

4 Planetary atmospheres and life

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Earth is *not* the only body in the Solar System that is habitable. Life as we know it requires liquid water and free energy gradients, both of which probably also exist on Mars and Europa, although liquid water on those bodies is restricted to the subsurface. Earth is, however, the only planet in the Solar System that has liquid water at its surface. Similar planets may exist around other stars (Chapter 21) and would be of profound interest for two reasons. First, biology on such planets might resemble life on Earth. Second, the biosphere on such planets would interact with the planet's atmosphere and could modify it in a way that may be detectable remotely. Today, life may be thriving on Mars or Europa but its discovery will require subsurface exploration. In contrast, we might be able to tell whether a distant Earth-like planet is inhabited by measuring the spectrum of its atmosphere.

Thus, from an astrobiological standpoint, one of the most fundamental characteristics of a planet is its surface temperature T_s . If T_s is not within the range in which liquid water can exist, remotely detectable life will probably not exist there. Consequently, the first part of this chapter is concerned with planetary surface temperatures. The constraint on temperature is not as obvious as $0 < T_s < 100^\circ\text{C}$. Water boils at 100°C at Earth's surface because the overlying atmospheric pressure is 1 bar ($= 10^5 \text{ N/m}^2 = 10^5 \text{ Pascal}$) and because the atmosphere is not in equilibrium with water at this temperature. If Earth's entire surface were at 100°C , the oceans would still not boil because the overlying atmospheric pressure would then be 2 bars (1 bar $\text{N}_2\text{-O}_2$ and 1 bar H_2O). Thus, planetary atmospheres act like pressure cookers, with gravity taking the place of the pressure cooker's lid. In general, liquid water is stable all the way up to a temperature of 374°C (647 K) for pure water, or even higher for salt water.

More practical upper limits on T_s for a habitable planet can be considered. The currently known lower limit for microbial activity is $\sim -20^\circ\text{C}$ (in very salty solutions; Chapter 15). The currently known upper limit for prokaryotic microbial life is 121°C (Kashefi and Lovley, 2003) while that for more complex eukaryotic life is 60°C (Rothschild and Mancinelli, 2001) (Chapter 14). The latter temperature is also about the point where a 1-bar atmosphere like Earth's rapidly begins to lose its water because the molecules can move efficiently to the upper atmosphere. This process involves energetic solar ultraviolet photons dissociating (breaking up) water molecules at the top of the atmosphere, after which the light H atoms escape to space (Section 4.2.2).

In summary, from about -20°C to 60°C would seem to be a probable temperature range of interest for habitable planets populated by organisms similar to those found on Earth.

Planetary habitability is also affected by atmospheric composition. There are several factors to consider here, which are best discussed within the context of our own planet Earth, for which we have considerable data. Was a certain atmospheric composition necessary for the origin of life? How did atmospheric composition change once life had originated? When and why did O_2 become an abundant atmospheric constituent? Could we infer the presence of life by remotely analyzing Earth's atmosphere, now or in the past? And did the availability of O_2 set the tempo for the evolution of complex life? These questions will form the basis of the second half of the chapter.

4.1 Fundamentals of global climate

We begin by outlining a few fundamental concepts governing planetary climates. These will prove useful in understanding how Earth's climate has evolved and why the climates of Mars and Venus evolved so differently.

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4.1.1 Planetary energy balance and the greenhouse effect

Earth is warmed by absorption of visible and near-infrared radiation from the Sun and is cooled by emission of thermal infrared radiation. If we treat the Earth as a *blackbody radiator*¹ with *effective temperature* T_e , we can equate the emission of thermal infrared radiation F_{IR} (given by the Stefan–Boltzmann law) with the average solar radiation absorbed by the Earth. Let us denote the annual mean solar flux at Earth's orbit by S ($=1366 \pm 3 \text{ W/m}^2$). The Earth, with radius R , presents an area πR^2 normal to the solar beam and has a total surface area $4\pi R^2$. Thus, the globally averaged flux of solar radiation received per unit area is $S/4$, but a fraction of that flux, called the *albedo* A ($\cong 0.3$ for Earth), is reflected back to space and does not warm the Earth. Thus, the planetary energy balance (energy flux out = energy flux in) is

$$F_{IR} = \sigma T_e^4 = \frac{S}{4}(1 - A), \quad (4.1)$$

where σ is the Stefan–Boltzmann constant. Solving for Earth's effective temperature yields $T_e = 255 \text{ K}$. Earth, however, is *not* a blackbody, but instead has an atmosphere that warms the surface by the *greenhouse effect*. Thus, the globally averaged surface temperature T_s is in fact $\sim 288 \text{ K}$. The difference between T_e and T_s gives the magnitude of the greenhouse effect:

$$\Delta T_g \equiv T_s - T_e = 33 \text{ K}. \quad (4.2)$$

In the greenhouse effect, the atmosphere warms as it absorbs upwelling infrared radiation from the Earth below. Because the atmosphere is warm it radiates. Some of this radiation is emitted downwards towards the Earth. Consequently, the Earth's surface is warmer than it would be in the absence of an atmosphere because it receives energy from two sources: the Sun and the heated atmosphere. The additional heating from the atmosphere is called the greenhouse effect.

In Earth's atmosphere today, the two most important contributors to greenhouse heating are CO_2 and H_2O . H_2O is responsible for about two-thirds of the

warming, although it acts in a different manner than CO_2 because it is near its condensation temperature, at least in the lowest layer of the atmosphere (the *troposphere*, up to 8 km at the poles and 17 km at the equator). CO_2 accounts for most of the remaining third of the greenhouse effect. The remaining $\sim 2\text{--}3 \text{ K}$ comes from CH_4 , N_2O , O_3 , and various human-produced chlorofluorocarbons (CFCs). Although the total of these trace constituents is small, they are very efficient greenhouse gases: for example, each CH_4 molecule is ~ 20 times more effective than a CO_2 molecule in the modern atmosphere (Schimel *et al.*, 1996). This is because they absorb within the $7.5\text{--}12 \mu\text{m}$ wavelength region, an otherwise transparent “window” through which most of the Earth's thermal infrared radiation energy escapes to space.

Equations (4.1) and (4.2) show that the mean planetary temperature T_s depends on only three factors: (a) the solar flux (set by astronomical geometry and solar physics), (b) the albedo, and (c) the greenhouse effect. Any changes in T_s during Earth's history (e.g., as evidenced by low-latitude glaciation) can only be understood by appealing to changes in one or more of these factors. The most difficult factor to estimate well is the planetary albedo because $\sim 80\%$ of it is caused by clouds. Clouds can be observed and parameterized in Earth's present atmosphere, but their properties for other atmospheres are uncertain. Climate calculations for early Earth or for other Earth-like planets are thus subject to considerable uncertainty.

4.1.2 Climate feedbacks and feedback loops

Water vapor acts as a feedback on the climate system because it is near its condensation temperature. As the atmosphere cools, the saturation vapor pressure (the maximum vapor pressure possible before water condenses) drops. If the relative humidity² remains constant, then the water vapor concentration in the atmosphere will decrease proportionately. Less water vapor results in a smaller greenhouse effect, which in turn results in further cooling. Just the opposite happens if the climate warms: atmospheric H_2O increases, thereby increasing the greenhouse effect and amplifying the initial warming.

The interaction between water vapor and surface temperature can be expressed by means of a feedback diagram such as Fig. 4.1a. Here, the boxes represent

¹ A *blackbody radiator* is an ideal body that reradiates all of the electromagnetic energy that it absorbs. The spectral distribution of this radiated energy depends only on the temperature of the body and is given by the Planck distribution formula. If a body's spectrum is only approximately that of a blackbody (as is typical for planets and stars), one can still define the *effective temperature* as the

² The *relative humidity* is the ratio of vapor pressure to saturation vapor pressure, usually expressed as a percentage.

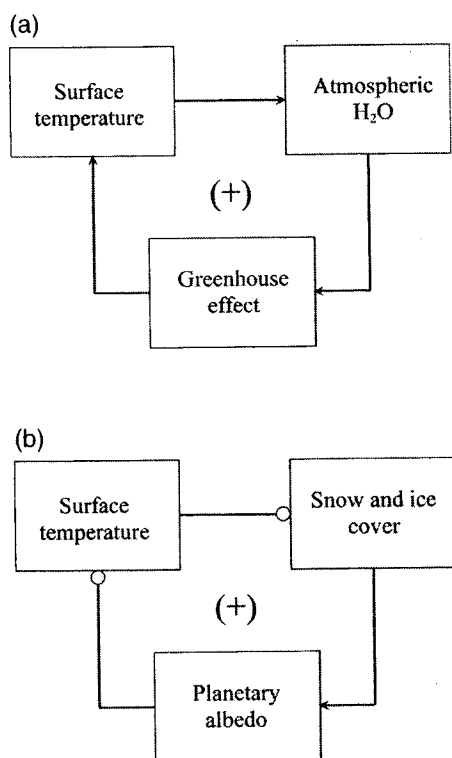


FIGURE 4.1 Feedback loops for the Earth's climate. (a) The water vapor positive feedback loop. (b) The H₂O and snow-and-ice albedo positive feedback loop.

three components of a simplified climate model: surface temperature, atmospheric H₂O, and the greenhouse effect. The arrows connecting them represent *positive couplings*, meaning that an increase (decrease) in one component causes a corresponding increase (decrease) in the next. All the couplings are positive in this diagram, so it constitutes a *positive feedback loop*. This particular feedback loop is very important for Earth's climate, essentially doubling the effect of any climatic perturbations such as changes in solar flux or in atmospheric CO₂.

A second important feedback loop is shown in Fig. 4.1b. This loop describes the interaction between surface temperature and the fraction of Earth's surface covered by snow and ice. The lines with circular endings represent *negative couplings*, e.g., an *increase* in surface temperature causes a *decrease* in snow and ice cover. The second coupling is positive, however, because more snow and ice causes more reflection of sunlight (compared to rock or vegetation) and thus increases the albedo. But an increase in albedo causes a decrease in surface temperature, so the third coupling is again negative. Two negatives make a positive in this type of diagram, so the overall feedback loop is again *positive*. The snow-and-ice albedo feedback loop has played a major role in the advances and retreats of the ice sheets over the past 2 Myr.

Positive feedbacks are unstable because they tend to make a parameter such as T_s greatly change, rather than stay near an equilibrium value. Since Earth's climate system is stable, there must also be negative feedbacks for T_s . The most basic negative feedback (not shown) is the interaction between surface temperature and the outgoing infrared flux F_{IR} . As T_s increases, F_{IR} increases, which is a loss of energy leading to a cooler surface (lower T_s). This creates a negative feedback loop that is so fundamental that it is often overlooked, although it is the reason that Earth's climate is stable on short timescales. On long timescales, however, factors that influence climate can change, and we need to look for something else to ensure stability. We will argue below that the most important long-term climate feedback involves the interaction between atmospheric CO₂ and surface temperature. Let us consider what factors affect climate over the long term and see why negative feedbacks are required to stabilize it.

4.2 The faint young Sun problem

Detailed models of the Sun's evolution indicate that it, like other stars, gets brighter as it ages in its *main sequence* phase. During this long-lasting, relatively stable phase, the Sun produces energy by fusing four hydrogen nuclei ^1H (4 protons) into one ^4He nucleus deep within its core. Ionized matter in the interior of the Sun behaves like an ideal gas. Thus, the relationship between its pressure P and temperature T is $P = nkT$, where n is the number density of all particles (electrons and nuclei) and k is Boltzmann's constant. But when hydrogen nuclei fuse to form helium, n decreases slightly. This causes contraction as the weight of overlying material presses inward. As the core contracts, gravitational acceleration g increases because $g \propto (\text{radius})^{-2}$. Core pressure P increases with g because $P = \text{force per unit area} = (\text{mass per unit area in a column}) \times g$, where the amount of overlying material remains constant. Thus, T must also increase to maintain a pressure balance and the core is heated. Higher core temperatures cause fusion reactions to proceed faster, so the Sun produces more energy. The solar luminosity (total power output) must therefore increase with time. Standard models predict that the Sun's luminosity was about 30% less when it formed 4.6 Ga and that it has increased roughly linearly with time ever since (Fig. 4.2). This theoretical prediction is considered robust because it arises from basic physics, namely nuclear fusion and hydrostatics, and is

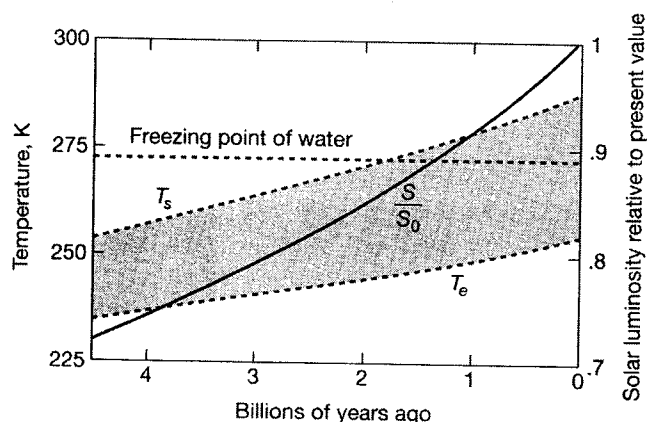


FIGURE 4.2 Calculations of the surface temperature of the Earth over its lifetime, illustrating the “faint young Sun problem.” T_s is the surface temperature assuming a present-day atmospheric composition, T_e is the planetary equilibrium temperature, S is the solar luminosity at times in the past and S_0 is the present solar luminosity. (From Kasting *et al.*, 1988.)

