

Frontiers of
Astrobiology

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Evolution of a Habitable Planet

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Introduction

We saw in the previous chapter that Earth developed a climate that supported liquid water at its surface very early in its history, probably within the first few hundred million years. That was good for life, of course, because all life that we know about on Earth requires liquid water at least episodically. There are good chemical reasons for thinking that this requirement might be universal, some of which were discussed earlier in this volume.

Here we are concerned with a somewhat later stage in Earth's history, starting from when the rock record begins, around 3.8–4 billion years ago, or 3.8–4 Gyr ago, and continuing on until the rise of atmospheric oxygen, around 2.3 Gyr ago. This time interval overlaps almost precisely with the geologic time period called the Archean Eon. Although not formally defined as such, the beginning of the Archean corresponds with the beginning of the rock record, as marked by the oldest dated fragments of continental crust at Earth's surface. We know that Earth had older rocks, based on crystals of the mineral, zircon, which survive today as sand grains in mid-Archean quartzites from Western Australia, and can be dated as far back as 4.4 Gyr ago (Valley *et al.* 2002). Defining the end of Archean time to be precisely 2.5 Gyr ago was a somewhat arbitrary decision of the geological community: at about this time, the dominant type of sedimentary basin switches from the granite-greenstone belt configuration (dominated by ultramafic, magnesium-rich volcanics and chemically immature sedimentary rocks) to basins controlled by thermal subsidence along passive margins. This switch in rock types may or may not have influenced the rise of O₂, as discussed later in this chapter. We will

henceforth use the term "Archean" to refer to the time period preceding the rise of O_2 , recognizing that astrobiological and geological terminologies have slightly different meanings.

Earth's climate history

When we say that Earth's climate was clement after the first few hundred million years, we should acknowledge that there is large uncertainty in the mean surface temperature throughout much of Archean time. Liquid water is actually stable on Earth's surface at all temperatures below its critical temperature, 374°C .¹ This is because the pressure of a fully vaporized ocean, ~ 300 bar, exceeds the critical pressure of 220.6 bar. So, the temperature constraint implied by the presence of liquid water is not as strong as is sometimes thought. Valley *et al.* (2002) argue that surface temperatures must have been lower than 200°C to explain the oxygen isotope ratios in the ancient zircons that they have studied (see the discussion of these isotopes below). But this still does not tell us much about the potential for life.

Dubious constraints from oxygen isotope ratios in cherts

Somewhat tighter constraints are provided by oxygen isotope ratios in cherts. Chert is a particular mineral form of silica, SiO_2 . The O atoms in chert can be either the normal isotope, ^{16}O , or one of the minor isotopes, ^{17}O or ^{18}O . We only care here about the ratio of the more abundant of these, ^{18}O , compared to ^{16}O . High temperatures in the water from which the chert is precipitated lead to lower $^{18}\text{O}/^{16}\text{O}$ ratios in the chert. Conversely, low temperatures lead to high $^{18}\text{O}/^{16}\text{O}$ ratios. If one examines cherts of different geologic ages, one finds that the older cherts have significantly lower $^{18}\text{O}/^{16}\text{O}$ ratios, suggesting that the early Earth was hotter than today (see e.g. Knauth 2005). Indeed, the mid-Archean appears to have been quite hot, $\sim 70^\circ\text{C}$, according to these data. By contrast, the present mean surface temperature is 15°C .

Unfortunately, the isotopic data from cherts also suggest that Earth's surface remained impossibly warm until much more recently. For example, the same methods imply that temperatures at the beginning of the Cambrian Period, 542 Myr ago, were still around 55°C , which is far above the temperature limits for growth of any known animal, and most eukaryotes. The molluscan fossils that appear around this time would have been cooked in their shells! Exactly which assumption is wrong remains unclear. Perhaps most or all cherts had their isotopic ratios reset during *diagenesis* (heating and chemical alteration of buried

1 All values given are for pure water. The behavior of saltwater is more complex, but the differences are not important for the arguments presented here.

sediments). Alternatively, the oxygen isotopic composition of seawater may have varied with time (Kasting *et al.* 2006), or the calculated temperatures may actually reflect those of widespread hydrothermal vent fluids, rather than that of the ocean. This last interpretation may be the most likely, as it might also explain systematic variations in silicon isotope ratios over time (van den Boorn *et al.* 2007). Whatever the case, there are good reasons to think that Archean surface temperatures were much cooler than 70 °C, some of which are discussed in the next section.

The long-term glacial record: firmer constraints on climate

Glaciers leave at least four very distinctive features in the rock record that do not form through any other known process. For example, rocks frozen into the ice at the base of a glacier are often scraped along the bedrock, gradually being ground down into glacial dust. If the rock is hard – such as a piece of chert or quartzite – it can become scratched and nicked with subparallel ridges across a surface. The ice, however, is dynamic and any individual stone will be tilted and tumbled numerous times and in different orientations before coming to rest. This produces a type of stone called a *multiply striated cobble*, which has only been found in glacial settings. Similarly, the surface of the bedrock over which the glacier moved also gets covered with long, parallel scratches as it is gradually sanded away, producing distinctive *glacial pavements* like those that grace Central Park in New York City. These pavements are often overlain by a pile of debris known as a *diamictite*, which is a rock that has two distinct grain sizes (typically fine rock flour and larger clasts). *Glacial till* is a type of diamictite that forms as the glaciers melt and drop the dust and stones they are carrying into a jumbled pile, usually with the stones “floating” in the finer-grained mud. Although debris flows can sometimes generate a diamictite, they tend to be local features. Glacial tills, in contrast, will form all along the edge of a melting ice sheet, leaving a much more extensive blanket of debris over the landscape. Finally, when a glacier reaches open water it will break up into icebergs that drift away, slowly melting and releasing the dust and rock that they hold. When a large rock slams into the mud at the bottom it deforms the sediment below and around it, and is then gradually buried by overlying sediment. Such distinctive *drop stones* can be as small as a pebble or as large as a house.

