CHAPTER

2

Origins

INTRODUCTION

Six elements, H, C, N, O, P, and S, are the major constituents of living tissue and account for 95% of the mass of the biosphere. At least 25 other elements are known to be essential to at least one form of life, and it is possible that this list may grow slightly as we improve our understanding of the role of trace elements in biochemistry (Williams and Fraústo da Silva 1996).[1] In the periodic table (see inside front cover), nearly all the elements essential to life are found at atomic numbers lower than that of iodine at 53. Even though living organisms affect the distribution and abundance of some of the heavier elements, the biosphere is built from the "light" elements (Deevey 1970, Wackett et al. 2004). Ultimately, the environment in which life arose and the arena for biogeochemistry today was determined by the relative abundance of chemical elements in

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[1] Arsenic is known to be an essential trace element for some species, but recent reports of bacteria that are able to grow using arsenic as a substitute for phosphorus (Wolfe-Simon et al. 2011) are largely discounted (Erb et al. 2012).

our galaxy and by the subsequent concentration and redistribution of those elements on Earth's surface.

In this chapter we will examine models that astrophysicists suggest for the origin of the elements. Then we will examine models for the formation of the solar system and the planets. There is good evidence that the conditions on the surface of the Earth changed greatly during the first billion years or so after its formation—before life arose. Early differentiation of the Earth, the cooling of its surface, and the composition of the earliest oceans determined the arena for the origins of life. Later changes caused by the evolution and proliferation of life strongly determined the conditions on our planet today. In this chapter, we will consider the origin of the major metabolic pathways that characterize life and affect Earth's biogeochemistry. The chapter ends with a discussion of the planetary evolution that has occurred on Earth compared to its near neighbors—Mars and Venus.

ORIGINS OF THE ELEMENTS

Any model for the origin of the chemical elements must account for their relative abundance in the Universe. Estimates of the cosmic abundance of elements are made by examining the spectral emission from the stars in distant galaxies as well as the emission from our Sun (Ross and Aller 1976). Analyses of meteorites also provide important information on the composition of the solar system (Figure 2.1). Two points are obvious: (1) with three exceptions—lithium (Li), beryllium (Be), and boron (B)—the light elements, that is, those with an atomic number <30, are far more abundant than the heavy elements; (2) especially among the light elements, the even-numbered elements are more abundant than the odd-numbered elements of similar atomic weight.

A central theory of astrophysics is that the Universe began with a gigantic explosion, "the Big Bang," about 13.7 billion years ago (Freedman and Madore 2010). The Big Bang initiated the fusion of hypothetical fundamental particles, known as quarks, to form protons (^{1}H) and neutrons, and it allowed the fusion of protons and neutrons to form some simple atomic nuclei (^{2}H, ^{3}He, ^{4}He, and a small amount of ^{7}Li). See Malaney and Fowler (1988), Pagel (1993), and Copi et al. (1995). After the Big Bang, the Universe began to expand outward, so there was a rapid decline in the temperatures and pressures that would be needed to produce heavier elements by fusion in interstellar space. Moreover, the elements with atomic masses of 5 and 8 are unstable, so no fusion of the abundant initial products of the Big Bang (i.e., ^{1}H and ^{4}He) could yield an appreciable, persistent amount of a heavier element. Thus, the Big Bang can explain the origin of elements up to ^{7}Li, but the origin of heavier elements had to await the formation of stars in the Universe—about 1 billion years later.

A model for the synthesis of heavier elements in stars was first proposed by Burbidge et al. (1957), who outlined a series of pathways that could occur in the interior of massive stars during their evolution (Fowler 1984, Wallerstein 1988, Trimble 1997). As a star ages, the abundance of hydrogen (H) in the core declines as it is converted to helium (He) by fusion. As the heat from nuclear fusion decreases, the star begins to collapse inward under its own gravity. This collapse increases the internal temperature and pressure until He begins
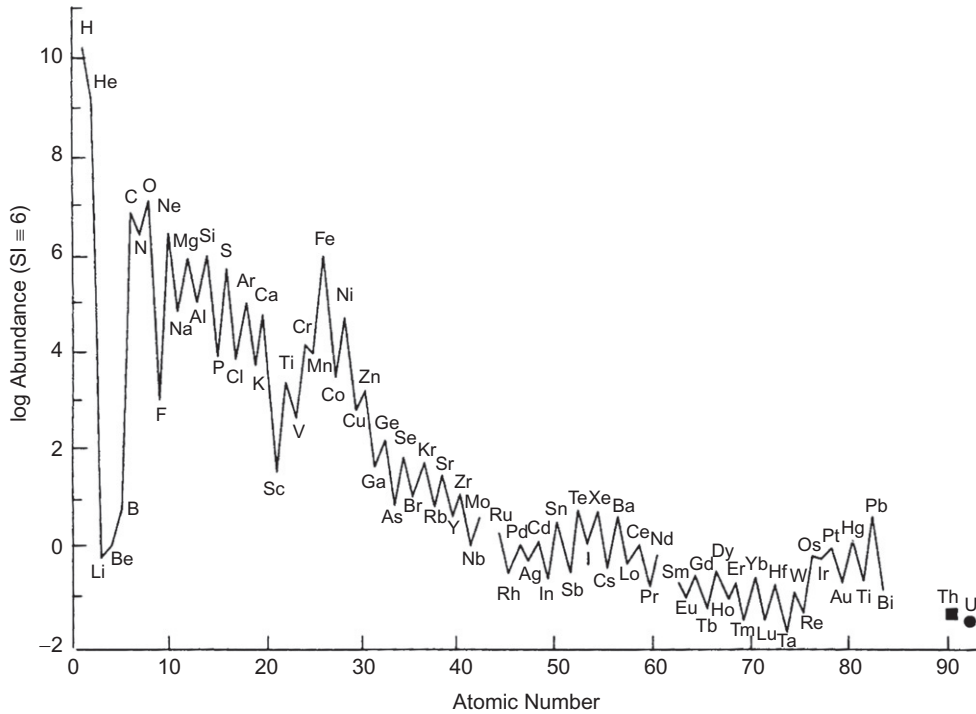
FIGURE 2.1   The relative abundance of elements in the solar system, also known as the cosmic abundance, as a function of atomic number. Abundances are plotted logarithmically and scaled so that silicon (Si) = 1,000,000. *Source: From a drawing in Brownlee (1992) based on the data of Anders and Grevesse (1989).*

to be converted via fusion reactions to form carbon (C) in a two-step reaction known as the triple-alpha process. First,

$$^{4}\text{He} + {}^{4}\text{He} \rightleftarrows {}^{8}\text{Be}. \tag{2.1}$$

Then, while most ^{8}Be decays spontaneously back to helium, the momentary existence of small amounts of ^{8}Be under these conditions allows reaction with helium to produce carbon:

$$^{8}\text{Be} + {}^{4}\text{He} \rightarrow {}^{12}\text{C}. \tag{2.2}$$

The main product of this so-called helium "burning" reaction is ^{12}C, and the rate of this reaction determines the abundance of C in the Universe (Oberhummer et al. 2000). ^{16}O is built by the addition of ^{4}He to ^{12}C, and nitrogen by the successive addition of protons to ^{12}C. As the supply of helium begins to decline, a second phase of stellar collapse is followed by the initiation of a sequence of further fusion reactions in massive stars (Fowler 1984). First, fusion of two ^{12}C forms ^{24}Mg (magnesium), some of which decays to ^{20}Ne (neon) by loss of an alpha (^{4}He) particle. Subsequently, oxygen burning produces ^{32}S, which forms an appreciable amount of ^{28}Si (silicon) by loss of an alpha particle (Woosley 1986).

A variety of fusion reactions in massive stars are thought to be responsible for the synthesis—known as stellar nucleosynthesis—of the even-numbered elements up to iron (Fe) (Fowler 1984, Trimble 1997). (Smaller stars, like our Sun, do not go through all these reactions and burn out along the way, becoming white dwarfs.) These fusion reactions release energy and produce increasingly stable nuclei (Friedlander et al. 1964). However, to make a nucleus heavier than Fe requires energy, so when a star's core is dominated by Fe, it can no longer burn. This leads to the catastrophic collapse and explosion of the star, which we recognize as a supernova. Heavier elements are apparently formed by the successive capture of neutrons by Fe, either deep in the interior of stable stars (s-process) or during the explosion of a supernova (r-process; Woosley and Phillips 1988, Burrows 2000, Cowan and Sneden 2006). A supernova casts all portions of the star into space as hot gases (Chevalier and Sarazin 1987).

This model explains a number of observations about the abundance of the chemical elements in the Universe. First, the abundance of elements declines logarithmically with increasing mass beyond hydrogen and helium, the original building blocks of the Universe. However, as the Universe ages, more and more of the hydrogen will be converted to heavier elements during the evolution of stars. Astrophysicists can recognize younger, second-generation stars, such as our Sun, that have formed from the remnants of previous supernovas because they contain a higher abundance of iron and heavier elements than older, first-generation stars, in which the initial hydrogen-burning reactions are still predominant (Penzias 1979). We should all be thankful for the fusion reactions in massive stars which have formed most of the chemical elements of life.

Second, because the first step in the formation of all the elements beyond lithium is the fusion of nuclei with an even number of atomic mass (e.g., ^{4}He, ^{12}C), the even-numbered light elements are relatively abundant in the cosmos. The odd-numbered light elements are formed by the addition of neutrons to nuclei in the interior of massive stars (s-process) and by the fission of heavier even-numbered nuclei. In most cases an odd-numbered nucleus is slightly less stable than its even-numbered "neighbors," so we should expect odd-numbered nuclei to be less abundant. For example, phosphorus is formed in the reaction

$$^{16}O + {}^{16}O \rightarrow {}^{32}S \rightarrow {}^{31}P + {}^{1}H. \tag{2.3}$$
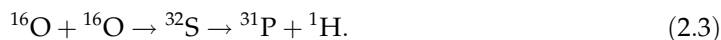
Thus, phosphorus is much less abundant than the adjacent elements in the periodic table, Si (silicon) and S (sulfur) (Figure 2.1). It is interesting to speculate that the low cosmic abundance of P (phosphorus) formed by this and other reactions of nucleosynthesis may account for the fact that P is often in short supply for the biosphere on Earth today (Macia et al. 1997).

Finally, the low cosmic abundance of Li, Be, and B is due to the fact that the initial fusion reactions pass over nuclei with atomic masses of 5 to 8, forming ^{12}C, as shown in Eqs. 2.1 and 2.2. Apparently, most Li, Be, and B are formed by spallation—the fission of heavier elements that are hit by cosmic rays in interstellar space (Olive and Schramm 1992, Reeves 1994, Chaussidon and Robert 1995).

This model for the origin and cosmic abundance of the elements offers some initial constraints for biogeochemistry. All things being equal, we might expect that the chemical environment in which life arose would approximate the cosmic abundance of elements. Thus, the evolution of biochemical molecules might be expected to capitalize on the light elements that were abundant in the primordial environment. It is then of no great surprise that no element heavier than Fe is more than a trace constituent in living tissue and that among

the light elements, no Li or Be, and only traces of B, are essential components of biochemistry (Wackett et al. 2004). The composition of life is remarkably similar to the composition of the Universe; as put by Fowler (1984), we are all "a little bit of stardust."

ORIGIN OF THE SOLAR SYSTEM AND THE SOLID EARTH

The Milky Way galaxy is about 12.5 billion years old (Dauphas 2005), indicating that the first stars and galaxies had formed within a billion years after the Big Bang (Cayrel et al. 2001). By comparison, as a second-generation star, our Sun appears to be only about 4.57 billion years old (Baker et al. 2005, Bonanno et al. 2002, Bouvier and Wadhawa 2010). Current models for the origin of the solar system suggest that the Sun and its planets formed from a cloud of interstellar gas and dust, possibly including the remnants of a supernova (Chevalier and Sarazin 1987). This cloud of material would have the composition of the cosmic mix of elements (Figure 2.1). As the Sun and the planets began to condense, each developed a gravitational field that helped capture materials that added to its initial mass. The mass concentrated in the Sun apparently allowed condensation to pressures that reinitiated the fusion of hydrogen to helium.

The planets of our solar system appear to have formed from the coalescing of dust to form small bodies, known as planetesimals, within the primitive solar cloud (Beckwith and Sargent 1996, Baker et al. 2005). Collisions among the planetesimals would have formed the planets. The process is likely to have been fairly rapid. Several lines of evidence show planetesimals forming during the first million years of the solar system (Srinivasan et al. 1999, Yin et al. 2002, Alexander et al. 2001), and most stars appear to lose their disk of gases and dust within 400 million years after their formation (Habing et al. 1999). Recent observations suggest that a similar process is now occurring around another star in our galaxy, ß Pictoris (Lagage and Pantin 1994, Lagrange et al. 2010), and Earth-size and larger planets have been detected around numerous other stars in our galaxy (Gaidos et al. 2007, Borucki et al. 2010, Lissauer et al. 2011).