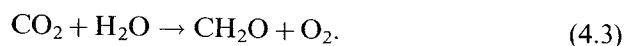
consistent with observations of many other solar-like stars of various ages.

Although an understanding of increasing solar luminosity began in the 1950s, it was not until much later that Sagan and Mullen (1972) noted the implications for planetary climates. If one lowers the value of S by 30% in Eq. (4.1), holding the albedo and greenhouse effect constant for simplicity, one finds that T_e drops to 233 K and T_s to 266 K = -7°C , below the freezing point of water. If one then repeats this calculation with a climate model that includes the positive feedback loop involving water vapor, the problem becomes even more severe. The dashed curves in Fig. 4.2 show T_e and T_s calculated using a one-dimensional, radiative-convective climate model, assuming constant CO_2 concentrations and fixed relative humidity (Kasting *et al.*, 1988). The results are similar to those predicted earlier by Sagan and Mullen: T_s is below the freezing point of water prior to ~ 2 Ga. Especially once the snow/ice-albedo feedback loop is taken into account, this would seem to imply that the Earth was then globally glaciated. However, geologic evidence tells us that liquid water and life were both present back to certainly 3.5 Ga and maybe even earlier. The presence of an ocean at 4.3 Ga has been deduced from ancient zirconium silicate minerals (zircons) (Wilde *et al.*, 2001; Mojzsis *et al.*, 2001). These zircons are enriched in heavy oxygen (^{18}O), which can result from interaction with liquid water at low temperature. The inference from the zircons is that the crust from which they formed interacted with an early liquid ocean, not a frozen one.

How can the faint young Sun problem be solved? The most likely solution involves a greater greenhouse effect in the past. A drastic decrease in cloudiness, leading to much less reflected light (a lower albedo), would also solve the problem (Rossow *et al.*, 1982), but this seems unlikely because the ancient climate appears to have been, if anything, even warmer than today, promoting evaporation and cloud formation. Instead, there are good reasons to believe that the faint young Sun problem is best solved by the presence of abundant greenhouse gases in the early atmosphere.

4.2.1 The carbonate-silicate cycle and CO_2 -climate feedback

Carbon dioxide is the second most important greenhouse gas today. Over long timescales, CO_2 is controlled by the *carbon cycle*, which has several different parts. The more familiar part is the *organic carbon cycle* in which plants (and many microbes) convert CO_2 and H_2O into organic matter and O_2 by photosynthesis. Organic matter on average can be represented as “ CH_2O ,” so the overall reaction for (oxygenic) photosynthesis can be written as



Photosynthesis is almost entirely balanced by the twin processes of respiration and decay, both of which are the reverse of the above reaction.

There are two reasons, however, why the organic carbon cycle cannot be the primary control on CO_2 levels over long timescales. First, the living biosphere is not a large carbon reservoir – it contains only about as much carbon as does the atmosphere. Second, any small imbalance that occurs when organic carbon is buried in sediments cannot be maintained for very long because it is controlled by a negative feedback loop involving atmospheric O_2 (e.g., Catling and Claire, 2005). Basically, an increase in organic carbon burial causes an increase in atmospheric O_2 , which in turn causes a decrease in organic carbon burial. Moreover, this cycle is controlled more by oxygen than by climate, so it cannot contribute appreciably to climate stability. Indeed, this cycle may have destabilized climate on more than one occasion, leading to possible global glaciation episodes (Section 4.2.4).

The part of the carbon cycle most important to long-term climate is the *inorganic carbon cycle*, also called the *carbonate-silicate cycle*. Beginning at the left-hand side of Fig. 4.3, CO_2 dissolves in rainwater

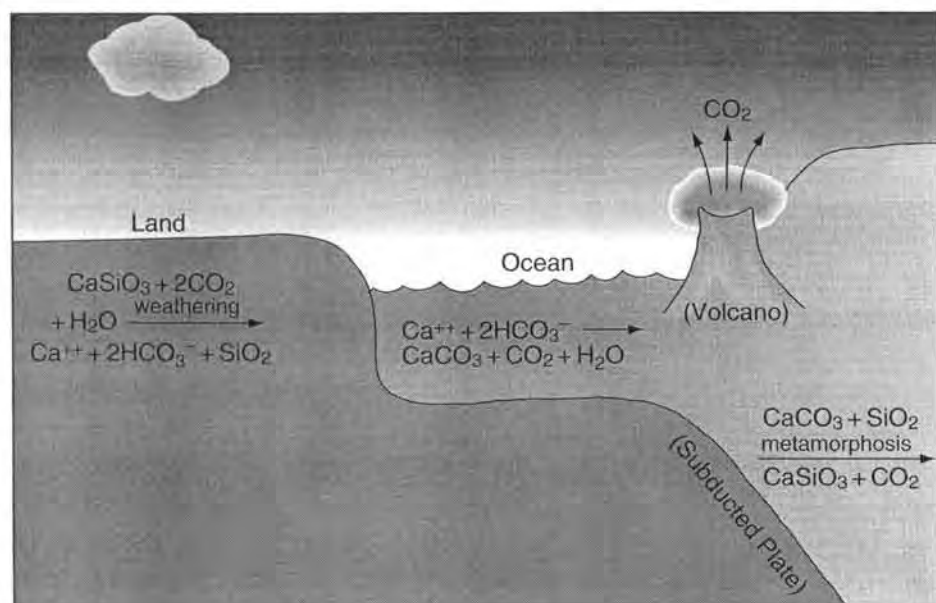
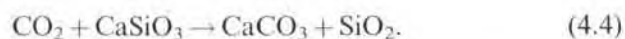


FIGURE 4.3 Earth's carbonate-silicate cycle.

to form carbonic acid, H_2CO_3 . Carbonic acid is a weak acid – it is the acid in soda pop – but over long times it is strong enough to dissolve silicate rocks. We will focus here on calcium silicates, which can be represented by the simplest silicate mineral, wollastonite (CaSiO_3). The products of this silicate *weathering*, including calcium (Ca^{++}) and bicarbonate (HCO_3^-) ions and dissolved silica (SiO_2), are transported by rivers to the ocean. There, organisms such as foraminifera use the products to make shells of calcium carbonate (CaCO_3), preserved, for example, as limestone. Other organisms such as diatoms and radiolarians make shells out of silica.³ When these organisms die, they fall into the deep ocean. Most of the shells redissolve, but a fraction survive to be buried in sediments on the seafloor. The combination of silicate weathering plus carbonate precipitation can be represented chemically by the reaction



If this was all that was happening, we would not have a complete cycle, and all of Earth's CO_2 would end up in carbonate rocks. But the seafloor is not static and is continuously being created at the mid-ocean ridges and subducted at plate boundaries where oceanic plates slide beneath less dense continental plates. When this happens, the carbonate sediments are

carried down to depths with high temperatures and pressures. Under these conditions, reaction (4.4) reverses itself: carbonate minerals recombine with silica (which by this time is in the form of quartz) to reform silicate minerals, releasing CO_2 in the process. This reaction is termed *carbonate metamorphism*.⁴ The CO_2 released from carbonate metamorphism re-enters the atmosphere, thereby completing the carbonate-silicate cycle. This cycle has a timescale of ~ 200 Myr and replenishes all of the CO_2 in the combined atmosphere-ocean system every ~ 0.5 Myr; at any time almost all of the carbon ($>99.99\%$) is in the Earth's crust.

Let us now consider the implications of this cycle for the faint young Sun problem. Suppose, for the sake of argument, that the oceans were completely frozen over. In this case, the *hydrological cycle*⁵ would have almost completely shut down. Some H_2O would still cycle by sublimation and snowfall, but surficial liquid water would be completely absent. Weathering of rocks requires liquid water to proceed at an appreciable rate, so the rate of silicate weathering would drop drastically. Volcanic activity, however, would continue unabated. Figure 4.3 makes it appear as if the volcanic CO_2 source might disappear, too, but in fact CO_2 would continue to be pumped into the atmosphere because (1) there are other types of volcanism that

³ Although the presence of life enhances the carbonate-silicate cycle on Earth, it would operate even on a sterile planet. Calcium carbonate would still become incorporated into ocean sediments through nonbiological chemistry when the mineral simply gets saturated in seawater.

⁴ *Metamorphism* refers to any geological process at depth leading to structural, mineralogical or chemical changes in rocks. In this chapter metamorphism (along with volcanism) is important as a source of *outgassing* to the atmosphere.

⁵ The *hydrological cycle* refers to the cycling of H_2O between liquid, solid, and vapor phases as a result of evaporation, sublimation, rain, snow, etc.

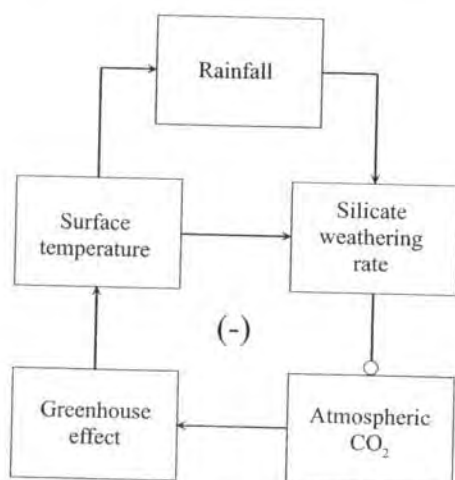


FIGURE 4.4 The negative feedback loop involving the silicate weathering rate, CO₂, and climate.

release CO₂ (e.g., mid-ocean ridge and hotspot volcanism); and (2) the mean lifetime of seafloor material is ~60 Myr between creation and subduction, and so there would be a long delay before all subducted material was carbon free. Thus, volcanic CO₂ would accumulate in the atmosphere until the greenhouse effect eventually became strong enough to melt the ice, allowing the hydrological cycle to resume. For a completely frozen Earth, about 0.3 bars of CO₂ (~1,000 times today's atmospheric amount) would be required to do this. At present rates of volcanism, this much CO₂ would take only ~10 Myr to accumulate.

Although there may indeed have been a few short times in Earth's history when such an extreme scenario actually occurred (the evidence for this is discussed at the end of Section 4.2.4), over the longest timescales this CO₂–climate negative feedback loop has also probably played a major role in *stabilizing* Earth's climate (Fig. 4.4). The key is that any change in temperature affects the silicate weathering rate, which counteracts that change. For example, a lowering temperature leads to less rain and a lower silicate weathering rate, which produces less atmospheric CO₂ and less greenhouse effect, thereby causing the temperature to rise.

4.2.2 Failure of climate stabilization on Mars and Venus

One way of evaluating the importance of the CO₂–climate feedback loop is by examining what happened to Venus and Mars. Neither planet has a habitable surface according to our previous definition. Venus has a mean surface temperature of 460 °C, well above the critical point for water, while Mars's mean temperature is –55 °C, well below freezing (Table 4.1).

What went wrong with the carbonate–silicate cycle on these planets?

Venus was close enough to the Sun that its higher temperature led to loss of water by photodissociation followed by escape of hydrogen to space (see Section 4.4.2 for a description of hydrogen escape for Earth). Once the water was lost, silicate weathering could not occur, so volcanic CO₂ simply accumulated in Venus's atmosphere and produced the hot, dry planet that we see today.

In the case of Mars, the situation was strikingly different. Mars formed farther from the Sun, so that for liquid water to exist a stronger atmospheric greenhouse effect would have been needed to warm its surface. It can be shown that gaseous CO₂ and H₂O by themselves could not have kept Mars warm enough early in its history when the Sun was less bright (Kasting, 1991; Colaprete and Toon, 2003). However, Mars had another, more serious problem: Mars is only 10% of Earth's mass and 15% of Earth's volume. Smaller objects cool down more rapidly, and thus widespread volcanism on Mars ceased long ago. Without volcanism, there was no mechanism for recycling CO₂, and what CO₂ there was should have accumulated in the crust. However, in spite of several spectroscopic searches, carbonate minerals have not been found in abundance on Mars. One explanation for this lack is that the early martian atmosphere (greatly aided by low martian gravity) was cumulatively blasted away to space by comet or asteroid impacts (Melosh and Vickery, 1989). For our purposes, the lesson to be drawn from Mars is that size matters: a small, geologically inactive planet is not likely to develop a stable climate or to hold on to its atmosphere.⁶

4.2.3 Complications to the faint young Sun story: methane

The explanation provided above for how early Earth avoided freezing is probably true to some extent. But silicate weathering feedback is not the only factor that helped keep the early Earth warm. As we discuss later, atmospheric O₂ concentrations are thought to have been low up until ~2.4–2.3 Ga. In a low-O₂ atmosphere, greenhouse gases such as methane (CH₄) could conceivably have been more abundant. In their 1972 paper, Sagan and Mullen proposed that high

⁶ See Chapter 18 for more discussion of Mars and Chapter 3 for discussion of the notion of a *habitable zone* for planets over a certain range of distance from a star.

