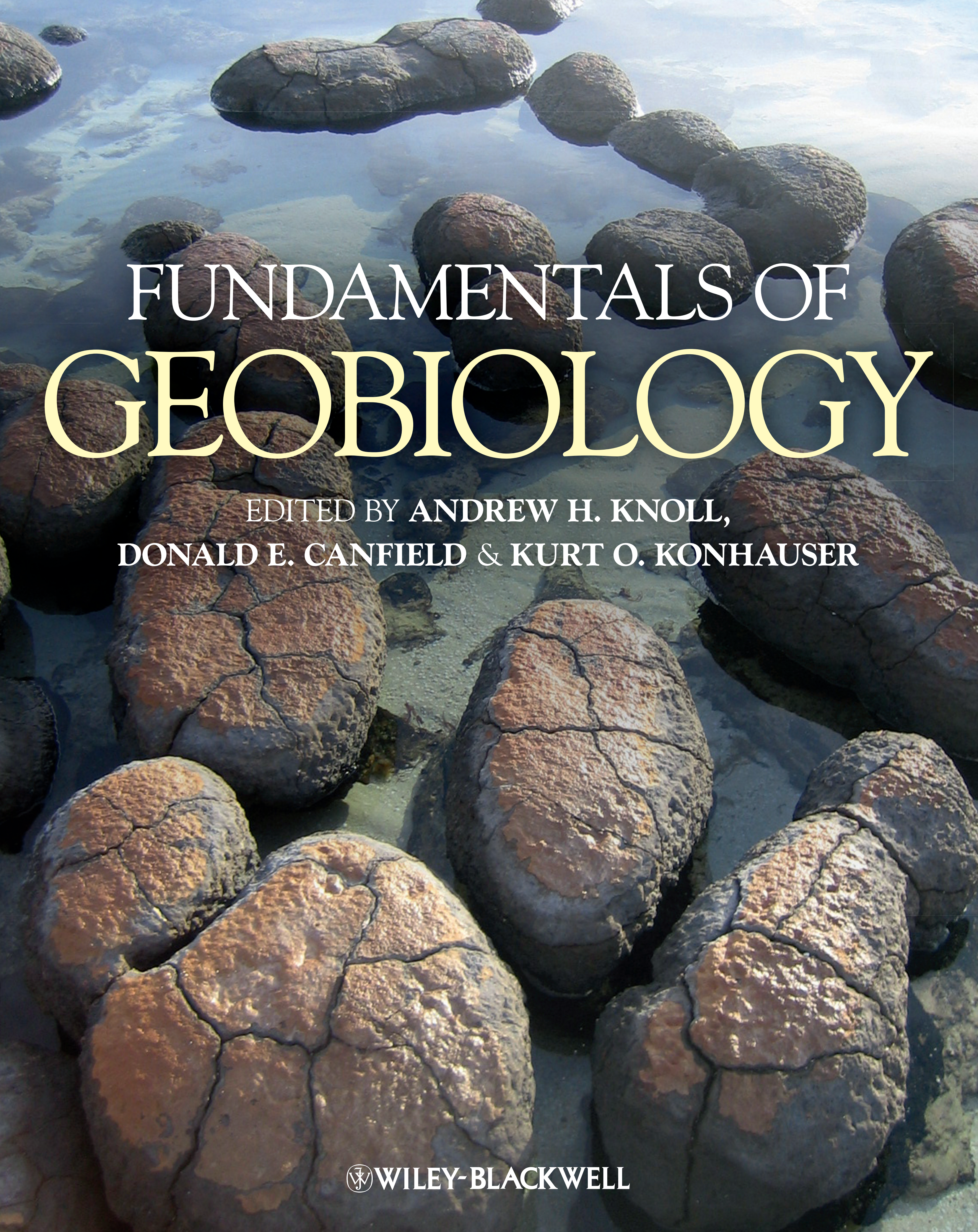

FUNDAMENTALS OF GEOBIOLOGY

EDITED BY ANDREW H. KNOLL,
DONALD E. CANFIELD & KURT O. KONHAUSER

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1
WHAT IS GEOBIOLOGY?

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1.1 Introduction

Geobiology is a scientific discipline in which the principles and tools of biology are applied to studies of the Earth. In concept, geobiology parallels geophysics and geochemistry, two longer established disciplines within the Earth sciences. Beginning in the 1940s, and accelerating through the remainder of the twentieth century, scientists brought the tools of physics and chemistry to bear on studies of the Earth, transforming geology from a descriptive science to a quantitative field grounded in analysis, experiment and modeling. The geophysical and geochemical revolutions both reflected and drove a strong disciplinary emphasis on plate tectonics and planetary differentiation, not least because, for the first time, they made the Earth's interior accessible to research.

While geochemistry and geophysics occupied centre stage in the Earth sciences, another multidisciplinary transformation was taking shape nearer to the field's periphery. Paleontology had long brought a measure of biological thought to geology, in no small part because fossils provide a basis for correlating sedimentary rocks. But while it was obvious that life had evolved on the Earth, it was less clear to most Earth scientists that life had actually shaped, and been shaped, by Earth's environmental history. For example, in *Tempo and Mode in Evolution*, paleontology's key contribution to the Neodarwinian synthesis in evolutionary biology, G.G. Simpson (1944) devoted less than a page to questions of environmental interactions. As early as 1926, however, the Russian scientist Vladimir Vernadsky had published *The Biosphere*, setting forth the argument that life has shaped our planet's surface environment throughout geologic time. Vernadsky also championed the idea of a noosphere, a planet transformed by activities of human beings. A few years later, the Dutch microbiologist Lourens Baas-Becking (1934) coined the term *geobiology* to describe the interactions between organisms and environment at the chemical level. Whereas most paleontologists stressed morphology and systematics, Vernadsky and Baas-Becking focused on metabolism – and in the long run that made all the difference.

Geobiological thinking moved to centre stage in the 1970s with articulation of the Gaia Hypothesis by James Lovelock (1979). Much like Vernadsky before him, Lovelock argued that life, air, water and rocks interact in complex ways within an integrated Earth system. More controversially, he posited that organisms regulate the Earth system for their own benefit. While this latter view, sometimes called 'strong Gaia,' has found little favor with biologists or Earth scientists, most now accept the more general view that Earth surface environments cannot be understood without input from the life sciences. The seeds of these ideas may have been planted earlier, but it was Lovelock who really captured the attention of a broad scientific community.

As the twentieth century entered its final decade, interest in geobiology grew, driven by an increasing emphasis within the Earth sciences on understanding our planetary surface, and supported by accelerating research on the microbial control of elemental cycling, the ecological diversity of microbial life under even

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the most harsh environmental conditions (commonly referred to as *extremeophiles*), the use of microbes to ameliorate pollution (bioremediation) or recover valuable metals from mine waste (biorecovery), Earth's ancient microbial history, and efforts to understand human influences on the Earth surface system. And, in the twenty-first century, universities are increasingly supporting research and education in geobiology, international journals (e.g., *Geobiology, Biogeosciences*) have prospered, textbooks have been published (e.g., Schlesinger, 1997; Canfield *et al*., 2005; Konhauser, 2007; Ehrlich and Newman, 2009), and conferences occur regularly. Without question, geobiology has come of age.

1.2 Life interacting with the Earth

Geobiology is predicated on the observation that biological processes interact with physical processes at and near the Earth's surface. Take, for example, carbon, the defining element of life. Within the *biosphere* – the sum of all environments that support life on Earth – carbon exists in a number of forms and in several key reservoirs. It is present as CO_2 in the atmosphere; as CO_2, HCO_3^- and CO_3^{2-} dissolved in fresh and marine waters; as carbonate minerals in soils, sediments and rocks; and as a huge variety of organic molecules in organisms, in sediments and soils, and dissolved in lakes and oceans. Physical processes move carbon from one reservoir to another; for example, volcanoes add CO_2 to the atmosphere and chemical weathering removes it. Biological processes do as well. In two notable examples, photosynthesis reduces CO_2 to sugar, and respiration oxidizes organic molecules to CO_2. Since the industrial revolution, humans have oxidized sedimentary organic matter (by burning fossil fuels) at rates much higher than those characteristic of earlier epochs, making us important participants in the Earth's carbon cycle. Given the centrality of the carbon cycle to both ecology and climate, its biological and geological components are explored in two early chapters of this book (Chapters 2 and 3) and revisited in the context of human activities in Chapter 22.

Other biologically important elements also cycle through the biosphere. Sulfur, nitrogen, and iron (Chapters 4–6) all link the physical and biological Earth, interacting with each other and, importantly, with the carbon cycle. And oxygen, key to environments that support large animals, including humans, is regulated by a complex and incompletely understood set of processes that, again, have both biological and physical components (Chapter 7).