Overall, the original solar nebula is likely to have been composed of about 98% gaseous elements (H, He, and noble gases), 1.5% icy solids (H_2O, NH_3, and CH_4), and 0.5% rocky solid materials, but the composition of each planet was determined by its position relative to the Sun and the rate at which the planet grew (McSween 1989). The "inner" planets (Mercury, Venus, Earth, and Mars) seemed to have formed in an area where the solar nebula was very hot, perhaps at a temperature close to 1200 K (Boss 1988). Venus, Earth, and Mars are all depleted in light elements compared to the cosmic abundances, and they are dominated by silicate minerals that condense at high temperatures and contain large amounts of FeO (McSween 1989). The mean density of Earth is about 5.5 g/cm^3. The high density of the inner planets contrasts with the lower average density of the larger, outer planets, known as gas giants, which captured a greater fraction of lighter constituents from the initial solar cloud (Table 2.1). Jupiter contains much hydrogen and helium. The average density of Jupiter is 1.3 g/cm^3, and its overall composition does not appear too different from the solar abundance of elements (Lunine 1989, Niemann et al. 1996). Some astronomers have pointed out that the hydrogen-rich atmosphere on Jupiter is similar to the composition of "brown dwarfs"—stars that never "ignited" (Kulkarni 1997).

From the initial solar cloud of elements, the chemical composition of the Earth is a selective mix, peculiar to the orbit of the incipient planet. The majority of the mass of the Earth seems

TABLE 2.1   Characteristics of the Planets

Planet Name[a]	Radius 10⁸ cm	Volume 10²⁶ cm³	Mass 10²⁷ gm	Density gm/cm³	Corrected density[b] gm/cm³
Mercury	2.44	0.61	0.33	5.42	5.4
Venus	6.05	9.3	4.9	5.25	4.3
Earth	6.38	10.9	6.0	5.52	4.3
Mars	3.40	1.6	0.64	3.94	3.7
Jupiter	71.90	15,560	1900	1.31	<1.3
Saturn	60.20	9130	570	0.69	<0.7
Uranus	25.40	690	88	1.31	<1.3
Neptune	24.75	635	103	1.67	<1.7

[a] *The mass of the Sun is 1.99×10^{33} gm, 1000× the mass of Jupiter.*
[b] *Density a planet would have in the absence of gravitational squeezing.*
Source: From Broecker (1985, p. 73). Published by Lamont Dougherty Laboratory, Columbia University. Used with permission.

likely to have accreted by about 4.5 bya—within about 100 million years of the origin of the solar system (Allègre et al. 1995, Kunz et al. 1998, Yin et al. 2002, Touboul et al. 2007, Jackson et al. 2010). Several theories account for the origin and differentiation of Earth. One suggests that Earth may have grown by homogeneous accretion; that is, throughout its early history, Earth may have captured planetesimals that were relatively similar in composition (Stevenson 1983, 2008).

Kinetic energy generated during the collision of these planetesimals (Wetherill 1985), as well as the heat generated from radioactive decay in its interior (Hanks and Anderson 1969), would heat the primitive Earth to the melting point of iron, nickel, and other metals, forming a magma ocean. These heavy elements were "smelted" from the materials arriving from space and sank to the interior of the Earth to form the core (Agee 1990, Newsom and Sims 1991, Wood et al. 2006).

As Earth cooled, lighter minerals progressively solidified to form a mantle dominated by perovskite ($MgSiO_3$), with some complement of olivine ($FeMgSiO_4$), and a crust dominated by aluminosilicate minerals of lower density and the approximate composition of feldspar (Chapter 4). Thus, despite the abundance of iron in the cosmos and in the Earth as a whole, the crust of the Earth is largely composed of Si, Al, and O (Figure 2.2). The aluminosilicate rocks of the crust "float" on the heavier semifluid rocks of the mantle (Figure 2.3; Bowring and Housh 1995).

An alternative theory for the origin of Earth suggests that the characteristics of planetesimals and other materials contributing to the growth of the planet were not uniform through time. Theories of heterogeneous accretion suggest that materials in the Earth's mantle arrived later than those of the core (Harper and Jacobsen 1996, Schönbächler et al. 2010), and that a late veneer delivered by a class of meteors known as carbonaceous chondrites was responsible for most of the light elements and volatiles on Earth (Anders and Owen 1977, Wetherill 1994, Javoy 1997, Kramers 2003). The two accretion theories are not mutually exclusive; it is
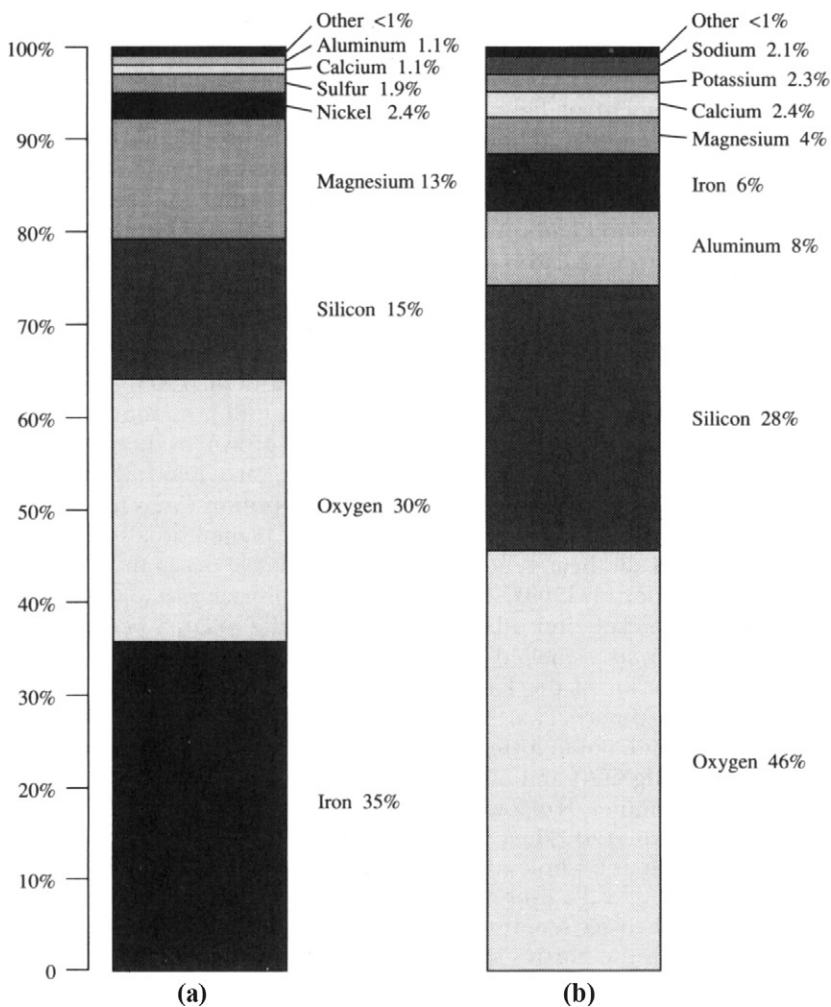
FIGURE 2.2   Relative abundance of elements by weight in the whole Earth (a) and Earth's crust (b). *Source: From Earth (fourth ed.) by Frank Press and Raymond Siever. Copyright 1986 by W.H. Freeman and Company. Used with permission.*

possible that a large fraction of the Earth mass was delivered by homogeneous accretion, followed by a late veneer of chondritic materials (Willbold et al. 2011).

It is likely that during its late accretion, Earth was impacted by a large body—known as Theia—which knocked a portion of the incipient planet into an orbit about it, forming the Moon (Lee et al. 1997). The Moon's age is estimated at 4.527 billion years (Kleine et al. 2005). Earth's early history was probably dominated by frequent large impacts, but based on the age distribution of craters on the Moon, it is postulated that most of the large impacts occurred before 2.0 bya (Neukum 1977, Cohen et al. 2000, Bottke et al. 2012). The present-day
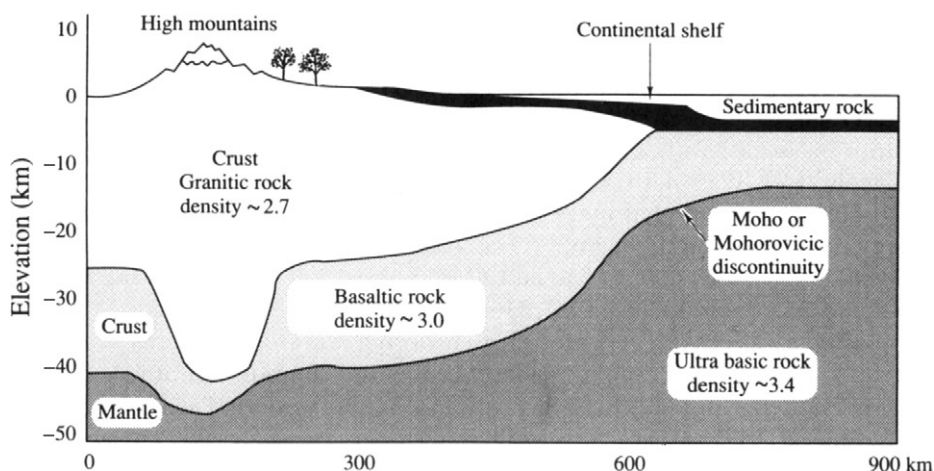
FIGURE 2.3   A geologic profile of the Earth's surface. On land the crust is dominated by granitic rocks, largely composed of Si and Al (Chapter 4). The oceanic crust is dominated by basaltic rocks with a large proportion of Si and Mg. Both granite and basalt have a lower density than the upper mantle, which contains ultrabasic rocks with the approximate composition of olivine ($FeMgSiO_4$). *Source: From Howard and Mitchell (1985).*

receipt of extraterrestrial materials (8 to 38×10^9 g/yr; Taylor et al. 1998, Love and Brownlee 1993, Cziczo et al. 2001) is much too low to account for Earth's mass (6×10^{27} g), even if it has continued for all of Earth's history.

   Consistent with either theory are several lines of evidence that the primitive Earth was devoid of an atmosphere derived from the solar nebula—that is, a primary atmosphere. During its early history, the gravitational field on the small, accreting Earth would have been too weak to retain gaseous elements, and the incoming planetesimals were likely to have been too small and too hot to carry an envelope of volatiles. The impact of Theia is also likely to have blown away any volatiles that had accumulated in Earth's atmosphere by that time. Today, volcanic emissions of some inert (noble) gases, such as ^{3}He, ^{20}Ne (neon), and ^{36}Ar (argon), which are derived from the solar nebula, result from continuing degassing of primary volatiles that must have been delivered to the primitive Earth trapped in pockets (fluid inclusions) in accreting chondrites (Lupton and Craig 1981, Burnard et al. 1997, Jackson et al. 2010). Otherwise, the Earth's atmosphere appears to be of secondary origin.

   If a significant fraction of today's atmosphere were derived from the original solar cloud, we might expect that its gases would exist in proportion to their solar abundances (refer to Figure 2.1). Here, ^{20}Ne is of particular interest because it is not produced by any known radioactive decay, it is too heavy to escape from Earth's gravity, and as an inert gas it is not likely to have been consumed in any reaction with crustal minerals (Walker 1977).[2] Thus, the

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[2] ^{20}Ne is one of the isotopes of neon. Isotopes of an element have the same number of protons in the nucleus, but differ in the number of neutrons, so they differ in atomic weight. Naturally occurring chemical elements are usually mixtures of isotopes, and their listed atomic weights are average values for the mixture. Most of the elements in the periodic table have two or more isotopes, with 254 stable (i.e. nonradioactive) isotopes for the first 80 elements.

present-day abundance of ^{20}Ne in the atmosphere is likely to represent its primary abundance—that derived from the solar nebula. Assuming that other solar gases were delivered to the Earth in a similar manner, we can calculate the total mass of the primary atmosphere by multiplying the mass of ^{20}Ne in today's atmosphere by the ratio of each of the other gases to ^{20}Ne in the solar abundance. For example, the solar ratio of nitrogen to neon is 0.91 (Figure 2.1). If the present-day atmospheric mass of neon, 6.5×10^{16} g, is all from primary sources, then $(0.91) \times (6.5 \times 10^{16}$ g) should be the mass of nitrogen that is also of primary origin. The product, 5.9×10^{16} g, is much less than the observed atmospheric mass of nitrogen, 39×10^{20} g. Thus, most of the nitrogen in today's atmosphere must be derived from other sources.