TABLE 4.1 Properties of Venus, Earth and Mars and their atmospheric compositions. Note the large disparity in the atmospheric pressures of the planets when interpreting their atmospheric composition. For example, 3.5% N₂ in the atmosphere of Venus represents 3.3 bars of N₂ (four times that of the Earth), indicating a planet that is either more volatile-rich than the Earth or much more efficiently outgassed. ppm = parts per million. (Sources: Lodders and Fegley (1998); Pollack (1991).)

Parameter	Venus		Earth		Mars	
Mean surface pressure (bar)	95.6		1.0		0.006	
Mean surface temperature (K)	735		288		218	
Mass relative to Earth (5.97 × 10 ²⁴ kg)	0.815		1.0		0.107 ≈ 1/9	
Mean radius relative to Earth (6371 km)	0.950		1.0		0.532 ≈ 1/2	
Key gases in atmosphere (by volume)	CO ₂	96.5%	N ₂ *	78.084%	CO ₂	95.32%
	N ₂	3.5%	O ₂ *	20.946%	N ₂	2.7%
	SO ₂	150 ± 30 ppm (22–42 km)	H ₂ O	0.1 ppm–4% (varies)	Ar	1.6%
		25 to 150 ppm (12–22 km)			O ₂	0.13%
	Ar	70 ± 25 ppm	Ar	9340 ppm	CO	0.08%
	H ₂ O [†]	30–70 ppm (0–5 km)	CO ₂ * [‡]	~280 ppm (pre-industrial)	H ₂ O	0.03%
	CO [†]	45 ± 10 ppm (cloud top)		~380 ppm (year 2006)		(varies)
		17 ± 1 ppm (12 km)			NO	~100 ppm
	He	12 (+24/–8) ppm			Ne	2.5 ppm
	Ne	7 ± 3 ppm	Ne	18.18 ppm	Kr	0.3 ppm
			⁴ He	5.24 ppm		
			CH ₄ *	1.7 ppm		
			Kr	1.14 ppm		
			H ₂ *	0.55 ppm		
			N ₂ O*	~230 ppb		
			CO*	125 ppb		

Notes:

[†]Altitude-dependent.

* Under varying degrees of biological influence.

[‡]CO₂ levels increased at a rate of ~1.9 ppm/yr over 1995–2005 due to fossil fuel burning by humans.

concentrations of ammonia (NH₃) were the solution to the faint young Sun problem. This idea now seems unlikely because NH₃ is easily dissociated by ultraviolet photons unless shielded by atmospheric O₂ and O₃. CH₄, though, is not subject to this problem, as it is broken up only by photons with wavelengths below ~145 nm, and this has led to the suggestion that CH₄ may have been an important greenhouse gas on the early Earth (Kiehl and Dickinson, 1987; Lovelock, 1988). Indeed, photochemical models (e.g., Pavlov *et al.*, 2001) predict a ~10,000–20,000-year lifetime for CH₄ in a low-O₂ atmosphere, as opposed to ~10 years today. The present biological methane flux could have supported an atmospheric CH₄ *mixing ratio*⁷ in the

past of several hundred ppm (Pavlov *et al.*, 2001), instead of the scant 1.7 ppm today (*ppm* is parts per million).

By itself this of course does not prove that CH₄ was abundant during the Archean eon (>2.5 Ga), because we have assumed that methane was produced at the same rate then as now. This is plausible, however, since microbes that make methane (*methanogens*) are thought to be evolutionarily ancient (Chapter 10). Virtually all methanogens can subsist by way of the reaction CO₂ + 4 H₂ → CH₄ + 2 H₂O. Furthermore, the energy sources used by methanogens – H₂, CO₂, acetate, and formate – are all thought to have been abundant during the Archean. Thermodynamic considerations suggest that methanogens should have converted most of the available atmospheric H₂ into CH₄

⁷ The *mixing ratio* is the fraction of particles of a given type in a gas.

by this pathway (Kasting *et al.*, 2001). H_2 mixing ratios without any biological processes present are thought to have been of the order of 10^{-3} (= 1,000 ppm), so CH_4 mixing ratios after methanogens evolved should have been about half that, given that the total number of hydrogen atoms would be preserved. This estimate is consistent with the one obtained in the previous paragraph, although the argument used is entirely different.

If CH_4 was an abundant constituent of the Archean atmosphere, then the greenhouse effect could have been large even in the absence of high CO_2 concentrations. Calculations of global mean surface temperatures (Pavlov *et al.*, 2000) for the Late Archean (2.8 Ga), when the solar flux was $\sim 80\%$ of its present value, indicate that if the CH_4 mixing ratio was 10^{-4} – 10^{-3} , as suggested above, then the surface could have been warm even if the mixing ratio of CO_2 was no higher than today. Furthermore, most methanogens are thermophilic (heat-loving), and those with higher optimum growth temperatures reproduce faster than those that grow best at lower temperatures. This creates a positive feedback loop that may have tended to keep the Archean climate warm. This positive feedback was limited, though, by an additional complication: when CH_4 becomes as or more abundant than CO_2 in a planet's atmosphere, photochemical models (e.g., Pavlov *et al.*, 2001) indicate that a hydrocarbon haze is formed similar to that observed today on Saturn's moon Titan (Chapter 20). This haze, in turn, can cool the planet's surface via the *anti-greenhouse effect*. In the anti-greenhouse effect, solar radiation is absorbed and reradiated high in the atmosphere without ever reaching the surface. The net effect is the same as having a higher albedo. Thus, if the haze became too thick on early Earth, the surface would have cooled, and conditions would have become less favorable for thermophiles such as methanogens.

All of this suggests that the Archean climate may have been regulated by a negative feedback loop similar to that depicted in Figure 4.5. Starting from the box labeled surface temperature (T_s) at the left, an increase in T_s increases atmospheric CH_4 from methanogens. At the same time T_s tends to decrease atmospheric CO_2 through silicate-weathering feedback. Both factors increase the atmospheric CH_4/CO_2 ratio, thereby promoting the formation of hydrocarbon haze. This haze, though, then cools the surface as soon as its transmission of visible light drops below 70–80%. Thus, the overall feedback of both sides of the loop is negative. So, one hypothesis (albeit speculative) is that Archean

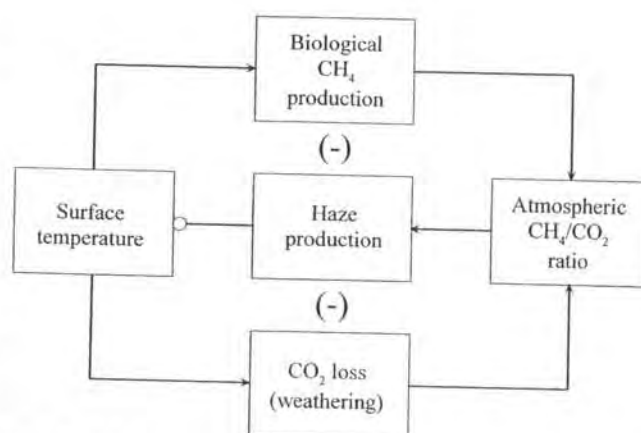


FIGURE 4.5 A negative feedback loop involving CO_2 , biologically produced CH_4 , and organic haze formation that may have operated in the Archean age on Earth (>2.5 Ga).

climate was stabilized by the presence of a thin organic haze layer.

An alternative hypothesis is that after oxygenic photosynthetic microbes had evolved (see Section 4.5.4), a CH_4 -mediated climate could have been stabilized in negative feedback with O_2 (Catling *et al.*, 2001). In this feedback, an increase of CH_4 causes greenhouse warming, which increases rain and continental weathering rates and, hence, sedimentation rates in the ocean. Many field measurements show that organic burial rates strongly correlate with sedimentation rates (Betts and Holland, 1991). These increased organic burial rates would then elevate O_2 fluxes (via $CO_2 + H_2O = CH_2O$ (buried) + O_2), and lower CH_4 levels by enhanced microbial oxidation in the water column or by atmospheric oxidation.

4.2.4 End of the methane greenhouse: the first Snowball Earth

We end our discussion of planetary climates at the point on which the remainder of the chapter is focused: the rise of O_2 in the Earth's early atmosphere. As discussed below, a variety of different geological indicators suggest that atmospheric O_2 increased abruptly from near zero prior to ~ 2.4 – 2.3 Ga to much higher values afterwards. If methane was an important contributor to the greenhouse effect during the Late Archean, then the rise of O_2 must have been significant for the climate. Indeed, the Canadian geologist Stuart Roscoe first suggested that drastic climate change occurred around the time of the rise of O_2 . He observed rocks in the Huronian sequence just north of Lake Huron in southern Canada (Roscoe, 1973; Prasad and Roscoe, 1996). The sequence spans 2.45–2.2 Ga

and contains evidence for glaciation, in fact three periods of glaciation, in the form of three layers of clusters of unconsolidated rock fragments bound up in a matrix (diamictites). Striations and dropstones provide further evidence of glaciers. The diamictite layers also appear to be separated by periods of intense weathering.

Roscoe also observed that the glacial layers were sandwiched by deposits indicating low O_2 conditions below and high O_2 levels above (more details are in Section 4.6.1.1). Thus, the glaciations and the rise of atmospheric O_2 appear to be related. This timing, of course, makes sense if CH_4 was an important part of the atmospheric greenhouse at this time. The rise of O_2 would have eliminated most of the methane by enabling more efficient oxidation of methane in the atmosphere,⁸ as well as by constraining the environments in which methanogens could survive. The loss of methane then led to much lower temperatures and glaciation. The fact that there were two initial glacial episodes, followed by a third, even larger glaciation, suggests that both the atmospheric redox state and the climate may have been oscillating during a 0.2–0.25 Gyr period.

Evidence for glaciation at ~ 2.4 –2.2 Ga is also found in Australia, India, Russia, Scandinavia, South Africa, and elsewhere in North America (Eyles and Young, 1994). However, apart from the Transvaal in South Africa, three discrete glacial layers are not generally evident, perhaps because the rock record from this early time is poorly preserved. Furthermore, some glacial deposits in South Africa are interbedded with rocks that apparently formed at low latitudes, according to paleomagnetic analysis.⁹

⁸ The first step in the atmospheric destruction of methane is an attack by hydroxyl OH. After the rate-limiting first step ($OH + CH_4 = CH_3 + H_2O$), a series of subsequent reactions produces net oxidation of methane: $CH_4 + 2O_2 = CO_2 + 2H_2O$. In today's troposphere, production of OH is linked to tropospheric ozone (O_3): ozone photolyzes and produces an excited oxygen atom that produces OH from water vapor (i.e., $O + H_2O = 2OH$). In turn, tropospheric ozone production is tied to the presence of O_2 in the atmosphere because the oxygen atoms within O_3 originate from O_2 . In the Archean, in the absence of a stratospheric ozone layer, short wavelength, energetic ultraviolet light would have penetrated into the troposphere, allowing OH to be produced directly from H_2O photolysis ($H_2O + h\nu = H + OH$). But without O_2 to remove the H, the OH would recombine with the H and not be such an effective oxidant for CH_4 as it is today. Thus, levels of O_2 control the CH_4 abundance, albeit indirectly, through oxidation mediated by OH.

⁹ The field lines of Earth's predominately dipole magnetic field are approximately perpendicular to the surface near the poles and

It is now also known that there were three glacial episodes between 720 and 580 Ma, of which the first two were low-latitude (Hoffman and Schrag, 2002; Halverson, 2005; Xiao and Kaufman, 2006). These two glaciations, as well as the earlier ones, have been dubbed *Snowball Earth* episodes by Joe Kirschvink (1992, 2000). In these episodes, Earth's surface may have frozen over entirely to a depth of a kilometer or more. Snowball Earth glacial deposits are also overlain in some places by thick layers of carbonate rocks ("cap carbonates") with unusual textures indicating rapid deposition and unusual ratios of carbon isotopes. These cap carbonates are thought to have formed when CO_2 that built up during the ice-covered-surface period was later removed in an episode of rapid carbonate and silicate weathering (as observed). In essence, the "thought experiment" described earlier in the chapter with respect to the faint young Sun problem appears to have actually happened on several separate occasions, although the question of whether the Earth froze over entirely remains controversial.

4.3 The coevolution of atmospheric oxygen and life

We now turn for the remainder of the chapter to discussing the partial pressure of atmospheric oxygen (pO_2) through time, which has been a major factor in the evolution of life on Earth. This section gives an overview of the history of atmospheric oxygen (summarized in Fig. 4.6), while later sections supply the details.