Firm evidence for glaciation exists both in the middle Archean at around 2.9–2.7 Gyr ago (Young *et al.* 1998), and near its end, between 2.45 and 2.22 Gyr ago (Young 1991), providing strong arguments that the early Earth was cool during the last half of Archean time (see Figure 6.1). The climate could, of course, have been hot in between these glaciations, much in the way that Earth has alternated between long (100 Myr scale) intervals of “ice-house” and “greenhouse” intervals for the past half billion years (Kump *et al.* 2010). The geological record supports

Geologic Time

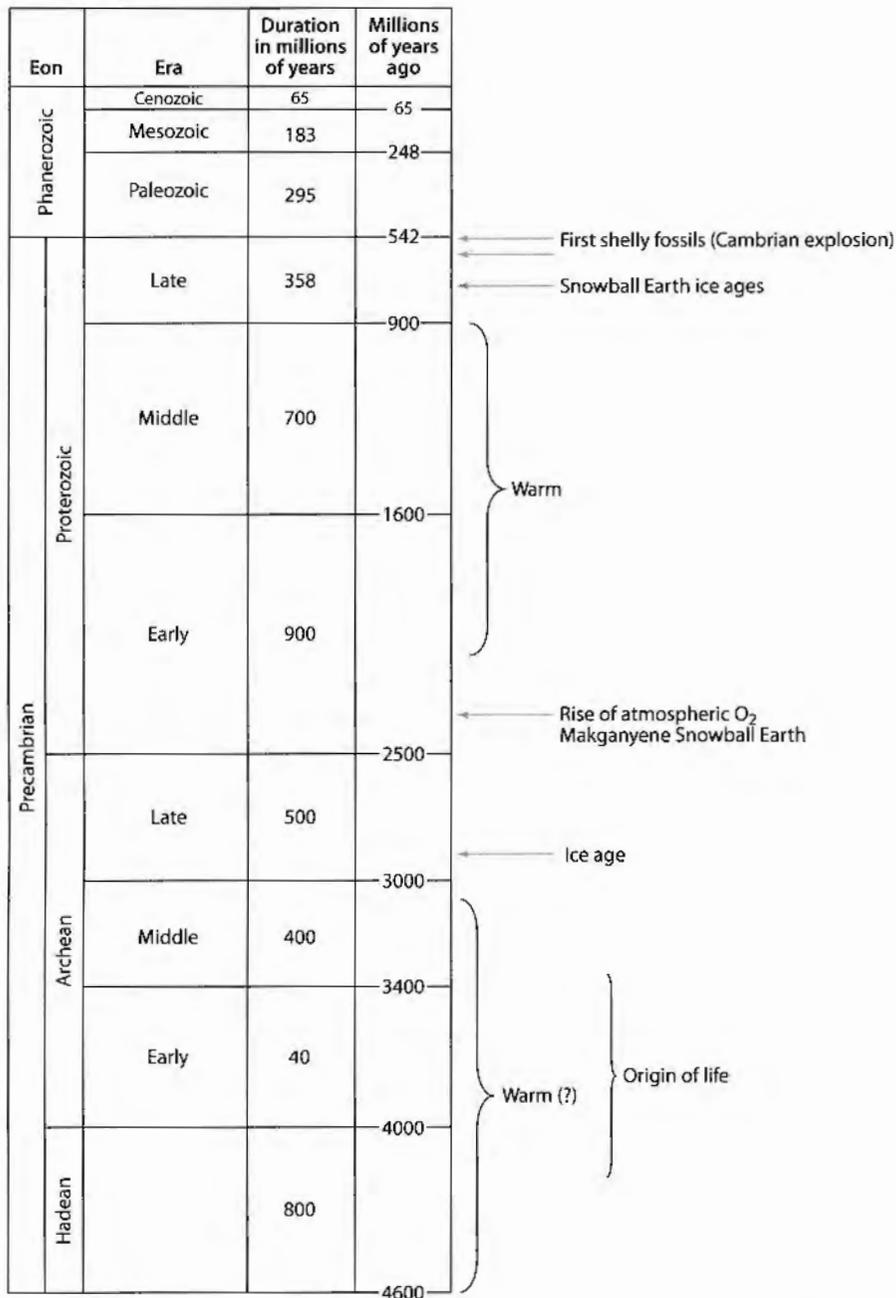


Figure 6.1 The geologic time-scale, showing major events in Earth's history back to its origin at 4.6 Gyr ago. Known periods of glaciation are indicated.



Figure 6.2 Example of a multiply striated cobble from the 2.22 Gyr old Makganyene diamictite of South Africa.

this concept. For example, the Pongola glaciation in Southern Africa at 2.9–2.7 Gyr ago has at least three distinct units of diamictite that can be traced laterally over hundreds of square kilometers and that contain occasional small drop stones. Similarly, early Proterozoic sediments (commonly known as the ‘Huronian’ interval from 2.45 to 2.22 Gyr ago) are globally characterized by all of these characteristic features, including multiple layers of laterally continuous diamictites, multiply striated cobbles (Figure 6.2), basal striated pavements (in both Canada and South Africa), and often abundant drop stones. Both the Huronian sequence in Canada and the Transvaal group in Southern Africa record several intervals of glacial advance and retreat. The total number of these glacial cycles is obviously unknown, but as discussed later, the last one – the Makganyene event in South Africa – reached down into low latitudes and most likely was a global ‘Snowball Earth’ event.

Because the geological record is incomplete, and because it becomes worse with increasing geological age, we have probably underestimated the extent and duration of these ancient glacial episodes. Indeed, most ice caps form at high latitudes, but the probability of a continental fragment being at the poles to record the presence of a glaciation is relatively small.

