

10.1 The Early History of Life

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10.1.1 Introduction

10.1.1.1 Strangeness and Familiarity – the Youth of the Earth

The youth of Earth is strange. Many of the most fundamental constraints on life may have been different, especially the oxidation state of the surface. Should people suddenly land on its Hadean or early Archean surface by some sci-fi accident, people would not recognize their home nor even be able to breathe. Overhead, the sky may have been green or some other unworldly color, and above that the weak young Sun unrecognizable to someone trying to identify it from its spectrum. Below, geophysical tests would show a hot, comparatively low-viscosity interior (Arndt and Nisbet, 2012). The core was present (Wood and Halliday, 2010), though perhaps rather smaller than today. The continents may have been small islands in an icy sea, mostly frozen with some leads of open water (Sleep et al., 2001). Into these icy oceans, huge protruding Hawaii-like volcanoes would have poured out vast far-spreading floods of komatiite lavas in immense eruptions that may have created sudden local hypercane storms to disrupt the nearby icebergs. And meteorites would rain down.

Or perhaps it was not so strange nor so violent. The child is father to the man; young Earth was mother to old Earth. Earth had hydrogen, silicate rock below and on the surface abundant carbon, which her ancient self retains today. Moreover, Earth was oxygen-rich, as today. Today, a tiny part of the oxygen is free, as air; then the oxygen would have been in the mantle, while the surface oxygen was used to handcuff the hydrogen as dihydrogen monoxide. Oxygen dihydride is dense, unlikely to fly off to space, and at the poles, hydrogen monoxide is rock-forming. Of all the geochemical features that make Earth unique, the sustained presence of liquid water is the defining oddity of this planet. Volatile degassing (Genesis 2:6) would have happened on all inner planets, but Earth kept its hydrogen and its water. Earth probably also kept much of its carbon, nitrogen, and sulfur as oxide or hydride.

After ~4.4 Ga ago, when the most cataclysmic events had passed (Halliday, 2000, 2001 see also Chapter 2.8), for the most part, the planet was peaceful. Even the flanks of the most active great volcanic plumes are very habitable (a Treatise editor does live in the state of Hawaii). For single-celled life, volcanic eruptions are a minor evolutionary challenge. Meteorites large enough to extinguish all dinosaurs may have hit as often as every few thousand years, but this is not enough to be a nuisance to a bacterium (except when the impact boiled the ocean); while to the photosynthesizer, long-term shifts in the solar spectrum may be less of a problem than cloudy hazy days. Even if the sky were hazy, it would have had useful wavelengths in its spectrum. Admittedly, green is junk light to

modern biology, the excretion from the photosynthetic antennae, but early Earth would have had reds and infrareds also, excellent when photosynthesis was in its infancy. This planet, then, had possibilities.

Most important of all, like all good houses, this planet had location: Earth was just in the right spot. Not too far from the faint young Sun (Sagan and Chyba, 1997; Sagan and Mullen, 1972), it was also far enough away still to be in the comfort zone (Kasting et al., 1993) when the maturing Sun brightened (Zahnle and Walker, 1982). As many have pointed out when Goldilocks arrived, she found everything just right. But what is less obvious is that as she grew and changed and the room changed too, Goldilocks commenced to rearrange the furniture to make it ever righter for her. Thus far, the bears have not arrived, though they may have reclaimed Mars from Goldilocks's sister (see Figure 1).

10.1.1.2 Evidence in Rocks, Moon, Planets, and Meteorites – the Sources of Information

The information about the early history of life comes from several sources: ancient relics, modern descendants, and models. The ancient material is in rocks, in meteorites, in what people can learn from other planets, and in solar system and stellar science. The Lucretian view of a planet, ramparts crumbling with age (Lucretius, circa –60, 1994) may apply to Mars, but as Hutton (1795) realized, virtually all of the surface of Earth is renewed every few hundred million years, and if it were not so, life would die from lack of resources.

But in the tiny fragment that has not been renewed, relics of early life remain. It is these relics that attract the geologist. Some of them are direct – specks of carbon or structures of biogenic origin. Other relics are indirect – changes in the isotopic ratio of inorganic material or oxidation states of material that is of inorganic origin. Yet other information is simply scene-setting: evidence, for example, that water was present or that volcanism was active.

Extraterrestrial sources of evidence are also important. From Venus, there is evidence that a planet can have water oceans and then lose all its hydrogen (Donahue et al., 1982; Watson et al., 1984). From Mars, there is evidence that planets can die geologically and can become unable to renew their surface by tectonics and volcanism. Perhaps they can also die biologically. From moons of outer planets come evidence that a wide variety of early conditions was possible. Meteorites (Ahrens, 1990; Taylor, 2001) provide clear signs that in the early part of the history of the solar system, there could have been significant exchange of surface material between the inner planets. Study of the Sun and of sunlike stars demonstrates that even stable stars do change, and over the past 4.6 billion years, the Sun has significantly increased in power (Sagan and Chyba, 1997) and has altered in spectrum.

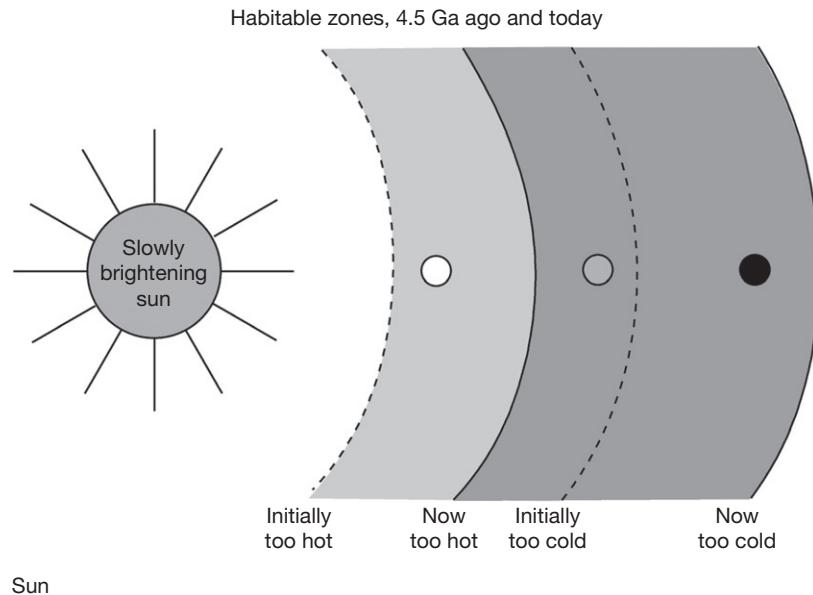


Figure 1 The habitable zone (Kasting et al., 1993). Too close to the Sun, a planet's surface is too hot to be habitable; too far, it is too cold. Early in the history of the solar system, the Sun was faint and the habitable zone was relatively close; 4.5 Ga later, with a brighter Sun, planets formerly habitable are now too hot, and the habitable zone has shifted out. Note that even given a constant star, boundaries can shift. By changing its albedo and by altering the greenhouse gas content of the air, the planet can significantly widen the bounds of the habitable zone (Lovelock, 1979, 1988).

10.1.1.3 Reading the Palimpsests – Using Evidence from the Modern Earth and Biology to Reconstruct the Ancestors and their Home

'Ontogeny,' the old saying went, 'recapitulates phylogeny.' Each human starts as a couple of lengths of DNA, one loose with a few attendants, the other comfortable in a pleasant container full of goodies, itself held in a warm and safe maternal universe. The DNA-, the RNA-based processing, the information-transfer systems, and the protein machinery of the cell all carry historical information. Every human cell lives in its own seawater – the blood – people's version of a warm kindly Archean ocean. Every oxygen-handling blood cell carries iron: people learned this trick in some setting where their ancestors could acquire iron, surely without the sophisticated metal-gathering equipment that is provided by modern biochemistry. At the very heart of the information transfer in the cell is the ribosome: this massive (compared to other enzymes) RNA-based superenzyme in a strange way is both chicken and egg. Though much modified by evolution, it is surely of the very greatest antiquity.

Modern life comes in very many forms: animals, plants, and single-celled eukaryotes in the Eukarya domain; prokaryotes in two great domains, archaea and bacteria (Woese, 1987; Woese et al., 1990); and not-life viruses (Moreira and Lopez-Garcia, 2009). Some not-life is even anthropogenic: the wild-type polio virus that used to be found in water bodies is now replaced in the pools and rivers of America and Europe by the altered vaccine-type virus. From all this information, deductions can be made. Clearly, multicelled life came from single-celled life; less obviously but most probably, each of the cells carries mitochondria that are descended from symbiotic purple bacteria. Plants, in addition, carry chloroplasts that are descended from partner cyanobacteria: indeed, from the

bacterial point of view, plants and animals are simply 'spacesuits' – survival structures to allow bacteria to live on dry land or, indeed, visit the Moon.

There is an enormous wealth of molecular information that is only partly deciphered. Indeed, the molecular record (Zuckerkandl and Pauling, 1965) may be the best route to the understanding of Archean palaeontology. Geological study interacts with this, both by calibrating the relative timing of the evolutionary steps (e.g., by dating the arrival of the multicelled organisms) and secondly by identifying the impact of each step (e.g., the onset of oxygenic photosynthesis). Both molecular and rock-based studies are needed: without calibration by the information and dating held in the rocks, molecular evidence can lead to (and has done so) very erroneous deduction; equally, the geological evidence cannot of itself give much detail about major steps. But there is also a danger of circularity of reasoning: just because something looks plausible biochemically, it is possible to reinterpret the geological evidence to fit, but wrongly; conversely, weakly supported geological models can, on occasion, unduly sway interpretation of complex and nonunique molecular evidence.

10.1.1.4 Modeling – The Problem of Taking Fragments of Evidence and Rebuilding the Childhood of the Planet

Model building is part of all science: lovely falsifiable hypotheses are built and then broken on the cold facts. Certain key components are common to all models of life's origins – water (though not necessarily in an ocean: aerosols are possible hosts of proto-life); inorganic supplies of thermodynamic drive (i.e., interface settings where two or more different conditions are accessible); and ambient temperatures in the 0–110 °C range.

Models of the early history of life come in two broad categories – models of the origin and first development of life itself (e.g., [Lane et al., 2010](#)) and models of the environmental settings of that life (e.g., [Sleep, 2010; Sleep et al., 2011](#)). The geologist can contribute much more to the second class of model than to the first: from the geological evidence, it is possible to make reasonable models of the early planets, including their surface condition and the supply of chemicals and nutrients from the interior and from space.

All information is fragmental, and the further back in time, the less the information. But enough is left that reasonable guesses may be made about the surface conditions of the four inner planets and the Moon as they evolved in the first two billion years of the solar system's history. These models set the scene for the biochemists: without them, the biochemical deductions can be unconstrained and can be wrong (e.g., a thick primaeval 'soup' is geologically very unlikely). Thus, the debate over the various models of origin is avoided here: for that, seek out google.com. The focus instead is on what geologists and geochemists can usefully contribute.

10.1.1.5 What Does a Planet Need to be Habitable?

Venus may have been in the right place once and is the right size, with a hot interior producing much volcanism, but in the long term, it was too close to the Sun. Mars may be in a tolerable place ([Nisbet et al., 2007b](#)) and on occasion had liquid water on its surface ([Baker, 2001; Carr, 1996](#)), but it has a small heart, almost dead of cold. Only Earth has a location suitable for long-term occupation and is large enough to keep a hot active interior.

What are the requirements? First, liquid water. It is difficult to imagine biology that does not include water. Nonbiological life may be possible (indeed, someday, computers may lead to an inorganic waterfree sentience that achieves genetic takeover from organic life) but not in nature as people presently know it. Externally, the planet needs to be far enough from the Sun not to overheat and close enough not to freeze entirely. The allowable bounds of the habitable zone ([Kasting et al., 1993](#)) are wide at any one moment, given the range of temperature control provided by changes in atmospheric greenhouse heat trapping.

But these bounds of habitability progressively shift outward as the Sun evolves and brightens. Thus, early in the history of the solar system with a faint young Sun, Venus was probably within the bounds of the habitability zone and was covered by oceans. But today, it may be too close to the bright old Sun to allow life. Even if water were added, it would be difficult to sustain liquid water on the planet with any plausible life-supporting atmosphere. However, that is not to say it is uninhabitable: someday, humanity may well add water supplies from an outer solar system source and may hang aluminum foil mirrors around the planet to reduce sunlight input. Mars, alternatively, is too cold to sustain liquid water but could, in future, be warmed by chlorofluorocarbon and methane greenhouse gases, such that it sustained puddle oceans.

These thought experiments with Venus and Mars demand teleological action not possible in Darwinian evolution, but there are persuasive arguments that feedbacks from nonteleological life have carried out very similar processes on Earth over

4 Ga ([Lovelock, 1979, 1988; Lovelock and Margulis, 1974](#)). Indeed, it is possible that the composition of the Earth's atmosphere over the past 2.9 Ga has been regulated by an evolutionarily stable set of feedback controls ([Nisbet et al., 2012](#)).

Planets need to be geologically active to sustain life over long periods, or they cannot provide the necessary supply of mineral nutrients. Nature needs to renew her face continuously or the chemical and thermodynamic resources behind life, especially early life, are rapidly exhausted. For example, DNA-based life is built on phosphates. If the available surface phosphorus supply is exhausted and not renewed continually by volcanism and tectonics, then life must become hungry for phosphorus and eventually die out. Life depends on a small number of essential housekeeping proteins, and many of these proteins use metals: if the geological metal supply ended, the proteins would not be formed and life would be unsustainable. This need for 'supply' places constraints on the physical evolution of a planet, if it is to be capable of sustaining life over many aeons. Planets vary ([Taylor, 2001](#)). The Moon is too small. It was once active but now has died. Mars is just about dead. Mercury may once have been larger but now seems to be a barren metal-rich relict of the innards of a planet. Jupiter and the outer gas giants are too large. Some of the tidally heated great moons (some with radii comparable to Mars) of the gas giants do remain very active geologically and offer possible future homes in an elderly solar system ([Zahnle et al., 2007](#)). But of the internally warm and hence geologically active bodies that also have a Sun-warm outer surface, only Earth and Venus are just the right size.

10.1.1.6 The Power of Biology: The Infinite Improbability Drive

What is just right in one moment becomes wrong in the next. The porridge that Goldilocks tasted would have been perfect in the first mouthful, but a little later, especially if she ate slowly as her mother would have taught her, it would have cooled.

Biology has the power to sustain, to draw out its environmental conditions ([Lovelock, 1979, 1988](#)), and indeed to remake them in an improbable path. Swiss travelers do not descend peaks by jumping over the cliffs. Instead, they use cable cars, and as they descend, they help others to ascend: only a small input of energy is needed to overcome frictional losses. Indeed, consider a hypothetical cable car that had an attached snowtank filled from a snowfield at the top. At the bottom, the snow would be dropped off so that the rising car was always somewhat lighter than the descending car. This system could work without extra input perpetually carrying tourists up to the peak and down again, as the potential energy transfer would make up for the frictional losses. Indirectly, this is solar power: the Sun lifts the water, evaporating it from the bottom and replacing it back on the top as snow.

Most microbial processes are like that – they move enormous numbers of traveling chemical species on cogways up and down the thermodynamic peaks and valleys, with only small extra inputs of externally sourced energy. Moreover, at the intermediate stations partway up (or down) the peaks, the microbial processes link with innumerable smaller cable car systems that scatter metabolic tourists around the ecological mountainsides in a complex web of ascents, descents,

and lateral movements. Thus, biology creates local order, primarily by using the high quality of sun-given energy, to exploit and to create redox contrast between the surface of Earth and its interior.