Animals and multicellular plants require O_2 to live. The atmosphere started out with virtually no oxygen ($pO_2 \sim 10^{-13}$ bar) before life existed but now contains about 21% O_2 by volume ($pO_2 \sim 0.21$ bar). Nursall (1959) first suggested that the appearance of macroscopic animals in the fossil record reflected the emergence of an oxygen-rich atmosphere able to support the higher energy requirements of animal metabolism. Preston Cloud (1988) championed a similar view, pointing out aspects of the geologic record that indicated secular increases in the level of O_2 . Today, the evidence is strong that not until about 2.4–2.3 Ga was pO_2 high enough to oxidize exposed continental rocks ubiquitously. Some also argue that there was a second increase in pO_2 around 0.8–0.6 Ga (Canfield and

parallel near the equator. Igneous rocks containing iron minerals such as magnetite (Fe_3O_4) become magnetized in the direction of the prevailing magnetic field when they cool. Thus, rocks in which the

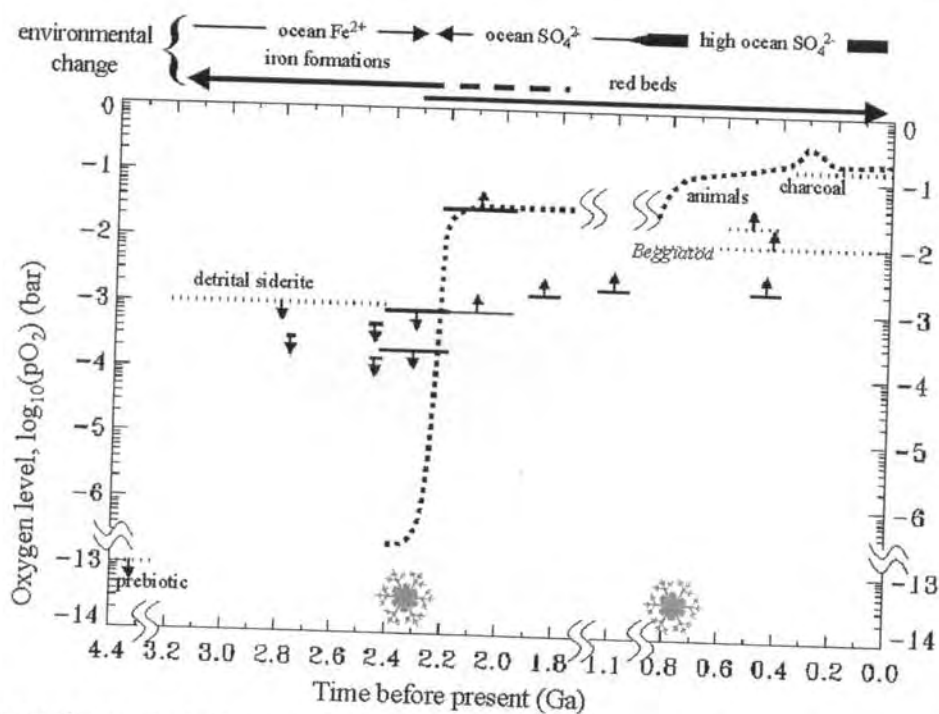


FIGURE 4.6 The history of atmospheric O_2 – note the indicated breaks in the timescale of the plot. The thick dashed line shows a possible evolutionary path for atmospheric O_2 that satisfies geochemical and biological constraints, as well as modeling results. Dotted upper and lower limits show the duration of geochemical and biological constraints, such as the occurrence of detrital siderite ($FeCO_3$) in ancient riverbeds. Arrows indicate upper and lower bounds on the level of oxygen. Unlabeled solid-line upper and lower bounds are from the evidence of specific paleosols (ancient soils), with the length of each line showing the uncertainty in the age of each. Bounds on pO_2 from paleosols are taken from Rye and Holland (1998). Biological lower limits on pO_2 are based on estimates for the requirements of the marine sulfur-oxidizing bacteria *Beggiatoa* (Canfield and Teske, 1996), and also the requirements of macroscopic animals that appear after 0.59 Ga (Runnegar, 1991). The upper bound on the level of pO_2 in the prebiotic atmosphere at ~4.4 Ga (shortly after the Earth had differentiated into a core, mantle, and crust) is based on photochemical calculations. A “bump” in the oxygen curve at 0.3 Ga (in the Carboniferous) is based on the model of Berner *et al.* (2000). Snowflake symbols indicate the occurrence of episodes of low-latitude glaciation (Snowball Earth events), which appear to have some broad correlation with the oxygen history of the atmosphere.

Teske, 1996; Canfield, 1998). A very small number of researchers have continually questioned the idea that pO_2 has changed at all (e.g., Ohmoto, 1997), but the great preponderance of evidence indicates a significant increase in O_2 at ~2.4–2.3 Ga (Section 4.6).

Paleontological evidence is also consistent with the hypothesis that a rise in O_2 at 2.3 Ga enhanced biological evolution. For example, the oldest known fossils of possible eukaryotic origin, found in shales from Michigan dated at 1.87 Ga, are remains of spirally coiled organisms resembling the extinct photosynthetic alga *Grypania spiralis* (see Section 12.2.1). Furthermore, molecular *phylogeny* (the reconstruction of evolutionary lineages using genes) suggests that several anaerobic lineages were lost in the range 2.5 to 1.6 Ga (the Paleoproterozoic) (Hedges *et al.*, 2001). This is consistent with the toxicity of O_2 to obligate anaerobes,¹⁰

The rise of O_2 may also be linked to the emergence of multicellular life. Fossils that are 4–5 mm long are found in northern China at 1.7 Ga, and may be multicellular (Shixing and Huineng, 1995). Then by 1.4 Ga, similar, often larger, carbonaceous fossils become abundant worldwide in marine sediments.

Another pivotal evolutionary event was the appearance of macroscopic animal fossils (Ediacara – Section 16.2.4.4) at ~575 Ma. Similar fossils appear on six continents in strata that lie above rocks from a glacial episode at ~580 Ma. Their appearance may be linked to a second rise in O_2 marked by increased sulfate levels in the ocean (Canfield and Teske, 1996; Knoll and Carroll, 1999; Fike *et al.*, 2006; Canfield *et al.*, 2007). Certainly pO_2 levels must have been at least 10% of present pO_2 to support large animal metabolism. The Neoproterozoic era (1,000–542 Ma) also bears many curious similarities to the Paleoproterozoic discussed above. Both eras are characterized by Snowball Earth episodes (Section 4.2.4), significant changes in the biota, and large oscillations of sedimentary carbon isotopes.

¹⁰ Anaerobes are microorganisms that do not require O_2 , as opposed to aerobes that require O_2 ; obligate (an)aerobes must have (a lack of) O_2 . Oxidic and anoxic environments refer to a presence or lack of O_2 .

Finally, ever since the rapid rise of complex animals starting in 542 Ma, pO_2 has probably always been 0.2 ± 0.1 bar. Charcoal is found in continental rocks from 350 Ma onwards, which indicates an O_2 mixing ratio of at least 15% for all recent epochs because wood cannot burn below this O_2 level (Lenton and Watson, 2000). The colonization of the land by plants began around ~ 450 Ma. Subsequently large amounts of organic carbon were buried on the continents in the Carboniferous (360–300 Ma), possibly because lignin, a structural compound in woody plants, was difficult to decompose until organisms like fungi evolved the means to do so. Because organic carbon burial is accompanied by a release of O_2 (Eq. (4.3)), organic burial may have led to peak $pO_2 \sim 0.3$ bar at ~ 300 Ma (Berner *et al.*, 2001). This may explain the presence of giant Carboniferous insects, such as 70 cm wingspan dragonflies, which must have relied on the diffusion of O_2 for respiration (Dudley, 1998).

After this quick overview of the history of atmospheric O_2 , we now proceed though it again more thoroughly.

4.4 The prebiotic atmosphere

What was the atmosphere like before life appeared? The *prebiotic* atmosphere was in all likelihood “weakly reducing,”¹¹ composed primarily of N_2 , CO_2 , and water, with relatively small quantities of H_2 , CO, and CH_4 , and negligible O_2 (Fig. 4.7) (Walker, 1977; Kasting and Brown, 1998). Pioneering laboratory experiments that produced complex organic molecules (such as amino acids) in CH_4 - NH_3 - H_2 atmospheres led some researchers to suggest that the early atmosphere was highly reducing to explain how life originated, but this view has now been largely abandoned (Chapters 6–9). The early atmosphere accumulated

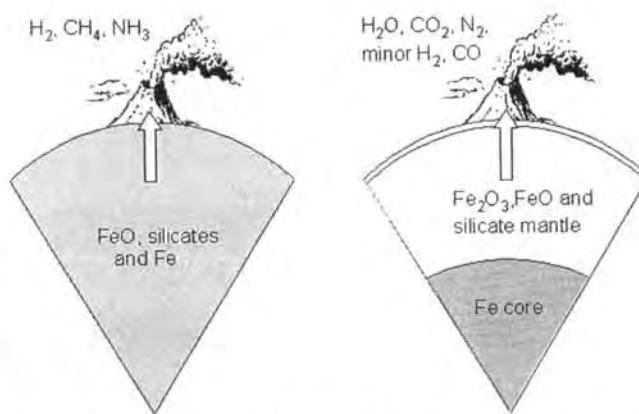


FIGURE 4.7 (Left) During 4.4–4.5 Ga when the mantle was Fe-rich during core formation, reduced volcanic gases were introduced into the atmosphere. (Right) From 4.4 Ga onwards, after the Earth had differentiated into a core, mantle, and crust, a weakly reducing mixture of volcanic gases fed the atmosphere.

from volcanic *degassing*, which arose from volcanic gases associated with melts and metamorphic gases from hot rocks that did not melt. But the major volatile gases introduced into today’s atmosphere are oxidized species such as H_2O , CO_2 , and N_2 rather than reduced forms such as H_2 , CO or CH_4 , and NH_3 . The reduced/oxidized gas ratio (H_2/H_2O , CO_2/CO , etc.) in volcanic gases, in particular, depends on the degree of oxidation in the upper mantle, the source region for such gases (Holland, 1984).

The basic composition of the upper mantle was set 4.4 Ga. The heat produced by impacts during Earth’s accretion melted the planet, and molten metals (mostly iron) separated from the surrounding mixture of silicates and oxides and sank to form the Earth’s core. Siderophile (“iron-loving”) elements segregated into the core and some were either radioactive or the decay products of radionuclides, leaving clues about the time of core formation that suggest it occurred within the first 100 Myr of Earth history (Halliday *et al.*, 2001). This by itself does not tell us the oxidation state of the mantle at that time. However, the molten mantle almost certainly contained water, some of which would have dissociated to produce hydrogen and oxygen. If the hydrogen became lost by volcanic outgassing followed by escape to space or by being incorporated into the metallic core, the overall mantle oxidation state would increase (Fig. 4.7). Exactly how fast this oxidation occurred is currently a matter of debate. We shall return to this topic later in the chapter because even small changes in volcanic gas composition could have been important for the origin of life and for later atmospheric evolution.

¹¹ Chemical reactions that involve an exchange of electrons, or more accurately, that change the degree of electronegativity (e.g. electrons becoming bound strongly to the oxygen nucleus, which is much more electronegative than, say, either C or H), are called reduction–oxidation or *redox* reactions. In such a reaction a *reducing agent* (often called an *electron donor* in biology) is *oxidized* while simultaneously an *oxidizing agent* (*electron acceptor*) is *reduced*. A “reducing” gas is composed of reducing agents, which for the Earth’s atmosphere are typified by H_2 , CH_4 , CO, and NH_3 , whereas an oxidizing mixture consists of N_2 , CO_2 , and/or H_2O . The redox state of an atmosphere is then the result of these opposing reactions; oxidizing atmospheres are generally “hydrogen poor” and reducing atmospheres “hydrogen rich.” Note that oxygen does *not* have to be involved to oxidize something, although it often is.

4.4.1 O₂ in the prebiotic atmosphere

The weakly reducing nature of volcanic emissions must have greatly limited pO₂ in the prebiotic atmosphere because reduced gases would have dominated over the only abiotic source of free O₂, namely *photolysis* of water (breaking up the molecule from irradiation by light) and the subsequent escape of hydrogen to space. (By itself, photolysis of H₂O or CO₂ does not provide a net source of oxygen because the oxygen soon recombines.) Hydrogen escape and O₂ production associated with water vapor destruction is severely limited because little water vapor is able to rise to the upper atmosphere because water condenses at the top of the troposphere. Such condensation is called *cold-trapping*, borrowing a laboratory term for cooling a gas to condense out water vapor. Consequently, the abiotic production rate of O₂ is very small.

It is useful to think of an oxidizing atmosphere as “hydrogen poor” and a reducing atmosphere as “hydrogen rich.” Even a small excess of H₂ tips the balance. Hydrogen exerts a control on the level of O₂ through a series of photochemical reactions that add up to a net reaction



To estimate pO₂ for the prebiotic atmosphere, we take outgassing rates as greater on early Earth than today because of increased heat flow from a hotter, more radioactive interior. Assuming that H₂ outgassing rates were in fact 3–5 times higher, detailed photochemical models indicate that the prebiotic atmosphere’s pO₂ was only $\sim 10^{-13}$ bar (Kasting, 1993).