The faint young Sun problem

The central theoretical problem of Archean climate is not to explain how it could have been cool; rather, it is to explain why the Earth was not completely frozen. Solar evolution models (e.g. Gough 1981) predict that the Sun was ~30%

less luminous when it first formed. The reason lies at the heart of the Sun's mode of energy production: The Sun fuses hydrogen into helium in its core. This makes the core denser, causing it to contract and heat up, and this in turn makes the fusion reactions go faster. At the beginning of the Archean (3.8 Gyr ago), solar luminosity is thought to have been about 75% of its present value, increasing to roughly 83% at the end of that time (2.5 Gyr ago). Straightforward calculations (e.g. Kump *et al.* 2010) show that, because of this change in solar luminosity, Earth's surface would have been frozen prior to ~2.0 Gyr ago if its atmospheric greenhouse effect had remained unchanged over time.

Numerous hypotheses have been proposed to explain why the early Earth did not freeze. Sagan and Mullen (1972), who identified this problem originally, suggested that high concentrations of the greenhouse gases, methane (CH_4) and ammonia (NH_3), were what kept the Earth warm. Both CH_4 and NH_3 are reduced gases, meaning that they can react with O_2 . Thus, when atmospheric O_2 concentrations were lower, it makes sense that the concentrations of CH_4 and NH_3 could have been higher. This expectation is borne out for CH_4 , which is predicted to have had a concentration of 100–1000 parts per million (ppm) during the Archean, as compared to only 1.6 ppm today (Pavlov *et al.* 2001, Kharecha *et al.* 2005). NH_3 , however, is photolyzed rapidly by solar ultraviolet (UV) radiation in the absence of shielding by atmospheric O_2 and O_3 (ozone) (Kuhn and Atreya 1979), and so until recently it was not thought to have played a significant role.

Sagan remained fond of this idea, however, and in a paper published posthumously (Sagan and Chyba 1997), he and his coauthor suggested that NH_3 was shielded from photolysis by an organic haze formed from CH_4 photolysis. Organic haze is observed in the CH_4 -rich atmosphere of Saturn's moon, Titan, and is predicted to have been present at least some of the time on the Archean Earth (Domagal-Goldman *et al.* 2008). Simple models of the haze failed to provide enough UV shielding to protect NH_3 (Pavlov *et al.* 2001, Haqq-Misra *et al.* 2008). Just recently, however, Wolf and Toon (2010) argued that these models may be misleading. Actual hydrocarbon particles are more like carbonaceous "snowflakes" rather than the simple spheres used in most radiative transfer calculations. By treating these snowflakes as *fractals* – many tiny spheres packed inside of large ones – Wolf and Toon showed that the UV shielding is dramatically improved. Indeed, preliminary unpublished calculations by Tian *et al.* suggest that the shielding is good enough to allow NH_3 to again become an important greenhouse gas.

This said, another important piece of the climate puzzle involves carbon dioxide, CO_2 . Along with water vapor, CO_2 is one of the two most important greenhouse gases in Earth's present atmosphere. Its concentration in the early Earth's

atmosphere may have been higher, for a variety of reasons.² CO₂ is produced from volcanism, and volcanic activity is predicted to have been higher on the hot, young Earth. Furthermore, removal of CO₂ by silicate weathering, followed by deposition of carbonate sediments, depends strongly on temperature (Walker *et al.* 1981, Kump *et al.* 2010). All other things being equal, lower solar luminosity early in Earth's history should have led to lower surface temperatures, slower weathering rates, and higher atmospheric CO₂. This negative feedback loop could easily have generated CO₂ concentrations 100–1000 times higher than today's level of ~300 ppm.³ If CO₂ was actually this high, then it could have kept Earth's surface temperature above freezing, even in the complete absence of reduced greenhouse gases (Owen *et al.* 1979, Kasting 1987, von Paris *et al.* 2008).

Theories about past atmospheric composition and greenhouse warming have begun to be tested by measurements made on ancient rocks. Rye *et al.* (1995) and Sheldon (2006) have published limits on atmospheric CO₂ concentrations based on *paleosols* (ancient soils). Sheldon's kinetic analysis is to be preferred, as the thermodynamic data used by Rye *et al.* are out of date and the analysis method itself is suspect. Sheldon's published pCO₂ estimate is equivalent to about 10–100 times present at 2.2 Gyr ago, decreasing to about 1–10 times present at 1 Gyr ago. This is less than would have been needed to keep the Earth warm at these times, and so it suggests that other warming mechanisms must have been present. More recently, Rosing *et al.* (2010) published a much lower limit on CO₂, about 3 times present, based on the mineralogy of *banded iron-formations*, or BIFs.⁴ BIFs contain a variety of iron-bearing minerals, including magnetite, Fe₃O₄, and siderite, FeCO₃. The Rosing *et al.* limit is based on equilibrium reactions between these two minerals



A number of objections to this idea have been raised, including the fact that neither magnetite nor siderite is a primary mineral and that organic carbon, not hydrogen, was the probable reductant (Dauphas and Kasting 2011). It remains to be seen which side will prevail in this debate. For our purposes here, the outcome of this dispute does not matter too much. We know empirically that Earth did remain habitable during

2 In the following discussion, we will ignore the short-term *organic carbon cycle*, which affects atmospheric CO₂ concentrations on time-scales of months to thousands of years. The slower *inorganic carbon cycle*, or *carbonate-silicate cycle*, is the chief process controlling atmospheric CO₂ on time-scales of millions of years or longer.

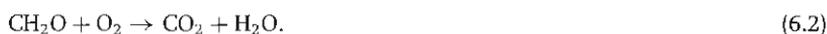
3 Today's CO₂ concentration is changing year to year as a consequence of fossil fuel burning. The pre-industrial (pre-1800) CO₂ concentration was about 280 ppm. Today's level is closer to 390 ppm.

4 Rosing *et al.* make up for the lack of greenhouse warming by postulating that the early Earth had a lower albedo, or reflectivity, caused by the lack of biogenic sulfur gases which could act as cloud condensation nuclei.

the Archean eon, and we understand that there are processes, particularly the CO₂-weathering feedback, that promote habitability. This bodes well for the prospects of eventually finding other Earth-like planets with stable, liquid-water-supporting climates.