10.1.2 The Chaotian and Hadean (~4.56–4.0 Ga Ago)

10.1.2.1 Definition of the Chaotian

Aeons are the largest divisions of geological time: Hadean, Archean, Proterozoic, and Phanerozoic. Goldblatt et al. (2009) sought to define the Chaotian aeon, from the first events that marked the start of the solar system to the cataclysmic collision that led to the formation of the Moon. The Chaotian aeon is defined as applying to the entire solar system. From its end, each planet has separate chronostratigraphy.

The start of the Chaotian, as defined by Goldblatt et al. (2009), is the beginning of the solar system, when the first significant planetesimals collected to begin the accretion. The time of formation of the oldest material in meteorites is conventionally taken to be representative of the start of accretion. Bouvier and Wadhwa (2010) report ^{207}Pb – ^{206}Pb evidence from a calcium–aluminium-rich inclusion in a meteorite, which suggests the inclusion formed 4.568 my ago. Very roughly then, the start of the solar system can be placed at 4.57 Ga, where 1 Ga is 1000 my (10^9). The end of the Chaotian and the start of the Hadean is placed at the time of the giant impact that led to the formation of the Moon. The Moon-forming event is thought to have been at a time close to 4.5 Ga ago (Halliday, 2001). This occurred relatively late in accretion, more than 30 Ma after the start of the solar system (Halliday, 2012; Halliday and Wood, 2009; Wood and Halliday, 2010; Yu and Jacobsen, 2011).

Goldblatt et al. (2009) suggest two Chaotian eras. In the Eochaotian, the solar nebula became a closed system, which contained the agglomeration of the solar system constituents from the solar nebula. Initially, the solar nebula was a cloud, from which the proto-Sun formed, but was yet to be luminous. The Neochaotian Era begins with the first light from the Sun. Gravitational collapse made the Sun's first light brighter than its subsequent main sequence. Collision of proto-planets occurred to form larger planets. Among these initial planets in the inner solar system was a Mars-sized body, named Theia (Halliday, 2000). This planet collided 4.5 Ga ago, with the proto-Earth, named Tellus by Goldblatt et al. (2009), which was then about the size of modern Venus. This giant impact created both the modern Earth and also the Moon, which accumulated from some of the ejecta that did not fall back to the main planet. This event is taken by Goldblatt et al. (2009) as the end of the Chaotian and the start of the Hadean.

10.1.2.2 Definition of the Hadean

The Hadean aeon includes, broadly, the time from about 4.5 Ga ago to about 4 Ga ago and is the first of the four aeons of history specific to Earth (Goldblatt et al., 2009; Nisbet, 1991). The Hadean includes the time from the impact that led to the formation of Earth–Moon system to the end of the aeon, when Earth had become an ordered, settled planet, with a cool surface under oceans and atmosphere, and with a hot

active interior mantle and core. The Hadean is ‘short’ compared to the other Precambrian aeons (if 500 Ma can be called short); the middle two aeons are billions of years long.

The start of the Hadean is a moment, about 4.5 Ga ago (Halliday, 2001), after which the bulk of Earth had accreted, including material both from the proto-Earth and for the late giant impactor. The end of the Hadean is more difficult to define, though the definition is more useful to the geologist, as this is within the terrestrial geological record. For the interim, as a rough guide, 4 Ga is used by many geologists. An alternative choice could be around 3.9 Ga (see discussion in Goldblatt et al., 2009). Fortunately, at present, the best guess for the origin of life is also ‘somewhen around 4 Ga ago.’

10.1.2.3 Building a Habitable Planet

The solar system accreted from a dust cloud, formed after a supernova explosion. From this primitive solar nebula condensed the Sun and the planets. This process is reviewed by Righter and O’Brien (2011). Among the oldest objects in the solar system yet found are Ca–Al-rich inclusions in meteorites, ~4.57 Ga old (Allegre et al., 1995; Bouvier and Wadhwa, 2010). It is possible that these grains predate the solar nebula and may have been formed in the expanding envelope of the supernova explosion (Cameron, 2002).

The formation of planetesimals may have been very rapid after the initial formation of the solar nebula. Objects as large as Mars would have grown within 10^5 years (Weatherill, 1990). The core of Mars may have formed as early as within 13 my. The core of the asteroid Vesta may have formed within only 3–4 my, and lava flows on its surface may have occurred at this time also (Yin et al., 2002). Bodies like Vesta would have collided rapidly, aggregating their cores to form larger planetoids and then planets.

The special events of our planet’s accretion (Ahrens, 1990; Newsom and Jones, 1990; Taylor, 2001; Weatherill, 1990) were crucial in making Earth habitable over billions of years. Segregation of the core physically separated reduction power in the iron-rich center of Earth, from a more oxidized mantle. Simultaneously, the early events controlling the surface environment made possible the development of a habitable ocean/atmosphere system. The date of core formation in Earth remains controversial but may have been as little as 30 my or less after the birth of the solar system (Kleine et al., 2002). Yin et al. (2002) suggest that the aggregation of the Earth’s core began within 29 my. However, Wood and Halliday (2010) showed from Pb isotopes that partitioning into Earth’s core took place throughout accretion, including some late addition at the time of and after the Moon-forming impact.

The most important single physical event was the Moon-forming impact, roughly 4.5 Ga ago. At this stage, proto-Earth (named ‘Tellus’ by Goldblatt et al., 2009) was probably a substantial fraction of its present mass, with a segregated core. Sunward of Earth, Venus and Mercury had formed; outward, were Mars-like planets. Then, the Earth suffered its largest collision: a defining moment in habitability. One model is that a planet at least double the mass of Mars hit a half-formed Earth in a double collision (Cameron, 2002); the alternative model mentioned above is that Theia, a Mars-sized body, hit the 90%-formed Earth (Canup and Asphaug, 2001; Halliday,

2000, 2001). When the impact took place, the Earth was transformed. Internally, it is likely that the entire planet would have become molten, even if primordial radiogenic and infall heat had not already melted it. The already-formed iron core of the impactor would have crashed to the center to join the core of the Earth. This large core, with its solid center and molten outer region, gave Earth its distinctive magnetic field, and life-protecting Van Allen belts. Arguably, planets without a strong protective field (e.g., Venus) are initially uninhabitable as the surface environment may be too severe for unstable early genomes.

The surface of Earth was completely changed. Any deep primordial atmosphere/ocean, possibly rich in noble gases, would have been removed by the impact. Presumably, the event was followed by further cometary infall and further degassing from the interior to produce our present thin, water-dominated inventory of volatiles. By this stage, the inner solar system was probably swept clear of volatiles and was a relatively gas-poor environment. Volatile influx would have come perhaps in larger planetesimals infalling from the outer solar system.

The mechanical effect of the impact was that Earth was tilted, creating winter and summer. This is very important in distributing heat evenly across the surface, as the intensity of solar radiation falling on any particular place varies in the annual cycle. Even more important for the habitability of the Earth is the spin: much faster immediately after the impact but now slowed by aeons of tidal friction to give the 24 h day. Thus, there is no hot eternal dayside and cold eternal nightside, but an even illumination. Moreover, the night-day cycle allows a variety of photosynthetic/respiratory cycles in cells and contributes greatly to the diversity of biota. Milton is thus incorrect in seeing this event as a punishment (Paradise Lost X:668):

Some say he bid his angels turn askance
The poles of Earth twice ten degrees and more
From the Sun's axle; they with labour push'd
Oblique the centric Globe...

The Moon was created from the mantle-derived ejecta. Physically, over the aeons, this may have played a useful sheltering role in protecting the planet from some meteorite impacts. Arguably more important, the presence of the Moon leads to the tides. These create the intertidal and near-subtidal habitat with rapidly varying geochemical settings, from wet submarine to dry subaerial, in which sediment is repeatedly flushed with fluid. Such cyclically varying habitats may have been vital in the early evolution of microbial biofilms and, eventually, microbial mats.

Other planets had varying histories (Taylor, 2001). Mercury also had a major collision, possibly being hit by an object ~ 0.2 Mercury masses, removing much of its silicate mantle and leaving a planet of high intrinsic density, with a major core and a thin rocky mantle, an uninhabitable planet. Mars and Venus had kinder gentler histories. On neither did a great impact eject splat; neither planet gained a significant Moon. Though subject to geological or impact catastrophe, both planets evolved sustainable systems within the constraints of kinetics and the thermodynamics of equilibrium; only Earth produced an intrinsically unsustainable disequilibrium system.

On Mars (a tenth of Earth mass and 38% of its radius), the present water inventory is much less than on Earth, enough to cover the planet to a few tens of meters: puddle oceans (Carr, 1996). Nisbet et al. (2007b) discussed potential habitats for life on Mars: by comparison with Earth, there are many potential environmental settings on Mars in which life may once have occurred or may even continue to exist. On Venus, which must have been very nearly the Earth's twin prior to the giant impact on Earth (0.815 modern Earth mass, 95% of its radius), the atmosphere evolved to its present runaway CO₂ greenhouse. There has been much speculation about early Venusian oceans, perhaps some kilometers deep, but possibly only a few meters if Venus formed too close to the Sun to inherit a large water inventory (see Taylor, 2001 for a brief summary of this dispute).

Zahnle et al. (2007) have summarized the events that took place after the Moon-forming impact, when Earth was left with a hot silicate atmosphere. This condensed as it cooled quickly over a brief span of the order of 1000 years. Simultaneously, Earth degassed volatiles into the air, which was changed from silicate (rock vapor) to hot gases, especially steam, that thermally blanketed Earth. Below this blanket, the magma eventually cooled, perhaps over ~ 2 my, to solidify on the surface. Once it had solidified, the new crust acted as an insulator, allowing the steam atmosphere to cool. Thereafter, surface temperature would be governed by how fast CO₂ was removed from the air by hydrothermal carbonation of the oceanic crust (Sleep et al., 2001, 2011; Zahnle et al., 2007). If this was rapid, within 10–100 my after the Moon-forming impact (Sleep et al., 2011), the surface thereafter could have been cold and icy, with thick ice caps blanketing and insulating the deeper liquid-water oceans, warmed from below by geothermal heat and trapped by the insulating ice. Mantle degassing continued, likely emitting a range of S gases including H₂S and carbon gases, such as CO, CO₂, and N₂ (Kasting, 1993). The oxidation state of the mantle may have been similar to modern mantle (Canil, 1997).

The main part of the accretion of Earth can be considered complete by ~ 4.45 Ga. By this stage, most of what now makes up Earth was in place. The then much nearer Moon orbited close by. Earth would have been molten except for a thin rocky outer crustal capace, possibly of broadly basaltic composition (komatiitic basalt or even komatiite). An early magma ocean may have existed in the deeper part of the upper mantle (Drake and Righter, 2002; Nisbet and Walker, 1982). Within the Earth, ongoing late precipitation of the core may have continued, with reaction between the water in the mantle and the infalling iron, adding oxygen to the iron and giving a mantle source of hydrogen that may have made its way eventually to the surface via mantle plumes and thence volcanoes.

The composition of Earth is unique, subtly different from the other rocky planets, and this suggests that different parts of the material of the inner solar system went to make each planet (Drake and Righter, 2002). The origin of Earth's water is particularly interesting (Yung et al., 1989). A significant fraction of Earth's early hydrogen endowment may have been lost to space in short-lived steam greenhouse events. Seawater has a D/H ratio of 150×10^{-6} in contrast to Mars water which has D/H of 300×10^{-6} . Perhaps, Mars lost more hydrogen to space, enriching D, but it also may be possible that the Martian interior has

water of very different D/H, since cooler Mars has outgassed less than Earth. One possibility is that temperatures were high in the inner part of the accretion disk: thus the Earth may have accreted as a dry planet, with water and carbon compounds delivered after the main accretion by comets and meteorites. Alternately, Earth did, indeed, accrete with a significant water content, and some geochemical evidence suggests the early magma ocean was hydrous (Drake and Righter, 2002).

Arndt and Nisbet (2012) suggest that from 4.4 to about 4 Ga ago, the planet may have been widely covered by lava flows that erupted under a deep but ice-covered ocean. There were likely continental nuclei (see below), but these may have been largely flooded. Kamber et al. (2005) and Kamber (2007) estimated heat production in Archean continental crust was 3–4 times greater than today, and presumably, even more so in the Hadean. In a generally hotter regime, the continental crust may have been more ductile and weaker than today, and not capable of sustaining high mountain ranges. Any exposed land could have been subject to acid rainfall in the high-CO₂ air, but (depending on the strength of the atmospheric greenhouse) the world may have been cold and very dry under the faint sun. In the water, however, there would have been habitable regions, both in deep water circulating around widespread hydrothermal systems and in shallow water made liquid around volcanoes.

The late Hadean Earth (say 4.2 to 4 Ga ago) was thus very unusual among the inner rocky planets in terms of its Moon, spin, tilt, likely magnetic field, and especially in its inventory of water and its location in the ‘habitable band.’ Such a planet is not improbable, given the allowable common accidents of accreting planets by collision, but perhaps may be found to be rare as knowledge of distant extrasolar planetary systems increases.

10.1.2.4 The Hadean Geological Record

The Jack Hills and the Mt. Narryer, Western Australia. Some of the oldest material found on Earth consists of a few crystals of detrital zircon (Figure 2) that are now preserved in quartzites in the Mt. Narryer and the nearby Jack Hills area, Western Australia (Compston and Pidgeon, 1986; Halliday, 2001; Maas et al., 1992; Wilde et al., 2001). The host sediment is ~3.3–3.5 Ga old, but some of the zircons themselves are up to 4.2–4.4 Ga old. There are several implications of the discovery. First, (also shown in many other successions) that about 3.3 Ga ago, in the mid-Archean, there was already old continental crust being eroded and redeposited by water. Secondly abundant zircons are typical of rocks broadly characteristic of continental crust. This line of reasoning thus suggests granitoid rocks and continental crust were present in the Hadean. Intuitive reasoning would suggest komatiitic and basaltic rocks would be expected to be typical of 4.4 Ga ago crust, rather than granitoids, but the existence of Hadean zircons implies otherwise, at least locally in what is now Western Australia. Moreover, to form granitoid nowadays, subduction of old hydrated oceanic plate is needed: water is needed to make granites, and subduction is needed to supply the water (Campbell and Taylor, 1983). Did subduction occur as early as 4.4 Ga ago, and did oceans of water exist to hydrate the crust? Oxygen isotope evidence (Mojzsis et al., 2001; Wilde et al., 2001) supports the deduction that oceans of liquid water were indeed present. The zircons contain isotopically heavy



Figure 2 Zircon grain, in part ~4.3 Ga old (Compston and Pidgeon, 1986). Jack Hills, Western Australia. Scale bar is 100 µm long (with thanks to W. Compston).

oxygen: suggesting derivation from liquid surface water. Sleep et al. (2011) consider that there was an early CO₂-rich atmosphere, which carbon was rapidly subducted in the first ~100 Ma or less. This is a speculation, and just as one swallow does not make a summer, one zircon does not make either a continent or an ocean of water (Moorbath, 1983). Yet the question remains open: did the Hadean continents exist, and oceans, and were hydrothermal systems present on continental land surfaces around andesitic volcanoes fed by water-mediated subduction?