4.4.2 The escape of hydrogen to space and H₂ in the prebiotic atmosphere

The severe depletion of noble gases in the composition of the Earth provides evidence that Earth did not retain gaseous volatiles from the original solar nebula (Chapter 3). Thus, Earth’s hydrogen does not derive from accreted H₂, and instead was accreted in an oxidized form in solids such as water ice (H₂O), water of hydration in silicates (-OH), or hydrocarbons (-CH).

The escape of hydrogen from the Earth (albeit via atmospheric gases other than H₂O) is important in the history of atmospheric O₂ (Section 4.7). When hydrogen escapes to space, the Earth as a whole is irreversibly oxidized. It is immaterial whether the hydrogen is transported through the atmosphere as H₂, H₂O, HCN, NH₃, or any other H-bearing

compound. For example, when hydrogen emanates from volcanoes and subsequently escapes to space, the upper mantle is oxidized through reactions such as $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$. Similarly, when hydrogen originates from metamorphic gases in the crust, the crust is oxidized.

The abundance of hydrogen in the atmosphere is set by a balance between H₂ outgassing (from volcanism and metamorphism) and escape of hydrogen to space. Because hydrogen atoms are so light, there are always some at the top of the atmosphere traveling fast enough ($>11 \text{ km s}^{-1}$) to escape Earth’s gravity, even today (Fig. 4.8).¹² Extreme ultraviolet radiation from the Sun is absorbed and converted into heat in the *thermosphere*, which on the modern Earth stretches from 85 km to ~ 500 km altitude and has temperatures of $\sim 1,000$ to $2,500$ K. Although the average hydrogen atom thermal velocity is insufficient to achieve escape, the high temperature at the top of the thermosphere induces a significant high-velocity “tail” in the Maxwellian distribution of velocities of hydrogen atoms, from which many atoms escape. This process is termed *thermal escape* because it represents escaping atoms from the thermal velocity distribution. However, *non-thermal escape* mechanisms are even more important, accounting for 60–90% of the H atom escape. Non-thermal escape results from hydrogen atoms being boosted above escape velocity by photolytic, electronic impact, or ionic reactions.

There are two principal bottlenecks as hydrogen atoms (either free or as part of molecules later to be photolyzed) work their way upwards and eventually escape. The first is the cold trap mentioned previously and the second is a slow diffusion process through the thermosphere. The thermosphere is analogous to a membrane with a certain partial pressure of hydrogen below and a vacuum above – the flux through the membrane is determined by the partial pressure below.

Calculations show that the amount of escaping H today is only $9 \times 10^{10} \text{ mol H yr}^{-1}$ (for details see Kasting and Brown, 1998); about half of these atoms originate from water vapor that makes its way above

¹² (1) In a mixed gas at a certain temperature, each species of atom or molecule can be characterized by an average kinetic energy of $0.5 m v^2$, where m is the mass of the species and v is its velocity. Those species of lower mass on average have higher velocities. (2) Basic dynamics shows that escape of an object from the gravity of another does not depend on the mass of the escaping object, only on its velocity. Thus one must achieve a velocity of 11 km/s to escape Earth’s gravity whether launching a rocketship or a hydrogen atom.



FIGURE 4.8 An ultraviolet image of Earth by NASA's Dynamics Explorer 1 spacecraft at 16 500 km altitude above 67°N latitude. The faint glow beyond the edge of the planet is entirely due to Earth's extended hydrogen atmosphere (geocorona) as seen in resonantly scattered Lyman- α (121 nm) solar radiation. Energetic hydrogen atoms in the geocorona are escaping to space. Features on the Earth's disk (dayglow from the sunlit atmosphere, the oval ring of the aurora borealis, and equatorial airglow) are due to emission from atomic oxygen and molecular nitrogen. Isolated points of light are background stars that are bright in the ultraviolet.

the cold trap and the other half from biogenic methane, which is not cold-trapped. For early Earth, an outgassing rate 5 times higher than today can be balanced with a hydrogen escape flux to space that depends on the hydrogen mixing ratio. This calculation yields a hydrogen mixing ratio of $\sim 10^{-3}$ for the prebiotic atmosphere, compared to today's value of 5.5×10^{-7} .

4.4.3 Atmospheric synthesis of formaldehyde and hydrogen cyanide

Formaldehyde

Reactions in the weakly reducing prebiotic atmosphere may have produced molecular precursors to life. One of the early self-replicating chemical systems may have been based on ribonucleic acid (RNA), a hypothesized biochemistry known as "RNA World" (Chapters 6–8). RNA consists of chains of monomers called nucleotides, each comprising a phosphate molecule, a ribose (sugar)

molecule, and a nitrogen-containing base. The phosphate molecule would likely be derived from phosphate released in weathering of rocks, whereas the other components might have had an atmospheric origin. Ribose is $C_5H_{10}O_5$, which can be formed from five molecules of formaldehyde, H_2CO . Photochemical reactions in weakly reducing CO_2 -rich atmospheres are predicted to produce large quantities of formaldehyde (Pinto *et al.*, 1980), which is soluble and would rain out. Subsequent spontaneous reactions could allow formaldehyde to form sugars, including ribose.

Hydrogen Cyanide

The simplest nitrogen-containing base is adenine, $C_5H_5N_5$, which is a chain of five hydrogen cyanide molecules (HCN). Substantial HCN can form in a primitive atmosphere with a few tens of parts per million of methane (Zahnle, 1986). N atoms can be produced by ionization of N_2 in the ionosphere ($N_2 + h\nu = N_2^+ + e^-$) followed by dissociative recombination ($N_2^+ + e^- = N + N$). The N atoms then flow down into the stratosphere where they combine with fragments produced in CH_4 photolysis to make HCN:



However, the rate constants for these reactions and their products have not yet been studied experimentally. Also, there may not have been enough prebiotic methane. Much of the methane entering today's atmosphere is biogenic. Today's abiotic source from mid-ocean ridges is $\sim 1.5 \times 10^{10}$ mol CH_4 yr^{-1} and would only produce 0.5 ppm CH_4 in a weakly reducing atmosphere. This would result in only 5.3×10^8 mol HCN yr^{-1} (Kasting and Brown, 1998).¹³ For comparison, consider extraterrestrial delivery. Today's flux of micrometeorites would produce only 1% as much HCN if all the N were converted to HCN by heating during atmospheric entry, but the flux may have been $\sim 10^2$ – 10^3 times higher before 4 Ga.

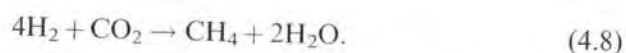
¹³ Fluids emanating from a new, off-axis hydrothermal vent field on the mid-Atlantic ridge (Lost City) are different in composition and in particular have high CH_4 concentrations (Kelley *et al.*, 2005). If other off-axis vent fluids have similar compositions, the resulting global CH_4 source today could be as high as 1×10^{11} mol/yr, but it is not clear how this process would scale for early Earth. A second possible source of abiotic CH_4 is impacts. Condensing particles in impact plumes catalyze the conversion of CO into CH_4 and CO_2 (Kress and McKay, 2004).

4.5 Effects of primitive life on the atmosphere

Today's biosphere affects the cycling of every major element of importance to biology, such as C, N, O, P, and S, and it is likely that early life behaved similarly (Chapter 12). Life modulates the cycle of carbon, the second most abundant volatile after water, by removing carbon from the atmosphere to synthesize organic matter. Life also modulates the cycle of Earth's third most abundant volatile, nitrogen, by extracting it from the air to make ammonium ions, and then recycling it back to N_2 in air. In fact, when different metabolisms evolved they must have affected several important volatiles, and we now consider H_2 , CO_2 , N_2 , and O_2 .

4.5.1 Methanogens and methane production

The simultaneous presence of reduced and oxidized gases in the early atmosphere would have provided a source of energy for primitive life because such gases can be catalyzed to react together. As discussed in Section 4.2, methanogens derive energy from hydrogen and carbon dioxide:

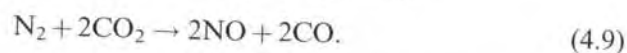


They use the energy to synthesize cell material from inorganic nutrients. Thus the early biosphere would have increased atmospheric CH_4 at the expense of more metabolically desirable H_2 (Section 4.2.3). Assuming that methanogens were thermodynamically energy-limited, $\geq 90\%$ of the H_2 would have been converted to CH_4 (Kasting *et al.*, 2001), and H_2 levels would have dropped from a prebiotic mixing ratio of 10^{-3} to $\sim 10^{-4}$. CO_2 levels would have also decreased because CH_4 is a powerful greenhouse gas, which would have led to increased warming and loss of CO_2 via increased continental weathering in the carbonate-silicate cycle (Section 4.2.1).

4.5.2 Biological nitrogen fixation and atmospheric N_2

Despite abundant atmospheric N_2 , nitrogen is often a limiting nutrient for life. Life would fall apart without proteins, DNA and RNA, all of which contain N, an essential structural element. Nitrogen is contained in the peptide bond-CO-NH- that links amino acids along a protein. Peptide bonds are so mechanically effective that chemists utilize them to make plastics like nylon. Yet few microorganisms can metabolize nitrogen

unless it is *fixed* from the atmosphere, i.e., acquired and turned into a more soluble form. So how did the very first organisms obtain nitrogen? In the anoxic prebiotic atmosphere (Section 4.4), N_2 would have been oxidized with CO_2 by lightning:



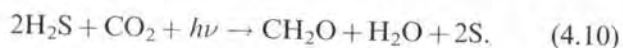
NO then gets converted to soluble nitrosyl hydride (HNO). Thus, early lightning would have provided a modest flux of fixed nitrogen to the ocean that may have been important for the origin of life. The above reaction depends on the abundance of CO_2 . For CO_2 mixing ratios ranging from 0.04 to 0.5, the rate of fixation would be 2.6×10^9 to 3×10^{11} g N yr $^{-1}$ at Earth's present lightning rate (Navarro-Gonzalez *et al.*, 2001). In the ocean, the end products of dissolution would have been NO_3^- and NO_2^- (Mancinelli and McKay, 1988). The latter can be reduced by ferrous iron (Fe^{2+}) dissolved in the early ocean to produce ammonia, NH_3 (via $6Fe^{2+} + 7H^+ + NO_2^- = 6Fe^{3+} + 2H_2O + NH_3$), some of which would flux to the atmosphere. NH_3 would then be quickly photolyzed to N_2 and H_2 , completing the cycle (Fig. 4.9a). Another way that nitrogen could have been fixed abiotically was through HCN synthesis in atmospheres containing trace levels of CH_4 (Section 4.4.3). HCN is hydrolyzed in solution to form NH_4^+ (ammonium).

Nitrogen fixation is strictly anaerobic and its origin perhaps even predates the divergence of the three domains of life. It may have been derived from an earlier biochemical function such as an enzyme for detoxifying cyanides like HCN present in the early environment (Section 4.4). In any case, once anaerobes developed nitrogen fixation, NH_4^+ would likely have become the dominant combined form of nitrogen in the ocean. In the absence of oxygen, early nitrogen fixation may have been more effective and nitrogen recycling diminished relative to the present day. This would have resulted in a lower atmospheric pressure than today, but currently there are no constraints from geologic data on total atmospheric pressure.

After oxygenic photosynthesis arose (next section), nitrification would have become important. *Nitrification* happens when ammonium ions (NH_4^+) are oxidized to nitrite (NO_2^-) and then nitrate (NO_3^-) by aerobic bacteria. *Denitrification* is the microbial reduction of NO_3^- to N_2O and N_2 . Denitrifiers use organic matter as a reductant, and inhabit anoxic zones such as continental margin sediments. Thus, after the ~ 2.4 – 2.3 Ga rise of O_2 , the nitrogen cycle was probably similar to today's (Fig. 4.9b). However, the evolution of the nitrogen cycle on early Earth is

Section 12.3.3, organic molecules in the geological record and certain fossils (stromatolites) provide good evidence that oxygenic photosynthesis had evolved by 2.7 Ga.

In *anoxygenic photosynthesis* no O_2 is released and microorganisms use another electron donor (e.g., Fe^{2+} , H_2S , H_2 , S) instead of H_2O to reduce CO_2 to organic carbon. For example, anoxygenic photosynthesis using H_2S is



Anoxygenic photosynthesis predates the evolution of oxygenic photosynthesis (Blankenship and Hartman, 1998; Xiong *et al.*, 2000). *Cyanobacteria* are eubacteria that evolved the capability of oxygenic photosynthesis (although they can also accomplish anoxygenic photosynthesis if reductants are readily available). Plants and other modern photosynthetic eukaryotes all have ancestors that acquired photosynthesis when a cyanobacterium became resident inside a larger cell and the whole cell evolved into a single organism with an intracellular, photosynthesizing structure (now called a chloroplast) descended from the cyanobacterium.