Atmospheric composition and redox state

Besides climate and the availability of liquid water, the other environmental variable that has most affected life throughout Earth's history is the atmospheric and oceanic redox state. Today, Earth's atmosphere is rich in O₂ – a powerful oxidant (electron acceptor) that drives the metabolism of aerobic organisms through *respiration*. Chemically, we can express respiration as



The symbol “CH₂O” is geochemists' shorthand for organic matter, which contains carbon, hydrogen, and oxygen in roughly a 1:2:1 ratio. To a geochemist, respiration is the opposite of *oxygenic photosynthesis*, which is just reaction (6.2) run backwards. All higher organisms, including plants, animals, and single-celled, *eukaryotic* organisms⁵ such as algae, depend on respiration to drive their metabolism. Hence, the origin of oxygenic photosynthesis, and the subsequent rise in atmospheric O₂, played a major role in the evolution of advanced life on Earth.

Curiously, O₂ is actually an incredibly poisonous molecule. If it can grab an electron from a common biological cation like Fe⁺² or Mn⁺², it will form a superoxide radical, O₂^{*}, which will then react with water and generate hydroxyl radicals, OH^{*}. Although they have an extremely short lifetime, hydroxyl radicals can attack almost any organic substance in their path, including the backbone of DNA. These and similar O₂^{*}-induced reactions had to be contained before Earth's biosphere could exploit the enormous chemical energy potential provided by the availability of O₂. The puzzle of how this might have evolved is addressed at the end of this chapter.

Atmospheric composition prior to the rise of O₂

Prior to the “Great Oxygenation Event”, somewhere around 2.4 Gyr ago (Farquhar *et al.* 2000), the atmosphere must have had a very different composition. Reduced gases, such as molecular hydrogen (H₂) and methane, should have been more abundant, and free O₂ should have been virtually absent at ground level. Some O₂ would have been produced from photolysis of CO₂ up in the stratosphere, followed by recombination of O atoms to form O₂; however, the amount formed

⁵ *Eukaryotic* organisms are those that have cells with nuclei. *Prokaryotic* organisms, including Bacteria and Archea, lack cell nuclei.

was too small to block out short-wavelength solar UV radiation or to form an effective ozone screen.

Just because oxygenic photosynthesis had not yet been invented does not mean, however, that life had no effect on the early atmosphere. Prior to the origin of life, the main reduced gas in the atmosphere was probably H_2 .⁶ As first pointed out by Walker (1977), the H_2 concentration of the prebiotic atmosphere should have been determined largely by the balance between outgassing of H_2 and other reduced gases from volcanoes and loss of hydrogen to space. Volcanoes today release mostly H_2O and CO_2 , but H_2 is a minor component, along with CO and various sulfur gases (SO_2 and H_2S). The present H_2 outgassing rate is of the order of 1×10^{12} mol/yr, or roughly 4×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$ (Holland 2009). If hydrogen escapes to space at the *diffusion-limited rate* (Walker 1977), then its atmospheric mixing ratio, f_{H_2} , can be estimated from the equation

$$\Phi_{\text{esc}}(\text{H}_2) \cong 2.5 \times 10^{13} f_{\text{H}_2} \text{ molecules cm}^{-2} \text{ s}^{-1}. \quad (6.3)$$

Here, we are for the moment neglecting the contribution of other hydrogen-bearing gases to the volcanic outgassing rate (which is probably a safe assumption for the prebiotic atmosphere). Using this formula, and assuming that the H_2 escape rate equals the present outgassing rate, yields an atmospheric H_2 mixing ratio of about 1.6×10^{-4} , or 160 ppm. Higher volcanic release rates during the Archean could yield H_2 mixing ratios of 10^{-3} or higher, or about 0.1%. This creates what is typically referred to as a *weakly reduced atmosphere* (Figure 6.3).

Effect of early life on the atmosphere

Although 0.1% H_2 may not sound like a lot, it is enough to power several different forms of *anaerobic* metabolism, or those that occur in the absence of oxygen. One of these is *methanogenesis*, which produces methane. Methanogenesis is carried out by a type of anaerobic Archaea called *methanogens*. Methanogens produce methane by a variety of different pathways. Most, or all, of them, however, can utilize the reaction



The H_2 threshold at which methanogenesis can occur depends on the amount of CO_2 that is present, but it is at least 10–100 times lower than the 0.1% H_2 that is thought to

⁶ Although we have not discussed it explicitly, we assume that the bulk of the atmosphere was composed of molecular nitrogen, N_2 , as it is today. N_2 is relatively inert and has likely been partitioned mostly into the atmosphere since early in Earth's history. Indeed, Goldblatt (2009) has argued that N_2 partial pressures could have been 2–3 times higher than today, and that nitrogen has subsequently been sequestered in the mantle by subduction of N-bearing sediments. We acknowledge this possibility but point out that it probably has little bearing on Earth's habitability, other than providing a few degrees of warming by pressure broadening of other greenhouse gas absorption lines.

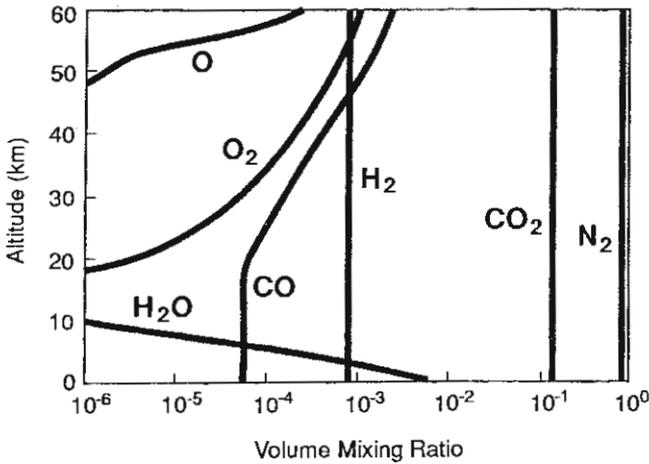


Figure 6.3 Vertical profiles of atmospheric species for a typical, weakly reduced, "prebiotic" atmosphere. The hydrogen abundance is determined by balancing volcanic outgassing with hydrogen escape. O_2 concentrations are predicted using a one-dimensional photochemical model (from Kasting 1993).