Acacia Gneiss, Canada. Among the next oldest rocks is the Acacia Gneiss, close to 4 Ga old (Bowring et al., 1989). This is a rock, of sorts, though highly deformed and metamorphically recrystallized. The oldest rocks form a small part of a 20 km² terrain of old rocks. There are various such terrains worldwide: examples include the Nain province in Labrador (~3.9 Ga), the Napier complex in Antarctica (up to ~3.7 Ga), and the Narryer complex, Australia (host rock up to ~3.7 Ga, hosting the older zircons). Some of these terrains are up to several thousand square kilometers, though the datable older rocks may only be a small proportion of the whole. The implication is that massifs of continental crust at least up to the size of, say, Luxembourg or Rhode Island existed in the latest Hadean and earliest Archean.

Nuvvuagittuq (Porpoise Cove), Canada. Nd isotopic evidence has demonstrated that the series of 3.8 Ga old metavolcanic and metasedimentary rocks in the Nuvvuagittuq region, Canada, were derived from still older Hadean (>4 Ga) continental crustal sources (O'Neil et al., 2007). The supracrustals include mafic and ultramafic rocks, oxide- and quartz-rich iron formations, and possible conglomerates (David et al., 2009).

10.1.2.5 When and Where Did Life Start?

Enough has been said of the origin of life to show that the problem is as far from solution as it was in Charles Darwin's time. The debate continues (Line, 2002). The geologist can make little contribution to this debate, except to point out possible habitats where the first life could have been born.

There are many possibilities: in the air, in the sea, on the shallow seafloor, on the deep seafloor, near on-land hydrothermal systems around andesite volcanoes (variable, intermediate to low pH), near on-land hydrothermal systems around komatiite volcanoes and hot ultramafic rocks (alkaline), near deep-water hydrothermal systems (acid), near carbonatite-driven hydrothermal systems (which could be phosphorus-rich), in hydrothermal systems under ice caps, in shallow-water tidal muds, and anywhere else that is fancied. The key essential for life is the presence of water. For life to begin, local meltwater around a volcano is arguably enough.

There are five planets on which life could have begun (Nisbet and Sleep, 2001, 2003). Earth is the most likely, as it is the only place where Cartesian logic suggests life exists today. Next most likely on the list is Mars, which could at one stage have had an early wet environment under a strong greenhouse. Mars would have been hit by many impacts capable of ejecting relatively unshocked rocks that could have carried a living cell to Earth, surviving the transit frozen in space. There would have been a numerically vast early flux of such rocks in the Hadean, and it is thus very reasonable to infer that if Mars had been habitable (e.g., see Nisbet et al., 2007b) and life had indeed begun on Mars, it would have been transferred to Earth. The logic that applies to Mars also applies to Venus, except that it is a very much deeper gravity well, and thus the outward flux of ejecta would have been much less and those ejecta would be more shocked. The Moon is a possible though unlikely candidate, early on. Finally, a candidate is Theia, the postulated impactor planet that hit the Earth. This Mars-sized object could have hosted life. On the great impact, ejected cells could have gone into space, either seeding Mars or much later falling back to Earth or new Moon. The most likely first homes are Earth or Mars; the other candidates are varying shades of improbable, only entertained because life is itself so improbable.

There is no direct evidence for the existence of life before 4 Ga ago. Even if a living organism had appeared in the very early history of the planet, life might have been obliterated within a few million years, killed in the intense Hadean bombardment. This was a time when from time to time (say every few million to tens of millions of years), large meteorite impact events would have occurred that so heated the oceans and the atmosphere as to make the Earth briefly uninhabitable, sterilized at several hundred °C (Sleep et al., 2001). However, and that said, it is also possible that the early Hadean, tens to

100 Ma after the Moon-forming impact, may have offered a surprisingly favourable prebiotic setting in which life could have begun, provided by 'white-smoker hydrothermal vents.' Sleep et al. (2011) pointed out that the early Hadean environment may have had abundant CO₂ in the air (perhaps up to 25 bar). In this setting, with seawater weakly acidic (pH around 6), hydration of ocean floor ultramafic rocks to serpentinite would have produced fluid with pH 9–11, venting from the seabed. Later on in the Hadean, the massive CO₂ atmosphere would have been subducted into the mantle, CO₂ less available in water, and the pH gradient between ocean water and fluids would have less.

10.1.3 The Archean (~4–2.5 Ga Ago)

10.1.3.1 Definition of Archean

The intereon boundary between the Hadean and the Archean is presently not defined (Nisbet, 1991). There are various options: (1) the date of the first life on Earth; (2) the date of the last universal common ancestor (LUCA); (3) a 'round number,' such as exactly 4 Ga – 4 000 000 000 years ago; (4) the oldest record of a terrestrial rock (~4 Ga ago); (5) the oldest record of a terrestrial mineral crystal (~4.3–4.4 Ga ago); and (6) the time of the postulated 'Late heavy bombardment,' around 3.9 Ga ago.

Each option has attractions and problems. The choice of a 'round number' goes sharply against long-held stratigraphic logic, which firmly maintains any definition should be 'in the rock.' Dating calibrations shift when decay constants are remeasured and are made more precise: such changes would reclassify material across the boundary. But a definition rooted in rock does not shift. The choice of a particular 'oldest' rock or 'oldest' mineral has more logic, but inevitably, the candidate would be supplanted as a new 'oldest' is discovered.

Life-based definitions are more satisfying. After all, the word 'Archean' comes from the Greek for beginning: St. John's gospel starts with the words "In the Archae..." One option is the start of life: it is not clear when this was, yet, but given life's impact on carbon isotopes, it is perhaps not overoptimistic to hope that the geological record may eventually provide some insight into when life began. A second option – perhaps better – is suggested by phylogenetic studies that infer a LUCA of life – the cell or group of cells from which all modern cells are descended (Woese, 1987, 1999). Any such successful cell would spread rapidly across the globe to inhabit all accessible habitats within a geological moment – and thus there is a hope that a global signature of its metabolism could be found. Moreover, there are clocks in the genetic divergence, and the rRNA record has already been used for this. The clocks may not be very accurate at present, but there is the hope that they can be calibrated better. The date of the LUCA is thus perhaps the most attractive candidate for the definition of the Hadean/Archean boundary.

Once life had begun, the early Archean bombardment during later phases of accretion would have imposed a major constraint on its survival (Gogarten-Boekels et al., 1995; Sleep et al., 2001). The 'Late heavy bombardment' of the Moon took place 3.9–3.8 Ga ago. The face of the Moon, like a ravaged battlefield, dates from this time. This should have affected the Earth dramatically, though signs are absent. The bombardment

is postulated (Gomes et al., 2005) to have been a consequence of resonance of the orbits of Jupiter and Saturn, disrupting asteroids into orbits entering the inner solar system. If Earth was indeed bombarded at this time by large meteorites, there may have been episodes in which the ocean was significantly warmed to a temperature high enough to eliminate cryophile and perhaps mesophile life forms.

10.1.3.2 The Archean Record

10.1.3.2.1 Greenland

The most informative old sequence is the Itsaq Gneiss complex of southern West Greenland (Nutman et al., 1996). This complex includes a wide variety of rocks older than 3.6 Ga and ranging up to 3.9 Ga (early Archean): components are the Isua Belt, the Amitsoq gneisses, and the Akilia association. The Isua Belt is especially interesting because it is supracrustal: it was laid down on the surface of the planet. The rocks include mafic pillow lavas, felsic volcanics, and volcaniclastic rocks, some of which were deposited from turbidity currents. The ensemble is reminiscent of material deposited today in volcanic island arcs, for example, in the western Pacific volcanic island chains. The implications are profound. There was clearly an ocean present and land masses (at least volcanoes, possibly other older crust). Erosion occurred, sediments were deposited; volcanic eruptions must have been normal features of the geological setting. Moreover, this was a time early enough that Earth was still under heavy bombardment by meteorites. There is good evidence from Isua of a meteoritic component in sediment (Schoenberg et al., 2002).

With volcanoes come hydrothermal systems, and there is good evidence for these in Isua. Localized low-strain zones in ~3.75 Ga rocks show many primary features (Appel et al., 2001), including mafic lavas with fine-grained cooling rims, and in pillow breccias, quartz globules occur. These globules are interpreted as former gas vesicles infilled with quartz from hydrothermal veins that formed during and immediately after volcanism. These quartz infills contain rare fluid inclusions. Appel et al. (2001) describe inclusions containing remnants of two independent fluid/mineral systems, comprising pure methane and highly saline (25% NaCl) aqueous fluids, and co-precipitating calcite. These fluids strongly resemble modern seafloor hydrothermal fluids. The conclusion reached by Appel et al. (2001) is thus that methane–brine hydrothermal systems operated 3.75 Ga ago, in the early Archean. If correct, the implications are twofold: that as common sense already tells people, hydrothermal systems existed and that they emitted methane, useful for metabolism.

There have been various claims of evidence for very early life in the rocks of west Greenland. These have been reviewed by Myers and Crowley (2000) and also studied by van Zuilen et al. (2002) and Fedo and Whitehouse (2002). Significantly, they contest claims (Mojzsis et al., 1996) for evidence of very early life at Akilia Island. Fedo and Whitehouse (2002) showed that the rock studied by Mojzsis et al. was not sedimentary but an ultramafic igneous rock. They further considered that the isotopic ratios of the carbon particles at Akilia recorded high-temperature metamorphic processes, not life, and yielding abiotic hydrocarbons. Thus the Akilia rock, though interesting, is not a guide to early life.

Rosing (1999) reported carbon microparticles from >3700 Ma rocks in Isua that are strongly depleted in ^{13}C relative to bulk Earth. $\delta^{13}\text{C}$ in these particles is in the range of $-10\text{\textperthousand}$ to $-20\text{\textperthousand}$, strongly indicative of organic fractionation though inorganic processes can also fractionate carbon isotopes (Pavlov et al., 2001). This work is not contested by Fedo and Whitehouse (2002). The carbon is present as 2–5 μm graphite globules that appear to be biogenic detritus. They are hosted in turbiditic sediments and in pelagic muds. The simplest interpretation is that these carbon particles were originally (before deformation and metamorphism) organic remains and represent the bodies of settled planktonic organisms. The implication is that plankton and, hence, mesothermophilic organisms were present globally before 3.7 Ga ago. Currently, this is the oldest claimed evidence for life on Earth that has as yet withstood critical scepticism.

Rosing and Frey (2004), in a further investigation, reported pelagic shale with up to 0.4% reduced carbon, with $\delta^{13}\text{C}$ values as light as $-25.6\text{\textperthousand}$. Pb isotope evidence suggested the shale was deposited in a local reducing setting, which precipitated U that had been transported via oxidized seawater. From this, they inferred oxygenesis and that oxygenic photosynthesis had evolved prior to 3.7 Ga ago. This conclusion remains very controversial. Also in the Isua Belt's sedimentary sequences, Grassineau et al. (2006) reported sulfide minerals with $\delta^{34}\text{S}$ from -3.8 to $+3.4\text{\textperthousand}$. Carbon dust in banded iron formations, turbidites, and conglomerate gave $\delta^{13}\text{C}_{\text{red}}$ from -29.6 to $-14.7\text{\textperthousand}$. They interpreted this as evidence that hyperthermophilic and chemotrophic species were most likely present in transient settings and possibly pelagic photoautotrophic microbes.

10.1.3.2.2 Barberton

Evidence for early life comes from the Barberton Mountain land of South Africa (Byerly et al., 1986; Tice and Lowe, 2004), in material from 3.3 to 3.5 Ga Swaziland Supergroup.

Byerly et al. (1986) described probable stromatolites in the Fig Tree Group preserved in gray–black finely laminated chert. The structures are made primarily of microcrystalline chert, forming low-relief laterally linked domes and in places pseudo-columnar structures. Byerly et al. did not find evidence of microfossils but inferred an organic origin from the morphology of the structures. Lowe (1994) disputed this evidence and concluded that the structures were not demonstrably of biotic origin. However, Tice and Lowe (2004) do report evidence for 3.4 Ga old photosynthetic microbial mats in Barberton.

Elsewhere in the Barberton Mountain Land is a wide array of mid-Archean volcanic and sedimentary rocks, ranging up to >3.5 Ga old. Some material is clearly biogenic (Westall et al., 2001), with highly fractionated carbon isotopes ($\delta^{13}\text{C} -27\text{\textperthousand}$), but may be of non-Archean age. Westall et al. (2006a,b, 2011) reported evidence for a complex microbial ecosystem. In the ~3.3 Ga Josefsdal Chert, Westall et al. (2011) described a complex microbial biofilm, formed by a consortium of anoxygenic microorganisms, probably including both photosynthesizers and also sulfur-reducing bacteria.

10.1.3.2.3 Western Australia

Several notable pieces of evidence for early life come from Western Australia. Rocks of similar age to Barberton occur in the 3.4–3.5 Ga Warrawoona Group, Pilbara, Western Australia.

A wide range of rock types is present, both lavas and sediments. There is a strong controversy as to whether or not microfossils are present in the Apex cherts of the Warrawoona Group (Buick et al., 1981): this controversy is summarized by the debate between Schopf et al. (2002) and Brasier et al. (2002) (see also Gee (2002) and Kerr (2002) for excellent reporting on the debate, and Buick, 1990). Lowe (1994) also dismissed claims that structures described as stromatolites in the Warrawoona Group are actually of organic origin.

Schopf et al. (2002) and earlier work cited therein, found evidence for microbial fossils in Pilbara and Barberton materials. The laser-Raman imagery reported by Schopf et al. (2002) demonstrated that the material was made of kerogen, and they interpreted this as evidence for remains of microbial life. Brasier et al. disputed the earlier work by Schopf and Packer (1987) and Schopf (1993) on Warrawoona material, constructing a detailed case in which they reinterpreted the supposed microfossils of the earlier study as secondary artifacts of graphite in hydrothermal veins. However, Brasier et al. (2002) did report C isotopic results that are most easily (though not conclusively) interpreted as microbial. Thus although the ‘microfossils’ earlier reported by Schopf may not be organic, there is isotopic evidence suggesting biological activity, though of uncertain age (possibly later than the host country rock).

Allwood et al. (2006, 2007) studied the 3.43 Ga Strelley Pool cherts in detail. These exhibit extensive dolomite/chert stromatolitic laminae. The cherts probably formed as a reef in a transgressive marine setting, with frequent very saline or evaporative episodes. There was proximal hydrothermal activity. Shen et al. (2001) found isotopic evidence for microbial sulfate reduction in 3.47 Ga barites from the North Pole in the Pilbara. Intuitively, sulfate reduction would be expected to be very old: this confirmatory evidence is strong. Also notable is the discovery by Rasmussen (2000) of filamentous microfossils in a 3.235 Ga old volcanogenic massive sulfide deposit, a type of deposit that only forms under deep water. The implication is that hyperthermophile microbial life was certainly present on Earth by this date and in deep water.

One diversion is of interest here. The abundant microbial life around mid-ocean ridge (MOR) vents would have meant that considerable amounts of reduced carbon were preserved under the lava flows. This would have affected the net balance of the atmosphere, leaving an excess of oxygen. It would also have introduced reduced carbon down subduction zones. Interestingly, some diamonds have light carbon isotopes that may have ‘organic’ ratios prior to metamorphism and also contain ‘ophiolite-like’ inclusions, palimpsests of a MOR origin. Just possibly, some diamonds may be carbon from ancient microbial colonies (Nisbet et al., 1994).

In younger rocks of the Pilbara and Yilgarn cratons of Western Australia, there is considerable evidence for life. The ~2.8 Ga old Mount Roe palaeosol contains highly fractionated organic carbon, probably recording the activity of methanotrophs living near ephemeral ponds: this implies that significant biological methane sources existed in the late Archean (Rye and Holland, 2000). Oil is also present in some Archean sandstone (Dutkeiwicz et al., 1998; Rasmussen and Buick, 2000). Of particular interest are stromatolites from the Tumbiana Formation, in the 2.7 Ga Fortescue Group (Buick, 1992).