Unlike physical processes, life evolves, and so the array of biological processes in play within the biosphere has changed through time. The state of the environment supporting biological communities has changed as well. Indeed, given the close relationship between environment and population distributions on the present day Earth, it is reasonable to hypothesize that evolving life has significantly influenced the chemical environment through time and, conversely, that environmental change has influenced the course of evolution.

While metabolism encompasses many of the biological cogs in the biosphere, other processes also play important roles. For example, many organisms precipitate minerals, either indirectly by altering local chemical environments (Chapter 8), or directly by building mineralized skeletons (Chapter 10). Today, skeletons dominate the deposition of carbonate and silica on the seafloor, although this was not true before the evolution of shells, spicules and tests. More subtly, organisms interact with clays and other minerals in a series of surface interactions that are only now beginning to be understood (Chapter 9). While much of geobiology focuses on chemical processes, organisms influence the Earth through physical activities as well – think of microbial communities that can stabilize sand beds (Chapter 16) or worms that irrigate sediments as they burrow (Chapter 11). The example of burrowing reminds us that while microorganisms garner much geobiological attention, plants and animals also act as geobiological agents, and have done so for more than 500 million years (Chapter 11).

In short, Earth surface processes once considered to be largely physical in nature – for example weathering and erosion – are now known to have key biological components (Chapter 12). Life plays a critical role in the Earth system.

1.3 Pattern and process in geobiology

Geobiologists, then, study how organisms influence the physical Earth and vice versa, and how biological and physical processes have interacted through our planet's long history. Much of this research focuses on illuminating *process*: field and experimental studies of how organisms participate in the Earth system, and what consequences these activities have for local to global environmental state. Geobiological research can be fundamental – that is, aimed at achieving a basic understanding of the Earth system and its evolution – or it can be applied. In the case of the latter, microbial populations have been deployed and even engineered to perform tasks that range from concentrating gold dispersed in the talus piles of mines, and removing arsenic from the water supply of Los Angeles, to respiring vast amounts of the petroleum that gushed into the Gulf of Mexico in 2010. Building on earlier chapters, Chapters 13–16 focus on techniques that are prominent in modern geobiological research.

Elucidating the changing role of life through Earth history, sometimes called *historical geobiology*, begins with a basic understanding of geobiological processes, but from there takes on a distinctly geological slant. We would like to interpret the geologic record in terms of active processes and chemical states, but rocks preserve only pattern. Thus, the geobiological interpretation of ancient sedimentary rocks requires that we understand how biological processes and aspects of the ambient environmental state are reflected in the geologically preservable patterns they create. For example, we can use the sulfur isotopic composition of minerals in billion-year-old shales to constrain the biological workings of the ancient sulfur cycle and sulfate abundance in ancient seawater, but can do so only in light of present day observations and experiments that show how biological and physical processes result in particular isotopic patterns.

Of course, there are at least two features that complicate this linkage of geobiological process to geologic pattern. For one, populations evolve, so biological processes observable today may not been active during the deposition of ancient sedimentary rocks. For this reason, historical geobiology has among its goals the establishment of evolutionary pattern in Earth history. The second complication is that many environmental states on the ancient Earth have no modern counterpart. Most obviously, modern surface environments are permeated with oxygen in ways unlikely to have existed during the first two billion years of our planet's development. Other differences exist, as well. Therefore, the present-day Earth system is far removed from the earliest systems where life evolved and then spread out across the planet; it represents a long accumulation of biological, physical and chemical changes through Earth history. Following a chapter on the origin of life (Chapter 17), perhaps the ultimate example of the intimate relationship between biological and physical processes, we present three chapters that outline Earth's geobiological history (Chapters 19–21). Oxygen, biological evolution and chemical change dominate these discussions, but there are other aspects to the story. For example, Chapter 18 discusses how the diversity of minerals found on Earth has expanded through time as the biosphere has changed, providing a twenty-first century account of an intriguing subject suggested long ago by Vernadsky.

Finally, there is the question of us. Either directly or indirectly, humans appropriate nearly half of the total primary production on Earth's land surface. We fix as much nitrogen as bacteria do, and shuttle phosphate from rocks to the oceans at unprecedented rates. As Vernadsky predicted in his early discussion of the noosphere, humans have become extraordinarily important agents of geobiological change. In areas that range from climate change to eutrophication, from ocean acidification to Earth's declining supplies of fossil fuels and phosphate fertilizer, the human footprint on the biosphere is large and growing. Our societal future depends in part on understanding the geobiological influences of humans and in governing the technological processes that have come to play such important roles in the modern Earth system (Chapter 22).

1.4 New horizons in geobiology

It is difficult, if not impossible, to predict the future, and while it would be fun to attempt a forecast of the status of geobiology in say 20 years, we will avoid this. Rather, we highlight that under all circumstances, geobiology will increasingly look to the heavens. *Astrobiology* can be thought of as the application of geobiological principles to the study of planets and moons beyond the Earth. At the moment, claims about life in the universe largely constitute under-constrained statistical extrapolations from our terrestrial experience: some hold that life is abundant throughout the universe, but intelligent life is rare (Ward and Brownlee, 2000), while others suggest that life is rare, but intelligence more or less inevitable wherever life occurs (Conway Morris 2004). Clearly, the way forward lies in exploration. Both remote sensing and lander operations have made remarkable strides during the past decade (e.g., Squyres and Knoll, 2006), so we can be confident that on planets and moons within our solar system, direct observation of potentially geobiological patterns will sharply constrain arguments about life in our planetary neighborhood. And arguments about life in nearby solar systems will be framed in terms of geobiological models of planetary atmospheres glimpsed by Kepler and its technological descendents (Kasting, 2010).

This book, then, is a status report. It contains detailed but accessible summaries of key issues of geobiology, hopefully capturing the state and breadth of this emerging discipline. We have tried to be inclusive in our choice of topics covered within this volume. We recognize, however, that the borders defining geobiology are fluid, and we have likely missed or underrepresented some relevant geobiological topics. We apologize in advance for this. We also hope and trust that in the future, geobiology will expand in both depth and breadth well beyond what is offered here. Our crystal ball is cloudy, but we can be certain that a similar book written twenty years from now will differ fundamentally from this one.

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2
THE GLOBAL CARBON CYCLE: BIOLOGICAL PROCESSES

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2.1 Introduction

Carbon is the fourth most abundant element in our solar system and its chemistry forms the basis of all life on Earth. It is used both as the fundamental building block for all structural biological molecules and as an energy carrier. However, the vast majority of carbon on the surface of this planet is covalently bound to oxygen or its hydrated equivalents, forming mineral carbonates in the lithosphere, soluble ions in the ocean, and gaseous carbon dioxide in the atmosphere. These oxidized (inorganic) forms of carbon are moved on time scales of centuries to millions of years between the lithosphere, ocean and atmosphere via tectonically driven acid-based reactions. Because these reservoirs are so vast (Table 2.1) they dominate the carbon cycle on geological time scales, but because the reactions are so slow, they are also difficult to measure directly within a human lifetime.

The 'geological' or 'slow' carbon cycle is critical for maintaining Earth as a habitable planet (Chapter 2), but entry of these oxidized forms of carbon into living matter requires the addition of hydrogen atoms. By definition, the addition of hydrogen atoms to a molecule is a chemical reduction reaction. Indeed, the addition or removal of hydrogen atoms to and from carbon atoms (i.e., 'redox' reactions), is the core chemistry of life. The processes which drive these core reactions also form a second, concurrently operating global carbon cycle which is biologically catalysed and operates millions of times faster than the geological carbon cycle (Falkowski, 2001). In this chapter, we consider the 'biological', or 'fast' carbon cycle, focusing on how it works, how it evolved, and how it is coupled to the redox chemistry of a few other elements, especially nitrogen, oxygen, sulfur, and some selected transition metals.

2.2 A brief primer on redox reactions

When carbon is directly, covalently linked to hydrogen atoms, the resulting (reduced) molecules are called *organic*. Like acid–base reactions, all reduction reactions must be coupled to a reverse reaction in another molecule or atom; that is the reduction of carbon is coupled to the oxidation of another element or molecule. Under Earth's surface conditions, the addition of hydrogen atoms to carbon requires the addition of energy, while the oxidation of carbon-hydrogen (C–H) bonds yields energy. Indeed the oxidation of C–H bonds forms the basis of energy production for all life on Earth.

Although biologically mediated redox reactions (see Box 2.1) occur rapidly, the products are often kinetically inert. Hence, while it is relatively easy to measure the rate at which a plant converts carbon dioxide into sugars, the product, sugar, is stable. It can be purchased from a local grocery store and kept in a jar in sunlight. It does not spontaneously catch fire or explode. Yet when you eat it, your body extracts the energy from the C–H bonds, and oxidizes the sugar to CO_2 and H_2O.