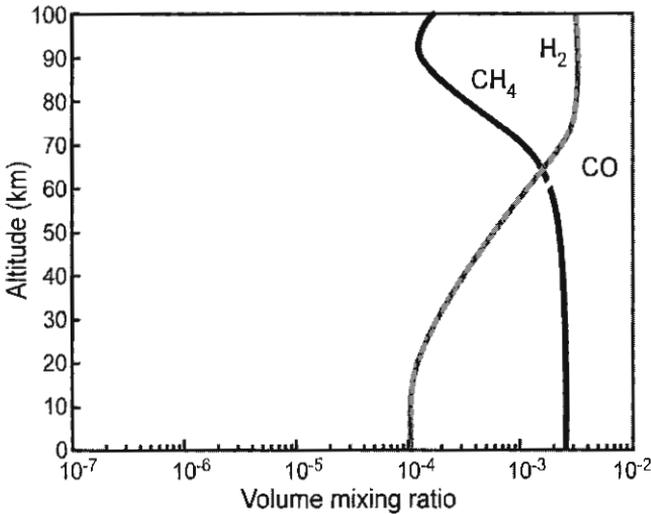


Figure 6.4 Vertical profiles of CH_4 , CO , and H_2 for a typical postbiotic, but "pre-photosynthetic", atmosphere (from Kharecha *et al.* 2005, Fig. 7c).

have been available. Hence, as Walker (1977) suggested many years ago, methanogens, once they evolved, probably converted much of the existing H_2 into CH_4 . This prediction has been quantified by Kharecha *et al.* (2005), who used a numerical model to estimate the rate at which methanogens could have metabolized, along with the coexisting concentrations of H_2 and CH_4 (Figure 6.4). In this model, the rate of methanogenesis is limited by the rate at which H_2 can diffuse downward through the atmosphere–ocean

interface and by the rate at which CH_4 can diffuse upward. A surprising result is that the predicted rate of methane production is within a factor of 3 of the present value, 3.6×10^{13} mol/yr (Prather *et al.* 2001), despite the fact that the Archean and modern ecosystems bear little resemblance to each other.

Methanogenesis was probably an early metabolic invention, according to most phylogenetic analyses (e.g. Woese and Fox 1977), and there is direct evidence of biogenic methane trapped in “bubbles” from 3.5 Gyr old cherts in Australia (Ueno *et al.* 2006). But other forms of anaerobic metabolism likely evolved at about the same time, including various forms of *anoxygenic photosynthesis*. Unlike oxygenic photosynthesis, in which the electrons needed to reduce CO_2 to organic carbon are derived from water (reaction 2 in reverse), in anoxygenic photosynthesis the electrons are provided by various reduced species, such as ferrous iron (Fe^{+2}), sulfide (S^{2-}), or H_2 . Fe^{+2} and H_2 were the most widely available reductants (Kharecha *et al.* 2005, Canfield *et al.* 2006), and they fueled marine biological productivity at rates that were of the order of 0.01 times today’s value, $\sim 4 \times 10^{15}$ mol/yr (Prentice *et al.* 2001). As many other authors have pointed out previously, this illustrates the gigantic leap in productivity that became available once cyanobacteria learned to split the water molecule. The Archean Earth was probably teeming with life, but it was still only a fraction as “alive” as today.

What influence would such anoxygenic photosynthesizers have had on the atmosphere? Surprisingly, their predicted effect is not greatly different from that of methanogens (Kharecha *et al.* 2005). H_2 -based photosynthesizers living in the oceans would have been limited by the downward flux of H_2 from the atmosphere, as before. Their productivity would have been roughly 10 times higher than that of methanogens, because they obtained their energy from sunlight rather than from chemical reactions. However, the organic matter that they produced would likely have decayed by *fermentation* and methanogenesis, and the rate of cycling of H_2 and CH_4 was still limited by diffusion. Hence, the flux of CH_4 into the atmosphere could not have been substantially higher than it was previously.

Finally, we should tie this discussion back to the earlier one concerning climate. Methane, as pointed out previously, is a reasonably good greenhouse gas on its own; furthermore, it photolyzes to produce organic haze, which can shield other greenhouse gases like ammonia from photolysis. Hence, the methane-producing Archean biosphere likely played a significant role in warming Earth’s climate right up to the point when atmospheric O_2 concentrations began to rise. At that point, the photochemical lifetime of methane dropped, atmospheric CH_4 concentrations declined precipitously, and Earth was thrown into a series of glaciations – the Paleoproterozoic glaciations discussed above. So, the methane-rich Archean atmosphere discussed here is broadly consistent with Earth’s inferred climate history. That does not mean it is necessarily right, but it provides at least a starting point for thinking about the Archean environment.

The great debate about the Great Oxygenation Event

As pointed out many years ago by Roscoe (1969), the Paleoproterozoic glaciations appear to have occurred right when atmospheric O₂ concentrations increased for the first time – the so-called “Great Oxidation Event” (Holland 2006). Naturally, this makes us suspect that the two events are causally connected, and indeed, two separate hypotheses have been proposed to explain how this might have occurred. In the first (Kasting *et al.* 1983, Pavlov *et al.* 2000), the rise of O₂ caused a decline in atmospheric CH₄ concentrations. CH₄ is a greenhouse gas that helps to warm Earth’s surface; thus, when CH₄ levels fell, the climate cooled and Earth was thrown into glaciation.