These have diverse morphology and occur in lacustrine sediments. Texturally, they closely resemble younger microbialites, and they are most probably the product of phototrophic microbial life, living by oxygenic photosynthesis in shallow water with negligible sulfate concentrations.

From a wide variety of lines of evidence, Anbar et al. (2007) concluded that a ‘whiff’ of oxygen was present – in other words, oxygenic photosynthesizers existed, and locally oxidized water bodies occurred, though the wider environment was still broadly anoxic. Czaja et al. (2010) found a wide range in $\delta^{13}\text{C}$ excursions, which they concluded were produced by C cycling in a variety of anaerobic and aerobic methane pathways. There is also a wide variety of geochemical evidence for oxygenesis, including $\Delta^{33}\text{S}$, molybdenum, iron, rhenium, and uranium studies (Duan et al., 2010; Kendall et al., 2010; Raiswell, et al., 2011). Despite this evidence for local oxygen ‘oases,’ there is also strong evidence for anoxic water (Rasmussen et al., 2008). It is clear that a complex array of microbial consortia was present, using many biochemical pathways.

The late Archean of Australia contains many carbonate rocks with $\delta^{13}\text{C} \sim 0\text{\textperthousand}$. This is a strong circumstantial evidence for global oxygenic photosynthesis. The logic depends on the strong fractionation imposed by rubisco as it selects carbon from the ocean/atmosphere system to incorporate it into living organisms (Schidlowski, 2002; Schidlowski and Aharon, 1992). Though some rubisco-using cells are not photosynthetic, most are, and the energy that allows rubisco to incorporate carbon into life is photosynthesis. Carbon emitted from the mantle has $\delta^{13}\text{C} \sim -5\text{\textperthousand}$ to $-7\text{\textperthousand}$. This is emitted into the air and ocean mainly as carbon dioxide. From this mantle-derived carbon, carbon is acquired into organic matter by rubisco, using the harvest of thermodynamic reduction power from the apparatus of oxygenic photosynthesis in the presence of abundant ambient atmospheric CO₂. This carbon chosen by life is strongly selected for ¹²C and thus has $\delta^{13}\text{C} \sim -28\text{\textperthousand}$ to $-30\text{\textperthousand}$. Thus, the residue left in the air/sea system is enriched in ¹³C. In modern-day carbonates, $\delta^{13}\text{C} \sim 0\text{\textperthousand}$, implying by balance ($-7\text{\textperthousand}$ source, partitioning into $-28\text{\textperthousand}$ organic life and 0\textperthousand inorganic sinks) that about a quarter to a fifth of primitive carbon is captured by organic matter, and three-quarters to four-fifths is left as carbonate with $\delta^{13}\text{C} \sim 0\text{\textperthousand}$. Because carbon dioxide is globally mixed, the presence of carbonate with $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ implies a global fractionation of carbon by oxygenic photosynthesis. This indeed is what is recorded in the late Archean (Nisbet et al., 2007a).

10.1.3.2.4 Steep Rock, Ontario, and Pongola, South Africa

The evidence from the 3.0 Ga sequence at Steep Rock, Northwest Ontario, Canada, is very different (Figure 3; Nisbet, 1987; Nisbet et al., 2007a; Wilks and Nisbet, 1985). Here is a large limestone reef, some kilometers long, displaying a wide variety of structures interpreted as formed by life, and also with a range of isotopic evidence that is not greatly dissimilar to modern sequences. The structures vary from large stromatolites (several meters long) to smaller (1–20 cm) stromatolitic structures (sadly some of the loveliest of these have been fractured by unknown collectors), deposited close to a major unconformity. These are among the oldest unchallenged examples of stromatolites: claims of older examples have been strongly criticized (Lowe, 1994). Isotopic evidence from Steep Rock

(Nisbet et al., 2007a) indicates that rubisco-mediated carbon capture (i.e., oxygenic photosynthesis) controlled the global carbon partitioning between carbon dioxide and carbonate: this is some of the oldest evidence for global oxygenic photosynthesis.

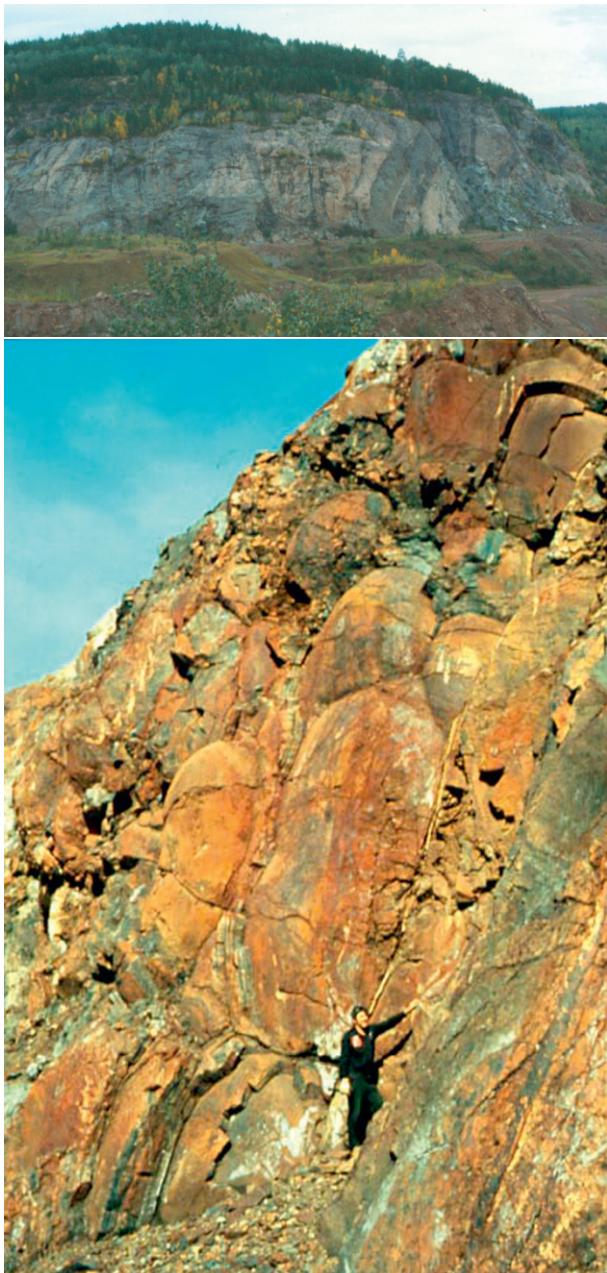


Figure 3 (a) The surface of the 3 Ga Earth, Steep Rock, NW Ontario, Canada. The hill-face is very close to a 3 Ga unconformity surface, and the rocks (granitoids and mafic dikes) exposed on the hill-face are immediately below the unconformity. Above them are assorted sediments, including thick stromatolitic limestones. (b) Stromatolitic limestone, Steep Rock, Ontario, Canada (c.3 Ga old), overlying the surface of (a) (Wilks and Nisbet, 1988). The palaeohorizontal surface dips ~70°. Stromatolitic domes are up to 4–5 m long and 2 m high (Wilks and Nisbet, 1985).

The Pongola sequence in South Africa (Matthews and Scharrer, 1968; von Brunn and Hobday, 1976) also includes stromatolites above a major unconformity (Eglington et al., 2003). The Pongola sequence is uncannily like Steep Rock both in age and sequence: it is tantalizing to wonder if they were once contiguous before the vagaries of continental breakup and reassembly.

10.1.3.2.5 Belingwe

The evidence for life in the sediments of the Belingwe belt, Zimbabwe, was described by Martin et al. (1980), Nisbet (1987), Grassineau et al. (2001, 2002), and Nisbet (2002). The Belingwe Greenstone Belt has a wide and diverse array of evidence for the late Archean life. In this, it is not unique – many Australian and South African sequences also have abundant evidence of life. What makes the Belingwe belt fascinating is the range of features outcropping in a small area, coupled with some extremely well-preserved igneous rocks (Bickle et al., 1975; Nisbet, 1987).

The rocks of the Belingwe belt span a range of ages, but the sequence that carries the most detailed evidence for life (Figures 4 and 5), the Ngesi Group, is 2.7 Ga old (Nisbet et al., 2007a). The base of the group includes shallow-water sediment locally rich in carbon and sulfur that is highly fractionated isotopically, suggesting the original presence of methanogens and the operation of complex sulfur



Figure 4 Stromatolitic limestone, Cheshire formation, Belingwe belt, Zimbabwe (2.6–2.7 Ga old; Martin et al., 1980): (a) outcrop surface – structures occur on a variety of scales from microscopic to meter relief; (b) detail of one outcrop. Reproduced from Nisbet EG (1987) *The Young Earth*. London: George Allen and Unwin. 402 pp.

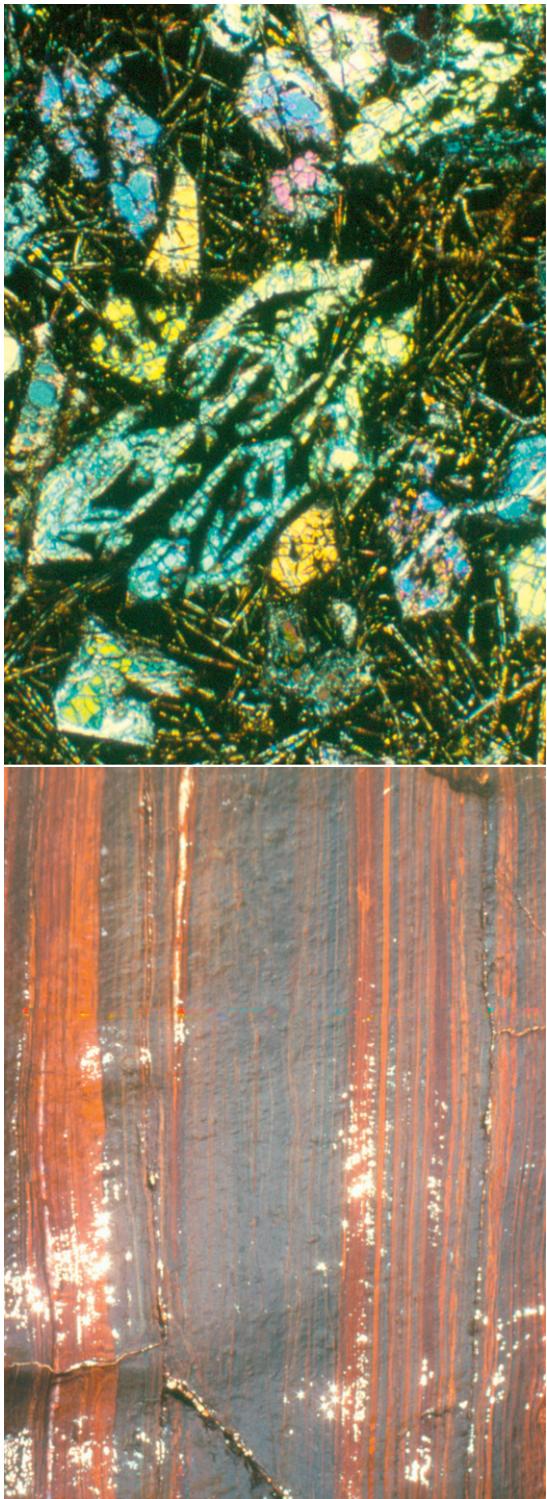


Figure 5 (a) Thin section of 2.7 Ga komatiite lava, Reliance Fm, Belingwe belt, Zimbabwe. About 6.5 mm across photo. Olivine crystals set in fine grained to once-glassy groundmass. For details see Nisbet et al. (1987). (Photo W. E. Cameron). (b) Alternating iron-rich and carbon-rich shales. White bands are chert: this lithology is transitional to banded ironstone. Approximately 20 cm across picture. Belingwe belt, Zimbabwe (see Bickle and Nisbet, 1993).

fractionating processes (Grassineau et al., 2001, 2002, 2006). Oil is present in some rocks (Grassineau and Nisbet, own observations). Locally associated with this stratigraphic unit are stromatolites made of calcite with $\delta^{13}\text{C} \sim 0\text{\textperthousand}$, with kerogen that contains carbon which is strongly fractionated isotopically, implying the selection of carbon by rubisco (see Section 10.1.7.2). Immediately above the basal sediments are komatiite pillow lavas and flows (Figure 5). Close to the contact with the lavas, in the uppermost sediments, are sediments that in places are very rich in kerogen and sulfides, with highly variable fractionated carbon and sulfur isotopes, different in very small physical distances. The simplest interpretation of this (Grassineau et al., 2002; Nisbet, 2002; Nisbet et al., 2007a) is that the complex isotopic fractionation is a record of consortia of prokaryotes, some reducing sulfate, and some perhaps oxidizing sulfur, others generating methane (Thomazo et al., 2013), some photosynthesizing and capturing carbon by using rubisco, and perhaps carrying out other microbial biochemistry (using metal enzymes). Both in shallow-water photosettings and in deeper water below the photic zone, microbial mats may have cycled sulfur in sulfur-eta, as in modern parallels (Fenchel and Bernard, 1995).

Above the komatiites are thick basalt pillows and flows. At the top of the sequence is a further sequence of shallow-water sediments, including limestones that locally have extensive and very well-preserved stromatolites (Figure 4). These probably grew in luxuriant stromatolite reefs, in shallow-water lagoons, with episodic evaporitic events (Martin et al., 1980). These too have evidence for rubisco fractionation (Nisbet et al., 2007a; see Section 10.1.7.2), both in kerogen carbon and in carbonate with $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ (Nisbet et al., 2007a). Evidence from Fe isotopes and Mo isotopes (Archer and Vance, 2006; Siebert et al., 2005) imply that the shallow water was locally oxic.

10.1.4 The Functioning of the Earth System in the Archean

10.1.4.1 The Physical State of the Archean Planet

The map of the surface of the Archean planet remains largely blank, populated by imagined beasts and perhaps some features seen dimly but truly (Macgregor, 1949). The main input from the mantle to the surface is via volcanism. The late Hadean and the early Archean volcanism would have provided thermodynamic contrast, placing relatively reduced material that had equilibrated with the hot mantle in contact with the ocean-atmosphere system that was open at the top to photolytic loss of hydrogen to space. In the latest Hadean and the earliest Archean, this redox contrast would have been most likely thermodynamic basis of life.

The early Archean volcanism was probably largely basaltic or komatiitic, but perhaps with some andesitic and alkaline centers. The mantle may have been somewhat hotter than today (Arndt and Nisbet, 2012; Nisbet et al., 1993), and thus the primary melt at MOR would likely have been more magnesian than today. Moreover, a hotter mantle would likely have sourced more plume volcanoes than today. These volcanoes would have been comparable to modern Hawaii but may have ranged up to much larger sizes. The plumes would have emitted komatiite lava flows. These are less viscous than basalt,

and would have flowed long distances on relatively flat surfaces, creating huge flat shields, perhaps as large wide islands emerging as the upper fraction of enormous volcanic platforms resting on oceanic plate.

Komatiite lava flows are very rich in MgO. They contain significant iron oxide, and are typically associated with nickel sulfides (NiS) and chromite. Hydrothermal systems in highly magnesian rocks can be very alkaline, with very high pH. Thus, it would be expected that rain falling onto komatiite flows, or flows into shallow (low-pressure) seawater, would generate very alkaline outflows of hot or warm water.