2.3 Carbon as a substrate for biological reactions

Approximately 75 to 80% of the carbon on Earth is found in an oxidized, inorganic form either as the gas carbon dioxide (CO_2) or its hydrated or ionic equivalents,

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Table 2.1 Carbon Pools in the major reservoirs on Earth

Pools	Quantity (Gt carbon)
Atmosphere	835
Oceans	38,400
Total inorganic	37,400
Surface layer	670
Deep Layer	36,730
Total organic	1,000
Lithosphere	
Sedimentary carbonates	>60,000,000
Kerogens	15,000,000
Terrestrial biosphere (total)	2,000
Living biomass	600–1,000
Dead biomass	1,200
Aquatic biosphere	1–2
Fossil Fuels	4,130
Coal	3,510
Oil	230
Gas	~300
Other (peat)	250

namely bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (see Fig. 2.1). These inorganic forms of carbon are interconvertible, depending largely on pH and pressure, and the three forms partition into the lithosphere, ocean and atmosphere[1] (see Chapter 3). Virtually all inorganic carbon in the oceans is in the form of HCO_3^- with an average concentration of about 2.5 mM. This carbon is removed in association with calcium and magnesium as carbonate minerals. Although the precipitation of carbonates is thermodynamically favourable in the contemporary ocean, it is kinetically hindered, and virtually all carbonates are formed by organisms. The biological precipitation of carbonates is *not* a result of redox reactions, but rather of acid-base reactions; hence, although virtually all carbonates are biologically derived, they remain as oxidized, inorganic carbon. The mineral phases of inorganic carbon are inaccessible to further biological reactions. The total reservoir of inorganic carbon in the ocean is approximately 50 times that of the atmosphere. Indeed, the ocean controls the concentration of CO_2 in the atmosphere on time scales of decades to millennia.

2.3.1 *Carbon fixation*

Entry of inorganic carbon into biological processes involves a process called carbon 'fixation', and there are only two biological mechanisms that lead to the fixation of inorganic carbon: chemoautotrophy and photoautotrophy. Before we consider these in turn, let us first examine what carbon 'fixation' is.

[1] Pure forms of carbon as (e.g.) diamond or graphite are relatively rare and do not undergo biological reaction.

The term carbon 'fixation' is an anachronism that means 'to make non-volatile'. It applies when a gaseous CO_2 is biochemically converted to a solute. There are several enzymatically catalysed reactions that can lead to carbon fixation, however, by far the most important is based on the activity of ribulose 1,5-bisphosphate carboxylase/oxygenase, or Rubisco (Falkowski and Raven, 2007). This enzyme is thought to be the most abundant protein complex on Earth, and it specifically reacts with CO_2 (i.e., it does not recognize hydrated forms of the substrate). Rubisco catalyses a reaction with a 5 carbon sugar, ribulose 1,5 bisphosphate, leading to the formation of two molecules of 3-phosphoglycerate (see Figs 2.2 and 2.3). This reaction, discovered in the late 1940s and early 1950s by Melvin Calvin, Andrew Benson and Jack Bassham, forms the basis of the pathway of carbon acquisition by most photosynthetic organisms (Benson and Calvin, 1950).

It should be noted that Rubisco imprints a strong biological isotope signature that is used extensively in geochemistry. There are two stable isotopes of C in nature: ^{12}C, containing 6 protons and 6 neutrons, accounts for 98.90%, and ^{13}C, containing 6 protons and 7 neutrons, accounts for 1.10%. In the fixation of CO_2 by Rubisco, the enzyme preferentially reacts with the lighter isotope; the net result is that 3-phosphogycerate is enriched by about 25 parts per thousand in ^{12}C relative to the CO_2 in the air or water (Park, 1961). This isotopic fractionation provides a basis for understanding the impact of the biological carbon cycle over geological time (Kump and Arthur, 1999).

The fixation of CO_2 by Rubisco is *not* an oxidation/reduction reaction; the carboxylic acid group has the same oxidation state as CO_2. The biochemical

Box 2.1 Redox reactions

The term *oxidation* was originally used by chemists in the latter part of the 18th century to describe reactions involving the addition of oxygen to metals, forming metallic oxides. For example:

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \qquad \text{(B2.1.1)}$$

The term *reduction* was used to describe the reverse reaction, namely the removal of oxygen from a metallic oxide, for example, by heating with carbon:

$$Fe_3O_4 + 2C \rightarrow 3Fe + 2CO_2 \qquad \text{(B2.1.2)}$$

Analysis of these reactions established that the addition of oxygen is accompanied by the removal of electrons from an atom or molecule. Conversely, reduction is accompanied by the addition of electrons. In the specific case of organic reactions that involve the reduction of carbon, the addition of electrons is usually balanced by the addition of protons. For example, the reduction of carbon dioxide to formaldehyde requires the addition of four electrons *and* four H^+ – that is, the equivalent of four hydrogen atoms.

$$O{=}C{=}O + 4e^- + 4H^+ \rightarrow (CH_2O)_n + H_2O \qquad \text{(B2.1.3)}$$

Thus, from the perspective of organic chemistry, oxidation may be defined as the addition of oxygen, the loss of electrons, or the loss of hydrogen atoms (but not hydrogen ions, H^+); conversely, reduction can be defined as the removal of oxygen, the addition of electrons, or the addition of hydrogen atoms.

Oxidation–reduction reactions only occur when there are pairs of substrates, forming pairs of products:

$$A_{ox} + B_{red} \leftrightarrow A_{red} + B_{ox} \qquad \text{(B2.1.4)}$$

Photosynthesis uses energy from the sun to reduce inorganic carbon to form organic matter; i.e., photosynthesis is a biochemical reduction reaction. In oxygenic photosynthesis, CO_2 is the recipient of the electrons and protons, and thus becomes reduced (it is the A in Equation B2.1.4). Water is the electron and proton donor, and thus becomes oxidized (it is the B in Equation B2.1.4). The oxidation of two moles of water requires the addition of 495 kJ of energy. The reduction of CO_2 to the simplest organic carbon molecule, formaldehyde, requires 176 kJ of energy. The energetic efficiency of photosynthesis can be calculated by dividing the energy stored in organic matter by that required to split water into molecular hydrogen and oxygen. Thus, the maximum overall efficiency of photosynthesis, assuming no losses at any intermediate step, is 176/495 or about 36%.

reduction of 3-phosphoglycerate is the second step in the carbon fixation pathway, and leads to the formation of an aldehyde. This is the only reduction step in the so-called Calvin cycle. The rest of the pathway is primarily devoted to regenerating ribulose 1,5-bisphosphate, and leaves no discernable geochemical signal.

2.3.2 *Chemoautotrophy*

Chemoautotrophs (literally, 'chemical self feeders') are organisms capable of reducing sufficient inorganic carbon to grow and reproduce in the absence of light energy and without an external organic carbon source. Chemoautotrophs likely evolved very early in Earth's history and this process is exclusively carried out by prokaryotic organisms in both the domains Archaea and Bacteria (Stevens and McKinley, 1995).

Early in Earth's history, H_2 was probably an important constituent of the atmosphere a major reductant used by organisms to reduce inorganic carbon to organic biomass (Jørgensen, 2001). Although this process can still be found in marine sediments, where H_2 is produced during the anaerobic fermentation of organic matter, and in hydrothermal environments, where the gas is produced as a byproduct of serpentization, free H_2 is scarce on Earth's surface. Rather, most of the hydrogen is combined (oxidized) by microbes with other atoms, such as sulfur or oxygen, and to a much lesser extent, nitrogen. Hence, most contemporary chemoautotrophs oxidize H_2S or NH_4^+, but also other reduced compounds such as Fe^{2+}.

The driver for chemoautotrophic carbon fixation ultimately depends on a thermodynamically favourable redox gradient. For example, the oxidation of H_2S by microbes in deep sea vents is coupled to the reduction of oxygen in the surrounding water. Hence, this reaction is dependent on the chemical redox gradient between the ventilating mantle plume and the ocean interior that thermodynamically favours oxidation of the plume gases (Jannasch and Taylor, 1984) (Box 2.2).