The first successful oxygenic photosynthesizers must have overcome the toxic effects of O_2 . But what drove microbes to develop defenses against O_2 in an anoxic world? Also, if oxygenic photosynthesis, which extracts hydrogen from water, perhaps developed in response to a lack of electron donors such as H_2 and H_2S , what oxidants were available before oxygenic photosynthesis to remove such reductants? An answer may reside in the early atmosphere (McKay and Hartman, 1991), where a series of photochemical reactions produce H_2O_2 , a powerful oxidant. The net effect is:



H_2O_2 is soluble and, after rainout, could have accumulated locally, for example, in lakes. Alternatively, non-atmospheric H_2O_2 may have been produced by surface-mediated reactions between H_2O and pyrite (FeS_2) in anoxic environments. The presence of H_2O_2 would have exerted a selective pressure for anoxygenic photosynthetic organisms to evolve enzymes, such as peroxidase, which reduces H_2O_2 to H_2O , and catalase, which converts $2H_2O_2$ to $2H_2O$ and O_2 . These enzymes are analogues to structures that facilitate electron transfer in today's oxygenic photosynthesis. Hence, H_2O_2 , perhaps from the atmosphere, may have promoted the evolution of oxygenic photosynthesis.

4.5.4 Oxygen oases in an anoxic environment

Globally low levels of *atmospheric* O_2 in the Archean (Section 4.6) do not imply that O_2 levels were everywhere and always low. Underground or underwater oases or strata where pO_2 was locally high were no doubt common, in the same way that today one easily finds places (e.g., muds) where H_2S or CH_4 is locally high despite the O_2 -rich atmosphere.

O_2 in microbial communities probably triggered evolution in symbiotic heterotrophs. Methanotrophy (methane oxidation) is one such innovation that was probably global by ~ 2.8 Ga (Hayes, 1994), although methanotrophs may have utilized sulfate rather than O_2 . Free-living aerobic bacteria that were the ancestors of mitochondria (structures in eukaryotes that perform aerobic respiration) probably evolved in response to locally available O_2 . Much of the early photosynthetic O_2 would then have been efficiently respired by symbiotic aerobes. O_2 oases may have also facilitated the evolution of eukaryotes with mitochondria. Phylogeny suggests that eukaryotes acquired mitochondria before chloroplasts (Knoll, 1992), perhaps before the rise of O_2 .

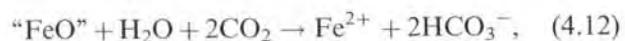
4.6 Geological evidence for the rise of oxygen

Geological evidence suggests that O_2 rose at ~ 2.4 – 2.3 Ga, and again at ~ 0.8 – 0.6 Ga (Fig. 4.6). There are no pristine samples of air trapped in rocks from these times, so the history of atmospheric O_2 has to be reconstructed from indirect tracers left behind by the chemical action of O_2 . On the continents, weathering processes release chemicals from rocks in a manner that depends upon atmospheric CO_2 and O_2 concentrations. Also atmospheric gases are mixed into the oceans, so that the chemistry of marine sediments depends on atmospheric composition.

4.6.1 Non-marine environments

*Paleosols*¹⁴ indicate that at ~ 2.4 – 2.3 Ga atmospheric pO_2 rose from <0.0008 bar to >0.002 atm (Rye and Holland, 1998). Paleosols before ~ 2.4 – 2.3 Ga show that iron was leached during weathering by the reaction

¹⁴ *Paleosols* are the lithified remains of ancient soils. They are useful for studies of the atmosphere because we know they were in contact with it at one time.



where “FeO” represents ferrous iron bound in unweathered material, but that after ~ 2.2 Ga, iron was rendered immobile. Ferrous iron (Fe^{2+}) is soluble whereas oxidized (ferric) iron (Fe^{3+}) is not. Consequently, iron is flushed through a soil or porous rock if rainwater has little dissolved oxygen but is immobile with oxygenated rainwater. The degree of weathering also depends on the rainwater’s pH, which is related to pCO_2 because CO_2 dissolves in water to make carbonic acid. Consequently, paleosols constrain the O_2/CO_2 ratio in the atmosphere rather than O_2 independently, requiring a separate estimate of pCO_2 . The pCO_2 can also be deduced from paleosol chemistry (Section 4.2.3). Cerium also indicates low pO_2 because it changes from Ce^{3+} to Ce^{4+} to form cerianite (CeO_2) in oxic weathering. Thus the presence of Ce^{3+} -rich phosphates in a 2.6–2.45 Ga granite paleosol implies a largely anoxic atmosphere (Murakami *et al.*, 2001). Figure 4.6 includes a compilation of pO_2 values deduced from paleosol studies.

Detrital grains are sedimentary minerals that never completely dissolve in weathering. Such grains in pre-2.4 Ga riverbeds commonly contain reduced minerals that would only survive at low pO_2 (Rasmussen and Buick, 1999). Grains of pyrite (FeS_2), uraninite (UO_2), and siderite (FeCO_3) place upper bounds on Archean pO_2 of roughly 0.1 bar, 0.01 bar, and 0.001 bar, respectively. Given their roundness, such grains were transported long distances in aerated waters. In oxic waters, uraninite dissolves to form soluble U^{6+} ions, pyrite oxidizes to sulfate (SO_4^{2-}) and ferric iron (Fe^{3+}), and siderite oxidizes to produce ferric iron (Fe^{3+}). After about 2.2 Ga the occurrence of reduced detrital grains becomes rare and restricted to locally anoxic environments.

Red beds provide further evidence for atmospheric redox change. They derive from windblown dust or river-transported particles coated with red-colored hematite (Fe_2O_3). After ~ 2.3 Ga, red beds are ubiquitous. Occasionally, red beds that appear to be very old actually result from much more recent oxidation. For example, the deep burrowing of subterranean termites, which have existed for at least 100 Myr, has sometimes allowed the penetration of O_2 into groundwater.

4.6.2 Marine environments

A transition in O_2 levels at ~ 2.4 – 2.3 Ga is consistent with the distribution of *banded iron formations* (BIFs)

through time. BIFs are laminated, marine sedimentary rocks containing ≥ 15 wt% iron, usually with alternating iron-rich and silica-rich layers. They occur prominently in the Archean (> 2.5 Ga), and then decline in abundance and disappear after ~ 1.8 Ga. The iron in large part originated from hydrothermal input into the anoxic, deep ocean, probably mostly at mid-ocean ridges (Holland, 1984). Ocean upwelling then carried Fe^{2+} to the continental shelves where it was oxidized to insoluble Fe^{3+} , typically forming magnetite (Fe_3O_4). However, even in today’s oxic world, there is a significant flux of reduced iron to the ocean in river particulates and windblown dust, so there was probably also such a contribution to Archean BIFs (Canfield, 1998). Many researchers believe that it was microbes that oxidized Fe^{2+} to Fe^{3+} . For the late Archean BIF in Hamersley, Australia, the estimated iron deposition rate requires an ancient oxygen supply of $\sim 1\%$ of the global, modern O_2 flux from the burial of organic carbon. The eventual disappearance of the BIFs may have happened when the deep ocean became oxygenated as pO_2 rose to $\sim 1/3$ to $1/2$ of present levels.

Alternatively, Canfield (1998) has proposed that iron disappeared in the oceans when sulfate concentrations became sufficient to increase the rate of microbial sulfate reduction. Because sulfate reduction produces sulfide (S^{2-}), the deep ocean would then have been swept free of iron by the precipitation of insoluble pyrite (FeS_2), perhaps continuing until the 0.8–0.6 Ga rise in O_2 .

4.6.2.1 Marine carbon isotopes

Marine carbon isotopes indicate drastic environmental change in the Paleoproterozoic era (2.5–1.6 Ga). The average $\delta^{13}\text{C}_{\text{in}}$ value of carbon entering into the atmosphere–ocean system from volcanism, metamorphism, and weathering is about -5.5‰ ¹⁵ (Holser *et al.*, 1998). On timescales that are long compared to the carbon residence time in the ocean, $\sim 10^5$ yr, the number of ^{12}C atoms and ^{13}C atoms entering the system must equal the number exiting the system either as carbonate or organic carbon sediments, implying

$$\delta^{13}\text{C}_{\text{in}} = f_{\text{carb}}\delta^{13}\text{C}_{\text{carb}} + f_{\text{org}}\delta^{13}\text{C}_{\text{org}}, \quad (4.13)$$

¹⁵ The notation $\delta^{13}\text{C} = -5.5\text{‰}$ means that the isotope ratio $^{13}\text{C}/^{12}\text{C}$ is depleted by 5.5 parts per thousand relative to a standard calibration value. Metabolic reactions in organisms preferentially use lighter isotope molecules because reactions using them are very slightly energetically favored. Therefore these and other *fractionation* ratios in the geologic record are used as indicators of biotic processes. Also see Section 12.2.3.

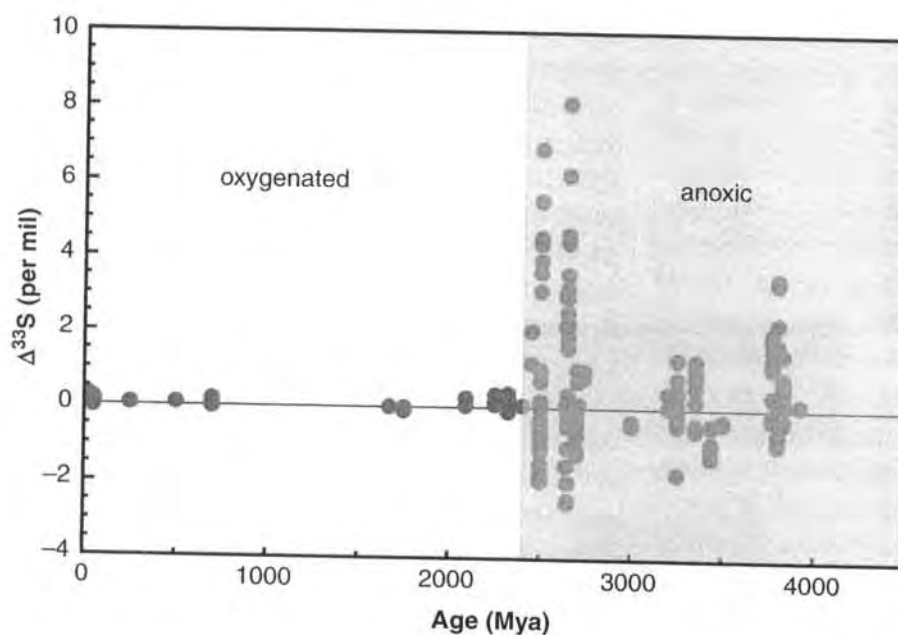


FIGURE 4.10 $\Delta^{33}\text{S}$ vs. time. $\Delta^{33}\text{S}$ expresses the deviation, in parts per thousand, from a standard sulfur isotope mass fractionation line: $\Delta^{33}\text{S} \equiv \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$. Samples younger than 2.1 Ga are considered consistent with fractionation by purely mass-dependent processes. In contrast, the samples older than 2.0–2.5 Ga are mass-independent. (Farquhar *et al.*, 2000.)

where f_{carb} is the fraction of carbon buried in carbonate minerals with a global average isotopic composition $\delta^{13}\text{C}_{\text{carb}}$, and f_{org} is defined similarly. One mole of buried organic carbon generates one mole of O_2 (Eq. (4.3)), so f_{org} provides the O_2 global production rate relative to the amount of carbon entering the atmosphere and ocean. Throughout geologic time, $\delta^{13}\text{C}_{\text{org}}$ is about -30‰ and $\delta^{13}\text{C}_{\text{carb}}$ is about 0‰ . Solving Eq. (4.13) with $\delta^{13}\text{C}_{\text{in}} = -6\text{‰}$ gives f_{org} about 0.2. In other words, $\sim 20\%$ of the CO_2 coming into the ocean–atmosphere system is fixed biologically and exits as buried organic carbon, whereas the remaining 80% exits as carbonate carbon.

The largest excursions in $\delta^{13}\text{C}_{\text{carb}}$ in Earth history occurred between 2.4 and 2.1 Ga, with positive and negative oscillations between $+10\text{‰}$ and -5‰ (see Fig. 12.8). But the Snowball Earth episodes that also occurred during 2.4–2.2 Ga (Section 4.2.4), combined with sparse $\delta^{13}\text{C}$ data, complicate the interpretation of $\delta^{13}\text{C}_{\text{carb}}$ fluctuations. Positive excursions of $\delta^{13}\text{C}_{\text{carb}}$ can be interpreted as resulting from increased organic burial on a global scale, leading to pulses of O_2 . However, given the geologically short residence time of atmospheric O_2 (today, a few million years), pulses of organic burial would merely cause atmospheric O_2 to rise and decay, and cannot be responsible for the permanent rise of O_2 (Section 4.7.1). The $\delta^{13}\text{C}$ record is further discussed in Section 12.2.3.