The zircon evidence (Wilde et al., 2001) from Australia and the existence of 4 Ga gneiss in Canada provide evidence for the existence of Hadean continental crust, but this may have been of limited areal extent. Given the very low likelihood of preservation of any rocks older than about 2.9 Ga (Hawkesworth et al., 2009), it is hard to make conclusions about the exposed area of the Hadean and the early Archean continents. Significantly, by the early Archean there had probably been inadequate time for deep continental lithosphere to develop. Yet in contradiction of this view, by 2.7 Ga, the late Archean diamonds are known in the Witwatersrand record (Nisbet, 1987). Diamonds imply lithosphere at least 150 km or so thick and suggest kimberlite and probably a spectrum of alkali volcanism on land. Alkaline volcanism is indeed known to have occurred, a source of high pH and perhaps phosphatic environments. There is a small but significant record of Archean alkali volcanics (Nisbet, 1987), for example, in the Timiskaming Group in Northern Ontario (Cooke and Moorhouse, 1969), which includes leucitic flows and pyroclasts. Just possibly phosphatic volcanics did occur—arguably the most likely setting for constructing sugar-phosphate chains in an inorganic process.

The early Archean continents were subject to erosion. Rocks from Isua include sediments, implying the action of rain and the existence of subaerial exposure, as well as the presence of wide oceans capable of evaporating the rainwater. The nature of the sediment was different from today, however. Nowadays, most surface rock is actually recycled previous sediment, and aluminous clay-containing muds (mature sediments) are common. Most of what little there is of the early Archean sedimentary record is not mature: primary volcanic terrains were being eroded. Clays would have been widely present but were probably mainly magnesium-rich clays derived from weathering of volcanic rock, not aluminum-rich material. This scarcity of mud may be important in considering likely biologic host environments.

10.1.4.2 The Surface Environment

The sedimentary evidence implies the existence of oceans. Although the initial deep volatile inventory of the planet would have been removed by the late great impact that formed the Moon, much of the water presently in the Earth's oceans would have degassed from the hot mantle or infallen as comets soon after that great impact, and the ongoing volcanism would have added more. However, at ridges water is rapidly returned to ocean crust by serpentinization and metamorphic hydration of basalt. As soon as old oceanic plate developed, cold plate and hence crustal water would begin to fall back in to the interior down subduction zones, returning more water than

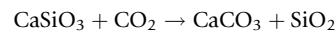
MOR volcanism emitted. Given the high mantle temperature, subduction zone volcanism probably rapidly restored the subducted water to the surface. Nisbet and Sleep (2003) suggest that in effect the Earth's mantle is self-fluxing. The net annual contribution of primary new water to from the deep interior the surface (ocean) would thus be set by the inputs of volcanism at ridges and plumes, plus infall of cometary material, minus net loss back into the interior from the small net amount of water that was carried down into the deep interior, and net loss by loss of hydrogen to space.

The controls on carbon dioxide would have been somewhat different. Today, carbon dioxide is stored in carbonate minerals in the ocean floor and on the continental shelf. Subduction, followed by volcanism, cycles the carbon dioxide to the mantle and then restores the CO₂ to the air. Metamorphic decarbonation of the lower crust also returns carbon dioxide. The carbon dioxide is then cycled back to the water, some via rain some dissolved via wave bubbles. Erosion provides calcium and magnesium, eventually, to precipitate the carbonate. In the earliest Archean, parts of this cycle may have been inefficient. The continental supply of calcium may have been limited; however, subseafloor hydrothermal systems would have been vigorous and abundant, exchanging sodium for calcium in sputilization reactions, and hence providing calcium for in situ precipitation in oceanic crust.

The early history of atmospheric CO₂ is controversial. Much depends on the timing of the onset of subduction. One argument is that in the earliest Hadean, before significant thicknesses of lithosphere had cooled over large areas, subduction may have been limited, and hence the return of carbonate-held carbon dioxide to air, via subduction volcanoes, would have been hindered. Zahnle et al. (2007) and Sleep et al. (2011) argued that a massive CO₂ atmosphere existed in the first tens to 100 Ma after the Moon-forming impact and that this created clement conditions (warm oceans) for life. These early clement conditions may have begun only a few tens of million years or less after the Moon-forming impact and lasted perhaps as much as 100 Ma.

However, by late Hadean subduction should have become the general fate of old oceanic plate, and with it, the rapid removal of CO₂ back to the interior. Cooling of plate depends on having a cool surface. The temperature of the late Hadean Earth's surface is unknown, but Sleep and Zahnle (2001) and Sleep et al. (2001) have made an excellent circumstantial case that the ambient surface environment was glacial, ice over cold ocean.

Formation of early continental material would have allowed the crustal Urey cycle to begin. The crust buffers carbon dioxide in the air. Where CaSiO₃ (wollastonite) is a proxy for clinopyroxene-containing crustal rocks, then:



In the Urey cycle, if global warming occurs, silicate weathering is speeded up, more calcium, magnesium, and strontium cations are released and hence carbonate is formed: thus the carbon dioxide greenhouse is reduced, ending the warming. Carbon dioxide is also cycled via the mantle: outgassing at the MOR adds carbon dioxide to the air, while alteration of ocean floor basalt precipitates carbonate, and the subsequent

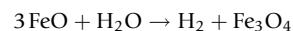
subduction of carbonated oceanic crust returns carbon dioxide to the Earth's interior. More generally, Walker et al. (1981) argued that the long-term clemency of the planetary climate over the aeons is simply an inorganic geochemical consequence of the nature of weathering/CO₂ feedbacks on the planetary surface.

To return now to the carbon dioxide question, in the late Hadean and early Archean, degassing would have been vigorous but so would have been the return of carbon to the interior and it is likely that the mantle cycle would have dominated (Sleep and Zahnle, 2001; Sleep et al., 2011; Zahnle et al., 2007). Moreover, frequent meteorite impacts would have created vast quantities of basalt ejecta that would also have reacted with carbon dioxide to precipitate carbonate. Sleep and Zahnle (2001) concluded that so much carbon dioxide would have been held in the mantle that the greenhouse warming would have been small: the Earth was probably heavily glaciated – the Hadean was probably a Norse ice hell. Possibly, the early Hadean Earth risked loss of atmospheric carbon dioxide to the interior more than dehydration by hydrogen loss to space, though this would depend on how much methane was in the air.

If so, the likely ambient conditions in the late Hadean (Nisbet and Sleep, 2001; Sleep, 2010; Sleep et al., 2001) would have included a dry troposphere with little water vapor (and hence little OH) in the low temperatures, and wide ice cover only locally broken by water leads on the sea surface (Figure 9(a)). The earth was probably cool (Valley et al., 2002). The air would have had very high dust content from the volcanic eruptions and meteorite impacts, possibly being so dusty as to inhibit rainfall (especially given the dryness). Continents would have been covered by dirty ice or perhaps dry permafrost (given the very low humidity). If conditions were cold enough and CO₂ concentration high enough, possibly carbon dioxide was present in polar ice. From time to time, perhaps millions of years apart, massive meteorite impacts would have ejected huge amounts of water and dust, melting ice and changing albedo (Sleep et al., 2001). Brief warm episodes would result, with water-aided greenhouse conditions, and then slowly, the ice cover would return. In this oscillating climate, there would be many local oases of warmth around volcanic hydrothermal systems (Nisbet et al., 2007a,b). Some of these would operate under ice cover (as in Iceland today), offering an interesting and very diverse variety of chemical settings very closely juxtaposed in space and perhaps repeatedly replacing each other in time as the hydrothermal systems fluctuated. These settings would include all possible phases: warm rock surfaces in warm or hot water/brine, fumaroles with various vapor phases, locations in ice, and locations in warm water (Nisbet and Sleep, 2001).

In addition to plate boundary and plume-related hydrothermal systems, the chemistry of the prebiotic world would have had strong redox contrasts in the restricted areas that had tidal coasts, and perhaps within the oceans where differing water masses interacted, or under ice. These redox contrasts were ultimately driven by photolysis in the atmosphere/ocean (presumably made of water and carbon gases) and escape from the top of the system and also by magmatic interaction at the bottom (around komatiitic vents), where reduced species such

as H₂ would have been generated by the reaction between FeO in rock and water to give hydrogen in solution and magnetite:



Likely terrestrial sources of redox contrast included: hydrogen emitted from serpentinization reactions when water reached hot ultramafic rock (Nisbet et al., 2007a,b; Sleep et al., 2011); sulfates in air and water versus sulfides in hydrothermal deposits; carbon dioxide in air versus methane or CO in hydrothermal systems; nitrogen oxides in air and water versus ammonia in hydrothermal emissions; and the contrast between water and magmatic hydrogen. Meteorites would have provided reduced iron and carbon particles. Hot iron, falling into water, could generate hydrogen.

A world is only interesting to biology if it offers a way of making a living. The first life must have been unskilled, not equipped to search out the necessities of life: thus it must have existed where a strong redox contrast was accessible, either spatially (over a few microns) or temporally (in a fluctuating setting, where regular variation took place between one redox regime and another, within hours or even minutes, e.g., as in a geyser). Obviously, the Hadean Earth offered these on a plate. Identifying the plate and determining if it was tectonic, however, is not easy.

10.1.5 Life: Early Setting and Impact on the Environment

10.1.5.1 Origin of Life

Over the origin of life, nature has chosen to draw a veil. A basic criterion in science is that the result should be reproducible, falsifiable. Not one of the notions of the origin of life has led to reproduction, not one can be falsified. No doubt success will soon come in the effort to understand the detailed step-by-step molecular controls of reproduction. There are many notions about the origin of life. Where there is little fact, imagination is allowable and profitable, but where there is no fact, then even imagination is best left unimagined here. Similarly, the question "what is life?" is perhaps best left to the consideration of Hades by trouser-role opera singers of uncertain reproductive status, seeking Eurydice. Life is more than reproduction, which clay minerals also achieve. Defining the boundary between life and nonlife is, to quote N. H. Sleep, like searching for the world's smallest giant.

Nevertheless, despite these warnings, the questions are of supreme interest. Given that life bends the rules, a slight digression is warranted. A definition of life is perhaps best approached via thermodynamics (Nisbet, 1987). Life is growth – it is always in disequilibrium with its surroundings, and its actions are such as to increase that disequilibrium. Sustainable equilibrium molecules are dead molecules. In practice, the boundary is set between the cell and the virus. The cell must be active and can in principle reproduce; it must maintain disequilibrium by increasing the universal chaos. In contrast, the virus can crystallize and thus set itself in a fixed point on the entropy scale.

There are several favorite notions of the site of the origin of life (Nisbet, 1987). The best known is the Marxist hypothesis of

the ‘primaeval soup’ – that the early ocean was a soup of organic molecules that had fallen in from meteorites (which frequently contain complex carbon-chain compounds: organic chemicals but made by prebiotic inorganic processes). In this soup, lipid blobs somehow evolved into living cells. The discovery of hydrothermal systems led to the realization that early oceans would have pervasively reacted with basalt, both in hydrothermal systems and also with basalt ejecta after impacts. Thus, the late Hadean ocean was most unlikely to be a festering broth, but more likely a cool clean ocean not greatly dissimilar to the modern ocean: exit the primaeval soup.

Other hypotheses note the properties of minerals, especially clay minerals (Bernal, 1951, 1967), iron oxides, and zeolites. Hooker, in a letter to Darwin that provoked the ‘warm little pond’ hypothesis (Darwin, 1859, 1959 edition), noted the characteristics of modern hydrothermal systems: abiotic formation of hydrocarbons may occur today in MOR systems (Holm and Charlou, 2001). An interesting variant is the idea of ‘genetic takeover’ (Cairns-Smith, 1982). This is based on the notion that some minerals are not greatly different from viruses – as Schrodinger (1944) pointed out, life is based on molecules that can be crystallized as aperiodic crystals. Mineral crystals reproduce, in a sense, when they grow – each crystal surface seeds new copies of itself. In one version of the genetic takeover hypothesis, the earliest replicating structures were simply minerals, which replicated just as clays minerals grow. These structures bound proteins, which helped in the reproduction. Then nucleic acid took over the role of the mineral template and occupied the central direction of the reproducing body.

The ‘panspermia’ hypothesis is simple (Crick, 1981) – Earth was seeded by little green men from outer space, who spread life cells by sending rockets throughout the galaxy. This hypothesis has the attraction of avoiding the impossible task of elucidating how life began on Earth by transferring the problem to another planet far away and long ago; it also achieves a happy congruence with Star Trek’s DNA-based universe. However, although littleness has great advantages, it is not discussed why the men were green or why they were men: pan-oo would be perhaps more likely than pan-sperm.

10.1.5.2 RNA World

Of the many origin of life ideas, the ‘RNA-first’ idea (Gilbert, 1986) is worth noting in more detail: the idea that prior to DNA, the genetic code was held in RNA. This does not necessarily mean that life began as RNA (a takeover is possible), but at some stage, it seems likely that life was RNA-based. All cells today use ribosomes – a giant RNA enzyme – to read the DNA tape, and RNA retains the key role of carrying messages in the cell. It may be that at one stage life was a few self-replicating RNA molecules.

If so, how did these RNA molecules exist? Possibly they were sophisticated enough already to have outer bags and thus containers for the protein they made. But it is also possible to imagine an early RNA world (Gilbert, 1986; Nisbet, 1986) in vesicles in a rock, where the container was provided either by the rock itself or by minerals with large tubular shapes, such as faujasitic zeolites or some of the iron oxide minerals. Chemicals and redox drive would be provided by fluids flushing through the setting. Any RNA molecules that

accidentally managed to self-replicate would be protected and would be propagated; one might next accidentally develop the ability to synthesize proteins that could be assembled to act as enzymes aiding replication, increasing the population. Volcanic accident could spread the molecules from the first container into other parts of the system. Finally, any molecule that accidentally acquired the ability to enclose itself with a lipid bag would be preadapted to life in the open environment, away from the rock vesicle. But this is a notion – many other notions have equal or greater validity.

10.1.5.3 Hydrothermal World

Geologically, some inferences can be made. Where hot rock and magma meet water, then hydrothermal systems develop. These are driven by density contrasts (hot water and steam are less dense than cold water) and can move vast quantities of water through rock, dissolving chemical species where the water is heated and precipitating where the water ejects into a colder setting. The environment in which the first life to use nucleic acids evolved would presumably have had abundant local phosphate sources and accessible phosphorus, sugars, and nitrogen bases. Here, the evidence of the existence of komatiite plumes and the antiquity of continents is just possibly relevant. Carbonatite volcanism and associated very unusual rocks (such as phosphatites) occur today mainly on ancient continental crust, but alkali volcanism is a feature of plume volcanoes (e.g., Mauna Kea in Hawaii). Whether phosphate-rich volcanism could have been possible as early as the Hadean is a moot point. Then the lithosphere may have been thin and limited to a segregated cooled-melted earliest crust, plus giant plume volcanic centers, fractionated in their upper stages. Assuming phosphate-rich igneous rocks did exist, then phosphorus-rich hydrothermal systems may have occurred.

More generally, alkaline hydrothermal systems (pH as high as 10 or more) would have occurred around the widespread cooling ultramafic rocks, such as the enormous komatiite flows that would have issued from komatiitic plume volcanoes, and also at distal sites near early MOR (themselves possibly fed by komatiitic basalt liquid). These hydrothermal systems would emit high-pH hot fluids and had many settings in which models of early life can be imagined (Holm et al., 2006; Lane et al., 2010; Martin et al., 2008; Russell et al., 1993). Here, ammoniacal hydrothermal systems (Hall, 1989; Hall and Alderton, 1994) would probably have occurred. Under such high-pH conditions, metal atoms (e.g., iron and copper) can form compounds within cages of four nitrogen atoms. Possibly, the cytochrome family of proteins, which is clearly very ancient, may have had its origins in such a setting. These proteins have at their heart a metal surrounded by four nitrogen atoms: heme with iron and four nitrogens and chlorophyll with magnesium surrounded by four nitrogens.

