volatile Beginnings</b>	<b>23</b>
1 The Major Volatiles	23
2 Primordial Atmosphere-Ocean System	35
3 Carbon Dioxide	40
4 Summary and Speculations	45
5 An Early Biosphere	49
<b>3 Heat Balance of the Atmosphere and Carbon Dioxide</b>	<b>61</b>
1 Heat Sources at the Earth's Surface	62
2 Solar Heating and Radiation Balance	63
3 Greenhouse Effect	69
4 Temperature of a Prebiotic Atmosphere	80
5 CO <sub>2</sub> and Climate Change	83
<b>4 Mineralogy, Chemistry, and Reaction Kinetics of the Major Carbonate Phases</b>	<b>89</b>
1 Carbonate Minerals	90
2 Calcites	93
3 Dolomite	101
4 Aragonite	105
5 Carbonate Dissolution and Precipitation Kinetics	110
6 Carbonate Precipitation and Dissolution in Marine Ecosystems	115
7 Some Geological Considerations	116
	xix

<b>5</b>	<b>Carbon Dioxide in Natural Waters</b>	123
	1 Dissolution and Dissociation of CO <sub>2</sub> in Water	124
	2 CO <sub>2</sub> Transfer from Atmosphere to Water	133
	3 Calcite and Aragonite in Natural Waters	137
	4 Degree of Saturation with Respect to Carbonate Minerals	138
	5 CO <sub>2</sub> Phases: Gas, Liquid, Hydrate, Ice	142
	6 Air-Sea CO <sub>2</sub> Exchange due to Carbonate and Organic Carbon Formation	147
<b>6</b>	<b>Isotopic Fractionation of Carbon: Inorganic and Biological Processes</b>	165
	1 Isotopic Species and Their Abundance	165
	2 Isotopic Concentration Units and Mixing	167
	3 Fractionation in Inorganic Systems	170
	4 Photosynthesis and Plant Physiological Responses to CO <sub>2</sub>	174
	5 Isotopic Fractionation and <sup>13</sup> C Cycle	184
	6 Long-Term Trends	188
<b>7</b>	<b>Sedimentary Rock Record and Oceanic and Atmospheric Carbon</b>	193
	1 Geologic Time Scale and Sedimentary Record	194
	2 The Beginnings of Sedimentary Cycling	195
	3 Broad Patterns of Sediment Lithologies	197
	4 Differential Cycling of the Sedimentary Mass and Carbonates	199
	5 Sedimentary Carbonate System	202
	6 Evaporites and Fluid Inclusions	208
	7 Isotopic Trends	211
	8 Summary of the Phanerozoic Rock Record in Terms of Ocean Composition	220
<b>8</b>	<b>Weathering and Consumption of CO<sub>2</sub></b>	225
	1 Weathering Source: Sedimentary and Crystalline Lithosphere	226
	2 Dissolution at the Earth's Surface	232
	3 Mineral-CO <sub>2</sub> Reactions in Weathering	237
	4 CO <sub>2</sub> Consumption from Mineral-Precipitation Model	242
	5 CO <sub>2</sub> Consumption from Mineral-Dissolution Model	247
	6 Environmental Acid Forcing	252
<b>9</b>	<b>Carbon in the Oceanic Coastal Margin</b>	255
	1 The Global Coastal Zone	256
	2 Carbon Cycle in the Coastal Ocean	262
	3 Inorganic and Organic Carbon	267
	4 Marine Calcifying Organisms and Ecosystems	278
	5 Present and Future of the Coastal Ocean Carbon System	284



<b>10</b>	<b>Natural Global Carbon Cycle through Time</b>	289
1	The Hadean to Archean	289
2	The Archean to Proterozoic	293
3	The Phanerozoic	297
4	Pleistocene to Holocene Environmental Change	303
<b>11</b>	<b>The Carbon Cycle in the Anthropocene</b>	319
1	Characteristics of the Anthropocene	319
2	Major Perturbations of the Carbon Cycle: 1850 to the Early 21st Century	321
3	Partitioning of the Carbon, Nitrogen, and Phosphorus Fluxes	326
4	The Fundamental Carbon Problem of the Future	336
	Bibliographic References	343
	Index	383

## Chapter 1

### Brief Overview of Carbon on Earth

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1	An Unusual Look at Earth's Shells .....	2
2	Global Carbon Cycle .....	7
2.1	Cycle Structure .....	7
2.2	Historical Note on the Carbon Cycle .....	12
3	Fundamental Equation of a Cycle and Carbon Flows .....	14
3.1	The Cycle Equation .....	14
3.2	General Pattern of Carbon Flows .....	14
3.3	Production and Remineralization of Organic Matter .....	16
3.4	Carbonate System and Air-Sea Exchange .....	17
4	Carbon in Fossil Fuels .....	18
5	Feedbacks in the Carbon Cycle .....	21

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In the minds of the broad public, carbon dioxide is associated primarily, if not exclusively, with considerations of global warming. This topic has been the focus of undoubtedly great attention in the last decades of the 20th and in the early 21st century owing to the coverage of the subject of global warming and climate change by the news media drawing their information from the results of scientific studies. The role of carbon dioxide as one of the gases that warm the Earth's atmosphere by absorption of infrared or longwave, outgoing Earth radiation has been known since the work of the French scientist Jean-Baptiste-Joseph Fourier in the early nineteenth century and that of the Irish polymath John Tyndall in the middle part of that century. The similar role of water vapor as a greenhouse gas was also recognized by John Tyndall in 1863. In his studies of the riddle of the causes of the ice ages, the Swedish chemist Svante Arrhenius in the mid-1890s did a series of mathematical calculations and showed that if the amount of atmospheric CO<sub>2</sub> were cut in half, the world would be 4° to 5°C cooler. He also concluded that a doubling of the CO<sub>2</sub> concentration would lead to a 5° to 6°C increase in global mean temperature. Furthermore, he recognized the fact that the burning of coal and oil emits CO<sub>2</sub> to the atmosphere and could lead to warming of the planet because of human activities (Chapter 3). However, it was only an increase in the concentration of atmospheric carbon dioxide, measured systematically by Charles D. Keeling of the Scripps Institution of Oceanography in California since the mid-1950s in the air over the mountain Mauna Loa on the Island of Hawaii, that drew widespread attention to this gas as a product of fossil-fuel burning and land-use changes by the increasingly industrializing world.