ORIGIN OF THE ATMOSPHERE AND THE OCEANS

Much of the Earth's inventory of "light" elements is likely to have been delivered to the planet as constituents of the silicate minerals in carbonaceous chondrites, perhaps in a late veneer of accretion (Javoy 1997). Even today, many silicate minerals in the Earth's mantle carry elements such as oxygen and hydrogen as part of their crystalline structure (Bell and Rossman 1992, Meade et al. 1994). Of particular interest to biogeochemistry, carbonaceous chondrites typically contain from 0.5 to 3.6% C (carbon) and 0.01 to 0.28% N (nitrogen) (Anders and Owen 1977), which may represent the original source of these elements for the biosphere.

The origin of the Earth's atmosphere is closely tied to the appearance and evolution of its crust, which differentiated from the mantle by melting and by density separation under the heat generated by large impacts and internal radioactive decay (Fanale 1971, Stevenson 1983, Kunz et al. 1998). During melting, elements such as H, O, C, and N would have been released from the mantle as volcanic gases. Several lines of evidence point to the existence of a continental crust by 4.4 bya (Wilde et al. 2001, Watson and Harrison 2005, O'Neil et al. 2008), and its volume appears to have grown through Earth's history (Collerson and Kamber 1999, Abbott et al. 2006, Hawkesworth and Kemp 2006). Thus, the accumulation of a secondary atmosphere began early in Earth's history (Kunz et al. 1998).

Today, a variety of gases are released during volcanic eruptions at the Earth's surface. The emissions associated with the eruption of island basalts, such as on Hawaii, offer a good indication of the composition of mantle degassing, since they are less likely to be contaminated by younger crustal materials that have been subducted (Marty 2012). Table 2.2 gives the composition of gases emitted from various volcanoes. Characteristically, water vapor dominates the emissions, but small quantities of C, N, and S gases are also present (Tajika 1998). Volcanic emissions, representing degassing of Earth's interior, are consistent with the observation that Earth's atmosphere is of secondary origin—largely derived from solid materials. The earliest atmosphere is likely to have been dominated by H_2, H_2O, CO, and CO_2 depending on the mix of chondritic materials (Schaefer and Fegley 2010). Some elements, including H, can dissolve in magma so that a significant proportion of the Earth's inventory of water, carbon, and nitrogen may still reside in the mantle (Bell and Rossman 1992, Murakami et al. 2002, Marty 2012). The total extent of mantle degassing through geologic time is unknown, but perhaps is 50% based on the content of ^{40}Ar in Earth's mantle (Marty 2012).

TABLE 2.2 Composition of Gases Emitted by Volcanoes

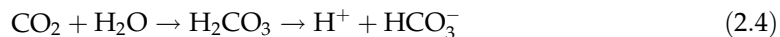| Volcano	Units	H_2O	H_2	CO_2	SO_2	H_2S	HCl	HF	N_2	NH_3	O_2	Ar	CH_4	References
Kudryavy, Russia	mole %	95.00	0.56	2.00	1.32	0.41	0.3700	0.030	0.21	–	0.03	0.002	0.002	Taran et al. (1995)
Nevado del Ruiz, Colombia	wgt. %	94.90		2.91	2.74	0.80	0.0052							Williams et al. (1986)
Kamchatka, Russia	vol. %	78.60	3.01	4.87	0.03	0.16	0.5700	0.056	11.87	0.11	0.01	0.060	0.440	Dobrovolsky (1994)

The isotopic ratio of argon gas on Earth (i.e., $^{40}Ar/^{36}Ar$) is suggestive of the proportion of our present atmosphere that is derived from mantle degassing. On Earth the isotope ^{40}Ar appears to be wholly the result of the radioactive decay of ^{40}K in the mantle (Farley and Neroda 1998), while the isotope ^{36}Ar was delivered intact from the original solar nebula. Like ^{20}Ne, this noble element is too heavy to escape the gravity of the Earth.[3] Thus, the atmospheric content of ^{36}Ar should represent the proportion that is due to the residual primary atmosphere (i.e. the solar nebula), whereas the content of ^{40}Ar is indicative of the proportion due to crustal degassing. The ratio of $^{40}Ar/^{36}Ar$ on Earth is nearly 300, suggesting that 99.7% of the Ar in our present atmosphere is derived from the interior of the Earth. In contrast, the Viking spacecraft measured a much higher ratio of 2750 for ^{40}Ar versus ^{36}Ar in the atmosphere on Mars (Owen and Biemann 1976). This observation supports the emerging belief that Mars lost a large portion of its primary atmosphere, and that most of the atmosphere on Mars today is derived from degassing (Carr 1987).

The ratio of N_2 to ^{40}Ar in the Earth's mantle is close to that of today's atmosphere (~ 80)—implying a common source for both elements at the Earth's surface (Marty 1995). Volcanic emissions and mantle degassing were undoubtedly greatest in early Earth history; the present-day flux of nitrogen from volcanoes (0.78 to 1.23×10^{11} g/yr; Sano et al. 2001, Tajika 1998) is too low to account for the current inventory of N at the Earth's surface ($\sim 50 \times 10^{20}$ g; Table 2.3) even if it has continued for all 4.5 billion years of Earth's history. Moreover, some nitrogen has also returned to the mantle by subduction (Zhang and Zindler 1993).

It is possible that a late impact of comets contributed to the gaseous inventory on Earth (Chyba 1990a). If so, the proportion must be small, because the isotopic ratio of H measured in the ices of the Hale Bopp and other comets does not match the ratio in the present inventory of water on Earth (Meier et al. 1998). Nevertheless, it is difficult to explain the presence of ice on the surface of the Moon, which has undergone only slight degassing other than by delivery in a late arrival of comets impacting its surface (Clark 2009, Sunshine et al. 2009, Colaprete et al. 2010, Zuber et al. 2012).

As long as the Earth was very hot, volatiles remained in the atmosphere, but when the surface temperature cooled to the condensation point of water, water could condense out of the primitive atmosphere to form the oceans. This must have been a rainstorm of true global proportion! Several lines of evidence point to the existence of liquid water on the Earth's surface 4.3 bya (Mojzsis et al. 2001, Wilde et al. 2001). Although heat from large, late-arriving meteors may have caused temporary revaporization of some of the earliest oceans (Sleep et al. 1989, Abramov and Mojzsis 2009), the geologic record suggests that liquid water has been present on the Earth's surface continuously for the past 3.8 billion years. Indeed, despite a few lingering meteor impacts, Earth may have harbored a temperate climate nearly 3.4 bya (Hren et al. 2009, Blake et al. 2010).

Various other gases would have quickly entered the primitive ocean as a result of their high solubility in water; for example:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{2.4}$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \tag{2.5}$$
$$SO_2 + H_2O \rightarrow H_2SO_3. \tag{2.6}$$

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[3] A small amount of ^{40}Ar has been destroyed by cosmic rays, producing ^{35}S in the atmosphere (Tanaka and Turekian 1991).

TABLE 2.3 Total Inventory of Volatiles at the Earth's Surface[a]

Reservoir	H_2O	CO_2	C	O_2	N	S	Cl	Ar	Total (rounded)
Atmosphere (see Table 3.1)	1.3	0.31	—	119	387	—	—	6.6	514
Oceans	135,000	19.3[b]	0.07	256[c]	2[d]	128[e]	2610	—	138,000
Land plants	0.1	—	0.06	—	0.0004	—	—	—	0.16
Soils	12	0.40[f,g]	0.15	—	0.0095	—	—	—	12.6
Freshwater (including ice and groundwater)	4850	—	—	—	—	—	—	—	4,850
Sedimentary rocks	15,000[h]	30000[g]	1560	4745[i]	200[j]	744[k]	500[h]	—	52,750
Total (rounded)	155,000	30,000	1560	5120	590	872	3100	7	196,000
See also	Fig. 10.1	Fig. 11.1	Fig. 11.1	Fig. 2.8		Table 13.1			

[a] All data are expressed as 10^{19} g, with values derived from this text unless noted otherwise.
[b] Assumes the pool of inorganic C is in the form of HCO_3^-.
[c] Oxygen content of dissolved SO_4^{2-}.
[d] Dissolved N_2.
[e] S content of SO_4^{2-}.
[f] Desert soil carbonates.
[g] Assumes 60% of $CaCO_3$ is carbon and oxygen.
[h] Walker (1977).
[i] O_2 held in sedimentary Fe_2O_3 and evaporites $CaSO_4$.
[j] Goldblatt et al. (2009).
[k] S content of $CaSO_4$ and FeS_2.

These reactions removed a large proportion of reactive water-soluble gases from the atmosphere, as predicted by Henry's Law for the partitioning of gases between gaseous and dissolved phases:

$$S = kP, \qquad (2.7)$$

where S is the solubility of a gas in a liquid, k is the solubility constant, and P is the overlying pressure in the atmosphere. Under one atmosphere of partial pressure, the solubilities of CO_2, HCl, and SO_2 in water are 1.4, 700, and 94.1 g/liter, respectively, at 25°C. When dissolved in water, all of these gases form acids, which would be neutralized by immediate reaction with the surface minerals on Earth. Thus, after cooling, the Earth's earliest atmosphere is likely to have been dominated by N_2, which has relatively low solubility in water (0.018 g/liter at 25°C).

Because many gases dissolve so readily in water, an estimate of the total extent of crustal degassing through geologic time must consider the mass of the atmosphere, the mass of oceans, and the mass of volatile elements that are now contained in sedimentary minerals, such as $CaCO_3$, which have been deposited from seawater (Li 1972). By this accounting, the mass of the present-day atmosphere (5.14×10^{21} g; Trenberth and Guillemot 1994) represents less than 1% of the total degassing of the Earth's mantle over geologic time (refer to Table 2.3). The oceans and various marine sediments contain nearly all of the remainder, and some volatiles have returned to the upper mantle by subduction of Earth's oceanic crust (Zhang and Zindler 1993, Plank and Langmuir 1998, Kerrick and Connolly 2001).

Despite uncertainty about the exact composition of the Earth's earliest atmosphere, several lines of evidence suggest that by the time life arose, the atmosphere was dominated by N_2, CO_2, and H_2O (Holland 1984), which were in equilibrium with the oceans, and by trace quantities of other gases from volcanic emissions that were continuing at that time (Hunten 1993, Yamagata et al. 1991). There was certainly no O_2; the small concentrations produced by the photolysis of water in the upper atmosphere would rapidly be consumed in the oxidation of reduced gases and crustal minerals (Walker 1977, Kasting and Walker 1981).

During its early evolution as a star, the Sun's luminosity was as much as 30% lower than at present. We might expect that primitive Earth was colder than today, but the fossil record indicates a continuous presence of liquid water on the Earth's surface since 3.8 bya. One explanation is that the primitive atmosphere contained much higher concentrations of water vapor, CO_2, CH_4, and other greenhouse gases than today (Walker 1985). These gases would trap outgoing infrared radiation and produce global warming through the "greenhouse" effect (refer to Figure 3.2). In fact, even today the presence of water vapor and CO_2 in the atmosphere creates a significant greenhouse effect on Earth—about 75% due to water vapor and 25% from CO_2 (Lacis et al. 2010, Schmidt et al. 2010a,b). Without these gases, Earth's temperature would be about 33°C cooler, and the planet would be covered with ice (Ramanathan 1988).

There are few direct indications of the composition of the earliest seawater. Like today's seawater, the Precambrian ocean is likely to have contained a substantial amount of chloride. HCl and Cl_2 emitted by volcanoes would dissolve in water, forming Cl^- (Eq. 2.5). The acids produced by the dissolution of these and other gases in water (Eqs. 2.4–2.6) would have reacted with minerals of the Earth's crust, releasing Na^+, Mg^{2+}, and other cations by chemical weathering (Chapter 4). Carried by rivers, these cations would accumulate in seawater until their concentrations increased to levels that would precipitate secondary minerals.

For instance, sedimentary accumulations of $CaCO_3$ of Precambrian age indicate that the primitive oceans had substantial concentrations of Ca^{2+} (Walker 1983). Thus, it is likely that the dominant cations (Na, Mg, and Ca) and the dominant anion (Cl) in Precambrian seawater were similar to those in seawater today (Holland 1984, Morse and MacKenzie 1998). Only SO_4^{2-} seems to have been less concentrated in the Precambrian ocean (Grotzinger and Kasting 1993, Habicht et al. 2002).