Chemoautotrophy supplies a relatively small amount of organic carbon to the planet (probably <1%), however this mode of nutrition is critically important in sediments, anoxic basins, and in completing several elemental cycles, including that of N and S. Thus, chemoautotrophy is common in sediments and anoxic water columns where strong redox gradients develop. A classic example would be the oxygen-sulfide interface in microbial mats where sulfide-oxidizing chemoautotrophs thrive, although countless other examples could also be named (Canfield and Raiswell, 1999). Reductants for chemoautotrophs can be generated within in the Earth's crust. An important example, as mentioned above, is the hydrothermal fluids generated in mid-ocean ridge spreading centres. Here, the sulfide and ferrous iron liberated with the fluids sup-

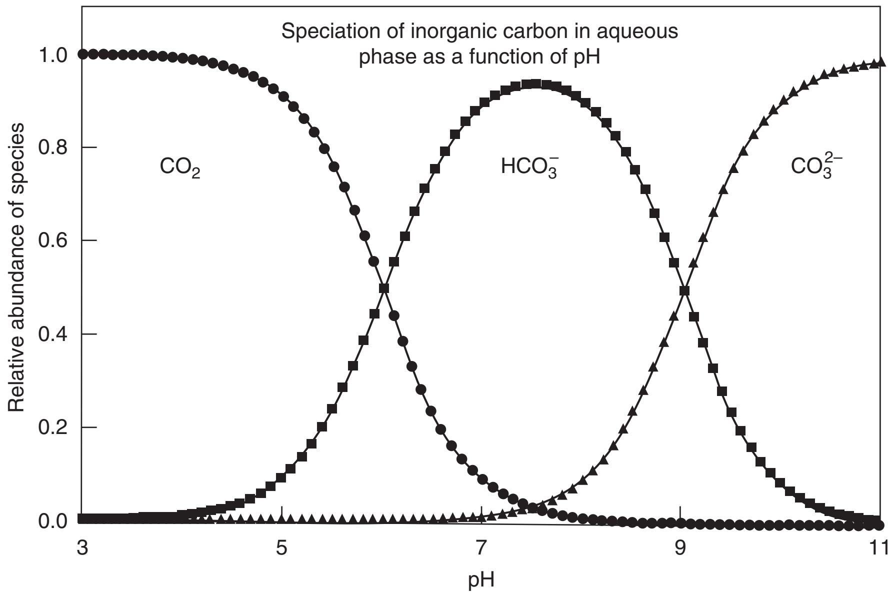

Figure 2.1 The relative distribution of the three major species of dissolved inorganic carbon in water as a function of pH. Note that at pH of seawater (~8.1), approximately 95% of the inorganic carbon is in the form of bicarbonate anion.

port the chemoautotrophic growth of sulfide- and Fe-oxidizers, which use oxygen as the oxidant.

However, early in Earth's history, due to the lack of oxygen, the redox gradients would have been small and hence there would have been no pandemic outbreak of chemoautotrophy. The vents themselves would have supplied H_2 and CO_2, for example, which could have supported the chemoautotrophic growth of methanogens (Canfield *et al.*, 2006), but this would have been on a much smaller scale than the chemoautotrophic sulfide oxidation supported in modern vents. Importantly, magma chambers, volcanism, and vent fluids are tied to either subduction or to spreading regions, which are transient features of Earth's crust and hence only temporary habitats for chemoautotrophs. In the Archean and early Proterozoic oceans, the chemoautotrophs would have had to have been dispersed throughout the oceans by physical mixing in order to colonize new vent regions (Raven and Falkowski, 1999).

2.3.3 Photoautotrophy

Photoautotrophy ('self feeding on light') is the biological conversion of light energy to the fixation of CO_2 in the form of organic carbon compounds. To balance the electrons, a source of reductant is also required. It should be noted that while all photoautotrophs are photosynthetic, not all photosynthetic organisms are photoautotrophs. Many organisms are capable of photosynthesis but can (and, sometimes must) supplement that metabolic strategy with the assimilation of organic carbon (Falkowski and Raven, 2007).

Photoautotrophy can be written as an oxidation–reduction reaction of the general form:

$$2H_2A + CO_2 + \text{Light} \xrightarrow{\textit{Pigment}} (CH_2O) + H_2O + 2A \tag{2.1}$$

In this representation, light is specified as a substrate, with some of the energy of the absorbed light stored in the products. All photoautotrophic bacteria, with the important exception of the cyanobacteria, are incapable of evolving oxygen. In these (mostly) anaerobic organisms, compound A is, for example, an atom of sulfur, and the pigments are bacteriochlorophylls (Van Niel, 1941; Blankenship *et al.*, 1995). All other photoautotrophs, including the cyanobacteria, eukaryotic algae, and higher plants, are oxygenic; that is, Equation 2.1 can be modified to:

$$\text{Chl } a + 2H_2O + CO_2 + \text{Light} \longrightarrow (CH_2O) + H_2O + O_2 \tag{2.2}$$

where Chl *a* is the ubiquitous plant pigment chlorophyll *a*. Equation 2.2 implies that chlorophyll *a* catalyses a reaction or a series of reactions whereby light energy is used to oxidize water:

$$\text{Chl } a + 2H_2O + \text{Light} \longrightarrow 4H^+ + 4e + O_2 \tag{2.3}$$

yielding gaseous, molecular oxygen. True photoautotrophy is restricted to the domains Bacteria and Eukarya. Although some Archaea and Bacteria use the pigment rhodopsin to harvest light, they require organic matter to fuel their metabolism (Beja *et al.*, 2000) and are not photoautotrophs.

2.4 The evolution of photosynthesis

We have discussed above the production of organic matter by photoautrophy, but photosynthesis is more

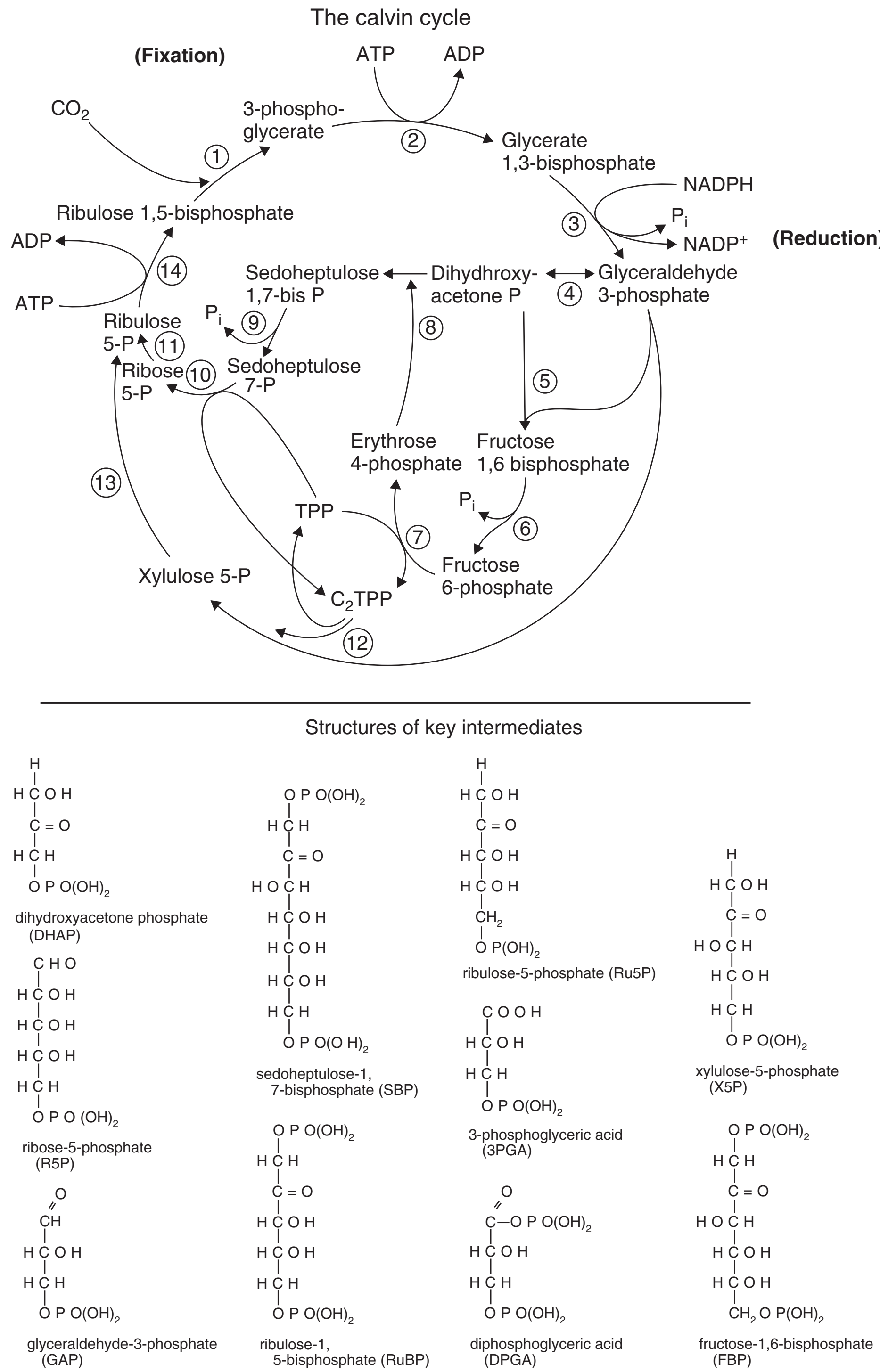

Figure 2.2 The reactions of ribulose 1,5 bisphosphate carboxylase/oxygenase. In the carboxylation process, the enzyme reacts with CO_2 to produce 2 molecules of 3-phosphogycerate, which is the first stable intermediate in the Calvin–Benson cycle. Alternatively, in the oxygenase process, the enzyme reacts with O_2, leading to the production 2 phosphoglycolate which ultimately is respired to CO_2.