In this first chapter of the book we describe the structure of the *Outer Shell of the Earth* on a global scale, the chemical composition of some of its parts on an atomic scale, the essentials of the carbon cycle in modern time, the connections between the inorganic and biological processes within the carbon cycle, and the estimated occurrences of the main types of fossil fuels that are believed to be the major source of the increase in atmospheric carbon dioxide in the industrial age of the last 150 years. This material provides an overview of the global carbon cycle and the framework for discussion of various aspects of the cycle in the chapters that follow.

In the concerns about global warming and the shorter-term increase of atmospheric carbon dioxide, three facts are nearly forgotten: one is the long-term cooling of the Earth's surface in the last 30 million years, since ice cover began to develop in Antarctica; another is the periodic glaciations during the last 1 million years that were accompanied by rises and declines in atmospheric carbon dioxide concentration; and the third is the primary importance of carbon dioxide to plant growth. The long history of carbon on Earth begins with the Earth's accretion 4.55 billion years ago (Fig. 1.1) and it underlies not only the beginning and evolution of organic life on Earth, but also a great variety of the processes that have shaped the geological environment since the early days of the planet.

## 1 An Unusual Look at Earth's Shells

We, as creatures living on the Earth's surface and capable of seeing things only of certain size that emit or reflect a certain narrow band of electromagnetic radiation, which we call visible light, have a certain perception of the appearance of our global habitat. A clean atmosphere is transparent to us, clear sky is blue, liquid water is of some color varying from blue to greenish or brown that depends on its absorption and reflection of parts of the visible light spectrum and on the presence of other dissolved or suspended materials in it. We see snow flakes and ice crystals as white or transparent, depending on their size and the reflecting quality of their surfaces. In the world of rocks and minerals, we can distinguish with an unaided eye individual mineral grains, but we do not see the atomic structure and different atoms making up the world around us, learning about it by other means. Our knowledge of the Earth's interior (Fig. 1.2) is neither a product of direct observations made on "journeys to the center of the Earth" nor is it based only on studies of rocks recovered from the deepest borehole of about 12 km drilled on land and a borehole of somewhat less than 2 km beneath the ocean floor. The picture of the Earth's interior as well as exterior shells, comprising the atmosphere, hydrosphere, sediments, and living organisms, is a product of researches that synthesize the observational, experimental, and theoretical knowledge gained over a long period of time. Figure 1.2 is a small-scale schematic view of our planet and its surface environment where most of the action involving carbon dioxide and other forms of carbon occurs. Carbon dioxide as the chemical species  $\text{CO}_2$  comprises only a very small part of all the carbon in the oceans, fresh waters, and sediments. Although it is a minor component of the atmosphere as a whole, it is the main form of atmospheric

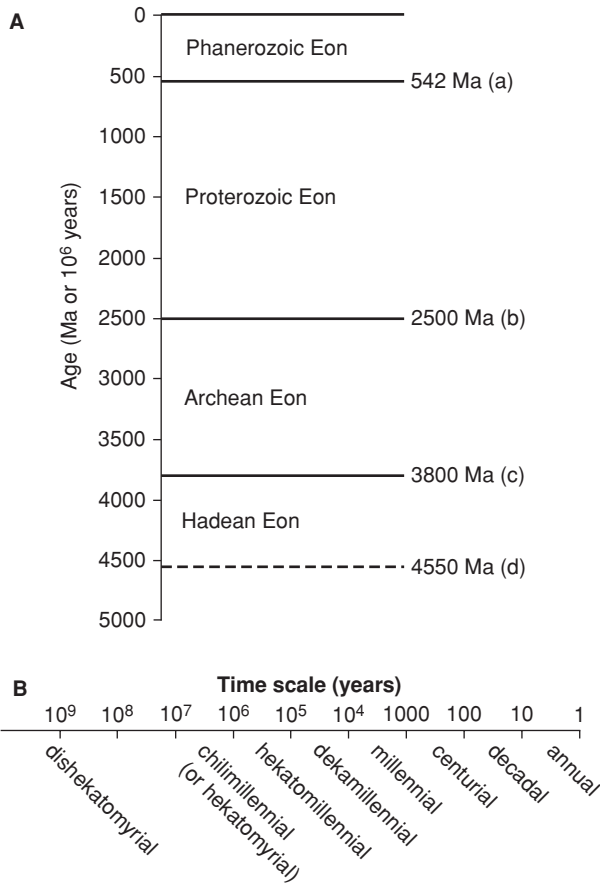


Figure 1.1 Geologic time scale. A. The four Eons. (a) The base of the Phanerozoic Eon is the base of the Cambrian Period; the age shown is that of the International Commission on Stratigraphy 2004 (Gradstein *et al.*, 2004); since 1937, age estimates of this boundary varied from 470 to 610 Ma (Harland *et al.*, 1990). (b) Gradstein *et al.* (2004). (c) The age of the Hadean-Archean boundary varies from 3800 to 4000 Ma because of insufficient age data for the Hadean (Harland *et al.*, 1990). (d) The age of the Earth taken as  $4.55 \pm 0.07$  Ga based on meteorite ages (Patterson, 1956); other meteorite ages between 4.504 and 4.568 Ga indicate a period of 64 million years when parent bodies of meteorites formed (Allègre *et al.*, 1995; Faure and Mensing, 2004). B. Terms used for some of the time segments. Compounds with the Latin-derived millennial are based on Greek terms (Smith, 1964; Woodhouse, 1910) and modern Greek for one billion or  $10^9$ . **Units:** 1 Ga =  $10^9$  yr, 1 Ma =  $10^6$  yr.