ORIGIN OF LIFE

Fundamental to all considerations of the origins of life are the characteristics of living systems as we know them today. To develop theories and a timeline for the evolution of life on primitive Earth, we need to be able to recognize some or all of these traits in fossil sediments and in the products of laboratory synthesis of organic materials. These characteristics include the presence of a physical membrane, metabolic machinery for obtaining energy from the environment, and genetic material allowing heritability. These fundamental characteristics separate life from abiotic organic materials. A surrounding or *plasma membrane* allows segregation of the building blocks of biochemistry, up to 30 elements, at concentrations and proportions that typically diverge substantially from the surrounding environment.

Internal membranes, such as the mitochondrial membrane, allow separation of materials within cells, facilitating the capture of energy as electrons flow from electron-rich (reduced) to electron-poor (oxidized) substances that are obtained from the environment (Figure 1.4). Autotrophic organisms produce their own organic materials by capturing energy from the Sun (photoautotrophy) or other external sources (chemoautotrophy); heterotrophic organisms consume the organic materials produced by others. Generic material allows these structural innovations to be repeatable and heritable so that organisms can grow and reproduce.

An initial constraint on the evolution of life was a lack of organic molecules on primitive Earth. In 1871, Darwin postulated that the interaction of sunlight with marine salts under a primitive atmosphere might have created these primordial organic building blocks.[4] Working with Harold Urey in the early 1950s, Stanley Miller carried out this experiment by adding the probable constituents of the primitive atmosphere and oceans to a laboratory flask and subjecting the mix to an electric discharge to represent the effects of lightning. After several days, Miller found that simple, reduced organic molecules had been produced (Miller 1953, 1957). This experiment, possibly simulating the conditions on early Earth, suggested that the organic constituents of living organisms could be produced abiotically.

This experiment has been repeated in many laboratories, and under a wide variety of conditions (Chang et al. 1983). Ultraviolet light can substitute for electrical discharges as an energy source; a high flux of ultraviolet light would be expected on primitive Earth in the absence of an ozone (O_3) shield in the stratosphere (Chapter 3). Additional energy for abiotic

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[4] From a letter from Charles Darwin to Joseph Hooker, 1871: "but if (and oh! what a big if!) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present, that a protein compound was chemically formed ready to undergo still more complex changes, at the present day such matter would be instantly devoured or absorbed, which would not have been the case before living creatures were formed."

synthesis may have been derived from the impact of late-arriving meteors and comets passing through the atmosphere (Chyba and Sagan 1992, McKay and Borucki 1997) or at hydrothermal vents in the deep sea (Russell 2006).

The mix of atmospheric constituents taken to best represent the primitive atmosphere is controversial. H_2 may have been an important component of Earth's earliest atmosphere (Tian et al. 2005), and the yield of organic molecules is greatest in such highly reducing conditions. Nevertheless, an acceptable yield of simple organic molecules is found in experiments using mildly reducing atmospheres, composed of CO_2, H_2O, and N_2 (Pinto et al. 1980), which are the more probable conditions on the primitive Earth (Trail et al. 2011). The experiments are never successful when free O_2 is included; O_2 rapidly oxidizes the simple organic products before they can accumulate.

Interstellar dust particles and cometary ices also contain a wide variety of simple organic molecules (Busemann et al. 2006, Carr and Najita 2008, Sloan et al. 2009), and various amino acids are found in carbonaceous chondrites (Kvenvolden et al. 1970, Cooper et al. 2001, Pizzarello et al. 2001, Herd et al. 2011), suggesting that abiotic synthesis of organic molecules may be widespread in the galaxy (Orgel 1994, Irvine 1998, Ciesla and Sandford 2012). Significantly, it is possible that a small fraction of the organic molecules in chondrites and comets survives passage through the Earth's atmosphere, contributing to the inventory of organic molecules on its surface (Anders 1989, Chyba and Sagan 1992). Even if the total mass received is small, exogenous sources of organic molecules are important, for they may have served as chemical templates, speeding the rate of abiotic synthesis and the assembly of organic molecules on Earth.

A wide variety of simple organic molecules have now been produced under abiotic conditions in the laboratory (Dickerson 1978). In many cases hydrogen cyanide and formaldehyde are important initial products that polymerize to produce simple sugars such as ribose and more complex molecules such as amino acids and nucleotides. Even methionine, a sulfur-containing amino acid, has been synthesized abiotically (Van Trump and Miller 1972). The volcanic gas carbonyl sulfide (COS) can catalyze the binding of amino acids to form polypeptides (Leman et al. 2004), and short chains of amino acids have been linked by condensation reactions involving phosphates (Rabinowitz et al. 1969, Lohrmann and Orgel 1973). An early abiotic role for organic polyphosphates in synthesis speaks strongly for the origin of adenosine triphosphate (ATP) as the energizing reactant in virtually all biochemical reactions that we know today (Dickerson 1978).

Clay minerals, with their surface charge and repeating crystalline structure, may have acted to concentrate simple, polar organic molecules from the primitive ocean, making assembly into more complicated forms, such as RNA and protein, more likely (Cairns-Smith 1985, Ferris et al. 1996, Hanczyc et al. 2003). Metal ions such as zinc and copper can enhance the binding of nucleotides and amino acids to clays (Lawless and Levi 1979, Huber and Wachtershauser 1998, 2006). It is interesting to speculate why nature incorporates only the "left-handed" forms of amino acids in proteins, when equal forms of L- and D-enantiomers are produced by abiotic synthesis (Figure 2.4). Apparently, the light of stars is polarizing, creating an abundance of L-enantiomers during organic synthesis in the interstellar environment (Engel and Macko 2001). If the organic molecules in meteorites served as a chemical template for abiotic synthesis on Earth, meteors may have carried the preference for L-enantiomers in organic synthesis at Earth's surface (Engel and Macko 1997, Bailey et al. 1998, Pizzarello and Weber 2004).

I. PROCESSES AND REACTIONS
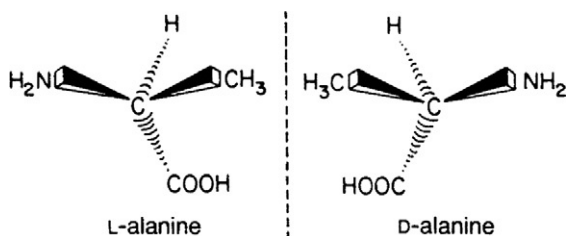
FIGURE 2.4   The left-handed (L) and right-handed (D) forms, known as enantiomers, of the amino acid alanine. No rotation of these molecules allows them to be superimposed. Although both forms are found in the extraterrestrial organic matter of carbonaceous chondrites, all life on Earth incorporates only the L form in proteins. *Source: From Chyba (1990b).*

Recently, scientists studying the origins of life have focused on submarine hydrothermal vent systems, which today harbor a diversity of life forms, as the arena for Earth's earliest life (Kelley et al. 2002, Russell 2006). Hydrothermal vents appear to support the abiotic synthesis of simple organic molecules, including formate, acetate (Lang et al. 2010), pyruvate (Cody et al. 2000), and amino acids (Huber and Wächtershäuser 2006). Indeed, the energetics of amino acid synthesis is favorable in these environments (Amend and Shock 1998). An origin of life in the high temperature, extreme pH, and high salinity of these habitats may explain how life persists in such a wide range of extreme habitats today (Rothschild and Mancinelli 2001, Marion et al. 2003).

Just as droplets of cooking oil form "beads" on the surface of water, it has long been known that some organic polymers will spontaneously form coacervates, which are colloidal droplets small enough to remain suspended in water. Coacervates are perhaps the simplest systems that might be said to be "bound," as if by a membrane, providing an inside and an outside. Yanagawa et al. (1988) describe several experiments in which protocellular structures with lipoprotein envelopes were constructed in the laboratory. In such structures, the concentration of substances will differ between the inside (hydrophobic) and the outside (hydrophilic) as a result of the differing solubility of substances in an organic medium and water, respectively. Mansy et al. (2008) show how primitive membranes may have allowed the transport of charged substances to the interior of protocells, allowing the evolution of heterotrophic metabolism.

Some organic molecules produced in the laboratory will self-replicate, suggesting potential mechanisms that may have increased the initial yield of organic molecules from abiotic synthesis (Hong et al. 1992, Orgel 1992, Lee et al. 1996). Other laboratories have produced simple organic structures, known as micelles, that will self-replicate their external framework (Bachmann et al. 1992). There is good reason to believe that the earliest genetic material controlling replication may not have been DNA but a related molecule, RNA, which can also perform catalytic activities (de Duve 1995, Robertson and Miller 1995).

Recent reports indicate some success in the abiotic synthesis of RNA precursors, which could subsequently support the abiotic synthesis of lengthy RNA molecules (Unrau and Bartel 1998, Powner et al. 2009). Vesicles that form around clay particles are found to enhance the polymerization of RNA (Hanczyc et al. 2003). Recently Gibson et al. (2010) inserted synthetic DNA into bacteria, where it replaced the native DNA and began reproducing. This work brings us one step closer to replicating the assembly of simple organic molecules into a complete self-replicating, metabolizing, and membrane-bound form that we might call life, with its origins in the laboratory.

A traditional view holds that life arose in the sea, and that biochemistry preferentially incorporated constituents that were abundant in seawater. For example, Banin and Navrot (1975) point out the striking correlation between the abundance of elements in today's biota and the solubility of elements in seawater. Elements with low ionic potential (i.e., ionic charge/ionic radius) are found as soluble cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in seawater and as important components of biochemistry. Other elements, including C, N, and S, that form soluble oxyanions in seawater (HCO_3^-, NO_3^-, and SO_4^{2-}), are also abundant biochemical constituents. Molybdenum is much more abundant in biota than one might expect based on its crustal abundance; molybdenum forms the soluble molybdate ion (MoO_4^{2-}) in ocean water. In contrast, aluminum (Al) and silicon (Si) form insoluble hydroxides in seawater. They are found at low concentrations in living tissue, despite relatively high concentrations in the Earth's crust (Hutchinson 1943). Indeed, many elements that are rare in seawater are familiar poisons to living systems (e.g., Be, As, Hg, Pb, and Cd).

Although phosphorus forms a soluble oxyanion, PO_4^{3-}, it may never have been particularly abundant in seawater, owing to its tendency to bind to other minerals (Griffith et al. 1977). Unique properties of phosphorus may account for its major role in biochemistry, despite its relatively low geochemical abundance on Earth. With three ionized groups, phosphoric acid can link two nucleotides in DNA, with the third negative site acting to prevent hydrolysis and maintain the molecule within a cell membrane (Westheimer 1987). These ionic properties also allow phosphorus to serve in intermediary metabolism and energy transfer in ATP.

In sum, if one begins with the cosmic abundance of elements as an initial constraint, and the partitioning of elements during the formation of the Earth as subsequent constraints, then solubility in water appears to be a final constraint in determining the relative abundance of elements in the geochemical arena in which life arose. Those elements that were abundant in seawater are important biochemical constituents. Phosphorus appears as an important exception—an important biochemical constituent that has been in short supply for much of the Earth's biosphere through geologic time.