broadly defined than this. Normally we consider photosynthesis to include all organisms that use light energy to synthesize new cells and this includes also photoheterotrophs which incorporate organic matter from the environment into their biomass. By far the most efficient and ubiquitous light harvesting systems for photosynthesis are based on porphyrins. The metabolic pathway for the synthesis of porphyrins is extremely old (Mauzerall, 1992); relic porphyrin molecules can be isolated from some ancient Archean (older than 2.5 billion years) rocks. It has been proposed that the porphyrin-based photosynthetic energy conversion apparatus originally arose from the need to prevent UV radiation from damaging essential macromolecules such as nucleic acids and proteins (Mulkidjanian and Junge, 1997). Indeed, most photosynthetic bacteria retain an ability to harvest UV light for

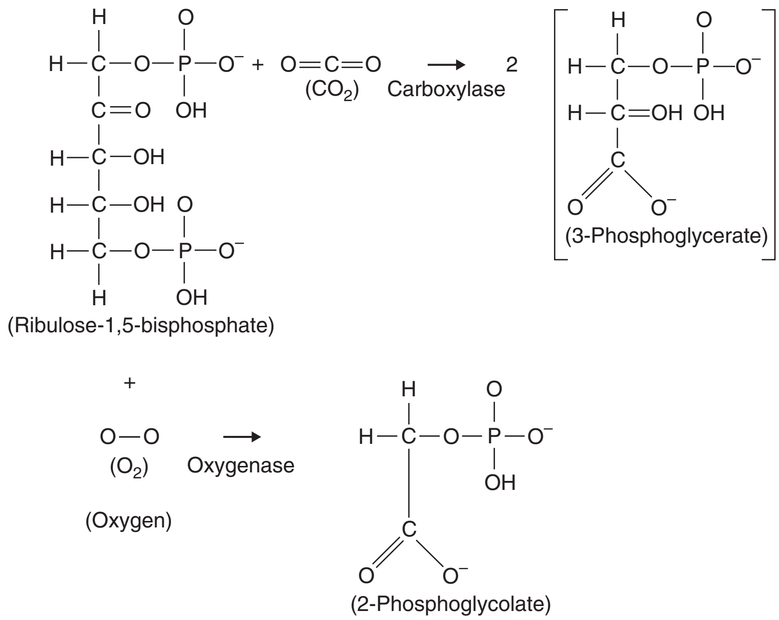

Figure 2.3 The basic Calvin–Benson cycle. CO_2 is condensed with ribulose 1,5 bisphosphate to form 3 phosphoglycerate (1), which is subsequently reduced to an aldehyde (reactions 2 and 3). The remaining reactions in the cycle are directed towards regenerating ribulose 1,5 bisphosphate; the intermediate structures are indicated.

Box 2.2 The Nernst Equation

As mentioned in the text, oxidation–reduction reactions involve the transfer of electrons. The tendency for a molecule to accept or release an electron is viewed relative to the ability of a 'standard' molecule to do the same, and this is normally the standard hydrogen electrode (SHE), which is represented by the following reaction:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad \text{(B2.2.1)}$$

The SHE is defined at 25 °C, and one atmosphere of H_2 gas, and for an $H^+_{(aq)}$ activity of 1 (pH = 0). The tendency of a species to accept or liberate electrons is formally known as *electrode potential* or *redox potential*, *E*. The SHE is arbitrarily assigned an *E* of 0. The redox potential of reactions at standard state (unit activity for reactants and products), and relative to the SHE are given the designation E_0. In comparing to the SHE, reactions are always written as reduction reactions after the following general form:

$$aA_{oxid} + be^- + cH^+ \rightarrow dA_{red} - gG \qquad \text{(B2.2.2)}$$

It is often more useful to define the redox potential at pH = 7, an environmentally relevant pH, and when so defined, the redox potential is denoted by the symbols E_0' or sometimes E_{m7}. The E_0' for a standard hydrogen electrode is −420 mV.

It is rare for organisms to live under standard-state chemical conditions (unit activity concentrations or reactants and products), and the electrode potential can be modified with the Nernst equation to reflect environmental conditions. With the general equation represented in B2.2.2, the Nernst equation is written as:

$$E = E_0 + 2.3(RT/nF)\log_{10}\left(a^{a}_{Aoxid}a^{c}_{H+}/a^{d}_{Ared}a^{g}_{G}\right) \qquad \text{(B2.2.3)}$$

Where *E* is the redox potential (in volts) under environmental conditions, E_0 is the standard redox potential, *F* is Faraday's constant (= 96 485 coulombs = the electical charge in 1 mole of electrons), *n* is the number of moles of electrons (Faradays) transferred in the half-cell reaction, *R* is the Boltzmann gas constant, *T* is temperature in Kelvin, and $a_y^{\,x}$ represents the activity (sometimes concentration is used, but this is not strictly correct) of species *y* raised to the stoichiomentric factor *x* in the balanced half reaction equation. The value of 2.3(*RT*/*F*) is 59 mV.

photosynthesis, but these bacteria cannot split water and evolve oxygen. These are termed 'anoxygenic' organisms, with light-mediated sulfide oxidation, as introduced above, a common (but not exclusive) metabolism.

In the ancient oceans, anoxygenic photosynthesis had profound biogeochemical consequences. It led not only to the formation of organic matter, but to the oxidation of such reductants as Fe^{2+} (to $Fe^{3+,}$ which precipitated as Fe oxides), which was found in abundance in ancient oceans and S^{2-} (to S^0 or SO_4^{2}), which was found in ancient hydrothermal springs, in ancient oceans during some time periods (Canfield, 1998; Brocks *et al*., 2005) and in contemporary analogs such as in Yellowstone National Park. While these reductants were ultimately resupplied via weathering in the case of Fe, or from hydrothermal fluids in the case of sulfide, the rate of supply was slow relative to the rate of at which organisms can photosynthesize. Hence there was a drive to find a reductant for photosynthesis that is virtually limitless. The obvious molecule is H_2O.

Liquid water contains ~55 kmol H_2O per m^3, and there are 10^{18} m^3 of water in the hydrosphere and cryosphere. However, the use of H_2O as a reductant for CO_2-fixation to organic matter requires a larger energy input than does the use of Fe^{2+} or S^{2-}. Indeed, for oxygenic photosynthesis to occur, several innovations on the old anoxygenic anaerobic photosynthetic machinery had to occur (Blankenship *et al*., 2007). Among these innovations were the evolution of: (a) a new photosynthetic pigment, chlorophyll *a*, which operates at a higher energy level than bacterial chlorophylls; (b) two photochemical reaction centres that operate in series, one of which splits water, the second of which forms a biochemical reductant that is used to reduce inorganic carbon; and (c) a unique complex comprised of four Mn atoms bound to a group of proteins that forms the 'oxygen evolving complex', i.e., the site in which four electrons are sequentially extracted from two molecules of liquid water, one at a time, via the absorption of four photons.

The photochemical apparatus responsible for oxygenic photosynthesis is the most complex energy transduction system found in nature; there are well over 100 genes necessary for its synthesis (Shi and Falkowski, 2008). It appears to have arisen only once, in a single clade of bacteria (the cyanobacteria), and has never been appropriated by any other prokaryote. The origin and evolutionary trajectory of oxygenic photosynthesis remains obscure (Falkowski and Raven, 2007). It almost certainly arose sometime in the Archean Eon, although the timing is uncertain (see Chapter 7). The two photosystems appear to have different origins: the water splitting system is derived from purple photosynthetic bacteria, while the second reaction centre is derived from green sulfur bacteria. How the two reactions became incorporated into a single organism is unknown.