carbon and very important to life and regulation of climate on our planet. Because of the chemical reactions that transform carbon dioxide into organic carbon and carbonate minerals in sediments, and the latter two back into carbon dioxide, the processes that affect the  $\text{CO}_2$  concentration in the atmosphere and natural waters extend far beyond the

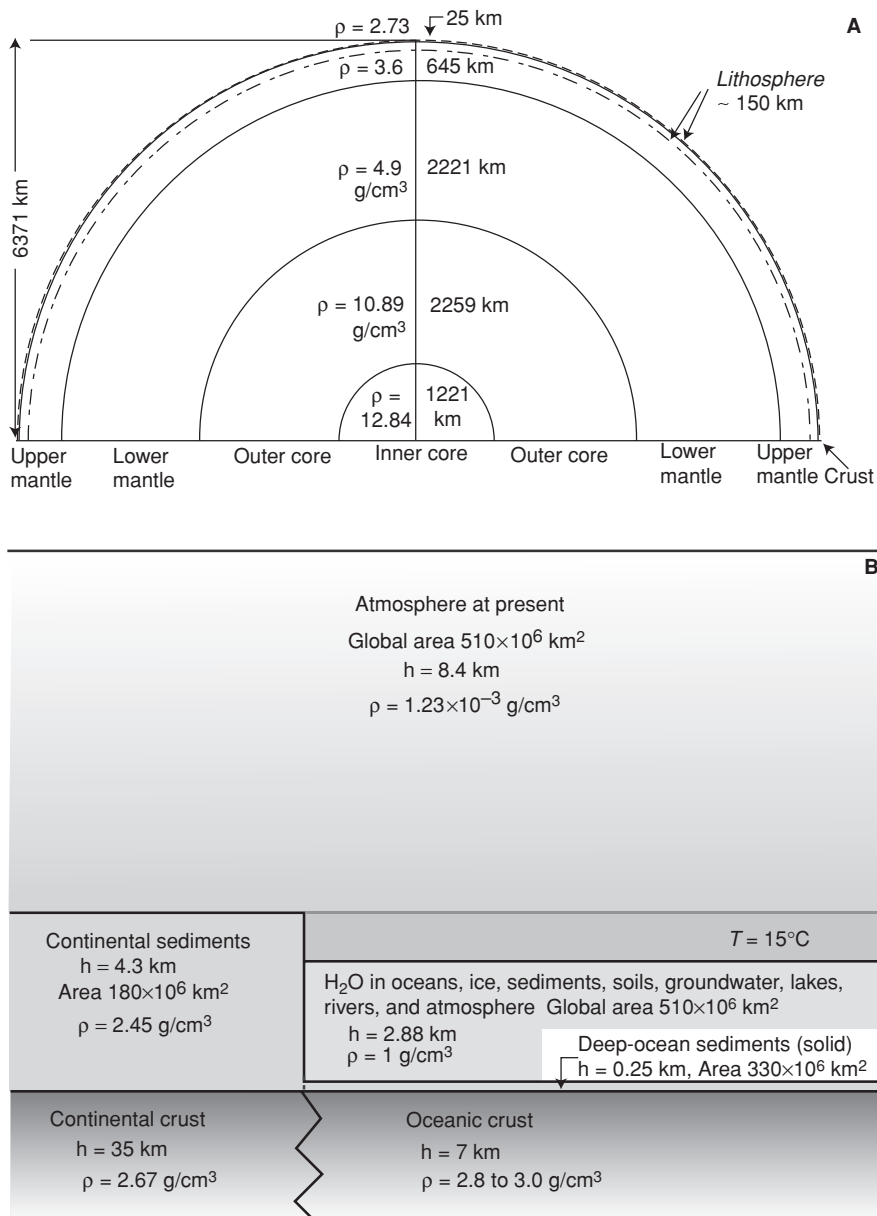


Figure 1.2 A. Earth’s interior shells. Shell thickness and densities are from E. A. Okal (*personal communication*, 2005), mean thickness of the lithosphere is from Gung *et al.* (2003). Note the average crust of 25 km thickness and a mean lithosphere of 150 km that includes the crust and part of the upper mantle. B. Atmosphere, water, and sediments above the continental and oceanic crust. Thickness of the atmosphere is its scale height, discussed in Chapter 2. Thickness of deep-ocean sediment is that of the solids in a layer of an average thickness of 500 m (Chester, 2000) and porosity 50%.