EVOLUTION OF METABOLIC PATHWAYS

In 1983, Awramik et al. reported that 3.5-billion-year-old rocks collected in Western Australia contained microfossils. While these observations were not without controversy (Brasier et al. 2004, Garcia-Ruiz et al. 2003), these and other specimens of about the same age may contain evidence of the first life on Earth (compare with Schopf et al. 2002). The earliest organisms on Earth may have resembled the methanogenic archaea that survive today in anaerobic hydrothermal (volcanic) environments at pH ranging from 9 to 11 and temperatures above 90°C (Rasmussen 2000, Huber et al. 1989, Kelley et al. 2005). Archaea are distinct from bacteria due to a lack of a muramic acid component in the cell wall and a distinct r-RNA sequence (Fox et al. 1980). Halophilic (salt-tolerant), acidophilic (acid-tolerant), and thermophilic (heat-tolerant) forms of archaea are also known (Figure 2.5). Kashefi and Lovley (2003) describe iron-reducing archaea growing at 121°C near a deep sea hydrothermal vent of the North Pacific—a potential analog of one of the earliest habitats for life on Earth.
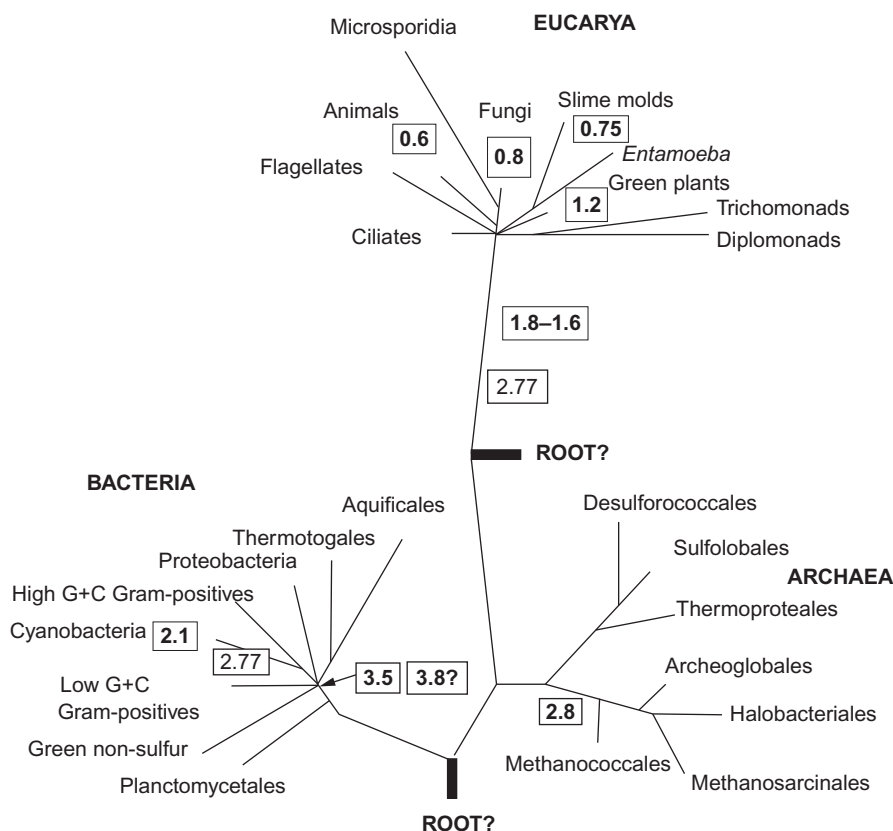
FIGURE 2.5   Relationship of the three domains of the tree of life, with boxes showing the estimated time (billions of years ago) for the first appearance of various forms. *Source: From Javaux (2006).*

The most primitive metabolic pathway probably involved the production of methane by splitting simple organic molecules, such as acetate, that would have been present in the oceans from abiotic synthesis:

$$CH_3COOH \rightarrow CO_2 + CH_4. \tag{2.8}$$

Organisms using this metabolism were scavengers of the products of abiotic synthesis and obligate heterotrophs, sometimes classified as chemoheterotrophs. The modern fermenting bacteria in the order Methanobacteriales may be our best present-day analogs.

Longer pathways of anaerobic metabolism, such as glycolysis, probably followed with increasing elaboration and specificity of enzyme systems. Oxidation of simple organic molecules in anaerobic respiration was coupled to the reduction of inorganic substrates from the environment. For example, sometime after the appearance of methanogenesis from acetate splitting, methanogenesis by CO_2 reduction,

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \tag{2.9}$$

probably arose among early heterotrophic microorganisms. Generally this reaction occurs in two steps: fermenting bacteria convert organic matter to acetate, H_2, and CO_2, and then

archaea transform these to methane, following Eq. 2.9 (Wolin and Miller 1987, Kral et al. 1998). Note that this methanogenic reaction is more complicated than that from acetate splitting and would require a more complex enzymatic catalysis.

Evidence for the first methanogens is found in rocks more than 3.5 billion years old (Ueno et al. 2006). Both pathways of methanogenesis are found among the fermenting bacteria that inhabit wetlands and coastal ocean sediments today (see Chapters 7 and 9). Without O_2 in the atmosphere, these early microbial metabolisms may have led to large accumulations of methane and an enhanced greenhouse effect on Earth (Catling et al. 2001).

Today, microbial communities performing methanogenesis by CO_2 reduction are also found deep in the Earth, where H_2 is available from geologic sources (Stevens and McKinley 1995, Chapelle et al. 2002). These microbial populations are functionally isolated from the rest of the biosphere, and indicate another potential habitat for the first life on Earth. Indeed, a vast elaboration of prokaryotes is found at great depths on land and in ocean sediments worldwide, where they persist with extremely low rates of metabolism (Whitman et al. 1998, Parkes et al. 2005, Krumholz et al. 1997, Fisk et al. 1998, Schippers et al. 2005, Lomstein et al. 2012, Røy et al. 2012).

Before the advent of atmospheric O_2, the primitive oceans are likely to have contained low concentrations of available nitrogen—largely in the form of nitrate (NO_3^-; Kasting and Walker 1981; but see also Yung and McElroy 1979). Thus, the earliest organisms had limited supplies of nitrogen available for protein synthesis. There is little firm evidence that dates the origin of nitrogen fixation, in which certain bacteria break the inert, triple bond in N_2 and reduce the nitrogen to NH_3, but today this reaction is performed by bacteria that require strict local anaerobic conditions. The reaction

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi \qquad (2.10)$$
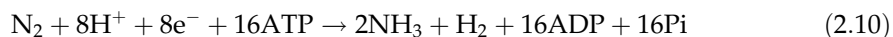
is catalyzed by the enzyme complex known as *nitrogenase*, which consists of two proteins incorporating iron and molybdenum in their molecular structure (Georgiadis et al. 1992, Kim and Rees 1992, Chan et al. 1993). The modern form of nitrogenase, containing molybdenum, may have appeared only 1.5 to 2.2 bya, having evolved from earlier forms in methanogenic bacteria (Boyd et al. 2011). A cofactor, vitamin B_{12} that contains cobalt, is also essential (Palit et al. 1994, O'Hara et al. 1988). Nitrogen fixation requires the expenditure of large amounts of energy; breaking the N_2 bond requires 226 kcal/mole (Davies 1972). Modern nitrogen-fixing cyanobacteria couple nitrogen fixation to their photosynthetic reaction; other nitrogen-fixing organisms are frequently symbiotic with higher plants (Chapter 6).

## Photosynthesis: The Origin of Oxygen on Earth

Despite various pathways of anaerobic metabolism, the opportunities for heterotrophic organisms must have been quite limited in a world where organic molecules were only available as a result of abiotic synthesis. Natural selection would strongly favor autotrophic systems that could supply their own reduced organic molecules for metabolism. Some of the earliest autotrophic metabolisms may have depended on H_2 (Schidlowski 1983, Tice and Lowe 2006, Canfield et al. 2006), namely:

$$2H_2 + CO_2 \rightarrow CH_2O + H_2O. \qquad (2.11)$$
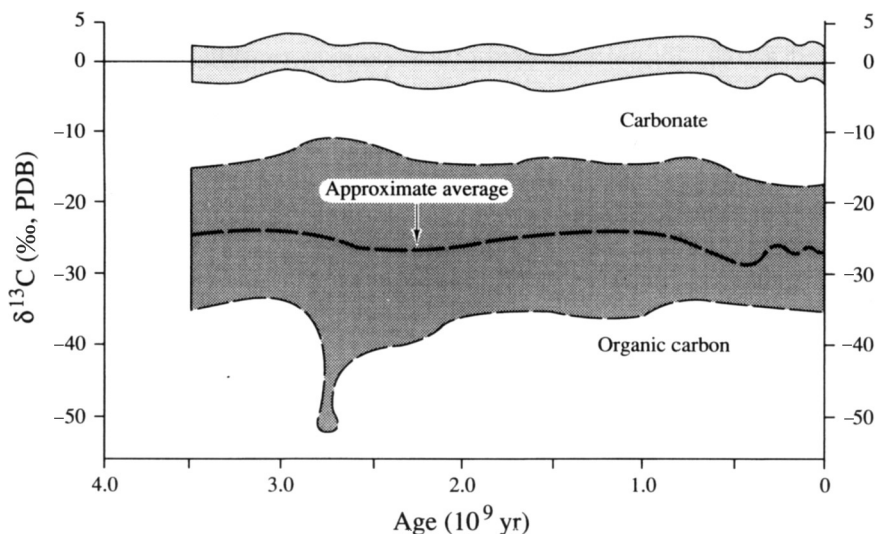
FIGURE 2.6   The isotopic composition of carbon in fossil organic matter and marine carbonates through geologic time, showing the range (*shaded*) among specimens of each age. The isotopic composition is shown as the ratio of ^{13}C to ^{12}C, relative to the ratio in an arbitrary standard (PDB belemite), which is assigned a ratio of 0.0. Carbon in organic matter is 2.8% less rich in ^{13}C than the standard, and this depletion is expressed as $-28‰$ $\delta^{13}C$ (see Chapter 5). *Source: From Schidlowski (1983).*

And we might also expect that one of the early photosynthetic reactions might have been based on the oxidation of the highly reduced gas, hydrogen sulfide (H_2S) (Schidlowski 1983, Xiong et al. 2000). For H_2S, the reaction

$$CO_2 + 2H_2S \rightarrow CH_2O + 2S + H_2O \qquad (2.12)$$
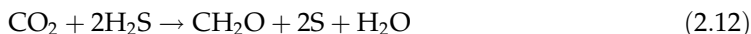
was probably performed by sulfur bacteria, not unlike the anaerobic forms of green and purple sulfur bacteria of today. These bacteria could have been particularly abundant around shallow submarine volcanic emissions of reduced gases, including H_2S.

Several indirect lines of evidence suggest that photosynthesis occurred in ancient seas of 3.8 bya. Photosynthesis produces organic carbon in which ^{13}C is depleted relative to its abundance in dissolved bicarbonate (HCO_3^-), and there are no other processes known to produce such strong fractionations between the stable isotopes of carbon.[5] Indeed, the carbon in carbonaceous chondrites is enriched in ^{13}C (Engel et al. 1990, Herd et al. 2011). Fossil organic matter with ^{13}C depletion is found in rocks from Greenland dating back to at least 3.8 bya (Mojzsis et al. 1996, Rosing 1999, Schidlowski 2001; Figure 2.6). This discrimination, which is about -2.8% ($-28‰$) in the dominant form of present-day photosynthesis, is based on

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[5] When two isotopes are available, here ^{12}C and ^{13}C, most biochemical pathways proceed more rapidly with the lighter isotope, which is often more abundant. This preferential use is known as mass-dependent fractionation, and it leaves metabolic products with a different ratio of isotopes than found in the surrounding environment.

the slower diffusion of $^{13}CO_2$ relative to $^{12}CO_2$ and the greater affinity of the carbon-fixation enzyme, ribulose bisphosphate carboxylase, for the more abundant $^{12}CO_2$ (see Chapter 5).

Some workers have suggested that the C-isotope depletion seen in these rocks is an artifact of metamorphism (Fedo and Whitehouse 2002, van Zuilen et al. 2002; but see Dauphas et al. 2004). But other evidence for the existence of oxygen-producing photosynthesis is also found in these and other deposits, which are known as *banded iron formations* (BIF; Figure 2.7). Under the anoxic conditions of primitive Earth, Fe^{2+} released during rock weathering and from submarine hydrothermal emissions would be soluble and accumulate in seawater. With the advent of oxygenic photosynthesis, O_2 would be available to oxidize Fe^{2+} and deposit Fe_2O_3 in the sediments of the primitive ocean, namely:

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 \downarrow + 8H^+. \tag{2.13}$$
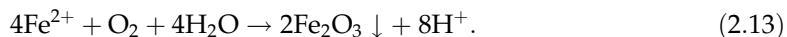
Massive worldwide deposits of the Fe_2O_3 in the banded iron formation are often taken as evidence for the presence of oxygen-producing photosynthesis based on the photochemical splitting of water in sunlight:

$$H_2O + CO_2 \rightarrow CH_2O + O_2. \tag{2.14}$$

Despite the relatively large energy barrier inherent in this photosynthetic reaction, there must have been strong selection for photosynthesis based on the splitting of water, particularly as the limited supplies of H_2S in the primitive ocean were removed by sulfur bacteria (Schidlowski 1983). Water offered an inexhaustible supply of substrate for photosynthesis.

Banded iron formations reach a peak occurrence in sediments deposited 2.5 to 3.0 bya (Walker et al. 1983). Most of the major deposits of iron ore in the United States (Minnesota), Australia, and South Africa are found in formations of this age (Meyer 1985). Presumably the deposition of BIF ended when the Earth's primitive oceans were swept clear of Fe^{2+} and excess oxygen could diffuse to the atmosphere.