10.1.5.4 LUCA – The Last Common Ancestor

The LUCA is more accessible to geology and molecular biology than the first ancestor. Though not less controversial than the first ancestor, it is at least the subject of testable hypotheses (Steele and Penney, 2010; Theobald, 2010). It stands at the base of the putative ‘Tree of Life’ (O’Malley et al., 2010). From

this ancestor, molecular phylogeny has been attempting to discover human descent (Pace et al., 2012; Woese and Fox, 1977).

Darwin (1859, 1959 edition) envisaged the descent of life as a tree of life, endlessly and progressively branching, with many branches dying off, a few branching onward. The Darwinian hypothesis of a Tree of Life (Figure 6) is broadly true for eukaryote descent, but for prokaryotes, the story is more complex (Doolittle, 2009). The real descent of prokaryotes may be more like a braided delta (Figure 6). In sexually reproducing animals, especially vertebrates, evolution comes about in vertical descent, generation upon generation by natural selection: parents die, and among their offspring advantaged siblings survive to procreate another generation, while less successful siblings fail to reproduce. In contrast in prokaryotes, Lamarck fights back by horizontal exchange within a coliving generation. Living organisms acquire new skills by lateral gene transfer. Prokaryote evolution is very hard to force into the notion of a Darwinian tree of life (Baptiste et al., 2009). Indeed, as far as prokaryotes are concerned, Doolittle (2009) goes so far as to pronounce the Darwinian hypothesis of a Tree of Life is false. Horizontal gene transfer also occurs from bacteria to eukaryotes and even between eukaryotes (Gladyshev et al., 2008), so in this sense, Darwin's hypothesis is generally false. Nevertheless, just as Newtonian physics has been shown by Einstein to be simply a special condition of a much wider hypothesis, so Darwinian

evolution remains a valid approximation for eukaryotes or for specific functional sets of genes. For example, in a comparative analysis of nearly 7000 phylogenetic trees, Puigbo et al. (2009) derived a consistent phylogenetic signal, especially among over a hundred 'nearly universal trees.' High levels of horizontal transfer occurred but seemed to be distributed randomly and did not obscure the central trend.

The LUCA is the notional cell, or population of cells, from which all modern living cells are descended (Woese, 1999). One definition of the Hadean/Archean boundary is the date of the LUCA. This last ancestor would have been a DNA-based organism, already complex, with many of so-called housekeeping proteins that are broadly common to nearly all modern types of cell. Note, however, that viruses, especially RNA viruses, may (or may not) be separately descended from an earlier ancestor.

There is much debate about the habitat – and hence metabolic processes – of the LUCA. The majority view is that the root was a prokaryote, more bacterial than anything else, from which diverged the sister domains of archaea and Eucarya (Figure 7; Ciccarelli et al., 2006; Puigbo et al., 2009; Theobald, 2010; Woese, 1987). In this view, the eukaryotes evolved later, from microbial prokaryotes (Gribaldo et al., 2010), possibly the archaea.

Added to this interpretation is the inference that the LUCA was a hyperthermophile, living in hot conditions ($>85^{\circ}\text{C}$) probably in close proximity to a hydrothermal system

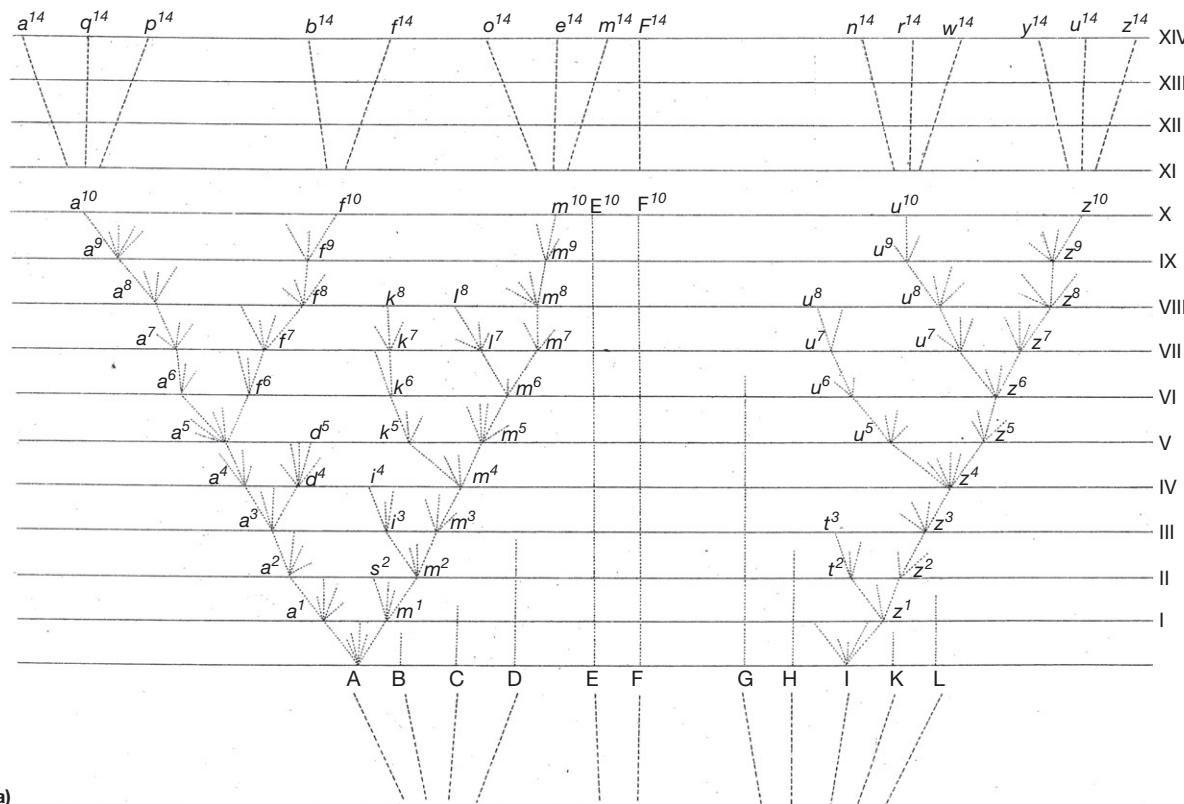


Figure 6 Models of the descent of life: (a) Darwin's single illustration in Origin of Species (Chapter IV) (Darwin, 1872, 1959); and (b) braided delta model, assuming large-scale lateral gene transfers and boundaries of nonviability. Recently the very concept of a 'tree of life' has been challenged, at least in the prokaryotic domains (Baptiste et al., 2009; Doolittle 2009).

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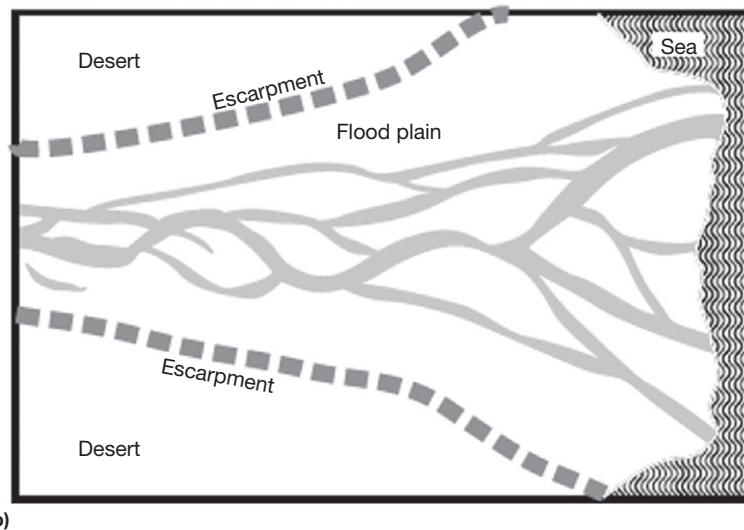


Figure 6 (Continued)

(Miyazaki et al., 2001; Nisbet and Fowler, 1996a, b; Stetter, 1996). In many early microbial phylogenies (e.g., Barnes et al., 1996; Pace, 1997; Woese, 1987), the most deeply rooted organisms all appeared to live in high-temperature settings. This view makes abundant geological sense, as the diversity and fluctuation of chemical settings in hydrothermal systems offer readily accessible thermodynamic drive for prephotosynthetic life, while the deep involvement of metals in the ubiquitous (and thus presumably ancient) enzymes responsible for the housekeeping biochemistry of cells strongly suggests hydrothermal supply. In particular Russell et al. (1993) and Russell and Arndt (2005) have argued that the emergence of life may have been linked to the presence of catalytic iron–sulfide membranes in and around hydrothermal systems. Moreover, heat shock proteins (HSP) are integral to protein shaping, suggesting the speculation that heat shock was a general problem for early life.

However, the argument in favor of a mesophile LUCA is also tenable (Boussau et al., 2008; Forterre, 1995; Forterre and Philippe, 1999; Galtier et al., 1999). Boussau et al. (2008) inferred two phases of environmental adaptation. They suggested that the first ancestor, LUCA, was mesophilic. From this first parent, its descendants became adapted to higher temperatures. Heat is a threat to life: it cooks it, and cells have HSP to restore them if slightly cooked. It seems counterintuitive to imagine that life started in a place so risky, before it could evolve protective mechanisms. Forterre suggested that life began in milder mesophile settings, with an initially poorly organized and complex structure. Then, when bacteria and archaea spread to the more dangerous but thermodynamically advantageous hyperthermophile settings, those that prospered were cells descended from lines that had evolved more efficient, streamlined genomes ('thermoreduction'). Forterre (1995) considered the RNA-world idea incompatible with the notion (e.g., Nisbet and Fowler, 1996a; Stetter, 1996) that early life was hyperthermophile. RNA is unstable at very high temperatures. Moreover, modern hyperthermophiles have very sophisticated mechanisms to sustain them in hot environments, unlikely in very primitive cells. Forterre (1995) suggested that early cells were complex

mesophiles, and those that strayed into hotter settings slowly adapted to the conditions by selection for reduced and streamlined genotypes, to produce the hyperthermophiles.

An analogy would be the comparison between geometrically complex early multiple-winged aircraft, such as Sopwith biplanes of the 1914–18 era, the streamlined Hurricane monoplanes of the Battle of Britain with protruding propellers and tail wheel, and the uncluttered Harrier still today in service, all built under the direction of a single designer, Thomas Sopwith. These airplanes simplified in shape as they became more powerful and internally complex over a century of rapid evolution. Yet they are all part of a single line. Or continuing the analogy, the officer commanding those Battle of Britain fighters, Marshal of the RAF Sholto Douglas, was the brother-in-law of author J. D. Salinger: close relations, utterly different careers. Extraordinary diversity can occur yet retain close linkages.

Derivation of molecular phylogeny from rRNA suffers from various mathematical pitfalls (Steele and Penney, 2010), especially where lateral gene transfer has been extensive. The difficulty of dealing with branches of the tree of life that evolve rapidly is severe. Any model that assumes uniform rates of evolution will make these branches appear inaccurately ancient (Graur and Martin, 2004). Moreover, there is massive evidence for multiple gene transfer between distinct lines within domains and across domain boundaries. For example, up to 18% of *E. coli*'s genes may be relatively recent foreign acquisitions (Martin, 1999). This complicates interpretation enormously (Doolittle, 1999, 2000, 2009) and leads to models not so much of 'trees' of descent but of 'mangrove roots' (Martin, 1999) or analogies with braided deltas (Nisbet and Sleep, 2001; Figure 6). Woese (1999) concluded that the communal ancestor was not so much a single discrete organism but a diverse community of cells that evolved together as a biological unit. In this view, the universal phylogenetic tree is not an organismal tree at its base, but becomes one as the peripheral branchings emerge.

The choice between explanations suggesting (1) shared ancestry between the lines, rather than (2) lateral transfer of information between contemporary but unrelated lines, is not

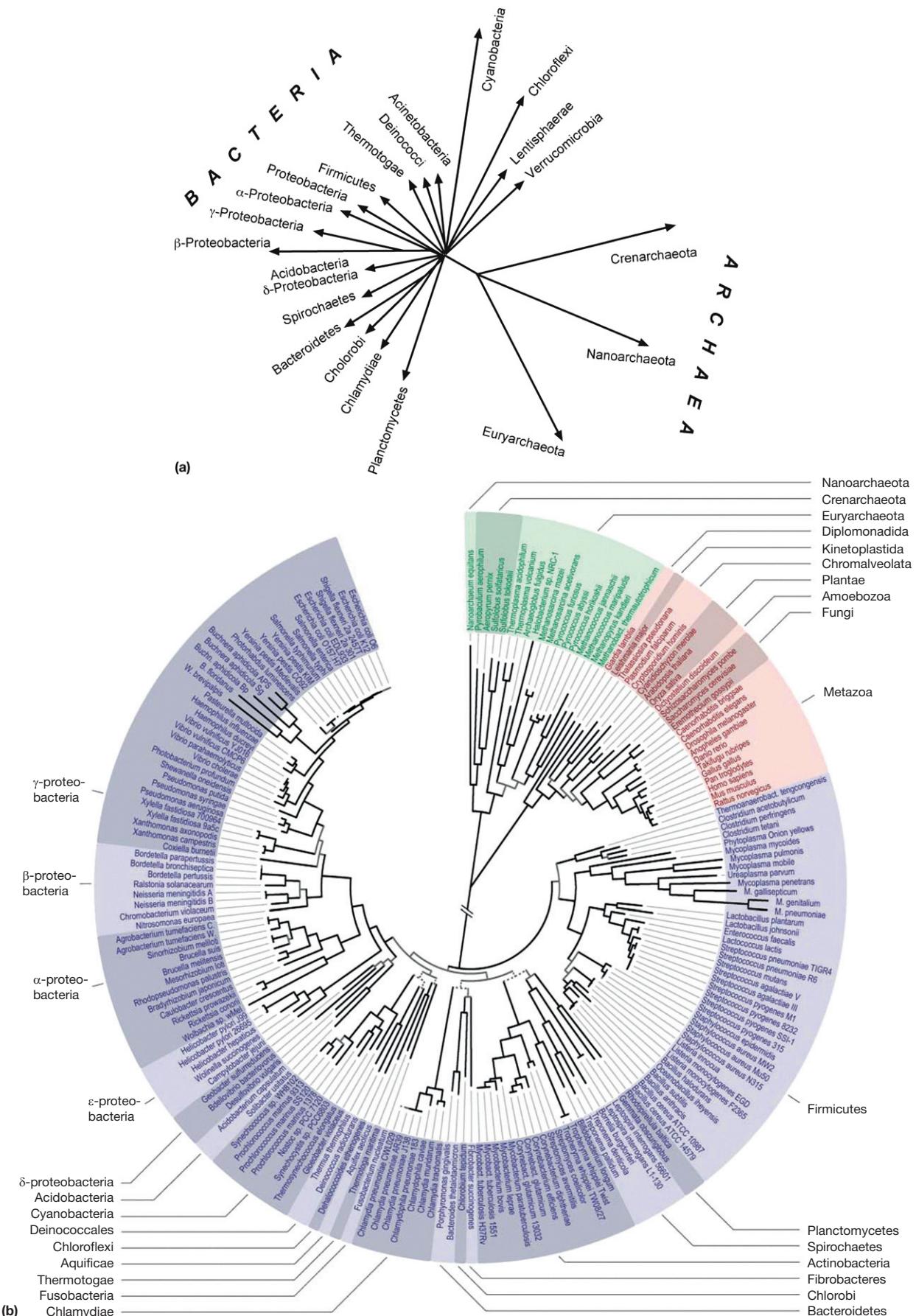


Figure 7 The descent of life. (a) The prokaryotic diversification between the bacterial and archeal domains, based on the network of nearly universal phylogenetic trees of Puigbo et al. (2009). (b) Global phylogeny of fully sequenced organisms from Ciccarelli et al. (2006); see also Letunic and Bork (2011). Phylogenetic tree is based on alignment of 31 universal protein families whose genomes have been fully sequenced. Green – Archaea. Red – Eukaryotes. Blue – Bacteria. In this unrooted tree the branch length linking Bacteria with Archaea and Eukaryotes is an artistic representation only. With permission from the American Association for the Advancement of Science.

easy (Abby et al., 2012; Steele and Penney, 2010). Thus the molecular record is very ‘noisy’ and the interpretation of descent is ambiguous. It is very difficult to be sure of the limited number of positions in an amino acid or nucleotide sequence that actually record true antiquity.