Kopp *et al.* (2005) extended this hypothesis by suggesting that the sudden evolution of oxygenic photosynthesis, followed by the exponential growth of the first cyanobacteria, was rapid enough to destroy this methane-based greenhouse faster than other feedbacks involving CO₂ could respond. In this case the net result would be a global freeze-over producing a “Snowball Earth”, consistent with paleomagnetic evidence for the low-latitude deposition of the Makganyene glaciation in South Africa between ~2.32 and 2.22 Gyr ago (Kirschvink *et al.* 2000, Evans *et al.* 1997). This later scenario is still consistent with the hard geological evidence for the onset of oxygenation of the atmosphere and oceans, including the massive Kalahari Manganese field that was deposited in the direct wake of the Makganyene Snowball (at 2.22 Gyr ago). This is the oldest unchallenged firm constraint on environmental oxidation (Kirschvink and Kopp 2008).

Alternative scenarios for global oxygenation hold that oxygenic photosynthesis might have evolved much earlier in Earth history, perhaps as far back as 3.8 Gyr ago (Rosing 1999), but that some environmental limitations on their growth kept them from oxidizing the planet until about 2.35 Gyr ago. Evidence in support of this scenario ranges from evidence of uranium mobility in highly metamorphosed black shales from the 3.8 Gyr old Isua province in Greenland (Rosing and Frei 2003), fossil biomarkers thought to require molecular oxygen in their biosynthetic pathways between 2.7 and 2.5 Gyr ago (Brocks *et al.* 1999, Summons *et al.* 1999), and elevated levels of redox-sensitive trace elements like Mo, Re, and various iron phases found in ~2.5 Gyr old cores from various Archean and early Proterozoic scientific drilling programs (Anbar *et al.* 2007).

However, every one of these arguments has cogent counter-arguments. The redox potential required to mobilize uranium⁷ is about the same as the ferric/ferrous couple, and both iron and uranium redox chemistry is done easily by anaerobic biochemistry. The biomarker constraints have been called into

7 Oxidized uranium, U⁺⁶, is soluble, while reduced uranium, U⁺⁴, is insoluble.

question both because of the ability of oils to migrate through porous sedimentary rock (Rasmussen *et al.* 2008), and the fact that many modern oxygen-dependent enzymatic steps in biochemical synthesis have replaced older, anaerobic versions (Kirschvink and Kopp 2008). Finally, all of the black shales that record a supposed “whiff of oxygen” signature (Anbar *et al.* 2007) have been completely remagnetized by subsequent hydrothermal events. As this remagnetization directly affects iron minerals through the growth of sulfide phases, and these in turn are known to scavenge these redox-sensitive trace elements, it is not surprising that the geochemistry could be misinterpreted as “oxygen whiffs.”

Although this is not the place to try to decide which of these two hypotheses is correct, there are some puzzles that need to be resolved. Growth requirements for cyanobacteria are actually rather simple and uniform across all divisions within this bacterial group, and hence were most likely present in their last common ancestor. It is clear that depriving them of the metals needed for growth and nitrogen fixation can provide a powerful check on their ability to oxidize the atmosphere and upper oceans (Fennel *et al.* 2005). However, Kopp and Kirschvink (2005) noted that glacial dust is rich in all trace elements needed for explosive cyanobacterial growth. The quantities of these elements being released into Earth’s oceans today (and during the ice ages for the past 2.5 million years) would have been more than sufficient to make the global environment jump over the nitrate limitation barrier of Fennel *et al.* into their oxic world. Estimates of the severity of the Pongola and Huronian glacial advances indicate that they were more intense than those of the Quaternary (Hambrey and Harland 1981). Hence, if cyanobacteria had evolved prior to either the Pongola (2.9–2.7 Ga) or the first two Huronian glaciations (2.45–2.35 Gyr ago), the “Great Oxygenation Event” should have happened sooner than the rock record suggests.

The final puzzle is a biochemical “chicken and the egg” problem. All oxygen in Earth’s atmosphere today is a product of oxygenic photosynthesis, released by the oxygen evolving complex of Photosystem-II. That complex system depends upon the ability to control the toxic byproducts of oxygen production, particularly the superoxide ($O_2^{\bullet -}$) and hydroxyl (OH^{\bullet}) free radicals, and yet the enzymes that do this clearly required the presence of this poison (O_2) in the environment to evolve in the first place! Although the authors of this chapter are still arguing about the exact mechanism involved, it is most likely that some product of UV light hitting Earth’s surface environment is responsible, either as trace levels of H_2O_2 frozen out onto the surface of ice sheets (Liang *et al.* 2006) or some nitrogen or sulfur-based compounds (Sagura *et al.* 2007). In either case it is worth noting that all known Precambrian glaciations are associated with mineralogical and/or geochemical indicators showing local oxidation increases (Raub and Kirschvink 2008), even though true vertical redox gradients in the sediments – like those

needed to support populations of magnetotactic bacteria – do not appear until after the Makganyene glaciation (Kopp and Kirschvink 2008). It is interesting to speculate that oxygenic photosynthesis might not evolve on Earth-like planets that are too close to their parent stars to have glaciation.

Summary

Although some aspects of Earth's early climate history and the rise of atmospheric O₂ are by now understood, the details of what controlled climate in the distant past and what triggered the rise of oxygen are still being debated. The discussion necessarily involves biologists, geologists, and even astronomers, and hence is a prime research area for the developing field of astrobiology. Understanding how Earth's environment has evolved over time will help us understand biological evolution on our planet and may eventually provide insights into atmospheres that we observe on planets orbiting nearby stars.