In order to oxidize water, the photochemical reaction must generate an oxidant with a potential of +0.8 V (Em_7) or more. This is significantly greater than is found in any extant anoxygenic photoautotroph (the highest is ca. +0.4 V). The oxidizing potential in oxygenic photosynthesis is the highest in nature, and ultimately, oxygenic photosynthesis became the primary mechanism for reducing CO_2 and forming organic carbon. Once established, it freed the microbial world from a limited supply of reductants for carbon fixation, and it decoupled the biological carbon cycle from the geological carbon cycle on time scales of millenia (Falkowski and Raven, 2007).

2.5 The evolution of oxygenic phototrophs

2.5.1 The cyanobacteria

Cyanobacteria are the only oxygenic phototrophs known to have existed before ~2 Ga. There is some suggestion that the 1.8 billion year old fossil *Grypania* may represent an eukaryotic algae (Han and Runnegar, 1992), but this has not been firmly established. Cyanobacteria numerically dominate the phototrophic community in contemporary marine ecosystems, and clearly their continued success bespeaks an extraordinary adaptive capacity.

By 2 billion years ago, cyanobacteria were probably the major primary producers (a primary producer is an organism that supplies organic matter to heterotrophs), with likely contributions from anoxygenic phototrophs and chemoautotrophs. In the contemporary ocean, the cyanobacteria fix approximately 60% of the ~45 Pg C assimilated annually by aquatic phototrophs (Falkowski and Raven, 2007). Their proportional contribution to 'local' marine primary productivity is greatest in the oligotrophic central ocean gyres that form about 70% of the surface waters of the seas. Two major groups of marine cyanobacteria can be distinguished. The phycobilin-containing *Synechococcus* are more abundant nearer the surface and the (divinyl) chlorophyll *b*-containing *Prochlorococcus* are generally more abundant at depth (Chisholm, 1992) (Table 2.2).

Some cyanobacteria not only fix inorganic carbon, but also fix N_2. Biological reduction of N_2 to NH_3 (i.e., 'fixation') is catalysed by nitrogenase, a heterodimeric enzyme that is irreversibly inhibited by O_2. Molecular phylogenetic trees suggest that N_2 fixation evolved in Bacteria prior to the evolution of oxygenic photosynthesis (Zehr *et al*., 1997) and was acquired by cyanobacteria relatively late in their evolutionary history (Shi and Falkowski, 2008). The early evolution of nitrogenase is also indicated by the very large Fe requirement for the enzyme; the holoenzyme contains 38 iron atoms. This transition metal was much more available in the water column of the oceans in the Archean and

Table 2.2 Annual and seasonal net primary production (NPP) of the major units of the biosphere (after Field *et al.*, 1998)

	Ocean NPP		Land NPP
Seasonal			
April–June	10.9		15.7
July–September	13.0		18.0
October–December	12.3		11.5
January–March	11.3		11.2
Biogeographic			
Oligotrophic	11.0	Tropical rainforests	17.8
Mesotrophic	27.4	Broadleaf deciduous forests	1.5
Eutrophic	9.1	Broadleaf and needleleaf forests	3.1
Macrophytes	1.0	Needleleaf evergreen forests	3.1
		Needleleaf deciduous forest	1.4
		Savannas	16.8
		Perennial grasslands	2.4
		Broadleaf shrubs with bare soil	1.0
		Tundra	0.8
		Desert	0.5
		Cultivation	8.0
Total	48.5		56.4

Source: Field *et al*. (1998). All values in GtC. Ocean NPP estimates are binned into three biogeographic categories on the basis of annual average C_{sat} for each satellite pixel, such that oligotrophic = $C_{sat} < 0.1\,mg\,m^{-3}$, mesotrophic = $0.1 < C_{sat} < 1\,mg\,m^{-3}$, and eutrophic = $C_{sat} > 1\,mg\,m^{-3}$ (Antoine *et al*., 1996). This estimate includes a 1 GtC contribution from macroalgae (Smith, 1981). Differences in ocean NPP estimates between Behrenfeld and Falkowski (1997b) and those in the global annual NPP for the biosphere and this table result from (i) addition of Arctic and Antarctic monthly ice masks; (ii) correction of a rounding error in previous calculations of pixel area; and (iii) changes in the designation of the seasons to correspond with Falkowski *et al*. (1998). The macrophyte contribution to ocean production from the aforementioned is not included in the seasonal totals. The vegetation classes are those defined by DeFries and Townshend (DeFries and Townshend, 1994).

early Proterozoic Eons than it is today (Berman-Frank *et al*., 2001). Indeed, iron has been suggested to limit nitrogen fixation in the contemporary ocean (Falkowski 1997).

2.5.2 *The eukaryotes*

Eukaryotes are unicellular or multicellular organisms whose cells possess nuclei that contain their DNA. All eukaryotes were derived from a symbiotic association between a host cell closely affiliated with the Archaea (Woese, 1998), and an organelle derived from the Bacteria. The symbiosis occurred via the engulfment of the latter cell by the former, after which most of the genes in the bacterium were either lost of transferred to the host. There appears to have been only two primary symbiotic events. The first involved a purple bacterium, which may have been photosynthetic (Woese *et al*., 1984); this organism ultimately came to be a mitochondrion, the primary energy producing system for eukaryotes. In a second symbiotic event, a host eukaryote engulfed a cyanobacterium. The cyanobacterium would, over time, lose many of its genes and become a plastid (or, specifically in green plants, a chloroplast) (Martin and Herrmann, 1998), leading the evolution of an oxygenic photosynthetic eukaryote. Because they lost so many genes, the endosymbiotic cyanobacteria became incapable of independent existence outside the symbiotic association; essentially they are enslaved by the host cell (Bhattacharya and Medlin, 1998). All eukaryotic photoautotrophs are oxygenic (Falkowski *et al*., 2004).

While there are eight major phyla of photosynthetic eukaryotes, they can be broadly lumped into two major groups: a green and a red clade. The former contain, in addition to chlorophyll *a*, a second photosynthetic pigment, chlorophyll *b*. The latter does not contain chlorophyll *b*, but rather other pigments, especially chlorophyll c. Regardless of the evolutionary history of the host, however, the core photosynthetic machinery is highly conserved. That is, the same basic structure that evolved in cyanobacteria is found in every oxygenic photosynthetic eukaryote. Indeed, in some cases, the gene sequences are so highly conserved across the ca. 3 billion years of evolution that they have been called 'frozen metabolic accidents' – genes that essentially have ceased evolving (Shi *et al*., 2005).

Approximately 500 million years ago, one green alga ultimately became the progenitor of all higher plants (Knoll, 1992; Kenrick and Crane, 1997). Although there are in excess of 250,000 species of extant higher plants, they are all relatively closely related to each other. Except for diatoms that live in soils, member of the red clade of photosynthetic eukaryotes successfully colonized land. These organisms, however, became extremely successful in aquatic ecosystems. All of the major photosynthetic eukaryotes in the ocean arose by *secondary* endosymbiosis, where eukaryotic phagotrophic flagellates ingested eukaryotic phototrophs (Falkowski *et al*., 2004). This process led to the evolution of diatoms and other closely related groups (including the kelps), haptophyte algae including coccolithophores, and dinoflagellates (Delwiche, 2000). These three groups, which are very distantly related, have left fossils that allow some physical reconstruction of their evolutionary history. There is fossil evidence that a (macrophyte) red alga existed 1.2 Ga, with unicellular (cysts) and macrophytic green algae from 1 and 0.6 Ga bp respectively.

While fossils referable to heterokonts (which include diatoms) are known from the late Proterozoic, it is possible that these are not photosynthetic, granted the much later (280 Ma bp) origin of *photosynthetic* heterokonts suggested by molecular clock data calibrated from the molecular phylogeny and fossil record of diatoms (Bhattacharya *et al*., 1992; Kooistra *et al*., 2007). The precursors of modern dinoflagellates probably originated more than 250 million years ago (Falkowski *et al*., 2004), while at least the coccolithophorid variants of the haptophytes are first known from fossils of the early Triassic period (de Vargas *et al*., 2007).

This brief account of the evolution and diversification of aquatic photoautotrophs reveals that there is much more higher-taxon diversity among aquatic than terrestrial primary producers; 95% or more of species involved in terrestrial primary producers are embryophytes derived from a single class (Charophyceae) of a single Division (Chlorophyta) among the eight Divisions of eukaryotic aquatic photoautotrophs. By contrast, there is no comparable taxonomic dominance of primary producers in aquatic ecosystems. Simply put, the land is green and the oceans are red (Falkowski *et al*., 2003).

2.6 Net primary production

Photosynthesis allows an organism to convert inorganic carbon to organic matter, yet the organism must also use some of that organic matter for its own metabolic demands. Hence, ecologists have devised another term: net primary production (NPP), defined as that fraction of photosynthetically produced carbon that is retained following all respiratory costs of the photoautotrophs and consequently is available to the next trophic level in the ecosystem (Lindeman, 1942).