Rather than taking banded iron formation as evidence of oxygenic photosynthesis, some workers have pointed out that it could also have been deposited by anaerobic, Fe^{2+}-oxidizing bacteria (Kappler et al. 2005, Widdel et al. 1993), namely:

$$4Fe^{2+} + HCO_3^- + 10H_2O \rightarrow CH_2O + 4Fe(OH)_3 + 7H^+. \tag{2.15}$$
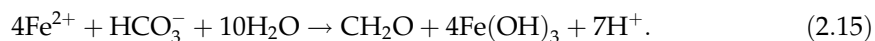
FIGURE 2.7 Banded iron formation from the 3.25-billion-year-old Barberton Greenstone Belt, South Africa. *Sources: Collected by M.M. Tice (Texas A&M University); photo © 2010, Lisa M. Dellwo.*

Invoking this reaction as an alternative, one might conclude that oxygen-evolving photosynthesis dates only to the first appearance of cyanobacteria, which are known oxygenic forms today. Evidence for the presence of cyanobacteria is found in sediments deposited 2.5 to 2.7 bya (Summons et al. 1999, Brocks et al. 1999) or younger (Rasmussen et al. 2008). Indeed, some workers believe that anoxygenic Fe-photosynthesis may have dominated primary production in the primitive ocean (Table 2.4). Note that these two pathways for the deposition of BIF (Eqs. 2.13 and 2.15) are not mutually exclusive; both Fe-photosynthesizers and cyanobacteria can precipitate iron oxides in marine environments today (Trouwborst et al. 2007).

Despite some doubts regarding an early evolution of oxygenic photosynthesis, there is strong evidence that some forms of photosynthetic microbes existed at least 3.4 bya (Tice and Lowe 2004), and robust reports of microfossils, 3.2 to 3.4 bya, are derived from rocks of South Africa (Javaux et al. 2010, Fliegel et al. 2010) and Australia (Wacey et al. 2011). Thus, life seems to have appeared about 500 million years after the last great impacts of Earth's accretion. Whenever it first appeared, oxygenic photosynthesis offered a higher energy yield than other forms of photosynthesis, so these autotrophs might be expected to proliferate rapidly in the competitive arena of nature (Table 2.4).

Even in the face of an early evolution of oxygen-producing photosynthesis, many lines of evidence indicate that the Earth's atmosphere seems to have remained anoxic until about 2.45 to 2.32 billion years ago (Farquhar et al. 2000, 2011, Bekker et al. 2004, Sessions et al. 2009). Until recently, most researchers attributed the lack of oxygen solely to its reaction with reduced iron (Fe^{2+}) in seawater and the deposition of Fe_2O_3 in banded iron formations (Cloud 1973). Oxidation of other reduced species, perhaps sulfide (S^{2-}), may have also played a role, accounting for the slow buildup of SO_4^{2-} in Precambrian seawater (Walker and Brimblecombe 1985, Habicht et al. 2002). It is also possible that the early deposition of iron oxides in the banded iron formation held phosphorus concentrations at low levels, slowing the proliferation of photosynthetic organisms (Bjerrum and Canfield 2002, but see also Konhauser et al. 2007).

Several recent papers postulate an early evolution of aerobic respiration, closely coupled to local sites of O_2 production, which may have held the concentration of O_2 at low levels (Towe 1990, Castresana and Saraste 1995). Aerobic oxidation of methane may have kept oxygen at low levels until 2.7 bya (Konhauser et al. 2009). Only when the oceans were swept clear of reduced substances such as Fe^{2+}, S^{2-}, and CH_4 could excess O_2 accumulate in seawater and diffuse to the atmosphere. Thus, what is known as the Great Oxidation Event began about 2.4 bya, achieving 1% of the present level of O_2 in the atmosphere about 2.0 bya (Kump et al. 2011).

TABLE 2.4   Estimates of Marine Primary Production about 3.5 Billion Years Ago

Process	Annual rate	See Equation
H_2-based anoxygenic photosynthesis	0.35×10^{15} gC/yr	2.11
Sulfur-based anoxygenic photosynthesis	0.03	2.12
Fe-based anoxygenic photosynthesis	4.0	2.15
Present day	~50.0	2.14; Chapter 9

*Source: Modified from Canfield et al. (2006).*

Chemoautotrophy

Oxygen also enabled the evolution of several new biochemical pathways of critical significance to the global cycles of biogeochemistry (Raymond and Segre 2006). Two forms of aerobic biochemistry constitute chemoautotrophy. One based on sulfur or H_2S,

$$2S + 2H_2O + O_2 \rightarrow 2SO_4^{2-} + 4H^+, \tag{2.16}$$
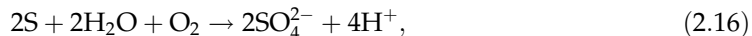
is performed by various species of *Thiobacilli* (Ralph 1979). The protons generated are coupled to energy-producing reactions, including the fixation of CO_2 into organic matter (refer to Figure 1.4). On primitive Earth, these organisms could capitalize on elemental sulfur deposited from anaerobic photosynthesis (Eq. 2.12), and today they are found in local environments where elemental sulfur or H_2S is present, including some deep-sea hydrothermal vents (Chapter 9), caves (Sarbu et al. 1996), wetlands (Chapter 7), and lake sediments (Chapter 8).

Also important are the chemoautotrophic reactions involving nitrogen transformations by *Nitrosomonas* and *Nitrobacter* bacteria:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{2.17}$$

and

$$2NO_2^- + O_2 \rightarrow 2NO_3. \tag{2.18}$$
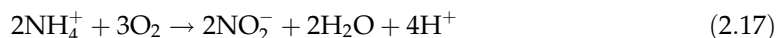
These reactions constitute *nitrification*, and the energy released is coupled to low rates of carbon fixation; that is, nitrifying bacteria are chemoautotrophs. Evidence for the first occurrence of sulfide oxidation and nitrification is indirect evidence for the presence of O_2 on Earth.

Anaerobic Respiration

With the appearance of SO_4^{2-} and NO_3^- as products of chemoautotrophic reactions, other metabolic pathways could evolve. The sulfate-reducing pathway, which depends on SO_4^{2-},

$$2CH_2O + 2H^+ + SO_4^{2-} \rightarrow H_2S + 2CO_2 + 2H_2O, \tag{2.19}$$

is found in archaea dating to 2.4 to 2.7 bya, on the basis of the S-isotope ratios in preserved sediments (Cameron 1982, Parnell et al. 2010). The late appearance of sulfate-reduction relative to photosynthesis may be related to the time needed to accumulate sufficient SO_4^{2-} in ocean waters, from the oxidation of sulfides, to make this an efficient means of metabolism (Habicht et al. 2002, Kah et al. 2004).

This biochemical pathway has been found in a group of thermophilic archaea isolated from the sediments of hydrothermal vent systems in the Mediterranean Sea, where a hot, anaerobic, and acidic microenvironment may resemble the conditions of primitive Earth (Stetter et al. 1987, Jorgensen et al. 1992, Elsgaard et al. 1994). In South Africa, simple microbial communities isolated at 2.8-km depth consist of sulfate-reducing archaea that fix nitrogen and are completely isolated from energy inputs from the Sun at the Earth's surface (Lin et al. 2006, Chivian et al. 2008).

Similarly, today an anaerobic, heterotrophic reaction called *denitrification* is performed by bacteria, commonly of the genus *Pseudomonas*, found in soils and wet sediments (Knowles 1982), namely:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_2O. \tag{2.20}$$

The denitrifying reaction requires NO_3^-, and its preferential use of $^{14}NO_3^-$ over $^{15}NO_3^-$ leaves the ocean enriched in $^{15}NO_3^-$. Rocks showing this enrichment are dated to at least 2.0 bya (Beaumont and Robert 1999, Papineau et al. 2005) and perhaps earlier (Garvin et al. 2009, Godfrey and Falkowski 2009). At that time, nitrate must have been present as products of nitrification reactions (Eqs. 2.17 and 2.18), providing another indirect line of evidence for the presence of O_2 on Earth.

Although the denitrification reaction requires anoxic environments, denitrifiers are facultatively aerobic—that is, switching to aerobic respiration when O_2 is present. This is consistent with several lines of evidence that suggest that denitrification may have appeared later than the strictly anaerobic pathways of methanogenesis and sulfate reduction (Betlach 1982). Denitrification would have been efficient only after relatively high concentrations of NO_3^- had accumulated in the primitive ocean, which is likely to have contained low NO_3^- at the start (Kasting and Walker 1981). Thus, the evolution of denitrification may have been delayed until sufficient O_2 was present in the environment to drive the nitrification reactions (Eqs. 2.17 and 2.18). It is interesting to note that having evolved in a world dominated by O_2, the enzymes of today's denitrifying organisms are not destroyed, but merely inactivated, by O_2 (Bonin et al. 1989, McKenney et al. 1994).

The first O_2 that reached the atmosphere was probably immediately involved in oxidation reactions with reduced atmospheric gases and with exposed crustal minerals of the barren land (Holland et al. 1989, Kump et al. 2011). Oxidation of reduced minerals, such as pyrite (FeS_2), would transfer SO_4^{2-} and Fe_2O_3 to the oceans in riverflow (Konhauser et al. 2011). Deposits of Fe_2O_3 that are found in alternating layers with other sediments of terrestrial origin constitute *red beds*, which are found beginning at 2.0 bya and indicative of aerobic terrestrial weathering (Van Houten 1973). It is noteworthy that the earliest occurrence of red beds roughly coincides—with little overlap—with the latest deposition of banded iron formation, further evidence that the oceans were swept clear of reduced Fe before O_2 began to diffuse to the atmosphere.

Canfield (1998) suggested that with O_2 in Earth's atmosphere, the oceans about 2 bya may have consisted of oxic surface waters and anoxic bottom waters, which only later became oxic throughout the water column (Reinhard et al. 2009). In this model, the bottom waters may have contained substantial concentrations of sulfide, produced by sulfate-reducing bacteria using SO_4^{2-} mixing down from above. Since most metals are scarcely soluble in the presence of sulfide (Anbar and Knoll 2002), Fe^{2+} would have been removed from these bottom waters. Deposition of the banded iron formation would cease because Fe^{2+} was precipitated as FeS_2 rather than Fe_2O_3 (but see Planavsky et al. 2011).

Oxygen began to accumulate to its present-day atmospheric level of 21% when the rate of O_2 production by photosynthesis exceeded its rate of consumption by the oxidation of reduced substances. Atmospheric oxygen may have reached 21% as early as the Silurian—about 430 mya (see inside back cover), and it is not likely to have fluctuated outside the range of 15 to 35% ever since (Berner and Canfield 1989, Scott and Glasspool 2006). What maintains the concentration at such stable levels? Walker (1980) examined all the oxidation/reduction

reactions affecting atmospheric O_2, and suggested that the balance is due to the negative feedback between O_2 and the long-term net burial of organic matter in sedimentary rocks. When O_2 rises, less organic matter escapes decomposition, stemming a further rise in O_2. We will examine these processes in more detail in Chapters 3 and 11, but here it is interesting to note the significance of an atmosphere with 21% O_2. Lovelock (1979) points out that with <15% O_2, fires would not burn, and at >25% O_2, even wet organic matter would burn freely (Watson et al. 1978, Belcher and McElwain 2008). Either scenario would result in a profoundly different world than that of today.

The release of O_2 by photosynthesis is perhaps the single most significant effect of life on the geochemistry of the Earth's surface (Raymond and Segre 2006). The accumulation of free O_2 in the atmosphere has established the oxidation state for most of the Earth's surface for the last 2 billion years. However, of all the oxygen ever evolved from photosynthesis, only about 2% resides in the atmosphere today; the remainder is buried in various oxidized sediments, including banded iron formations and red beds (see Figure 2.8 and refer to Table 2.3). The total inventory of free oxygen that has ever been released on the Earth's surface is, of course, balanced stoichiometrically by the storage of reduced carbon in the Earth's crust, including coal, oil, and other reduced compounds of biogenic origin (e.g., sedimentary pyrite). The sedimentary storage of organic
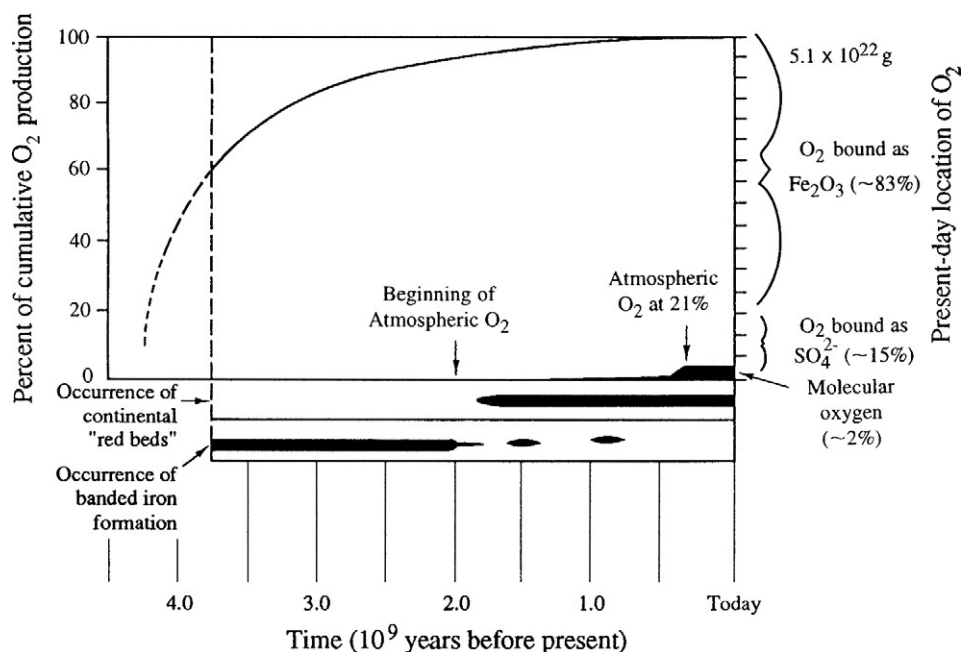
FIGURE 2.8 Cumulative history of O_2 released by photosynthesis through geologic time. Of more than 5.1×10^{22} g of O_2 released, about 98% is contained in seawater and sedimentary rocks, beginning with the occurrence of banded iron formation beginning at least 3.5 bya. Although O_2 was released to the atmosphere beginning about 2.0 bya, it was consumed in terrestrial weathering processes to form red beds, so that the accumulation of O_2 to present levels in the atmosphere was delayed to 400 mya. *Source: Modified from Schidlowski (1980).*

carbon is now estimated at 1.56×10^{22} g (Des Marais et al. 1992; see also Table 2.3), representing the cumulative net production of *bio*geochemistry since the origin of life.