4.6.2.2 Marine sulfur isotopes

Marine sulfur isotopes indicate an increase in sulfate concentrations at ~ 2.3 Ga consistent with a rise of O_2

(Fig. 12.9). Archean sulfides display $^{34}\text{S}/^{32}\text{S}$ that cluster around the unfractionated mantle value ($\delta^{34}\text{S} = 0\text{‰}$), implying Archean oceans with <0.2 mM sulfate, compared to 28.9 mM in today's surface seawater. Lack of sulfate is consistent with low $p\text{O}_2$, which would induce little oxidative weathering of sulfides, limiting the river supply of sulfate to the oceans. Further discussion is in Section 12.2.4.

Measurements of other sulfur isotope ratios, $\delta^{32}\text{S}$ and $\delta^{33}\text{S}$, in addition to $\delta^{34}\text{S}$, show a major change in the sulfur cycle occurring between 2.45 and 2.09 Ga, most probably related to the rise of O_2 (Fig. 4.10) (Farquhar *et al.*, 2000). Sulfur isotopes in rocks older than ~ 2.4 Ga are peculiarly fractionated. But in younger rocks, ^{32}S , ^{33}S , and ^{34}S obey “mass-dependent” fractionation, in which the difference in abundance between ^{33}S and ^{32}S is approximately half that between ^{34}S and ^{32}S . Such fractionation is produced by many aqueous chemical and biochemical reactions, such as sulfate reduction. In contrast, sulfur isotopes in pre-2.4 Ga rocks show large “mass-independent” fractionation, which is thought to result solely from gas-phase photochemical reactions such as photolysis of SO_2 . The isotopes in this case are still fractionated by mass, but their relative abundances deviate from what is expected in mass-dependent fractionation. In a high- O_2 atmosphere, sulfur gases are rapidly oxidized to sulfuric acid, H_2SO_4 , which rains out as dissolved sulfate, SO_4^{2-} . In the absence of O_2 and an ozone layer in the early atmosphere, shortwave ultraviolet light penetrated into the lower atmosphere and the photochemistry of S-bearing atmospheric species

would produce mass-independent signatures (Pavlov and Kasting, 2002).

From ~0.8–0.6 Ga, sulfides are increasingly found with ³⁴S-depletions exceeding the fractionation threshold of sulfate reducing bacteria. This has been interpreted as indicating a second rise of pO₂ from ~1–3% to greater than 5–18% of present levels (Canfield and Teske, 1996). This can be explained if sulfide was re-oxidized at the sediment–water interface to SO₄^{2–} and reduced again by bacteria, cyclically increasing the isotope fractionation. Possibly, O₂ increased to the point where it penetrated marine sediments, making the deep ocean aerobic for the first time (Canfield, 1998). This could supply the increase of O₂ thought necessary to explain the appearance of macroscopic animals in the fossil record after 590 Ma (Knoll and Carroll, 1999).

4.7 Models for the Earth's atmospheric O₂ history

There is still no consensus about why atmospheric O₂ levels increased in the manner indicated by the geologic record. Before discussing various hypotheses, we introduce some general principles in understanding how the number of moles of O₂ (R_{O_2}) changes with time. The rate of change of R_{O_2} in the atmospheric reservoir is

$$\frac{d(R_{O_2})}{dt} = F_{\text{source}} - F_{\text{sink}}, \quad (4.14)$$

where F_{sink} is the removal flux of O₂ from the atmosphere (in moles yr^{–1}) due to numerous oxidation reactions, and F_{source} is the source flux of oxygen. After the advent of oxygenic photosynthesis (and of corresponding respiration processes), F_{source} was dominated by the burial flux of organic carbon. Most organic carbon (today, ~99.9%) is rapidly oxidized via respiration, producing no net O₂. But the small leak of organic carbon to sediments, where it is segregated from O₂, contributes in effect to F_{source} . F_{sink} is due to several oxidation processes:

$$F_{\text{sink}} = F_{\text{volcanic}} + F_{\text{metamorphic}} + F_{\text{weathering}}. \quad (4.15)$$

These loss terms are the reaction of O₂ with various reductants: reduced volcanic gases (F_{volcanic}), reduced metamorphic gases ($F_{\text{metamorphic}}$), and reduced material on the continents ($F_{\text{weathering}}$).

The F_{source} and F_{sink} fluxes depend on R_{O_2} in complicated, nonlinear ways. If we knew these dependencies explicitly (and we do not) we could substitute Eq. (4.15) into Eq. (4.14) and integrate to derive R_{O_2} as a function of time. A simplifying assumption is that

at any instant, R_{O_2} will roughly be in “steady state,” which means that O₂ will have accumulated in the atmosphere to some value of R_{O_2} where the O₂ sink (F_{sink}) will be about equal to the O₂ source (F_{source}). In this case, $d(R_{O_2})/dt = 0$ in Eq. (4.14). Such a balance of source and sinks is how O₂ remains constant today.

The secret to how O₂ levels have evolved entails understanding how F_{source} and F_{sink} have altered over Earth's history. We argue below that the evidence is most consistent with the idea that the rise of O₂ was the consequence of the sink from reduced gases diminishing relative to the source of O₂. In the Archean, F_{sink} was dominated by rapid losses of O₂ to reduced volatiles such as H₂. Under such conditions, Eq. (4.14) was balanced in steady state at very low values of R_{O_2} . After the rise of O₂, oxidative weathering ($F_{\text{weathering}}$) became a more important sink, and the steady-state balance was at significantly higher values of R_{O_2} . To use an analogy, the amount of O₂ in the atmosphere can be likened to the water level in a bathtub. Even with water gushing out of the tap at a steady rate, the equilibrium level of the water in the bathtub depends on the size of the plughole. Similarly, the standing amount of O₂ in the air does not just depend on the source (the organic burial rate) but on the subsequent fate of the O₂ (the loss of O₂ to reductants).

4.7.1 The delay between the origin of cyanobacteria and the rise of O₂

Oxygenic photosynthesis surprisingly originated by 2.7 Ga (Section 4.5.3), 0.3–0.4 Gyr *before* the rise of O₂ (Section 4.6). One explanation is that a massive pulse of organic burial caused the rise of O₂, as evidenced by the large carbonate isotope excursions during 2.4–2.1 Ga (Section 4.6.2.1). However, given the geologically short residence time of O₂ (~2–3 Myr, even today) a pulse of organic burial would mean that O₂ would return to its previous low levels once burial and oxidation of previously buried carbon had re-equilibrated. For high O₂ to persist, a secular shift in source and sink fluxes of O₂ must occur. A second hypothesis is that as geothermal heat declined due to the decay of radioactive materials inside the Earth, the flux of volcanic gases dwindled, lessening the sink on O₂. However, increased past volcanic outgassing would have also injected proportionately more CO₂. Carbon isotopes from 3.5 Ga onwards show that ~20% of the CO₂ flux into the biosphere was fixed biologically and buried as organic carbon with the remainder buried as carbonate (Section 4.6.2.1). Consequently, increased

outgassing in the past, on its own, cannot explain the oxic transition because O_2 production due to organic burial would have paralleled O_2 losses. A third explanation of the rise of O_2 takes account of the problem with the previous idea by invoking a gradual, irreversible shift of outgassed volatiles from reduced to oxidized. This explanation is probably the most viable. Before discussing how and why the redox state of outgassed volatiles might change, we first consider the sinks for O_2 in the modern atmosphere.

4.7.2 Modern sinks for O_2 : reduced gases and oxidative weathering

The ultimate source of O_2 comes from burying organic carbon. However, burial of other (non-detrital) redox species can also effectively generate or consume oxygen. For example, marine sulfate is microbially reduced to sulfide, which is buried with overall reaction $2Fe(OH)_3 + 4H_2SO_4 = 2FeS_2 + 15O_2 + 7H_2O$. Today, the burial of organic matter and pyrite (FeS_2) each contribute about 50% to F_{source} in Eq. (4.14). The burial of ferrous iron also effectively adds oxygen ($2Fe_2O_3 = 4FeO + O_2$), whereas the burial of sulfate, which requires that SO_2 is oxidized, effectively removes O_2 (Holland, 2002).

About 80–90% of F_{source} is removed in oxidative weathering, while the remainder reacts with reduced outgassed volatiles. But in the Archean, the balance must have been different. First, the lack of red beds and presence of reduced detrital minerals means that oxidative weathering was small. Second, the scarcity of marine sulfate means that the sulfide burial rate was lower (consistent with low C/S in Archean shales). Third, the similar rate of organic carbon burial relative to carbonates means that the O_2 sink from reduced gases must have been larger than today. But how could reduced gases, which apparently account for only 10–20% of the O_2 sink today, have consumed nearly all the O_2 produced in the Archean?

4.7.3 Methane, hydrogen escape, and metamorphic gas fluxes

Catling *et al.* (2001) argue that the sink on O_2 from reductants emanating from the Earth was greater in the Archean because oxidation of the crust due to hydrogen escape may have been important. Low O_2 would stabilize biogenic methane to an abundance $\sim 10^2$ – 10^3 ppm. This methane level would promote rapid escape of hydrogen to space, oxidizing the

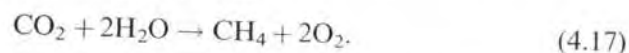
Earth, and it would also counteract the fainter Sun by greenhouse warming (Section 4.2.3). Thus, elevated Archean methane couples the “faint young Sun” and “rise of O_2 ” problems.

In the crust, the moles of excess oxygen locked up in minerals, such as sulfate or iron oxides, greatly exceeds reduced carbon (tabulated in Catling *et al.*, 2001). This can only be explained by a net hydrogen loss because otherwise photosynthesis would have produced organic carbon and oxygen in equimolar quantities (Eq. (4.3)). Thus, if the Archean crust oxidized due to hydrogen escape, the H_2/CO_2 ratio in metamorphic gases would drop, and O_2 would no longer be overwhelmed by reaction with CH_4 or H_2 . At this point, atmospheric O_2 would accumulate until balanced by oxidative weathering, and CH_4 levels would fall, inducing global cooling (Section 4.2.4).

In this model, microbial communities mediate the production of CH_4 (and ultimately hydrogen escape) via



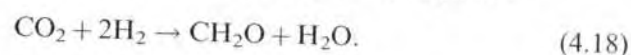
where the organic matter derives from photosynthesis. Consequently, addition of Eq. (4.16) to twice Eq. (4.3) gives the overall reaction



Although Eq. (4.17) mostly goes in the reverse direction, CH_4 can accumulate because O_2 reacts faster with outgassed H_2 and CO than it does with biogenic methane. A geological flux of H_2 is still needed to support high levels of CH_4 . If we add twice Eq. (4.5) to Eq. (4.17), we get $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$. Thus, dominance of CH_4 over O_2 requires excess H_2 supplied by the Earth regardless of the pathway of Eq. (4.16). This means that when hydrogen escapes to space via biogenic methane, the place where the hydrogen originated (the crust or the mantle (Section 4.4.2)) must ultimately be oxidized.

4.7.4 Excess hydrogen in the Archean

Holland (2002) has proposed a hypothesis for why the Archean atmosphere had excess hydrogen. He notes that the net reduction path of the biosphere is



Even if O_2 is generated by oxygenic photosynthesis (Eq. (4.3)), it is destroyed by Eq. (4.11) with hydrogen; Eqs. (4.3) + (4.11) produce the net reaction of Eq. (4.18). H_2 that remains in volcanic gas after the

reduction of 20% of its carbon to CH₂O (as inferred from sedimentary C isotopes) is available for the biosphere to reduce sulfur gases (principally SO₂) into sulfide. Sulfide then accumulates principally as sedimentary pyrite (FeS₂). Throughout the past 540 Myr, there has been enough H₂ left over from Eq. (4.18) to convert about 2/3 of the sulfur into pyrite (FeS₂), while the rest exits into sediments as sulfates. However, if Archean outgassing was H₂-rich, all of the sulfur could have been reduced to sulfide. In this case, there would be excess H₂ and the atmosphere would necessarily become “hydrogen-rich” and anoxic. Compared to modern volcanic gases, the increase in the proportion of hydrogen needed to flip to such an anoxic state would be a factor of ~2.4. Holland (2002) discusses possible ways in which this increased H₂ outgassing may have happened.

In summary, the most plausible explanation for why the late Archean atmosphere was anoxic is that excess reductants scavenged O₂. Hydrogen escape would have then oxidized the Earth, lowering the sink on O₂ until an oxic transition occurred. Explaining the second rise of O₂ at 0.8–0.6 Ga (Section 4.6.2.2) remains an area of future research. Perhaps methane persisted at a level of order about tens to a hundred ppm, and cumulative hydrogen escape over a further billion years helped shift another redox buffer beyond a critical threshold.

4.8 Formation of an ozone ultraviolet shield

An important consequence of the rise in O₂ at 2.4–2.3 Ga was the creation of an ozone (O₃) layer, which shielded the surface from biologically harmful solar ultraviolet (UV) radiation (but note that subterranean and marine organisms at depth do not require such protection). Radiation below a wavelength of ~200 nm is strongly absorbed by CO₂. For example, on Mars the CO₂-rich atmosphere prevents UV below 200 nm from reaching the surface, whereas biologically harmful radiation (in the 200–300 nm range) gets through (Cockell *et al.*, 2000). Today on Earth we are largely protected from radiation in the 200–300 nm range because of our atmosphere’s ozone layer.