In terrestrial ecosystems, NPP is derived from empirical measurements of leaf area (i.e., the ability of a plant to absorb light), leaf nitrogen content (a surrogate for the content of the photosynthetic machinery, as leaves are the photosynthetic organ of a plant), irradiance, temperature and water availability. To a first order, the distribution of plants on land is controlled by water availability (Mooney *et al*., 1987). When water is available, the productivity of terrestrial plants is mainly controlled by how much light is intercepted by the leaves (Nobel *et al*., 1993; Field *et al*., 1998). Models for NPP on land are relatively easy to verify; plants can be weighed and their carbon content can be measured.

In aquatic ecosystems, net primary production is generally estimated from incorporation rates of ^{14}C-labelled inorganic carbon (supplied as bicarbonate) into organic matter. Alternative approaches include oxygen exchange in an enclosed volume (a technique which is far less sensitive and much more time-consuming) and variable fluorescence (which embraces a variety of approaches) (Falkowski *et al*., 1998). As for terrestrial ecosystems, extrapolation of photosynthetic rates from any technique to the water column requires a mathematical model. The commonly used strategy is to derive an empirical relationship between photosynthesis and irradiance for a given phytoplankton or macrophyte community, and to integrate that (instantaneous) relationship over time and depth in the water column. Assuming some respiratory costs during the photo-period and during the dark, this approach gives an estimate of net primary production for the water column (Behrenfeld and Falkowski, 1997).

Using satellite-based images of terrestrial vegetation and ocean water leaving radiances (i.e., the visible light scattered back to space from the ocean), it is possible to construct maps of the global distributions of NPP. Briefly, the terrestrial NPP is constructed from estimates of leaf cover and irradiance. For the oceans, phytoplankton chlorophyll is derived based on the ratio of green to blue light that is reflected back to space. In the absence of photosynthetic pigments in the upper ocean, radiances leaving water would appear blue to an observer in space. In the presence of chlorophylls and other photosynthetic pigments, some of the blue radiation is absorbed in the upwelling stream of photons, thereby reducing the overall radiance; the water becomes ‘darker’. The fraction of blue light that is absorbed is proportional to the chlorophyll concentration. After accounting for scattering and absorption by the atmosphere, satellite-based maps of both terrestrial vegetation and ocean color can be used to infer the spatial and temporal variations of photosynthetic biomass from which NPP is derived (Behrenfeld and Falkowski, 1997).

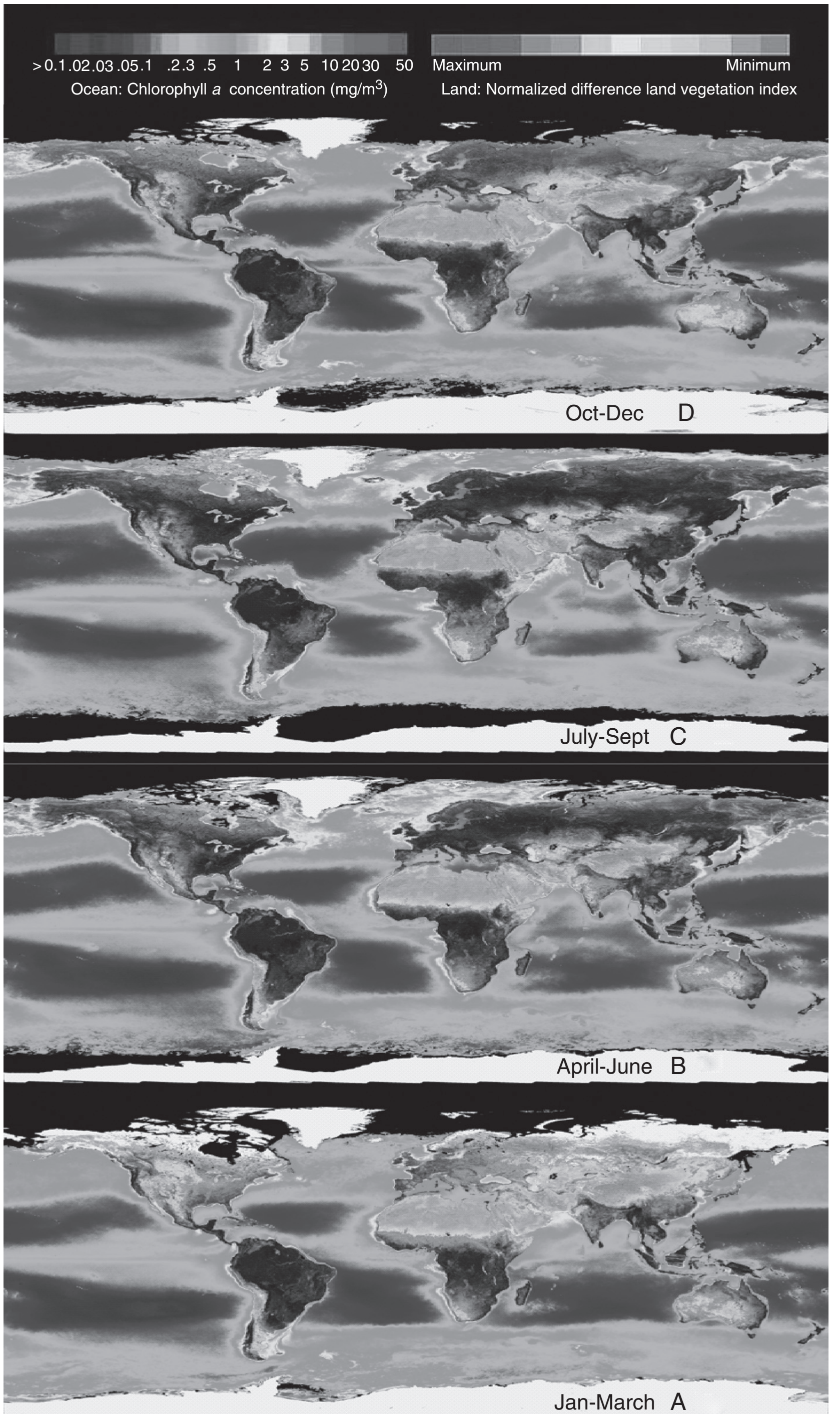

Figure 2.4 Seasonal, maps of global inventories of photosynthetic biomass in the oceans and on land as derived from satellite images. These data are used to construct global estimates of primary production (e.g. Field *et al*., 1998). Note the strong seasonal variations in biomass, especially at high latitudes in both hemispheres (data courtesy of NASA).

Monthly, seasonal and annual maps of global ocean net primary production have been developed that incorporate a primary production model into global ocean colour images of phytoplankton chlorophyll (Fig. 2.4). Such models suggest that annual net ocean photosynthetic carbon fixation is about 45±5GtC per annum (Behrenfeld and Falkowski, 1997a, b). This productivity is driven by a photosynthetic biomass that amounts to ca. 1GtC. Hence, phytoplankton biomass in the oceans turns over on the order of once every two weeks; the overwhelming majority (~85%) of the productivity is consumed by heterotrophs in the upper ocean, and about 15% sinks into the ocean interior where virtually all is consumed ('remineralized') and converted back to inorganic carbon (see also Chapter 3). Only a very small fraction of the organic matter produced is buried in marine sediments. Simply put, less than 1% of the photosynthetic biomass on Earth accounts for about 50% of the net primary productivity (Field *et al*., 1998). What about the other 50%?

Net primary production in terrestrial ecosystems accounts for approximately 52 GtC per annum, and is supported by a biomass of approximately 500 GtC (Field *et al*., 1998). Thus, the turnover time of terrestrial plant biomass is on the order of a decade. As in the ocean, the overwhelming majority of terrestrial plant production is recycled back to inorganic carbon, primarily by fungi and microbes which degrade dead plants. In terrestrial ecosystems, virtually all of the photosynthetic biomass is consumed by heterotrophs long after it was produced. For example, the leaves on deciduous trees remain until the autumn, when they then die and fall to the ground. Over the coming years, virtually 100% of the leaf litter will be consumed by microbes and fungi, but very little will have been eaten by an animal. Terrestrial ecosystems contain large amounts of carbon associated with living structures (e.g. wood in trees), but their photosynthetic rates are not sufficiently different than aquatic ecosystems, which have a much faster rate of ecological metabolism. Thus, although the recycling time for terrestrial plant production is much longer than that in the ocean, the fates are basically the same; virtually all of the organic matter is reprocessed by heterotrophs resulting in a biological cycle that has relatively small impact on the ocean/atmosphere inventory of CO_2 on time scales of decades or centuries (Falkowski *et al*., 2000).