Initially, it was thought that derivation of phylogeny from molecular information is intrinsically superior to phenotypic information. Forterre and Philippe (1999), Penny and Poole (1999), and Glansdorff (2000) pointed out that this is not necessarily true. The Microsporidae, for example, were originally misclassified as very ancient. More recently, these have been shown to be closely related to fungi, a much younger line (Hirt et al., 1999). The discovery of the error in placing the Microsporidae increases awareness that massive lateral gene transfer has occurred between the three domains of life. Each domain is distinct and monophyletic, but members of each domain have obtained genetic information from other domains.

Conceivably, if the last common ancestor were mesophile, the majority of bacteria may descend from an early mesophile prokaryote, perhaps via a genetically streamlined descendant that occupied a hyperthermophile setting. The archaea too may descend from the LUCA via a streamlined cell that had evolved to inhabit hyperthermophile settings. In contrast, the Eucarya may be directly descended from a mesophile. The PVC superphylum of eubacteria (Planctomycetes, Verrucomicrobia, and Chlamydia) have been particularly puzzling (Brochier and Philippe, 2002). For example, their internal membranes resemble eukaryote endomembranes. However, McInerney et al. (2011) showed that their similarity to some aspects of eukaryotes is apparently a result of convergent evolution, not common descent.

A possible geological scenario for this process may be that the LUCA lived on the warm (~40 °C) but not hot periphery of an alkaline hydrothermal system, on a glaciated planet. Descendants of the last common ancestor may have evolved to occupy hyperthermophile habitats, with sophisticated biochemical processes to ensure their survival. Other descendants may have spread to occupy planktonic mesophile habitats. Large meteorite impacts, capable of heating the oceans to nearly 100 °C, would have occurred occasionally prior to 3.8 Ga ago. Such impacts would have destroyed all life except two types of organism: those forms capable of living in high-temperature conditions, and perhaps also those organisms that had been accidentally preserved in especially thick ice caps. Modern organisms can survive up to half a million years or more in ice (Reeve et al., 2002), and there are probably cells preserved in ice that has crystallized from Lake Vostok, the great ancient lake under the Antarctic ice cap (Karl et al., 1999). Just possibly, some early mesophiles could have survived, having been subject to earlier preimpact freezing in thick ice cap and thus preferentially likely to survive a global heating event after a large meteorite impact.

10.1.5.5 A Hyperthermophile Heritage?

Whatever the setting of the LUCA, there are many aspects of modern cells that have a possible or likely hyperthermophile origin (Martin and Russell, 2003). To possess such a heritage, it is not necessary that a cell’s primary ancestral line once occupied a hyperthermophile habitat. There has been much genetic exchange between organisms both within lines and even massively between domains (Figure 6(b)).

Candidates for biochemical processes or molecules with hyperthermophile origins include the HSP and the metal enzymes (Nisbet and Fowler, 1996b; Nisbet and Sleep, 2001; Sleep, 2010). HSP are ubiquitous in all domains of life. They help repair damage after heat shock, but more generally, they help to shape new protein molecules so they can carry out their proper functions. The HSP are clearly of the greatest antiquity, given their involvement in very basic housekeeping processes. Their role as heat shock repairers may of course simply be a relatively late adaptation to life in hot settings. Alternately, however, HSP may indeed descend from an original function evolved to enable life to enter hyperthermophile settings around hot-water vents.

Like the HSP, the metal enzymes are central to many very basic cell functions. The metal-4N and Ni proteins have already been mentioned. Many other metal proteins involve metals, such as iron, copper, or zinc, often associated with four sulfur atoms. Such metals are characteristic of hydrothermal systems hosted by basaltic and andesitic volcanism. More generally, easily available metals in hydrothermal systems play a key role in many vital proteins, often but not always associated with four sulfurs. Examples include zinc in carbonic anhydrase; alcohol dehydrogenase; and RNA and DNA polymerases; copper in proteins used in respiration, such as cytochrome c oxidase; cobalt in transcarboxylase; Mo in many enzymes participating in the nitrogen cycle, in sulfite oxidase, in some dehydrogenases, and in dimethylsulfoxide-trimethylamine oxide reductase (which may have had an important role in early methane-linked atmospheric chemistry); selenium in hydrogenases; and iron in a wide range of catalases, peroxidases, ferredoxins, oxidases, and all nitrogenases.

Nickel, in particular, is interesting to the geologist, especially as Ni sulfides are frequently hosted by komatiites, characteristic Archean lavas. For example, carbon monoxide dehydrogenase, which is at the center of the acetyl-coA pathway of reducing carbon dioxide, characteristically contains nickel, zinc, iron, and molybdenum. Both coenzyme F₄₃₀ of methanogens and hydrogenase contain nickel. Consequently, nickel is essential to methanogens (Konhauser et al., 2009). Moreover, urease, a key part of the nitrogen cycle, converting urea to carbon dioxide and ammonia, is based on nickel. The most obvious supply of nickel in nature is komatiite: highly magnesian high-temperature lavas that would have been widespread in the late Hadean and the early Archean. Around komatiites, nickel sulfide would have been freely available. It could be that it was in this setting that nickel metal proteins evolved: perhaps it was around komatiite flows that hydrogenases, carbon monoxide dehydrogenase, and urease began. It may be that it was in such settings that methanogens first appeared, exploiting the hydrogen made from serpentinization reactions (Figure 8; Sleep et al., 2011). It is interesting to wonder if the cytochromes, methanogens, and the nitrogen cycle all first evolved on the flanks of komatiite volcanoes.

Today, metals are scavenged from water by extremely sophisticated biochemical processes (Morel and Price, 2003). Thus, seawater can have very low ambient levels of metal ions. Early Archean seawater would likely have been much richer in trace metals. But given that early organisms presumably had very unsophisticated processes for capturing metals, even in seawater rich in metal, it would have been difficult to access the metal. Perhaps the earliest distribution of

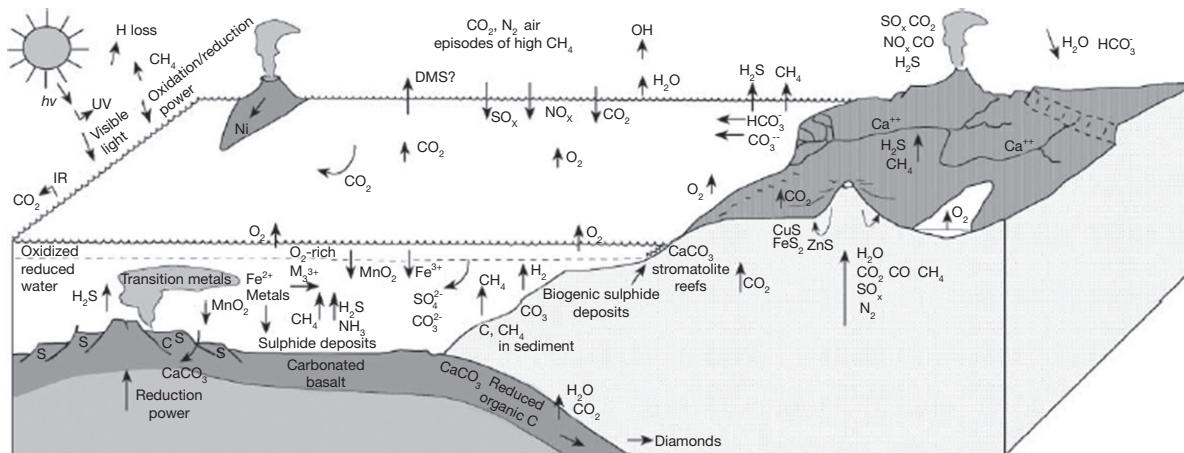


Figure 8 Sources of disequilibrium – possible geochemical (redox) resources for life in the early- to mid-Archean.

organisms was very restricted, with few cells living away from locations such as volcanoes that had readily accessible metals. Only the evolution of effective metal-gaining siderophores would have allowed the spread of life. There is thus reason to believe that even if the LUCA was not hyperthermophile but lived in somewhat cooler conditions, from it came volcano-hosted hyperthermophile ancestral lines, living in and around hydrothermal systems, that led to the Archaeal domain and perhaps also to most bacteria. There has been much gene exchange since then, and consequently enzymes of hyperthermophilic origin are ubiquitous in the housekeeping chemistry of all cell lines. The volcanic signature is written deeply into all life.

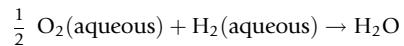
10.1.5.6 Metabolic Strategies

It is likely that the oldest organisms were not photosynthetic (see discussion in Nisbet et al., 1995; Nisbet and Sleep, 2001, and evidence in Grassineau et al., 2006). Prephotosynthetic organisms would have depended on natural redox contrasts and would thus have lived in habitats where such contrasts were accessible, either spatially or temporally (in fluctuating conditions). Air is never in chemical equilibrium and always contains both reduced and oxidized species. At the top of the atmosphere and in the higher levels, there would have been radiation-induced sources of oxidation power: the oxygen left after loss of hydrogen knocked out by UV, cosmic rays or solar wind, and also OH formed from water vapor in the lower air. The flux of UV in particular has major biological impact (Cockell, 2000). In addition to N₂ (Kasting, 1993), sulfate and nitrate from volcanic eruptions would have been present (Kasting et al., 1989; see also Alt and Shanks, 1998). Such transient species would have contributed vital oxidation power to the oceans; simultaneously, reduced species such as CO, H₂, and perhaps NH₃ would have been present also. The chief source of reduction power would be hydrothermal exchange with magma, providing reduced sulfur species, H₂, CH₄, CO, and NH₃.

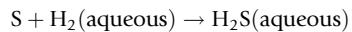
Major reactions supporting prephotosynthetic life (Reysenbach and Shock, 2002) may have included a series of

processes that depended on molecular hydrogen that was formed inorganically. Water/rock reaction at high temperature (Kaiser, 1995; Stevens and McKinley, 1995) produces molecular hydrogen when circulating groundwater reacts with ferromagnesian minerals (FeO silicate), producing iron oxide (e.g., Fe₂O₃) and quartz. Deeper in the earliest Earth hydrogen may also have been formed by water reaction with iron, as the iron precipitated to the core, producing an oxide component to the core and releasing molecular hydrogen to the mantle.

Such inorganically released hydrogen would have been available to be exploited by microbial life. Some archaea and bacteria use the 'knallgas' reaction:



Others reduce sulfur:



Methanogenesis (Thauer, 1998) is another process that involves H₂; in this,

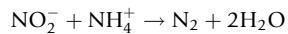


Methane likely was critical in sustaining a warm Archean climate (Catling et al., 2001).

These processes then allow sulfate chemistry to give many microbial possibilities: for example, an extreme option is:



Similarly, some planctomycetes can exploit ammonium and nitrogen oxides, likely to be found around volcanoes, to make dinitrogen:



Nature evolves by processing waste dumps. It is possible to imagine, for example, an early community of cells, as a single biofilm located on the site of a redox contrast, making its living from one of the hydrogen-using reactions. This would produce a waste of dead cells – reduced carbon – and also the by-products of metabolism such as sulfur or bicarbonate. Various specialist cells would evolve to tap into the new opportunities

afforded either by oxidizing the dead carbon or by using the by-product. These new cells would form a substrate, thickening the biofilm. Then, in turn, the waste of the new cells would be utilized, until the whole network resembled a complex clock with innumerable wheels cycling and recycling the thermodynamic possibilities provided by the basic metabolic redox-driven winding of the spring.

10.1.6 The Early Biomes

10.1.6.1 Location of Early Biomes

Replication of the last common ancestor would lead to mutation: in turn, mutation would create accidental preadaptation to life in diverse new habitats. Whatever the habitat of the LUCA, the spread of life across the more accessible other locations on Earth was probably rapid, when compared to a geological timescale.

The habitats available were disparate (Nisbet and Sleep, 2001). Examples include: hydrothermal high-temperature ($>85^{\circ}\text{C}$) settings; moderate thermophile settings ($\sim 40^{\circ}\text{C}$) on the fringes of hot areas, or in cooler, probably more alkaline springs; very cool ($\sim 0^{\circ}\text{C}$) water distal to hydrothermal vents but in the flux of metals and geochemical contrasts from hydrothermal plumes; in tidal waters where currents create a flux of nutrient; around terrestrial volcanoes; under ice; or even in air in dust clouds in frequent eruptions and meteorite impacts.

Lane et al. (2010) have argued persuasively that the earliest community was chemiosmotic. They suggested the earliest cells harnessed geochemically created proton gradients and then learned to make their own. Imagining a setting where this could occur, they pointed out that serpentinization produces hydrothermal fluids that are strongly alkaline (pH 9–11), are very rich in dissolved hydrogen and are capable of making abiotic hydrocarbons, methane, formate, and acetate. Methanogens depend on electron transfer from H_2 to CO_2 .

The first organisms to replicate in each habitat would immediately create new habitat by their very existence. Nature spreads on its own ordure. Dead cells would provide reduced organic matter that could be exploited by reoxidation by other cells, and specialist cells would rapidly evolve. Within a number of generations, mutation would lead to a diversified biofilm, relatively reduced at its base and relatively oxidized above (assuming that the redox gradient is between more reduced rock substrate and more oxidized air/ocean system).

This diversification would lead to distinct types of biofilms in specific habitats – the earliest biomes. They may have been only a few microns thick, but these would have been the first complex communities: the ancestors of interdependent ecologies.

10.1.6.2 Methanogenesis: Impact on the Environment

Life operates on a global scale. On a geological timescale, once the first cell had replicated, all habitats on the planet would immediately be filled. This would rapidly have consequences for the atmosphere.

Strong evidence for the Archean methanogens comes from highly fractionated carbon isotopes. As mentioned earlier, these have been found in 2.7 Ga material from Belingwe (Grassineau

et al., 2002, 2006) and also from similarly aged rocks in Australia (Rye and Holland, 2000). In samples from Isua, Greenland, relatively light carbon isotope values suggested, though not definitively, that methanogenesis was taking place even as early as ~ 3.8 Ga ago, (Grassineau et al., 2006).