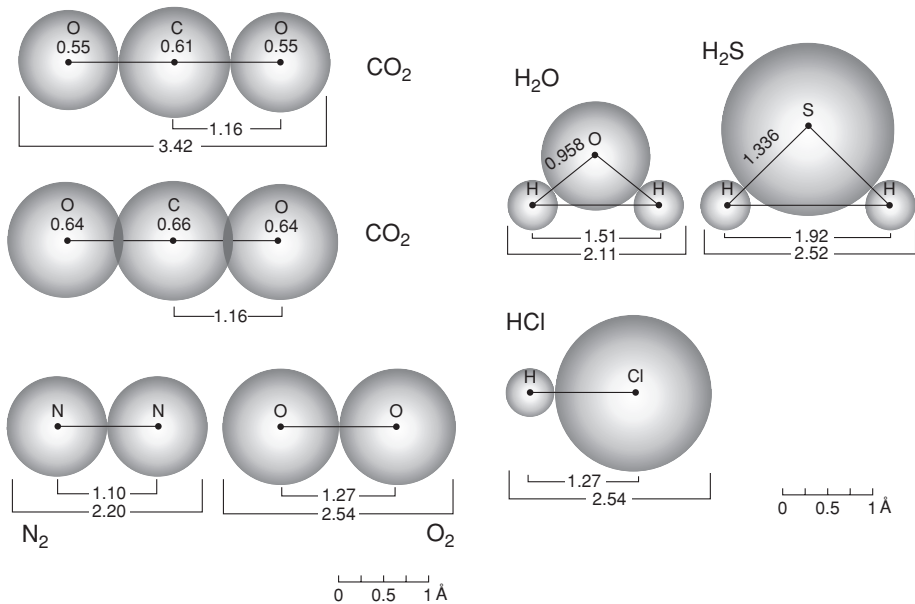


Figure 1.3 Molecules of some of the main atmospheric gases of the present and primordial past: CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, and HCl. Units of interatomic distances, atomic radii, and lengths are in ångströms ( $1 \text{ \AA} = 10^{-8} \text{ cm}$  or  $10^{-10} \text{ m}$  or  $100 \text{ pm}$ ). Interatomic distance, center to center, is the sum of two radii. This convention accounts for two representations of the CO<sub>2</sub> molecule: one, where the oxygen radius is  $0.549 \text{ \AA}$  and C radius is  $1.16 - 0.549 = 0.61 \text{ \AA}$ ; the other, where the C radius has the value for the double bond ( $0.66 \text{ \AA}$ , Table 1.1) and O radius is one-half of the interatomic distance in O<sub>2</sub> ( $0.636 \text{ \AA}$ ). The large sizes of S and Cl, in comparison to O, in single covalent bonding to the hydrogen atoms, may be noted.

last two centuries of the industrial age, as is discussed later in this and other chapters. For a view of our physical environment that is different from the one depicted in Fig. 1.2, we may imagine a fictional observer of our planet from space, who is capable of seeing individual atoms and looking through the thickness of the atmosphere, oceans, and some of the Earth's solid crust. This observer would see mostly oxygen atoms interspersed with other atoms occurring as smaller admixtures or impurities within the mass of oxygen that makes up more than 90% of the volume of the solid crust of the Earth and water in the oceans. The different chemical compounds of atomic and molecular species would be distinguishable to the atom-scale observer by their sizes and their composition that is represented by the different atoms. Volumes of molecules depend on the distances between the centers of their constituent atoms, which in turn depend on the nature of the chemical bonds between them.

The atmosphere would appear to our fictional observer as a mixture of the two most abundant gases, nitrogen and oxygen diatomic molecules of about the same size, as shown in Fig. 1.3, with 78% of the volume being nitrogen and 21% oxygen. The observer would also see the less abundant atoms of argon, about 0.9% of the volume, and small admixtures of carbon dioxide and water molecules, the latter appearing

as big oxygen atoms bonded to the much smaller hydrogen atoms in H<sub>2</sub>O. Because the volume fraction of water vapor in the atmosphere varies with location and climatic conditions from almost 0% in very dry air to nearly 3% in tropical humid air, and carbon dioxide constitutes currently about 0.038% of the atmosphere, both H<sub>2</sub>O and CO<sub>2</sub> would appear to our fictional observer as very small fractions of atmospheric oxygen tied up in a different form. Figure 1.3 shows some of the atmospheric gas molecules, drawn schematically to scale. Their physical dimensions and related parameters of the gases mentioned above are given in more detail in Table 1.1, as are the major gases

Table 1.1 Molecular dimensions of some atmospheric gases of the past and present (the ångström unit is 1 Å = 10<sup>-8</sup> cm or 10<sup>-10</sup> m or 100 pm)

<i>Species</i>	<i>Bond length</i> <sup>(1)</sup> (Å)	<i>Angle</i> <sup>(1)</sup> (degrees)	<i>Atomic radii in covalent bonds</i> (Å)	<i>Molecule dimension</i> (Å)
CO <sub>2</sub>	C—O 1.1600	∠OCO 180°	Double covalent bond: C 0.661, O 0.549 <sup>(2)</sup>	2.32 to 3.42 <sup>(4)</sup>
N <sub>2</sub>	N—N 1.0977	—	Triple covalent bond: N 0.545 <sup>(2)</sup>	2.20 <sup>(5)</sup>
O <sub>2</sub>	O—O 1.2716	—	Double covalent bond: O 0.549 <sup>(2)</sup> ; interatomic distance 1.2074 <sup>(3)</sup>	2.54 <sup>(5)</sup>
H <sub>2</sub> O	O—H 0.9575	∠HOH 104.51°	Single covalent bond: O 0.659, H 0.299 <sup>(2)</sup> ; O 0.73 and H 0.37 <sup>(3)</sup>	1.51 to 2.11 <sup>(4)</sup>
H <sub>2</sub> S	S—H 1.3356	∠HSH 92.12°	Single covalent bond: H 0.299 <sup>(2)</sup> ; H 0.37, S 1.02 <sup>(3)</sup>	1.92 to 2.52 <sup>(4)</sup>
SO <sub>2</sub>	S—O 1.4308	∠OSO 119.33°	Double covalent bond: O 0.549 <sup>(2)</sup>	2.47 to 3.57 <sup>(4)</sup>
HCl	Cl—H 1.2746		Single covalent bond: Cl 0.99 <sup>(3)</sup>	2.55 <sup>(5)</sup>
Ar			Atomic radius 0.71, radius for single covalent bond 0.97, van der Waals radius 1.88 <sup>(3)</sup>	1.42 <sup>(5)</sup>

NOTE: Atomic radii reported in the literature vary greatly, often without any explanation of what is meant by the atomic radius and its value. Publications and Web Sites by Alcock (1990) and Winter (2003) address such discrepancies.

<sup>(1)</sup> Lide (1994).

<sup>(2)</sup> Alcock (1990), with references therein.