Ozone today is formed in the *stratosphere* (ranging from 20 to 50 km altitude) from photochemical reactions involving O₂. Absorption of radiation below 240 nm dissociates O₂ into O atoms:

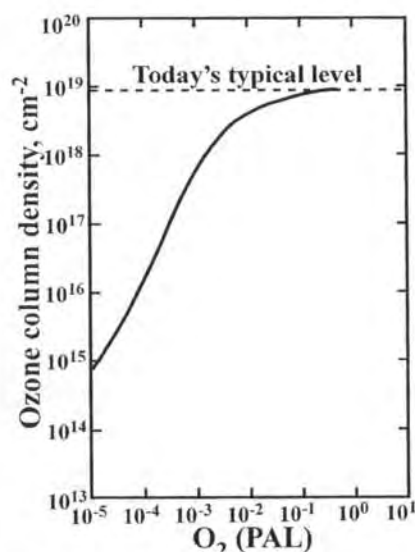


FIGURE 4.11 The ozone (O₃) layer column abundance as a function of pO₂ in the atmosphere. O₂ is expressed as a ratio to the Present Atmospheric Level (PAL). A typical ozone column abundance today is shown by the dotted line. The ozone layer’s protective absorption of ultraviolet light became significant at pO₂ of ~0.01 PAL, which occurred ~2.4–2.3 Ga. (After Kasting and Donahue, 1980.)

and the O atoms react with other oxygen molecules to form ozone:



Here M denotes any air molecule, usually N₂, which acquires the excess energy liberated by Eq. (4.20) and dissipates it through collisions with other air molecules. Ozone absorbs UV at longer wavelengths (200–310 nm) than O₂, and in the process the ozone is dissociated into O₂ and O and the absorbed energy heats the atmosphere. This is why the stratosphere increases in temperature with height, unlike the troposphere, where temperature decreases with height.

Photochemical models (Fig. 4.11) show that an atmosphere with pO₂ ≥ 0.002 bar (1% of present) creates an ozone layer that absorbs most harmful UV (Kasting and Donahue, 1980). Such a level occurred on Earth at ~2.4–2.3 Ga.

4.9 Advanced life and O₂ on other Earth-like planets

The high O₂ content of Earth’s atmosphere sets our planet apart from all others in the Solar System. But does Earth’s O₂-rich atmosphere differ from all other planets in the Galaxy or Universe? Is O₂ required for higher life? And would a high O₂ atmosphere, which results from biology on Earth, be diagnostic of life on another planet?

4.9.1 Is O₂ required for animal-like life?

There are several good reasons for believing that extraterrestrial multicellular life (comparable to animals on Earth) would metabolize molecular oxygen. Life anywhere in the Universe must be constrained by the chemistry possible within the periodic table. Advanced extraterrestrial life, like its terrestrial counterpart, would require substantial energy for chemical, electrical, osmotic, and mechanical work. Fluorine is the most energetic oxidant (per electron transfer) available in the periodic table, and aqueous chlorine is similar to oxygen. However, F is useless because it spontaneously explodes on contact with organic material! Similarly, Cl forms bleach in water. O₂ differs because its bond provides greater stability than the weak single bonds of the halogens. Given that F₂ and Cl₂ are not realistic oxidants, free O₂ in a planetary atmosphere allows life to utilize the greatest energy source per electron transfer. Oxygen is also plentiful in the cosmos, third in abundance behind H and He. Furthermore, oxygen occurs as a gas in the temperature–pressure range of liquid water. A solid (e.g., sulfur) or liquid terminal oxidant would have a confined distribution and thereby limit possible habitats. No such restriction applies with gaseous O₂, which can be ubiquitous throughout an atmosphere and within oceans. Consequently, given the constraints of the periodic table, aerobic respiration is the most energetic chemistry for advanced life. Thus high atmospheric O₂ is probably a necessary precursor for animal-like life anywhere (Catling *et al.*, 2005).

Consequently, the controls on the timescale for the rise of O₂ may be critical for the viability of advanced life on an extrasolar planet. For example, if a large, more chemically reducing planet around a Sun-like star took ~10 Gyr to undergo a significant rise in O₂ (much more than Earth's ~3.9 Gyr to reach the Cambrian), advanced life could be precluded because the star would have already evolved to a much more luminous red giant (Chapter 3).

4.9.2 Spectroscopic detection of life on extrasolar planets

In the future, life could be detected on extrasolar planets by remotely sensing their atmospheres (see Chapter 21 for plans to do this in the next decade). Compared to Venus and Mars, Earth has an anomalous atmosphere: water-rich, with strong ozone absorption at a wavelength of 9.6 μm (Fig. 4.12). Such an

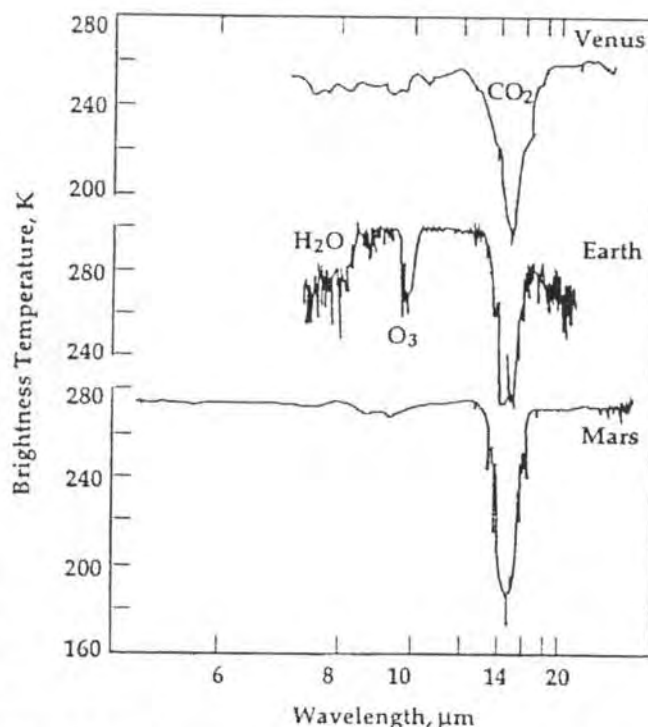


FIGURE 4.12 Remote sensing spectra obtained by orbiting spacecraft for Venus, Earth, and Mars. Brightness temperature is a measure of the temperature in the atmosphere or on the surface from where the emission originates. All atmospheric spectra show significant absorption due to CO₂ at 15 μm (Table 4.1). The spike in the center of the Earth's 15 μm band is characteristic of a warm layer of CO₂ in the stratosphere. The Earth's stratospheric ozone (O₃) layer is revealed by its absorption feature at 9.6 μm. Earth's spectrum also shows the presence of considerably more H₂O vapor than either Mars or Venus, indicative of Earth's oceans. (After Hanel *et al.*, 1975.)

atmosphere is diagnostic of life because the ozone implies a continuous biological source of O₂ (Sagan *et al.*, 1993). If photosynthetic life went extinct, O₂ would decrease to less than 1% of present levels in only ~10–15 Myr by reacting with reduced surface materials and reduced gases. Joshua Lederberg and James Lovelock first suggested that the presence of gases that are far removed from equilibrium is diagnostic of life (Lederberg, 1965; Lovelock, 1965; 1978). The problem, however, is that hot planetary interiors and stellar radiation, independent of life, provide other sources of free energy that produce disequilibrium, so discriminating life becomes a question of degree.

Ozone absorption at 9.6 μm is a good surrogate for the presence of O₂. Even at pO₂ only 1% of the present, the ozone column depth would be about a third of the present global average value (Fig. 4.11). Thus, astronomers on a distant planet with a powerful spectrometer-telescope could have deduced the presence on Earth of O₂ over the past 2.4–2.3 Gyr. But could substantial

O₂ arise in the absence of life (Leger *et al.*, 1999)? Today, Venus has <1 ppm of O₂ in its atmosphere, but it may have had much more in the past. Early Venus is thought to have lost its oceans due to a severe greenhouse effect (Section 4.2.2). With a wet upper atmosphere, the rate of water-induced hydrogen loss became correspondingly very high. Thus, Venus could have had a large abiotic production of O₂ from dissociation of water (noting that O₂ build-up may have been self-limiting by thwarting hydrogen escape). Earth could experience a similar fate when the oceans boil 1–2 Gyr from now as the Sun heats up. In observing extrasolar planets, we must therefore estimate the likelihood of such scenarios from orbital elements and the age and luminosity of the parent star (Chapter 21).

To detect life on planets resembling early Earth *before* O₂ became abundant, one could look for the strong 7.6 μ m absorption band of biogenic methane. However, abiological processes can also produce abundant methane. The atmosphere of Titan, Saturn's largest moon, has 4.9% CH₄ below 8 km altitude. The surface temperature of Titan is \sim 95 K – too cold for liquid water and conventional life – so it is believed that CH₄ emanates from geothermal processes in the subsurface (Chapter 20). Overall, the presence of methane as a spectroscopic biomarker is less certain than the presence of ozone.

4.10 Summary and conclusions

An Earth-like planet with liquid water on its surface is the most likely type of planet to be inhabited and to possess a biosphere that is detectable through remote atmospheric spectroscopy. Thus, a key aspect of a planet's biological potential is whether the planet's surface temperature is conducive to liquid water. The average surface temperature of a planet is determined by the planet's albedo, the atmospheric greenhouse effect, and the energy flux from its parent star. Negative feedbacks in a climate system tend to stabilize a planet's surface temperature within a particular range. Over geological time, the most important negative feedback for regulating the Earth's climate is the CO₂-climate feedback arising from the carbonate–silicate cycle. The rate of silicate weathering reactions, and therefore the consumption of CO₂, increases with the amount of CO₂ in the atmosphere. Given a source of CO₂ from volcanism and metamorphism that is independent of the amount of atmospheric CO₂, the climate tends to reach equilibrium at some equable level of CO₂ where the CO₂ sink balances the CO₂

source. However, such climate regulation failed on Venus, which was too close to the Sun and lost its water from dissociation and escape processes. Without water to remove CO₂ during weathering, CO₂ accumulated on Venus. Mars, being a small planet, shut down tectonically and failed to provide the necessary replenishment of CO₂ to the atmosphere. Mars probably also lost much of its atmosphere during early impact bombardment. For both reasons, Mars slipped into a permanent ice age.

Over geological history, the Earth's climate has been greatly affected by changes in the chemistry of the atmosphere coupled to the evolution of life. Today, apart from argon, all of the quantitatively important gases are at least in part biologically controlled (Table 4.1). Oxygen, in particular, has no significant abiological source. Consequently, before life evolved, Earth's atmosphere had negligible O₂. The prebiotic atmosphere probably consisted mainly of N₂, CO₂, and water, with relatively small amounts of H₂, CO, and CH₄. Reactions in such an atmosphere may have synthesized formaldehyde (H₂CO) and hydrogen cyanide (HCN), the basic building blocks for sugars and the nitrogen-containing bases required for RNA. Once life arose, microbes would have consumed H₂ and transformed it into CH₄. As a powerful greenhouse gas, CH₄ would have lowered the amount of CO₂ through temperature-dependent consumption of CO₂ in weathering. Thus, before O₂ became abundant in Earth's atmosphere, atmospheric models suggest that biogenic methane would have been stable at much higher levels than today and therefore was a more important greenhouse gas than CO₂.

The most significant biological event for the history of Earth's atmosphere was the evolution of oxygenic photosynthesis, a metabolism that dates back to at least 2.7 Ga. However, atmospheric O₂ remained below part per million levels until \sim 2.4–2.3 Ga. The history of O₂ can be characterized in terms of its chemical adversary: the collection of reducing, hydrogen-bearing atmospheric gases. Before the rise of O₂, hydrogen-bearing gases like CH₄ and H₂ must have tipped the redox balance in the atmosphere against O₂. A plausible mechanism for redox change is that the escape of excess hydrogen to space inexorably oxidized the Earth over geological time, shifting the redox balance in favor of an oxidizing atmosphere. Once O₂ finally rose, it created an ozone layer, shielding the surface from harmful ultraviolet radiation.

Given that atmospheric O₂ has no significant source other than from life, life on extrasolar Earth-like

planets can be detected using ozone as a proxy for abundant oxygen. On Earth, the amount of oxygen in the atmosphere must have set the tempo for the evolution of complex biology to some degree. Chemical arguments suggest that complex life forms elsewhere will probably also utilize oxygen in their metabolism. Thus, understanding the redox history of habitable planets and their atmospheres is critical for the question of whether humans are an improbable accident and the sole sentient beings in the universe or whether we are more typical. Planetary atmospheres thus run like a thread through some of the most important questions in astrobiology: life's origins, planetary habitability, and the distribution of complex life.

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