References

- Anbar, A. D., Duan, Y., Lyons, T. W. *et al.* (2007). "A whiff of oxygen before the great oxidation event?" *Science*, Vol. 317, pp. 1903–1906.
- Brocks, J. J., Logan, G. A., Buick, R., and Summons, R. E. (1999). "Archean molecular fossils and the early rise of eukaryotes," *Science*, Vol. 285, pp. 1033–1036.
- Canfield, D. E., Rosing, M. T., and Bjerrum, C. (2006). "Early anaerobic metabolisms," *Philosophical Transactions of the Royal Society, Series B: Biological Sciences*, Vol. 361, pp. 1819–1834.
- Crowell, J. C. (1999). *Pre-Mesozoic Ice Ages: Their Bearing on Understanding the Climate System*. Boulder, CO: Geological Society of America.
- Dauphas, N. and Kasting, J. F. (2011). "Low pCO₂ in the pore water, not in the Archean air" *Nature*, Vol. 474, pp. E2–E3.
- Domagal-Goldman, S. D., Kasting, J. F., Johnston, D. T., and Farquhar, J. (2008). "Organic haze, glaciations and multiple sulfur isotopes in the Mid-Archean Era," *Earth and Planetary Science Letters*, Vol. 269, pp. 29–40.
- Evans, D. A., Beukes, N. J., and Kirschvink, J. L. (1997). "Low-latitude glaciation in the Proterozoic Era," *Nature*, Vol. 386, pp. 262–266.
- Farquhar, J., Bao, H., and Thiemans, M. (2000). "Atmospheric influence of Earth's earliest sulfur cycle," *Science*, Vol. 289, pp. 756–758.
- Fennel, K., Follows, M., and Falkowski, P. G. (2005). "The co-evolution of the nitrogen, carbon and oxygen cycles in the Proterozoic ocean," *American Journal of Science*, Vol. 305, pp. 526–545.
- Goldblatt, C., Claire, M. W., Lenton, T. M. *et al.* (2009). "Nitrogen-enhanced greenhouse warming on early Earth," *Nature Geoscience*, Vol. 2, pp. 891–896.
- Gough, D. O. (1981). "Solar interior structure and luminosity variations," *Solar Physics*, Vol. 74, pp. 21–34.

- Hambrey, M. J. and Harland, W. B. (1981). *Earth's Pre-Pleistocene Glacial Record*. Cambridge: Cambridge University Press.
- Haqq-Misra, J. D., Domagal-Goldman, S. D., Kasting, P. J., and Kasting, J. F. (2008). "A revised, hazy methane greenhouse for the early Earth," *Astrobiology*, Vol. 8, pp. 1127-1137.
- Hayes, J. M. and Bengtson, S. (1994). "Global methanotrophy at the Archean-Preoproterozoic transition," in *Early life on Earth*, S. Bengtson (ed.). New York: Columbia University Press, pp. 220-236.
- Hayes, J. M. and Schopf, J. W. (1983). "Geochemical evidence bearing on the origin of aerobiosis: a speculative hypothesis," in *Earth's Earliest Biosphere: Its Origin and Evolution*, J. W. Schopf (ed.). Princeton, NJ: Princeton University Press, pp. 291-301.
- Holland, H. D. (2006). "The oxygenation of the atmosphere and oceans," *Philosophical Transactions of the Royal Society, Series B: Biological Sciences*, Vol. 361, pp. 903-915.
- Holland, H. D. (2009). "Why the atmosphere became oxygenated: a proposal," *Geochimica Cosmochimica Acta*, Vol. 73, pp. 5241-5255.
- Kasting, J. F. (1987). "Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere," *Precambrian Research*, Vol. 34, pp. 205-229.
- Kasting, J. F. (1993). "Earth's early atmosphere," *Science*, Vol. 259, pp. 920-926.
- Kasting, J. F., Zahnle, K. J., and Walker, J. C. G. (1983). "Photochemistry of methane in the Earth's early atmosphere," *Precambrian Research*, Vol. 20, pp. 121-148.
- Kasting, J. F., Howard, M. T., Wallmann, K. et al. (2006). "Paleoclimates, ocean depth, and the oxygen isotopic composition of seawater," *Earth and Planetary Science Letters*, Vol. 252, pp. 82-93.
- Kharecha, P., Kasting, J. F., and Siefert, J. L. (2005). "A coupled atmosphere-ecosystem model of the early Archean Earth," *Geobiology*, Vol. 3, pp. 53-76.
- Kirschvink, J. L. and Kopp, R. E. (2008). "Paleoproterozoic icehouses and the evolution of oxygen mediating enzymes: the case for a late origin of Photosystem-II," *Philosophical Transactions of the Royal Society, Series B*, Vol. 363, pp. 2755-2765.
- Kirschvink, J. L., Gaidos, E. J., Bertani, L. E. et al. (2000). "Paleoproterozoic Snowball Earth: extreme climatic and geochemical global change and its biological consequences," *Proceedings of the National Academy of Sciences of the USA*, Vol. 97, pp. 1400-1405.
- Kopp, R. E. and Kirschvink, J. L. (2008). "The identification and biogeochemical interpretation of fossil magnetotactic bacteria," *Earth-Science Reviews*, Vol. 86, pp. 42-61.
- Kopp, R. E., Kirschvink, J. L., Hilburn, I. A., and Nash, C. Z. (2005). "Was the Paleoproterozoic Snowball Earth a biologically-triggered climate disaster?" *Proceedings of the National Academy of Sciences of the USA*, Vol. 102, pp. 11131-11136.
- Knauth, L. P. (2005). "Temperature and salinity history of the Precambrian ocean: implications for the course of microbial evolution," *Palaeogeography, Palaeoclimatology, Palaeoecology*, Vol. 219, pp. 53-69.