<sup>(3)</sup> Winter (2003), with references therein.

<sup>(4)</sup> First figure is the distance between the centers of O atoms in CO<sub>2</sub> and SO<sub>2</sub>, and between H atoms in H<sub>2</sub>O and H<sub>2</sub>S (Fig. 1.2). Second figure is the longest dimension of the molecule, as shown in Fig. 1.3.

<sup>(5)</sup> Double of the interatomic distance for N<sub>2</sub>, O<sub>2</sub> (Fig. 1.1), and HCl, and atomic diameter of Ar.

occurring in the present-day and geologically old atmosphere shortly after the time of Earth's formation. Today's atmosphere contains molecular oxygen that was not present in the primordial atmosphere; the latter likely contained much higher concentrations of carbon dioxide and, initially, hydrogen chloride and sulfur in the form of either hydrogen sulfide or sulfur dioxide (Chapter 2).

The continental and oceanic crust, and the weathered products that constitute the inorganic mineral part of soils, are made of aluminosilicate minerals where oxygen is the volumetrically most abundant element owing to its ubiquitous presence as a chemical component and its crystal ionic radius that is large relatively to the smaller radii of other elements bonded to it. Crystal ionic radius depends on the chemical and nuclear characteristics of an element, and its coordination number in the crystal lattice. Although the ionic crystal radii reported by different authors have somewhat different values, they do not affect the general picture of a mineral lattice as made of big oxygens and other smaller elements (Ahrens, 1952; Evans, 1994; Faure, 1998; Moeller, 1952; Shannon, 1976; Whittaker and Muntus, 1970). The crystal ionic radius of  $O^{2-}$  in a 6-fold coordination is 1.32 to 1.40 Å, but the ionic radii of the major elements in such common rock-forming minerals as aluminosilicates and carbonates are smaller. Silicon and aluminum are each commonly surrounded by four oxygens (coordination number 4), with the ionic radii of  $Si^{+4}$  0.26 to 0.34 Å, and of  $Al^{+3}$  0.39 to 0.47 Å. For metal cations in a 6-fold coordination, sodium  $Na^+$  has the radius of 1.02 to 1.10 Å, and calcium  $Ca^{+2}$  1.00 to 1.08 Å. Carbon, occurring in the valence state of  $C^{+4}$  in carbonate minerals as anion  $CO_3^{2-}$ , is a much smaller ion, of radius 0.15 to 0.16 Å. As a whole, the continental granitic crust and the oceanic basaltic crust are 92 to 94% by volume elemental oxygen (Lerman, 1979; Mason, 1958) and they would appear to our fictional observer from space as a layer of oxygen atoms with other, mostly smaller, impurities in it.

## 2 Global Carbon Cycle

### 2.1 Cycle Structure

Life on Earth is based on carbon as one of the main components of organic matter. The occurrence of the various forms of carbon in different parts of the Earth's interior and its outer shell, and the processes that are responsible for the transfer of carbon between the different parts of the Earth make a conceptual model known as the geochemical or biogeochemical cycle of carbon. The latter name reflects combinations of geological, biological, chemical, and physical processes that variably control the flows and chemical transformations of carbon in the surface and interior reservoirs of the Earth.

The carbon cycle is usually divided into a deeper part, called the *endogenic cycle*, and the part that includes the surface reservoirs of the sediments, oceanic and continental waters, land and aquatic biomass, soils, and the atmosphere is referred to as the *exogenic cycle*. The main features of the global carbon cycle are shown in Fig. 1.4 and the carbon inventory on Earth is given in Table 1.2. The inventory of the reservoirs represents the geological near-Recent, with atmospheric carbon taken at the