2.7 What limits NPP on land and in the ocean?

All organisms are primarily composed of six major elements: H, C, N, O, P and S (Schlesinger, 1997). The ratios of these elements can vary widely, depending on the type of organism and the ecosystem; however, one or more of these elements often limits NPP. The limitations fundamentally differ between aquatic and terrestrial ecosystems.

Terrestrial plants have an absolute requirement for water, which clearly is not a problem for aquatic photoautotrophs. However, even when water is ample, carbon fixation is not necessarily maximal. One of the major limiting factors limiting NPP on land is the availability of CO_2 itself. Although Rubisco is the most abundant protein on Earth, it has a low affinity for CO_2. Saturation values for CO_2 in terrestrial ecosystems are in the order of ca. 500 parts per million, significantly above that found in the contemporary atmosphere (Mooney *et al*., 1991). To make matters even worse, the enzyme also 'mistakes' O_2 as a substrate (hence, the origin of the term 'oxygenase' in the appellation of the enzyme). Indeed, in most terrestrial plants, approximately 35% of the time, the enzyme reacts with O_2 leading to the immediate respiration of two carbon products which are never converted into biomass. This 'photorespiratory' process leads to a large loss in potential NPP when CO_2 is not saturating. Some terrestrial plants have overcome this limitation by developing a high-affinity carbon fixation process which allows them to use lower levels of CO_2; these so-called C_4 plants are primarily tropical grasses (such as cane sugar), and account for approximately 15% of global terrestrial NPP (Berry, 1999). Thus, on land, both water and CO_2 are major factors limiting NPP.

In aquatic ecosystems, water and inorganic carbon are not limiting. Although the concentration of gaseous CO_2 in the oceans is only ~10 μM, the total concentration of inorganic carbon is ~2.5 mM, of which 95% is in the form of HCO_3^-. Although HCO_3^- cannot be used by Rubisco directly, the anion can be transported into cells from the sea and converted to CO_2 by the enzyme carbonic anhydrase, which is one of the most catalytically active enzymes known. The transport and dehydration of HCO_3^- by aquatic photoautotrophs is called a 'carbon concentrating mechanism', and it virtually assures that carbon never limits NPP in aquatic ecosystems (Kaplan and Reinhold, 1999). If water or inorganic carbon are not limiting, what is?

Globally, nitrogen and phosphorus are the two elements that immediately limit NPP in both lakes and the oceans. It is frequently argued that since N_2 is abundant in both the ocean and the atmosphere, and since in principle it can be biologically reduced to the equivalent of NH_3 by N_2-fixing cyanobacteria, then nitrogen cannot be limiting on geological time scales (Redfield, 1958; Barber, 1992). Therefore, phosphorus, which is supplied to the ocean by the weathering of continental rocks, must ultimately limit biological productivity (Broecker and Peng, 1982; Tyrell, 1999). The underlying assumptions of these tenets should, however, be considered within the context of the evolution of biogeochemical cycles.

The main source of fixed inorganic nitrogen to the oceans is biological nitrogen fixation. This is strictly a prokaryotic process, and in the modern ocean, it is conducted mainly by cyanobacteria. On the early Earth, however, before the evolution of nitrogen fixers, electrical discharge or bolide impacts may have promoted NO formation from the reaction between N_2 and CO_2, but the yield for these reactions is extremely low. Moreover, any volcanogenic NH_3 in the atmosphere would have photodissociated from UV radiation (Kasting, 1990) while N_2 would have been stable (Warneck, 1988; Kasting, 1990). Biological N_2 fixation is a strictly anaerobic process (Postgate, 1971), and the genes encoding the catalytic subunits for nitrogenase are highly conserved in cyanobacteria and other prokaryotes that fix nitrogen, strongly suggesting a common ancestral origin (Zehr *et al*., 1995). Since fixed inorganic nitrogen was likely to have been scarce prior to the evolution of diazotrophic (nitrogen fixing) organisms, there was strong evolutionary selection for nitrogen fixation on the early Earth.

The formation of nitrate from ammonium by nitrifying bacteria requires molecular oxygen (see Chapter 7); hence, nitrification must have evolved following the formation of free molecular oxygen in the oceans by oxygenic photoautotrophs. Therefore, from a geological perspective, the conversion of ammonium to nitrate probably proceeded rapidly and provided a substrate, NO_3^-, that eventually could serve both as a source of nitrogen for photoautotrophs and as an electron acceptor for a diverse group of heterotrophic, anaerobic bacteria, the denitrifiers.

In the sequence of the three major biological processes that constitute the nitrogen cycle, denitrification must have been the last to emerge. This process, which permits the reduction of NO_3^- to (ultimately) N_2, requires hypoxic or anoxic environments and is sustained by high sinking fluxes of organic matter. With the emergence of denitrification, the ratio of fixed inorganic N to dissolved inorganic phosphate in the ocean interior could only be depleted in N relative to the sinking flux of the two elements in POM. Indeed, in all of the major basins in the contemporary ocean, the N:P ratio of the dissolved inorganic nutrients in the ocean interior is conservatively estimated at 14.7 by atoms (Fanning, 1992) or less (Anderson and Sarmiento, 1994), compared to the Redfield ratio of 16/1.

There are three major conclusions that may be drawn from the foregoing discussion. First, because the sinking flux of particulate matter has an organic N to P ratio (about 16/1) which exceeds the N to P ratio of the deep ocean dissolved inorganic pool (average 14.7/1 as noted above), the average upward flux of nutrients is slightly enriched in P relative to the requirements of the photoautotrophs (Redfield, 1958; Gruber and Sarmiento, 1997). Hence, with some exceptions (Wu *et al.* 2000), dissolved inorganic fixed nitrogen generally limits primary production throughout most of the world's oceans on ecological times scales (Barber, 1992); (Falkowski, 1998). Second, the N to P ratio of the deep-ocean inorganic dissolved pool was established by biological processes, not vice versa (Redfield, 1934; Redfield *et al.*, 1963). Third, if dissolved inorganic nitrogen rather than phosphate limits productivity in the oceans, then it follows that the ratio of nitrogen fixation to denitrification plays a critical role in determining primary production and the net biologically mediated exchange of CO_2 between the atmosphere and ocean (Codispoti, 1995).

On ecological time scales, primary production is limited by nutrient supply and the efficiency of nutrient utilization in the euphotic zone. There are three major areas of the world ocean where inorganic nitrogen and phosphate are in excess throughout the year, yet the mixed layer depth appears to be shallow enough to support active primary production (if the mixed layer depth extends below the depth where sufficient light is available for primary production, production becomes limited): these are the eastern equatorial Pacific, the subarctic Pacific, and Southern (i.e., Antarctic) Oceans. For the subarctic North Pacific, Miller *et al.* (1991) suggested a tight coupling between phytoplankton production and consumption by zooplankton. This grazer-limited hypothesis was used to explain why the phytoplankton in the North Pacific do not form massive blooms in the spring and summer like their counterparts in the North Atlantic (Banse, 1992).

In the mid-1980s, however, it became increasingly clear that the concentration of trace metals, especially iron, was extremely low in all three of these regions (Martin *et al.*, 1991). Indeed, in the eastern equatorial Pacific the concentration of soluble iron in the euphotic zone is only 100 to 200 pM, about an order of magnitude lower than found in other areas of the open ocean. Although iron is the most abundant transition metal in the Earth's crust, in its most commonly occurring form, Fe^{3+}, it is virtually insoluble in oxygenated water. The major source of iron to the euphotic zone of the ocean is aeolian dust, originating from continental deserts. In the three major areas of the world oceans with high inorganic nitrogen in the surface waters and low chlorophyll concentrations, the flux of aeolian iron is extremely low (Duce and Tindale, 1991). In experiments in which iron was artificially added on a relatively large scale to the waters in the equatorial Pacific, Southern Ocean, and subarctic Pacific there were rapid and dramatic increases in photosynthetic energy conversion efficiency and phytoplankton chlorophyll concentrations (Boyd *et al.*, 2007). Beyond doubt, NPP and export production in all three regions is limited by the availability of a single micronutrient – iron.

2.8 Is NPP in balance with respiration?

On long time scales, a very small fraction of net primary production escapes respiration to be become buried in sediments and transferred to the lithosphere. This process has profound influence on planetary redox state. As organic matter, by definition, contains reducing equivalents, its burial requires that oxidizing equivalents accumulate elsewhere in the system. Indeed, the net burial of organic matter on geological time scales implies the oxidation of the atmosphere and ocean; i.e., the accumulation of free molecular oxygen requires burial and sequestration of organic carbon (see Chapter 7). How can we assess how much organic carbon is buried?

Recall that Rubisco strongly discriminates against the heavier isotope of carbon, ^{13}C. The ultimate source of CO_2 to Earth's surface is volcanism with a distinct