- Kuhn, W. R. and Atreya, S. K. (1979). "Ammonia photolysis and the greenhouse effect in the primordial atmosphere of the Earth," *Icarus*, Vol. 37, pp. 207–213.
- Kump, L. R., Kasting, J. F., and Crane, R. G. (2010). *The Earth System*. Upper Saddle River, NJ: Pearson.
- Liang, M. C., Hartman, H., Kopp, R. E., Kirschvink, J. L., and Yung, Y. L. (2006). "Production of hydrogen peroxide in the atmosphere of a Snowball Earth and the origin of oxygenic photosynthesis," *Proceedings of the National Academy of Sciences of the USA*, Vol. 103, pp. 18896–18899.
- Owen, T., Cess, R. D., and Ramanathan, V. (1979). "Early Earth: an enhanced carbon dioxide greenhouse to compensate for reduced solar luminosity," *Nature*, Vol. 277, pp. 640–642.
- Pavlov, A. A., Kasting, J. F., Brown, L. L. *et al.* (2000). "Greenhouse warming by CH₄ in the atmosphere of early Earth," *Journal of Geophysical Research*, Vol. 105, pp. 11981–11990.
- Pavlov, A. A., Kasting, J. F., and Brown, L. L. (2001). "UV-shielding of NH₃ and O₂ by organic hazes in the Archean atmosphere," *Journal of Geophysical Research*, Vol. 106, pp. 23267–23287.
- Prather, M. *et al.* (2001). "Atmospheric chemistry and greenhouse gases," in *Climate Change 2001: The Scientific Basis*, J. T. Houghton *et al.* (eds.). New York: Cambridge University Press, pp. 239–288.
- Prentice, I. C., Farquhar, G. D., Fasham, M. J. R. *et al.* (2001). "The carbon cycle and atmospheric carbon dioxide," in *Climate Change 2001: The Scientific Basis*, J. T. Houghton *et al.* (eds.). Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. New York: Cambridge University Press, pp. 183–238.
- Rasmussen, B., Fletcher, I. R., Brocks, J. J., and Kilburn, M. R. (2008). "Reassessing the first appearance of eukaryotes and cyanobacteria," *Nature*, Vol. 455, pp. 1101–1104.
- Raub, T. D. and Kirschvink, J. L. (2008). "A pan-Precambrian link between deglaciation and environmental oxidation," in *Antarctica: A Keystone in a Changing World*, A. K. Cooper, P. Barrett, B. Story, E. Stump, and W. Wise (eds.). Washington, DC: National Academy Press, pp. 83–90.
- Roscoe, S. M. (1969). *Huronian Rocks and Uraniferous Conglomerates in the Canadian Shield*, Geological Surveys of Canada Paper 68–40.
- Rosing, M. T. (1999). "¹³C-depleted carbon microparticles in >3700-Ma sea-floor sedimentary rocks from West Greenland," *Science*, Vol. 283, pp. 674–676.
- Rosing, M. T. and Frei, R. (2003). "U-rich Archean sea-floor sediments from Greenland – indications of >3700 Ma oxygenic photosynthesis," *Earth and Planetary Science Letters*, Vol. 6907, pp. 1–8.
- Rosing, M. T., Bird, D. K., Sleep, N. H., and Bjerrum, C. J. (2010). "No climate paradox under the faint early Sun," *Nature*, Vol. 464, pp. 744–747.
- Rye, R., Kuo, P. H., and Holland, H. D. (1995). "Atmospheric carbon dioxide concentrations before 2.2 billion years ago," *Nature*, Vol. 378, pp. 603–605.
- Sagan, C. and Chyba, C. (1997). "The early faint Sun paradox: organic shielding of ultraviolet-labile greenhouse gases," *Science*, Vol. 276, pp. 1217–1221.

- Sagan, C. and Mullen, G. (1972). "Earth and Mars: evolution of atmospheres and surface temperatures," *Science*, Vol. 177, pp. 52–56.
- Sagura, A., Meadows, V. S., and Kasting, J. *et al.* (2007). "Abiotic production of O₂ and O₃ in high-CO₂ terrestrial atmospheres," *Astrobiology*, Vol. 7, pp. 494–495.
- Sheldon, N. D. (2006). "Precambrian paleosols and atmospheric CO₂ levels," *Precambrian Research*, Vol. 147, pp. 148–155.
- Summons, J. R., Jahnke, L. L., Hope, J. M., and Logan, G. A. (1999). "Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis," *Nature*, Vol. 400, pp. 554–557.
- Ueno, Y., Yamada, K., Yoshida, N. *et al.* (2006). "Evidence from fluid inclusions for microbial methanogenesis in the Early Archean Era," *Nature*, Vol. 440, pp. 516–519.
- Valley, J. W., Peck, W. H., King, E. M., and Wilde, S. A. (2002). "A cool early Earth," *Geology*, Vol. 30, pp. 351–354.
- van den Boorn, S. H. J. M., van Bergen, M. J., Nijman, W., and Vroon, P. Z. (2007). "Dual role of seawater and hydrothermal fluids in early Archean chert formation: evidence from silicon isotopes," *Geology*, Vol. 35, pp. 939–942.
- von Paris, P., Rauer, H., Lee Grenfell, J. *et al.* (2008). "Warming the early Earth – CO₂ reconsidered," *Planetary and Space Science*, Vol. 56, pp. 1244–1259.
- Walker, J. C. G. (1977). *Evolution of the Atmosphere*. New York: Macmillan.
- Walker, J. C. G., Hays, P. B., and Kasting, J. F. (1981). "A negative feedback mechanism for the long-term stabilization of Earth's surface temperature," *Journal of Geophysical Research*, Vol. 86, pp. 9776–9782.
- Wolf, E. T. and Toon, O. B. (2010). "Fractal organic hazes provided an ultraviolet shield for early Earth," *Science*, Vol. 328, pp. 1266–1268.
- Woese, C. R. and Fox, G. E. (1977). "Phylogenetic structure of the prokaryotic domain: the primary kingdoms," *Proceedings of the National Academy of Science of the USA*, Vol. 74, pp. 5088–5090.
- Young, G. M. (1991). *Stratigraphy, Sedimentology, and Tectonic Setting of the Huronian Supergroup*. Report of Annual Meeting, Toronto, 1991, Field Trip B5, Guidebook, Toronto: Geological Association of Canada.
- Young, G. M., von Brunn, V., Gold, D. J. C., and Minter, W. E. L. (1998). "Earth's oldest reported glaciation; physical and chemical evidence from the Archean Mozaan Group (~2.9 Ga) of South Africa," *Journal of Geology*, Vol. 106, pp. 523–538.