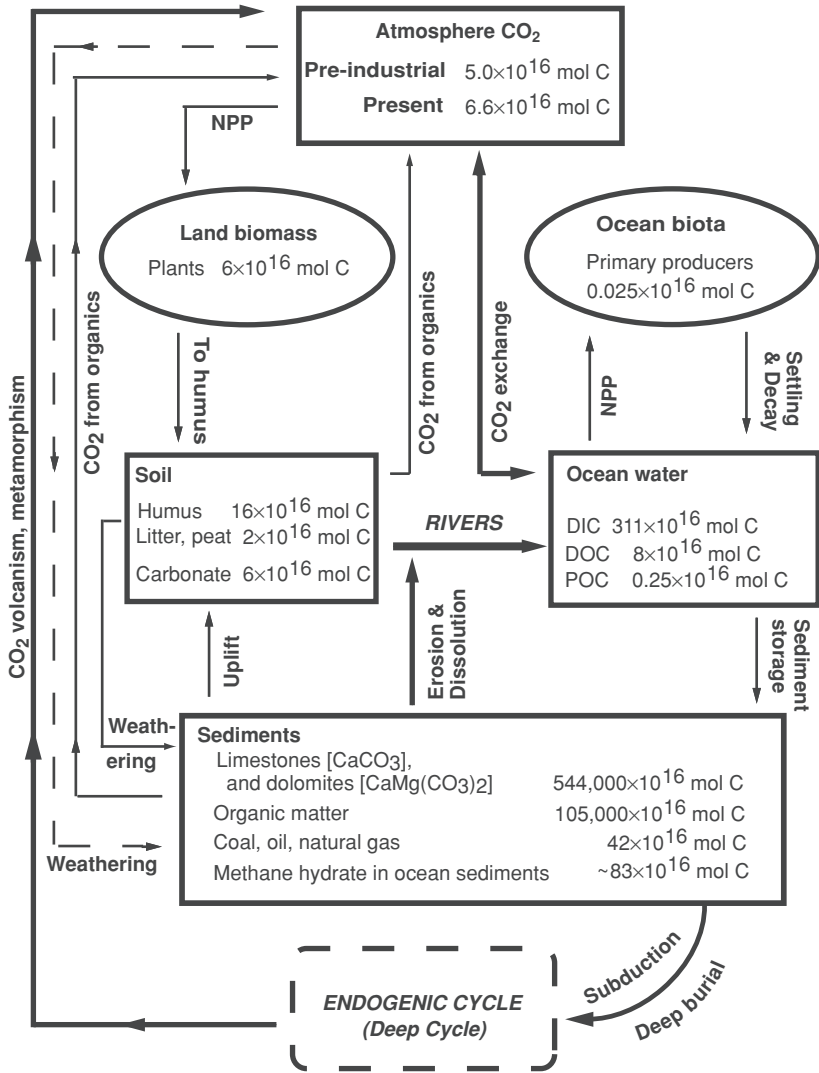


Figure 1.4 Global biogeochemical cycle of carbon. Reservoirs on the Earth surface represent the exogenic cycle. Masses of the major reservoirs are given in Table 1.2. NPP is net primary production, defined in the text. The CO<sub>2</sub> in weathering is shown as taken from the soil (solid line) or from the atmosphere (dashed line). Values of major fluxes are given in Table 1.3. Mass units: 1 mol C = 12.011 g C or  $1 \times 10^{16}$  mol C = 120 Gt C.

pre-industrial level of CO<sub>2</sub> that has probably varied significantly in the geologic past and has risen about 35% during the Industrial Age. Estimates of carbon masses in other reservoirs are subject to variable errors and greater uncertainties. The mass of carbon in land plants has been variably reported in the range of  $\pm 15$  to 20% of the value given

Table 1.2 Carbon masses in the major environmental reservoirs. From data in Li (2000), Ver *et al.* (1999), and Walker (1977)

<i>Reservoir</i>	<i>Mass of carbon</i>	
	<i>grams C</i>	<i>mols C</i>
Atmosphere		
CO <sub>2</sub> (at pre-industrial 280 ppmv)	$6 \times 10^{17}$	$5 \times 10^{16}$
Ocean		
Dissolved inorganic (DIC)	$3.74 \times 10^{19}$	$3.11 \times 10^{18}$
Dissolved organic (DOC)	$1 \times 10^{18}$	$8.33 \times 10^{16}$
Particulate organic (POC)	$3 \times 10^{16}$	$2.50 \times 10^{15}$
Ocean biota	$3 \times 10^{15}$	$2.50 \times 10^{14}$
Land biota		
Phytomass	$7 \times 10^{17}$	$6 \pm 1 \times 10^{16}$
Bacteria and fungi	$3 \times 10^{15}$	$2.50 \times 10^{14}$
Animals	$1 \text{ to } 2 \times 10^{15}$	$1.25 \times 10^{14}$
Land		
Soil humus	$1.92 \times 10^{18}$	$1.6 \pm 3 \times 10^{17}$
Reactive fraction of humus		$2 \times 10^{16}$
Dead organic matter, litter, peat	$2.5 \times 10^{17}$	$2.08 \times 10^{16}$
Inorganic soil (CaCO <sub>3</sub> )	$7.2 \times 10^{17}$	$6 \times 10^{16}$
Sediments		
Carbonates	$6.53 \times 10^{22}$	$5.44 \times 10^{21}$
Organic matter	$1.25 \times 10^{22}$	$1.05 \times 10^{21}$
Continental crust	$2.576 \times 10^{21}$	$2.14 \times 10^{20}$
Oceanic crust	$9.200 \times 10^{20}$	$7.66 \times 10^{19}$
Upper mantle	$(8.9 \text{ to } 16.6) \times 10^{22}$	$\sim 1.1 \times 10^{22}$

in Table 1.2, 700 Gt C (1 gigaton or 1 Gt =  $10^{15}$  g). Large variations in the estimated global mass of peat and soil humus have also been reported in the literature.

Carbon dioxide is emitted from the Earth's mantle through subaerial volcanism, in the spreading zones and ridges on the ocean floor, from magmatic plumes and hot spots, from subduction zones, and through thick piles of sediments. The occurrence of this chemically oxidized form of carbon in magmatic emissions indicates that CO<sub>2</sub> is not an exclusive product of carbon oxidation at the Earth's surface but it has a much longer geological history on our planet. This view is consistent with the chemical thermodynamic properties of carbon and oxygen that tend to combine and form carbon dioxide, as in the reaction



Over a wide range of temperatures, from those of the Earth's surface to those of the molten silicate melts, chemical equilibrium in reaction (1.1) is strongly shifted to the right, producing very high ratios of CO<sub>2</sub> to O<sub>2</sub>. In thermodynamic calculations of reaction equilibria that involve carbon, the standard form of carbon is, by convention, the mineral graphite and oxygen is diatomic gas. The reaction as written may be either

a reversible chemical reaction at equilibrium, where carbon dioxide forms from elemental carbon and oxygen, or it may also represent in shorthand notation the chemical balance for the process of one atom of elemental carbon and one molecule of oxygen combining to produce one molecule of carbon dioxide. Examples of the latter type of one-way processes at the Earth's surface are oxidation of carbon in organic matter and burning of carbon in fossil fuels or forest fires. At the relatively low temperature of the Earth's surface, many processes represented by reaction (1.1) do not go spontaneously from the left to the right, as predicted by chemical thermodynamics. A simple daily demonstration of this fact is in the starting of a fire when the temperature of the reactants, carbon and oxygen, has to be raised to the ignition temperature before they begin to combine one with the other and carbon burns. Common examples of such temporal stability or rather metastable existence of elemental carbon in the oxidizing atmosphere of the Earth are graphite and diamond.