The release of free oxygen as a byproduct of photosynthesis also dramatically altered the evolution of life on Earth. The pathways of anaerobic respiration by methanogenic bacteria and photosynthesis by sulfur bacteria are poisoned by O_2. These organisms generally lack catalase and have only low levels of superoxide dismutase—two enzymes that protect cellular structures from damage by highly oxidizing compounds such as O_2 (Fridovich 1975). Today, these metabolisms are confined to local anoxic environments. Alternatively, eukaryotic metabolism is possible at O_2 levels that are about 1% of present levels (Berkner and Marshall 1965, Chapman and Schopf 1983). Fossil evidence of eukaryotic organisms is found in rocks formed 1.7 to 1.9 bya (Knoll 1992; Figure 2.5), and perhaps even as much as 2.1 billion years ago (Han and Runnegar 1992). Large colonial organisms are reported from rocks 2.1 bya (El Albani et al. 2010). The rate of evolution of amino acid sequences among major groups of organisms suggests that prokaryotes and eukaryotes diverged 2 bya (Doolittle et al. 1996). All these dates are generally consistent with the end of deposition of the banded iron formation and the presence of O_2 in the atmosphere as indicated by red beds (Table 2.5).

TABLE 2.5   Milestones in the Deep History of the Earth

Milestone	When occurred (bya)
Origin of the Universe	13.7
Origin of the Milky Way Galaxy	12.5
Origin of the Sun	4.57
Accretion of the Earth largely complete[a]	4.5
Liquid water on Earth	4.3
Last of the great impacts	3.8
Earliest evidence of photosynthesis	
Depleted ^{13}C and banded iron formations	3.8
Earliest evidence of cellular structures	3.5
First evidence of cyanobacteria	2.7
First evidence of O_2 in the atmosphere	2.45
Evidence of seawater SO_4^{2-}, thus O_2	2.4
Evidence of denitrification, hence NO_3^- and O_2	2.5
Evidence of aerobic rock weathering (red beds)	2.0
First evidence of eukaryotes	2.0
End of banded iron formation	1.8
Land plants	0.43
Genus *Homo*	0.002

[a] *Impact of Theia at 4.527 bya forms the Moon.*

FIGURE 2.9 Cyanobacteria inhabit the space beneath quartz stones in the Mojave Desert, California, where they photosynthesize on the light passing through these translucent rocks. *Source: Schlesinger et al. (2003). Photo © 2010, Lisa M. Dellwo.*

O_2 in the environment allowed eukaryotes to localize their heterotrophic respiration in mitochondria, providing an efficient means of metabolism and allowing a rapid proliferation of higher forms of life. Similarly, more efficient photosynthesis in the chloroplasts of eukaryotic plant cells presumably enhanced the production and further accumulation of atmospheric oxygen.

O_2 in the stratosphere is subject to photochemical reactions leading to the formation of ozone (Chapter 3). Today, stratospheric ozone provides an effective shield for much of the ultraviolet radiation from the Sun that would otherwise reach the Earth's surface and destroy most life. Before the O_3 layer developed, the earliest colonists on land may have resembled the microbes and algae that inhabit desert rocks of today (e.g., Friedmann 1982, Bell 1993, Schlesinger et al. 2003, Phoenix et al. 2006; Figure 2.9). Although there is some fossil evidence for the occurrence of extensive microbial communities on land during the Precambrian (Horodyski and Knauth 1994, Knauth and Kennedy 2009, Strother et al. 2011), it is unlikely that higher organisms were able to colonize land abundantly until the ozone shield developed. Multicellular organisms are found in ocean sediments dating to about 680 mya, but the colonization of land by higher plants was apparently delayed until the Silurian (Gensel and Andrews 1987, Kenrick and Crane 1997). A proliferation of plants on land followed the development of lignified, woody tissues (Lowry et al. 1980) and the origin of effective symbioses with mycorrhizal fungi that allow plants to obtain phosphorus from unavailable forms in the soil (Pirozynski and Malloch 1975, Simon et al. 1993, Yuan et al. 2005; Chapter 6). Even primitive land plants are likely to have speeded the formation of clay minerals, which help preserve organic matter from degradation and thus further the accumulation of oxygen in the atmosphere (Kennedy et al. 2006, Chapter 4).

COMPARATIVE PLANETARY HISTORY: EARTH, MARS, AND VENUS

In the release of free O_2 to the atmosphere, life has profoundly affected the conditions on the surface of the Earth. But what might have been the conditions on Earth in the absence of life? Some indications are given by our neighboring planets Mars and Venus, which are the best replicates we have for the underlying geochemical arena on Earth. We are fairly

confident that there has never been life on these planets, so their surface composition represents the cumulative effect of 4.5 billion years of abiotic processes. Our understanding of the atmosphere of Mars has improved markedly since the Viking landing in 1976, followed by landings in 1997, 2004, and 2007 that further explored its atmosphere and surface properties with robotic instruments (Figure 2.10).[6]

Table 2.6 compares a number of properties and conditions on Earth, Mars, and Venus. Two properties characterize the atmosphere of these planets: the total mass (or pressure) and the proportional abundance of constituents. The present atmosphere on Mars is only about 0.76% as massive as that on Earth (Hess et al. 1976). We should expect a less massive atmosphere on Mars than on Earth because the gravitational field is weaker on a smaller planet. Mars probably began with a smaller allocation of the solar nebula during planetary formation, and we should expect that a small planet would have retained less internal heat to drive tectonic activity and outgassing of its mantle after its formation (Anders and Owen 1977, Owen and Biemann 1976). Estimates of the cumulative generation of magma are substantially lower for Mars ($0.17 \text{ km}^3/\text{yr}$) than for Earth ($26$–$34 \text{ km}^3/\text{yr}$) or Venus ($<19 \text{ km}^3/\text{yr}$) (Greeley and Schneid 1991).

We should also expect that the surface temperature on Mars would be colder than that on Earth because the planet is much farther from the Sun. The average temperature on Mars, $-53°C$ at the site of the Viking landing (Kieffer 1976), ensures that water is frozen on most of the Martian surface at all seasons. Ice is found at both poles of Mars and in Martian soils in other areas (Titus et al. 2003, Mustard et al. 2001, Smith et al. 2009). In the absence of liquid water, we would expect that the atmosphere on Mars would be mostly dominated by CO_2, which readily dissolves in seawater on Earth (Eq. 2.4). Indeed, CO_2 constitutes a major

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[6] The NASA lander, *Curiosity*, arrived safely on Mars on August 6, 2012.

TABLE 2.6   Some Characteristics of the Inner Planets

	Mars[a]	Earth	Venus[b]
Distance to the Sun (10^6 km)	228	150	108
Surface temperature (°C)	−53	16	474
Radius (km)	3390	6371	6049
Atmospheric pressure (bars)	0.007	1	92
Atmospheric mass (g)	2.4×10^{19}	5.3×10^{21}	5.3×10^{23}
Atmospheric composition (% wt.)			
CO_2	95	0.04	98
N_2	2.5	78	2
O_2	0.25	21	0
H_2O	0.10	1	0.05
$^{40}Ar/^{36}Ar$[c]	2840	296	1

[a] *From Owen and Biemann (1976).*
[b] *From Nozette and Lewis (1982).*
[c] *Wayne (1991).*

proportion of the thin atmosphere of Mars, and the observed fluctuations of the ice cap at the south pole of Mars appear due to seasonal variations in the amount of CO_2 that is frozen out of its atmosphere (Leighton and Murray 1966, James et al. 1992, Phillips et al. 2011a).

Several attributes of Mars are anomalous. First, with most of the water and CO_2 now trapped on the surface, why is N_2 such a minor component of the atmosphere on Mars? Second, why do the surface conditions on Mars indicate a period when small amounts of liquid water may have been present on its surface (Malin and Edgett 2000, 2003; Squyres et al. 2004; Solomon et al. 2005)—perhaps even recently (Malin et al. 2006, Christensen 2003, McEwen et al. 2011). Could it be that a more massive early atmosphere may once have allowed a significant "greenhouse effect" on Mars and warmer surface temperatures than today (Pollack et al. 1987)? Such a scenario could explain an early sporadic occurrence of liquid water on Mars, but if it is correct, why did Mars lose its atmosphere and cool to its present surface temperature of −53°C?

Losses of atmospheric gases from Mars may have resulted from several processes. A thick atmosphere on Mars may have been lost to space as a result of catastrophic impacts during its early history (Carr 1987, Melosh and Vickery 1989) or by a process known as "sputtering" driven by solar wind (Kass and Yung 1995, Hutchins and Jakosky 1996). Impacts are consistent with the low abundance of noble gases on Mars relative to the concentrations in carbonaceous chondrites and the Sun (Hunten 1993, Pepin 2006). Catastrophic loss of an early atmosphere is also consistent with the observation that nearly the entire atmosphere on Mars is secondary, as evidenced by a $^{40}Ar/^{36}Ar$ ratio of 2750 or more (Owen and Biemann 1976, Biemann et al. 1976, Wayne 1991, Yung and DeMore 1999). Mars shows some evidence of recent volcanic activity (Neukum et al. 2004), and a significant proportion of its thin atmosphere may have been derived <1 bya (Gillmann et al. 2011, Niles et al. 2010).

Loss of water from Mars may have also occurred as the water vapor in its atmosphere underwent photolysis by ultraviolet light. Observations of analogous processes on Earth are instructive. In the upper atmosphere on Earth, small amounts of water vapor are subject to photodisassociation, with the loss of H_2 to space. However, because the upper atmosphere is cold, little water vapor is present, and the process has been minor throughout Earth's history (Chapter 10). If this process were significant on Mars, we would expect that the loss of ^1H would be more rapid than that of ^2H, leaving a greater proportion of ^2H_2O in the planetary inventory. Owen et al. (1988) found that the ratio of ^2H (deuterium) to ^1H on Mars is about $6\times$ that on Earth, suggesting that Mars may have once possessed a large inventory of water that has been lost to space (de Bergh 1993, Krasnopolsky and Feldman 2001). The relative abundance of ^2H has potentially increased through time, as seen in measurements of putative Martian meteorites of various ages that have been collected on Earth (Greenwood et al. 2008). Although a small amount of O_2 is found in the Martian atmosphere (Table 2.6), most of the oxygen produced from the photolysis of water has probably oxidized minerals of the crust, namely:

$$4FeO + O_2 \rightarrow 2Fe_2O_3, \tag{2.21}$$

giving Mars its reddish color (Figure 2.10).

Nitrogen may have also been lost from Mars as N_2 underwent photodisassociation in the upper atmosphere, forming monomeric N. This process occurs on Earth as well, but even N is too heavy to escape the Earth's gravitational field and quickly recombines to form N_2. With its smaller size, Mars allows the loss of N. Relative to the Earth, a higher proportion of $^{15}N_2$ in the Martian atmosphere is suggestive of this process, since the escape of ^{15}N would be slower than that of ^{14}N, which has a lower atomic weight (McElroy et al. 1976, Murty and Mohapatra 1997). Both the Earth and Mars have a higher relative proportion of ^{15}N than the solar composition—Mars more so (Marty et al. 2011).

With losses of H_2O and N_2 to space, it is not surprising that the Martian atmosphere is dominated by CO_2. What is surprising is that the atmospheric mass is so low. As much as 3 bars of CO_2 may have been degassed from the interior of Mars, but only about 10% of that amount appears to be frozen in the polar ice caps and the soil (Kahn 1985). Some CO_2 may have been lost to space (Kass and Yung 1995), but during an earlier period of moist conditions, CO_2 may have also reacted with the crust of Mars, weathering rocks and forming carbonate minerals on its surface (Bandfield et al. 2003, Ehlmann et al. 2008, Boynton et al. 2009, Morris et al. 2010). With the loss of tectonic activity on Mars, there was no mechanism to release this CO_2 back to the atmosphere, as there is on Earth (refer to Figure 1.3).

In sum, various lines of evidence suggest that Mars had a higher inventory of volatiles early in its history, but most of the atmosphere has been lost to space or in reactions with its crust. The presence of water on Mars may have once offered an environment conducive to the evolution of life, especially in light of the relatively rapid appearance of life on Earth. Subsurface and hydrothermal environments are also possible sites for early life on Mars (Squyres et al. 2008), and today, intriguing emissions of CH_4 are observed from the Martian surface (Formisano et al. 2004, Mumma et al. 2009). Nevertheless, evidence for past life on Mars is rather scant (McKay et al. 1996), and there is no evidence of liquid water or life on Mars today. Even organic molecules received from meteoric impacts on the surface of Mars have been oxidized by the Sun's ultraviolet light (Kminek and Bada 2006).

Through geologic time, the loss of water from Mars would remove a large component of greenhouse warming from the planet. The thin atmosphere that remains is dominated by CO_2, but it offers little greenhouse warming—raising the temperature of Mars only about 10°C over what might be seen if Mars had no atmosphere at all (Houghton 1986). Our best estimate suggests that the volume of CO_2 now frozen in the polar ice caps (100 mbar) and soils (300 mbar) on Mars is insufficient to supply the 2 bars of atmospheric CO_2 that would be necessary for the greenhouse effect to raise the temperature of the planet above the freezing point of water (Pollack et al. 1987). Thus, it would be difficult to use planetary-level engineering to establish a large, self-sustained greenhouse effect on Mars, allowing humans to colonize the planet (McKay et al. 1991).

On Venus, the ratio of the mass of the atmosphere to the mass of the planet (1.09×10^{-4}) is only slightly less than the ratio of the total mass of volatiles on Earth (see Table 2.3) to the mass of the Earth (3.3×10^{-4}). These values suggest a similar degree of crustal degassing on these planets. Indeed, volcanism is observed on Venus today (Smrekar et al. 2010, Bondarenko et al. 2010), and the atmosphere on Venus is remarkably similar to the average composition of carbonaceous chondrites (Pepin 2006). Despite the evidence of outgassing, the $^{40}Ar/^{36}Ar$ ratio on Venus is close to 1.0, implying that, relative to the Earth, Venus may have also retained a greater fraction of gases from the solar nebula during its accretion (Pollack and Black 1982). Unlike the Earth, the high surface temperature of 474°C on Venus ensures that its present inventory of volatiles resides entirely in its atmosphere. The atmospheric pressure on Venus is nearly 100× that of Earth (Table 2.6). The hot, high-pressure conditions have made it difficult to land spacecraft for the exploration of the surface of Venus.

The massive atmosphere on Venus is dominated by CO_2, conferring a large greenhouse warming and surface temperatures well in excess of that predicted for a nonreflective body at the same distance from the Sun (54°C; Houghton 1986).[7] The relative abundance of CO_2 and N_2 in the atmosphere of Venus is roughly similar to that in the total inventory of volatiles on Earth (Oyama et al. 1979, Pollack and Black 1982, Lecuyer et al. 2000). What is unusual about Venus is the low abundance of water in its atmosphere. Was Venus wet in the past?

The ratio of ^2H (deuterium) to ^1H on Venus is >100× higher than that on Earth (Donahue et al. 1982, McElroy et al. 1982, de Bergh et al. 1991), suggesting that Venus, like Mars, may have possessed a large inventory of water in the past, but lost water through a process that differentiates between the isotopes of hydrogen. With the warm initial conditions on Venus, a large amount of the water vapor in the atmosphere may have been subject to photodisassociation, causing the planet to dry out through its history (Kasting et al. 1988, Lecuyer et al. 2000). The oxygen released during the photodisassociation of water has probably reacted with crustal minerals (Donahue et al. 1982, McGill et al. 1983, p. 87).

At the surface temperatures found on Venus, little CO_2 can react with its crust (compare with Figure 1.3), so high concentrations of CO_2 remain in the atmosphere (Nozette and Lewis 1982). Various other gases, such as SO_2, that are found dissolved in seawater on Earth also

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[7] One of the widely cited reports of the Intergovernmental Panel on Climate Change (IPCC) indicates that the surface temperature on Venus in the absence of a greenhouse effect would be −47°C (Houghton et al. 1990). This is lower than the value given here because the IPCC report accounts for the reflectivity of the thick cloud layer on Venus, whereas our value considers the equilibrium temperature for a black body absorber in the orbit of Venus. See Lewis and Prinn (1984, p. 97).

reside as gases in the atmosphere on Venus (Oyama et al. 1979, Svedhem et al. 2007, Marcq et al. 2011). Continuing volcanic releases of CO_2 have accumulated in the atmosphere to produce a runaway greenhouse effect in which increasing temperatures allow an increasing potential for the atmosphere to hold CO_2 and other gases (Walker 1977). Thus, the current temperature on Venus, 474°C, is much greater than we would predict if Venus had no atmosphere and is not conducive to life as we know it.

The proliferation of known planets around other stars and observations of organic molecules in interstellar dusts and meteorites beg for further exploration for the presence of extraterrestrial life in our galaxy and beyond (Lissauer et al. 2011, Cassan et al. 2012). At least one planet, Kepler-22b, which is 600 light years from Earth, shows a size and an orbit around its sun that might be conducive to life. The massive atmospheres on the outer planets of our solar system are not conducive to life, but Europa and the other moons of Jupiter show evidence of subsurface oceans beneath surface ice (Carr et al. 1998, Kivelson et al. 2000). Some of these habitats may be subjected to hydrothermal activity, providing a submarine habitat for the abiotic synthesis of organic materials and perhaps modest forms of metabolism (Gaidos et al. 1999, Marion et al. 2003). A small amount of O_2 is detected in the atmosphere of Europa (10^{-11} of that on Earth), where it may originate from a photolytic process similar to that leading to the loss of water from Mars and Venus (Hall et al. 1995).

The atmosphere of Saturn's moon Titan is dominated by nitrogen (96%) and methane (3%), with an $^{40}Ar/^{36}Ar$ ratio of 154, suggesting a secondary origin from outgassing (Niemann et al. 2005, Yung and DeMore 1999, p. 202). Huge lakes of liquid methane are potentially stable on its surface (Stofan et al. 2007, Lorenz et al. 2008), and liquid methane falls from its atmosphere as rain (Hueso and Sanchez-Lavega 2006, Turtle et al. 2011). On Saturn's moon, Enceladus, frozen water-ice covers much of the surface (Brown et al. 2006a), and geysers appear to spew water vapor into the atmosphere (Waite et al. 2006, Postberg et al. 2011). Habitats with liquid water, hydrothermal activity, and reduced gases (especially methane) on planets and planetary moons are likely places to look for extraterrestrial life within and outside our solar system (Swain et al. 2008). Subglacial lakes in Antarctica are analogous terrestrial habitats on Earth (Priscu et al. 1998).

Certainly the most unusual characteristic of the Earth's atmosphere is the presence of large amounts of O_2, which is an unequivocal indication of life on this planet (Sagan et al. 1993). Having examined the conditions on Mars, Venus, and other bodies of our solar system, we can now offer some speculation on the conditions that might exist on a lifeless Earth. At a distance of 150×10^6 km from the Sun, the surface temperature on the Earth, assuming no reflectivity to incoming solar radiation, would be close to the freezing point of water (Houghton 1986). Such cold conditions would seem to ensure that the atmosphere on the Earth has never contained much water vapor, so relatively little water has been lost to space as a result of photolysis in the upper atmosphere.

Despite the small amount of H_2O in Earth's atmosphere, the atmosphere confers enough greenhouse warming to the planet to have maintained liquid oceans for most of its history. Thus, even on a lifeless Earth, most of the inventory of volatiles would reside in the oceans. The atmosphere on a lifeless Earth would be dominated by N_2, which is only slightly soluble in water. The size of Earth and its gravitational field ensure that photolysis of N_2 does not result in the loss of N from the planet. Moreover, the rate of fixation of nitrogen by lightning

in an atmosphere without O_2 appears too low to transfer a significant portion of N_2 from the atmosphere to the oceans (Kasting and Walker 1981; Chapter 12). Thus, the main effect of life has been to dilute the initial nitrogen-rich atmosphere on Earth with a large quantity of O_2 (Walker 1984).

How long will the Earth be hospitable to life? Barring some unforeseen catastrophe, we can speculate that the biosphere will persist as long as our planet harbors liquid water on its surface. Eventually, however, a gradual increase in the Sun's luminosity will warm the Earth, causing a photolytic loss of water from the upper atmosphere, irreversible oxidation of the Earth's surface, and the demise of life—perhaps after another 2.5 billion years (Lovelock and Whitfield 1982, Caldeira and Kasting 1992). The Sun itself will burn out in 10 billion years. If we manage the planet well, studies of biogeochemistry have a long future.

SUMMARY

In this chapter we have reviewed theories for the formation and differentiation of early Earth. In the process of planetary formation, certain elements were concentrated near its surface and only some elements were readily soluble in seawater. Thus, the environment in which life arose is a special mix taken from the geochemical abundance of elements that were available on Earth. Simple organic molecules can be produced by physical processes in the laboratory; presumably similar reactions occurred in high-energy habitats on primitive Earth. Life may have arisen by the abiotic assembly of these constituents into simple forms, resembling the most primitive bacteria that we know of today. Essential to living systems is the processing of energy, which is likely to have begun with the heterotrophic consumption of molecules found in the environment. A persistent scarcity of such molecules is likely to have led to selection for the autotrophic production of energy by various pathways, including photosynthesis. Autotrophic photosynthesis appears to be responsible for nearly all the production of O_2, which has accumulated in the Earth's atmosphere over the last 2 billion years. The major biogeochemical cycles on Earth are mediated by organisms whose metabolic activities couple the oxidation and reduction of substances isolated from the environment.

Recommended Readings

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Hazen, R.M. 2012. *The Story of Earth: The First 4.5 Billion Years, from Stardust to Living Planet*. Viking Books.

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Kasting J.F. 2010. *How to Find a Habitable Planet*. Princeton University Press.

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Williams, G.R. 1996. *The Molecular Biology of Gaia*. Columbia University Press.

Yung, Y.L. and W.B. DeMore. 1999. *Photochemistry of Planetary Atmospheres*. Oxford University Press.

PROBLEMS

2.1. If the average carbon content of a carbonaceous chondrite is 3.5% by mass (compare with Anders and Grevesse 1989), what mass of such meteorites would have to be received to account for the total mass of carbon on Earth (Table 2.3)? How does this compare to the total mass of the Earth? What would be the % nitrogen content in these chondrites to account for the nitrogen inventory on Earth?

2.2. Assuming that the net primary production of today's biosphere (see Tables 5.3 and 9.2) has pertained to the Earth for the past 400,000,000 years, what is the cumulative amount of carbon that has at one time or another been held in living tissue over this interval? How does this compare to the carbon inventory on Earth and to the mass of the Earth's crust (estimate or cite a source for this number)? What is the significance of your conclusion?

2.3. On today's Earth, water at sea level (that is, under l atmosphere of pressure) boils at 100°C. If the total inventory of volatiles (Table 2.3) was present in the atmosphere of the Earth about 4.0 bya, at what temperature would liquid water have first condensed to form the oceans? Based on your calculation, what is the maximum fraction of today's inventory that could have been in the atmosphere when the condensation began? *Hint*: You will need to consult a table for the vapor pressure of water as a function of temperature.

2.4. The best estimates of the total amount of carbon (i.e., CO_2) released from volcanoes worldwide is about 0.05×10^{15} gC/yr. Using the data of Table 2.3, what does this suggest for the mean residence time for carbon in marine sediments? Why is this older than the oldest oceanic crust?

2.5. What is the N_2/Ar molar ratio in the volcanic emissions compiled in Table 2.2 and in the total inventory of volatiles on Earth (Table 2.3)? Why might you expect the N_2/Ar ratio to be higher in volcanic emissions than in the inventory?