As a whole, oxidized carbon is the more abundant form of the element at the Earth's surface where it occurs as carbon dioxide gas, dissolved carbonate ions in waters, and carbonate ions in sedimentary minerals. In addition to the sedimentary carbonates, two types of igneous rocks containing carbon occur in the Earth's crust: kimberlites, the main commercial source of diamonds that are an elemental crystalline form of carbon, and carbonatites, made mostly of calcite, dolomite, and iron-containing dolomite ankerite. Carbonatites are believed to form in the mantle, at high pressures of CO<sub>2</sub>, and extruded as volcanic rocks or intruded into the upper lithosphere at the later stages of magmatic differentiation. The occurrences of carbonatites are limited to small areas at about 330 locations worldwide (Barker, 1997), and their total mass is very small in comparison to the mass of sedimentary limestones and dolomites.

On Earth, the biological origin of organic matter is indicated by the abundance ratio of the two stable isotopes of carbon, <sup>13</sup>C/<sup>12</sup>C: the ratio is lower in biologically produced organic matter than in the source from which CO<sub>2</sub> is taken. This topic is discussed further in Chapter 6. However, organic compounds of non-biological origin are found in a class of meteorites known as chondrites, among which different types of carbonaceous chondrites contain between 0.26 and 3.5 wt % carbon in organic compounds coexisting with aluminosilicate minerals. This abundance of organic carbon in extraterrestrial materials may be compared with its mean abundance of about 0.75 wt % in the sedimentary mass on Earth. Fossil fuels—coal, petroleum, and hydrocarbon gases—are part of the global reservoir of sedimentary organic matter. The known recoverable reserves of fossil fuels (different coals, petroleum, and natural gas, recoverable with the present-day technology) account for only a very small fraction of the total organic carbon in sediments, and these are discussed further in Section 4 of this chapter.

The biggest carbon reservoir on the Earth's surface is sedimentary rocks. The mass of carbon stored over the geologic history of the Earth in sedimentary limestones, dolomites, and undecomposed organic matter exceeds by a very large factor, about 100,000, the mass of carbon in atmospheric CO<sub>2</sub> at the present time (Fig. 1.4, Table 1.2).

Next in size is the carbon reservoir of the oceans or, more generally, of the oceanic and continental surface and ground waters making the hydrosphere. The total mass of carbon in the global oceans, consisting mostly of dissolved inorganic carbon, is about

60 times greater than the mass of atmospheric carbon dioxide (Table 1.2). The main form of carbon in the global water reservoir is dissolved carbon dioxide and its ionic species, and generally less abundant dissolved organic carbon derived from incomplete decomposition of living and dead organic matter. These dissolved forms of carbon are usually denoted as DIC, for dissolved inorganic carbon, and DOC, for dissolved organic carbon (Fig. 1.4). Dissolved inorganic carbon (DIC) includes three major aqueous species— $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ —and, to a lesser degree, their complexes with metal ions in solution. On the other hand, dissolved organic carbon occurs as a great variety of organic compounds ranging in molecular weight from light, simple organic acids to much heavier and structurally more complex species. Besides the dissolved species of carbon, there are particles containing inorganic and organic forms of carbon in continental and ocean waters. Particulate inorganic carbon or PIC is mostly the grains of carbonate rocks carried by rivers and the calcium-carbonate skeletons of organisms forming in surface ocean waters and sinking to the ocean bottom. Its organic counterpart, particulate organic carbon or POC, consists of undecomposed cells, products of metabolic excretion, soft parts of dead plants and animals sinking through the water column, and organic matter adsorbed on mineral-particle surfaces, such as clays.

In the atmosphere that contains oxygen, carbon dioxide is the only chemically stable form of carbon. More reduced forms of carbon gases, such as carbon monoxide (CO), methane ( $\text{CH}_4$ ), and volatile hydrocarbons, produced by biological or inorganic processes or anthropogenic activities, are eventually oxidized to  $\text{CO}_2$ . At present, carbon dioxide is the most abundant of the carbon-containing gases and it makes a volume fraction of  $3.80 \times 10^{-4}$  or 380 ppmv (parts per million by volume)<sup>1</sup> of the atmosphere, increasing at a rate of approximately 1.5 ppmv per year. Other gases, such as methane ( $\text{CH}_4$ ) from natural sources or human agricultural and industrial activities, carbon monoxide (CO) and volatile organic compounds mainly from industrial activities, and the most recent emissions of the various synthetic chlorofluorocarbon compounds (CFCs, e.g., Freon 11 and 12) used as refrigerant and spray-propellant gases, are believed to have effects on atmospheric temperature, stratospheric and tropospheric ozone, and climate, despite their occurrences at concentrations much lower than atmospheric  $\text{CO}_2$ .

In the biosphere, a major part of carbon in living organic matter is represented by land plants. This very large and diversified group includes predominantly photosynthetic plants ranging in size from short-lived unicellular organisms to trees whose lifetimes average several decades. Forests are the main reservoir of biotic carbon on land. In the ocean, most of the photosynthesizing organisms live in the upper layer of the oceans where sufficient light is available. These free-floating organisms are known as the phytoplankton, and the phytoplanktonic group Coccolithophoridae is an important producer of calcium carbonate shells that constitute a major portion of ocean-floor carbonate sediments. Additional aquatic plants include the class of algae and bigger plants rooted to the bottom, known as macrophytes. The oceanic phytoplankton makes only a small fraction, about 0.5% of the carbon mass of global biota. However, amino

<sup>1</sup> Volume fraction of a gas in a mixture that is treated as an ideal gas is also its partial pressure. In the atmosphere of total pressure  $P = 1$  atm, partial pressure of  $\text{CO}_2$  is  $3.80 \times 10^{-4}$  atm.

acid-rich oceanic plants have a much shorter life cycle, about 20 days to 1 month, than the cellulose-rich land plants that turn carbon over approximately every 10 years. These differences account for the fact that fluxes of carbon through the land and oceanic phytomass are not too different.

## 2.2 Historical Note on the Carbon Cycle

The discovery of carbon dioxide as a gas that forms by fermentation and by burning of charcoal, under the name of *spiritus silvestris*, is attributed to Jan Baptista (or Baptist) van Helmont, a man of medicine, alchemy, and early chemistry in the then Spanish Netherlands, in the first half of the 1600s (e.g., Graham, 1974). The formation of organic matter from carbon dioxide and water under the action of light, the process known as photosynthesis, has been studied since the later part of the 1700s, when molecular oxygen was discovered in the process and carbon dioxide identified as a component of air. Presentation of the first general scheme of the carbon and nitrogen cycles was attributed to the French chemist, Jean Baptiste André Dumas, in 1841 (Rankama and Sahama, 1950). Dumas (1842) described the cycle of CO<sub>2</sub> consumption and production by respiration, pointing to the sources of “carbonic acid” in the air and soil where it forms from decomposition of manure or organic fertilizers. He made estimates of the residence time of atmospheric oxygen with respect to animal respiration and pointed out that it would cause very small changes in the oxygen content of the atmosphere at a centennial time scale. Significantly, he also pointed out (p. 5) that the Earth's primordial atmosphere must have contained all the carbon dioxide and nitrogen that have been taken up by living organisms.

As to geochemical cycles, an early treatment of the subject appeared in 1875, where several chapters on the cycles of chemical elements were included in a book on Earth's history by Friedrich Mohr, a professor at the University of Bonn, with short chapters on the silicon and carbon cycles among them (Mohr, 1875, pp. 397–398). In 1893 Professor Arvid Högbom, a colleague of Svante Arrhenius, presented a lecture at the Physical Society drawing the conclusion that the chief source of atmospheric CO<sub>2</sub> is in the release of the gas during the natural breakdown of limestone. He further theorized concerning the long-term geologic cycle of carbon by addressing the questions of how much of the CO<sub>2</sub> is retained in the atmosphere, how much is absorbed by the ocean, and how changes in the concentration of this gas in the atmosphere might affect climate (Christianson, 1999). By the 1920s, the cycles of the chemical elements that are involved in biological processes—carbon, nitrogen, and phosphorus—and are also transported between soil, crustal rocks, atmosphere, land and ocean waters, and the Earth's interior were well recognized by modern standards. Alfred Lotka's book, *Elements of Physical Biology*, published in 1925, has chapters on the cycles of carbon dioxide, nitrogen, and phosphorus that present a modern treatment of what we call today the biogeochemical cycles (Lotka, 1925). Furthermore, he wrote that his ideas of the nutrient element cycles and mathematical treatment of biogeochemical problems were developed as far back as 1902 and in his publications starting in 1907. The term biogeochemical reflects the fact that biological, physical, and chemical processes play important roles and interact

with each other in the element cycles that are mediated by photosynthetic primary production and respiration or mineralization of organic matter.

By 1950, the geochemical cycles of elements in the Earth's interior and on its surface became textbook material (Rankama and Sahama, 1950), with the variable degree of detail in each cycle that reflected knowledge of the igneous and sedimentary reservoir contents and some of the inter-reservoir fluxes at the time. This early, if not first, systematic textbook treatment of the geochemical cycles presented diagrams of the geochemical reservoirs as boxes and fluxes between them, and tabulations of the elemental concentrations or masses in some of the individual-reservoirs. Subsequent decades produced the knowledge we have today of the chemical speciation of the elements in the different compartments of the Earth, their abundances, and mechanisms responsible for their flows. While the earlier models of the global biogeochemical cycles of individual elements were static, describing the cycles without their evolution in time, developments in the mathematical treatment of time-dependent multireservoir systems (e.g., Meadows *et al.*, 1972) found their application in the analysis of geochemical cycles (e.g., Lerman *et al.*, 1975). Since then, there has been a great proliferation of cycle models, and in particular of carbon cycle models (e.g., Sundquist and Visser, 2004), at very different physical and time scales, aimed at interpretation of cycle evolution in the past and its projection into the future for the world as a whole, as well as for such global reservoirs as the atmosphere, land, coastal oceanic zone, and the open ocean.

Considerable attention became focused on the global sedimentary cycle and the cycling of salts in the ocean as a result of Kelvin's (William Thomson, later Lord Kelvin) estimates of the age of the Earth between 24 and 94 Ma, made between 1864 and 1899 (Carslaw and Jaeger, 1959), and the estimates of the age of the ocean from the rate of accumulation of sodium brought in by rivers, as was done, for example, by Joly (1899; Drever *et al.*, 1988) whose age of the ocean was about 90 Ma. Gregor (1988, 1992) summarized and discussed in detail the geological arguments in the second half of the 1800s and the early 1900s for the recycling of oceanic sediments after their deposition and for the existing sinks of dissolved salts in ocean water, such as their removal by adsorption on clays, entrapment in sediment pore water, and formation of evaporites that were contrary to the idea of the ocean continuously filling up with dissolved salts. Garrels and Mackenzie (1971) presented the concepts of the sedimentary cycling of materials, that had laid dormant for some years, in book form, and in 1972 these two authors developed a quantitative model of the complete sedimentary rock cycle. Quantitative estimates of sediment recycling rates, based on mass-age sediment distributions, have been made by Gregor (1970, 1980), Garrels and Mackenzie (1971, 1972), and Dacey and Lerman (1983): the total sedimentary mass has a mass half-age of 600 Ma. The differential weathering rates of different rock types gave the half-age of shales and sandstones of about 600 Ma, longer than the ages of more easily weathered rocks, such as carbonates of half-age 300 Ma and evaporites of about 200 Ma. Later work (Veizer, 1988) showed that the recycling rates of the sedimentary lithosphere and the various rock types within it are mainly a function of the recycling rates of the tectonic realms, such as active margin basins, oceanic crust, and continental basement, in which the sediments were accumulated.