In particular, if most molecular phylogenies are correct, methanogens are likely very ancient and may long predate methanotrophic bacteria. Methanogens most probably predate photosynthesizers if the evolutionary lengths in the standard models of molecular paleontology (Barnes et al., 1996; Pace, 1997; Woese, 1987) have value. Once methanogens had evolved, they would have occupied proximal and distal hydrothermal habitats and then perhaps wider habitats, such as open ocean (Sansone et al., 2001) and tidal habitats. Possibly, methanotrophs evolved quickly following the arrival of methanogens, to exploit the new opportunity: but, in the likely absence of abundant free molecular oxygen, they would have been severely limited by the supply of oxidant. The methane-oxidizing archaea operate by anaerobic oxidation of methane against sulfate, to produce bicarbonate, HS^- , and water: their impact would have been limited by the supply of sulfate oxidant. Thus it is conceivable that a large methane burden accumulated in the atmosphere. As methane is a very powerful greenhouse gas (Catling et al., 2001), it may have been capable of sustaining a clement atmosphere.

Biological methane emission to the air on a scale large enough to affect the atmosphere would have been possible if the hydrogen or acetate supply from inorganic and organic sources (and hence methanogenesis) had been adequate and on a larger scale than the methane removal flux (by atmospheric OH, supplemented by methanotrophy). Given the likely abundance of ultramafic rock near the early Archean seafloor, interacting with hydrothermal water, it is not unreasonable to suppose a major flux of inorganic hydrogen. If so, and there was a surplus of methane in the seabed biofilms, then much of the methane formed by the first methanogens would have been emitted directly to seawater and hence (because the water was anoxic) to the atmosphere. In the dry air on a cold glacial planet, this methane might rapidly overwhelm the OH. Over a few tens of millennia, if the air were anoxic, the atmospheric methane burden could build up and have a significant greenhouse impact (see Catling et al., 2001), until enough ice melted to permit OH in air and thus control the methane. It is indeed very likely, from $\Delta^{33}\text{S}$ evidence, that the Mesoarchean atmosphere was anoxic (Farquhar and Wing, 2003; Farquhar et al., 2007, and papers cited therein).

Methane may thus have played a crucial role in sustaining habitability on the early Earth (Catling and Claire, 2005; Catling et al., 2001; Pavlov et al., 2000, 2001). Methane emitted by organisms would have had a substantial greenhouse effect, and if the methane/carbon dioxide ratio in the air were high, methane could have fostered an organic smog that protected shallow-level life against UV radiation in sunlight (Lovelock, 1988). Thus there is a possible progression here, from the first methanogens, few in total number and confined to the immediate vicinity of hydrothermal systems on a very cold planet, then a warming trend, then development of planktonic life and much more widely spread methanogens, increasing the warming.

[Catling et al. \(2001\)](#) and [Kasting and Catling \(2003\)](#) pointed out that in the early Archean, biogenic methane may have saved Earth from permanent glaciation. On the modern Earth, on a 20 years timescale, emission of methane has an incremental greenhouse impact nearly 60 times, weight-for-weight, or 21 times, molecule-for-molecule, that of carbon dioxide. On the Archean planet, this ratio would have been very different, and the difference is nonlinear with burden. But whatever the greenhouse impact was, methane is a very powerful greenhouse gas. Indeed, unless abundant methane existed in the air, it is difficult to imagine how intense global glaciation was avoided. Thus geologically likely models of the early Archean atmosphere, that are consistent with the Isua evidence for water-eroded and water-transported sediments, would be expected to invoke high methane concentrations (10^2 – 10^3 ppm – compared to modern air with less than 2 ppm CH₄ and ~ 375 ppm of CO₂). Such high levels of methane would lead to hydrogen escape by photolysis and loss from the top of the atmosphere and hence irreversible net oxidation of the planetary surface environment ([Catling et al., 2001](#)), though not necessarily to significant ambient O₂ at any particular time.

The Archean surface temperature is very controversial. From isotopic evidence in cherts, [Knauth and Lowe \(2003\)](#), [Knauth \(2005\)](#), and [Robert and Chaussidon \(2006\)](#) inferred warm temperatures, possibly as high as 50–70 °C. This assumes ([Marin et al., 2010](#)) that the samples are seawater precipitates, not from hydrothermal fluids, and that seawater was similar in oxygen isotopes to modern values. From phosphate oxygen isotope values, [Blake et al. \(2010\)](#) came to the different conclusion that seawater temperature was around 26–35 °C, much the same as modern tropical ocean water.

Methanogenesis may have had the interesting consequence of triggering the evolution of nitrogen fixation ([Kasting and Siebert, 2001](#); [Navarro-Gonzalez et al., 2001](#)). On an early planet with CO₂ present in the air, nitrogen fixation would have occurred in lightning strikes, which would have used oxygen atoms from the carbon dioxide (or from water) to form NO. However, if CO₂ levels declined and CH₄ rose, the oxygen supply would be reduced, limiting the synthesis of NO. This would have created a crisis for the biosphere as usable nitrogen is essential. Out of this crisis, [Navarro-Gonzalez et al. \(2001\)](#) suggested what now appears to be the essentially ‘altruistic’ process of nitrogen fixation, which is very expensive in energy.

Another, not necessarily incompatible hypothesis is that nitrogenase first evolved as a manager of excess ammonia in the lower, anaerobic part of microbial mats, where hydrogen is present. The product, dinitrogen, could be safely bubbled away. Had a crisis occurred, in which there was a shortage of fixed nitrogen, any cell or consortium of cells able to reverse the process would have been advantaged. It is perhaps notable that in nitrogenase the N₂ is bound to a cluster of Mo–3Fe–3S. Molybdenum, iron, and sulfur are likely to be abundant together at hydrothermal systems, especially around andesite volcanoes, and this may be a protein with a hydrothermal heritage. [Falkowski \(1997\)](#) pointed out that the requirement for iron and the need for anoxia would have put severe limits on nitrogen fixation, such that fixed nitrogen supply (and hence the availability of iron), not phosphorus, may be the chief limitation on the productivity of the biosphere. Indeed, the vast scale of

human fixation of nitrogen and perhaps the pH change of the ocean may someday be seen as the greatest peril of modern global climate change, not the greenhouse.

The nitrogen budget is complex. [Vlaeminck et al. \(2011\)](#) discussed the suggestion that microbial nitrogen oxidation began in methanotrophic bacteria, while early nitrate production may have been via ammanox planctomycetes.

10.1.6.3 Prephotosynthetic Ecology

Early life most likely depended on exploiting the transient redox contrasts available from two sources: within the inorganic geological system – especially at hydrothermal vents ([Reysenbach and Shock, 2002](#)) – and secondly from inorganic light-driven reactions, such as the formation of transient oxidizing and reducing species in the atmosphere by incident radiation.

These sources of redox contrast would have been limited. The hydrothermal contrasts depend on local thermally driven juxtaposition (e.g., in vent fluids) of chemical species from differing environments. From the vents would come H₂, H₂S, and probably CH₄. The size and activity of the hydrothermal biosphere and hence its impact would have been considerable, as early Archean volcanism was probably much more common than today, with a higher heat flow out of Earth. Nevertheless, the total potential productivity of an early hydrothermal biosphere would have been small on a global scale compared to the modern photosynthetically driven biosphere. Moreover, modern biota at hydrothermal vents depend on the supply of sulfate, oxidized in the photosynthetic biosphere: before photosynthesis, the sulfate supply may have been limited. Thus, as a first guess, with a planetary heat flow higher than today but not massively so, and with a limited supply of oxidation power, it is unlikely that the early Archean chemolithotrophic biosphere would have been vastly greater than the sum of today’s hydrothermal communities.

In addition, there would have been redox consequences from the formation of transient chemical species in the air. The solar radiation, expelling H from the top of an atmosphere containing water vapor, would likely have produced OH and probably some O₂. Volcanic gases, taking part in atmospheric chemistry, would produce a small but important supply of sulfur oxides – and hence sulfate and sulfide in the sea, as well as nitrates and nitrites. Moreover, H₂ and CO would have been present. Together, the inorganic sources of redox contrast probably would have been capable of sustaining a small global biological community.

Life must be continuous – it must always have habitat. Volcanoes, however, become extinct. Thus, life must either have been able to live in the open ocean or must have hopped from dying volcano to new volcano. Volcanic vents were probably abundant enough, close enough, and accessible enough (especially to cells capable of floating in cool water or blowing in wind) that they could host migrant cells that were perpetually seeking a new home as the old one was exhausted. For life to be sustained over billions of years, large tracts of liquid water are necessary – oceans – and with them, water in the air also, to sustain erosion, supplying recycled essentials such as metal ions and helping control carbonate deposition. In the long term, a planet without rainbows is a planet without life.

My heart leaps up when I behold
 A rainbow in the sky
 So was it when first life began
 So is it in Earth's rich full span
 So be it when our home grows old
 Nor let her die!
 The cell is parent of the Man
 And Woman too, in days to be
 Bound each to each by natural piety.

Modified after Wordsworth

Nonphotosynthetic plankton are abundant today (Karl, 2002). Many of these are eukaryote zooplankton, but there is also a massive population of planktonic archaea that live near the base of the photic zone. Indeed, in the Pacific, the archaea dominate the deeper waters below ~ 1000 m depth, where pelagic crenarchaeota are abundant (Karner et al., 2001). In the early Archean, there may have been a significant boundary between deeper, more reduced water, and shallower water in sunlight. This boundary, as it shifted diurnally, would provide a fluctuating redox contrast for organisms that could exploit it. For example, the planctomycetes form macroscopic aggregates (>0.5 mm) of detritus in which they create tiny microaerobic or microanaerobic habitats in otherwise aerobic environments (Fuerst, 1995). They can thus exploit local redox contrast. Among the diverse and interesting properties of the planctomycetes is their ability to react nitrate with ammonia, evolving dinitrogen (the anammox process: Jetten et al., 2001; Fuerst, 1995). This too may be of long antiquity.

10.1.6.4 Geological Settings of the Early Biomes

Geological evidence for the early distribution of life is fragmentary. In the early Archean of the Isua belt, Rosing (1999) reported isotopic and textural evidence of planktonic life, presumably occupying mesophile or cool, even near-freezing habitats, from prior to 3.7 Ga. A possible (though not robust) inference is that from the LUCA, fairly early in Earth's history, came the occupation of a diversity of habitats (Figure 9). If Rosing's evidence is correctly interpreted, by ~ 3.7 Ga, mesophile plankton existed. On the modern Earth, Archaeal plankton are abundant in the deeper parts of the upper ocean, in the deep photic zone and below. Though ill-studied, the planctomycetes have marine examples. Thus, a marine biome, occupied by free-living cells and perhaps making N_2 by ammanox processes, was probably well established and diversified by the mid-Archean.

The geologic evidence for the presence of sulfur-processing microbial life and for methanogens goes back to the early Archean Isua sequence (Grassineau et al., 2006). Rocks containing highly fractionated sulfur isotopes, closely spatially associated with highly fractionated carbon, are known from many other Archean localities (Goodwin et al., 1976). For example, in the late Archean 2.7 Ga sediments of the Belingwe belt, Grassineau et al. (2001, 2002) describe what is interpreted as evidence for a complex biological sulfur cycle. Fractionated pyrite, implying sulfur-processing bacteria, is also known from 3.4 Ga Barberton rocks in South Africa (Ohmoto et al., 1993).

The rRNA molecular phylogeny (Barnes et al., 1996; Pace, 1997; Stetter, 1996; Woese, 1987; Wu et al., 2009) implies the antiquity of hyperthermophile organisms. Though there has

been much dispute about the interpretation of rRNA, there is some consensus that, whether or not it is the very most ancient habitat, life around hot-water vents is certainly of great antiquity. The implication is that by the mid-Archean, hyperthermophile habitats around hot vents were populated by microbial mats, and the waters around hot vents were likely occupied by motile cells, free-swimming in the water. Mesophile prephotosynthetic plankton probably existed in the open seas, and distal to the thermophile life in the surroundings of vents, the mesophile habitats further from the hot springs were also occupied.

The reactions that involve sulfur oxidation states leave isotopically fractionated sulfur and hence sulfide is a target for investigation by the geologist. Though there is controversy about sulfur isotope fractionation (Farquhar et al., 2000, 2007), the strong fractionation of $\delta^{34}S$ seen in the best-preserved Archean organo-sedimentary rocks can only be biological. Sulfate reducers are probably very old, present 3.5 Ga ago in the early Archean (Shen et al., 2001) and probably 3.8 Ga ago (Grassineau et al., 2006) and may have provided sulfur deposits, which in turn supported an increase in the supply of HS and H_2S at the bottom of the biofilm: the biofilm would have thickened, diversified, and turned to a microbial mat, created by structured consortia of prokaryotes (Fenchel and Bernard, 1995; Nisbet and Fowler, 1999). Such mats could have had a large impact on the production of reduced gases added to the air (Hoehler et al., 2001) and could have had a global significance in keeping the planet warm (Kasting and Siefert, 2002). Methane generated at the bottom may have been recycled nearer the top of the mat, in processes such as those described in the modern ocean by Boetius et al. (2000) in which archaea and sulfate-reducing bacteria consort.

The evolution of photosynthetic oxidation of sulfur compounds permitted the development of the full microbial sulfur cycle in sulfureta. In this cycle, some bacteria and archaea reduce oxidized sulfur compounds, pumping them downward in the microbial mat, while other bacteria reoxidize them photosynthetically. The development of this cycle coupled with the use of stored sulfur as a redox bank balance that could be exploited either way, the redox budget swung during tidal and diurnal cycles, would have greatly expanded the thermodynamic power of the biosphere.

The thermodynamic drive for this life would have come from various sources. In hot-spring settings, reduced species such as CH_4 , H_2S , and H_2 would have emanated from inorganic reactions around hot magma. These could have provided the basis of methanogenic life; quickly the supply of dead biomass would provide opportunity for other organisms to generate H_2 organically, thus multiplying the opportunities of the methanogens. At the top of the biofilms, sulfate was probably available in water. In the open seas, prephotosynthetic Archaeal and planctomycete planktonic life probably spread ubiquitously even before the advent of photosynthesis – it is a small evolutionary hop from a cell loosely bound to a microbial biofilm and a cell that lives in the sea, floating up and down between redox settings. Possible sources of life support, though limited in total flux, would have been widespread. They would have come from volcanic sources, especially in plumes of hot water, creating the contrast between, above, SO_x and NO_y chemical species dissolved in seawater from the

atmosphere, and below, reduced chemical species emanating from hydrothermal vents on the seafloor. Structured consortia of archaea and sulfate-reducing bacteria (Boetius et al., 2000) may have had global distribution.

10.1.7 The Evolution of Photosynthesis

10.1.7.1 The Chain of Photosynthesis

Photosynthesis is the source of the redox power that allowed life to escape from confinement to the very restricted early settings, where inorganic redox contrast existed, and to occupy the planet. Without access to light energy, life would have been permanently restricted to a few narrow and unstable settings, probably as thin biofilms and as plankton near upwellings.

Photosynthesis involves a complex chain of events, each of which must have its roots in the remote Archean (Blankenship,

2001; Hohmann-Marriott and Blankenship, 2011). The chain is of great interest, as each unit presents a separate puzzle in explaining its evolutionary history. Light is captured by pigments, such as chlorophylls (in oxygenic photosynthesis by eukaryotes and cyanobacteria) or bacteriochlorophylls (in other bacteria) and accessory pigments such as phycobiliproteins. The light is harvested by an array of chlorophyll molecules (say 300) that form an antenna, around a light-harvesting complex. This array passes the energy of the absorbed photon from molecule to molecule until it reaches a photosynthetic reaction center. In purple bacteria, the photosynthetic reaction center consists of special bacteriochlorophyll molecules, linked to other molecules and a central Fe(II) atom. In the overall process in purple bacteria, the net result of two photons hitting the reaction center is the transfer of four H⁺ from the interior cytoplasm to the external medium.

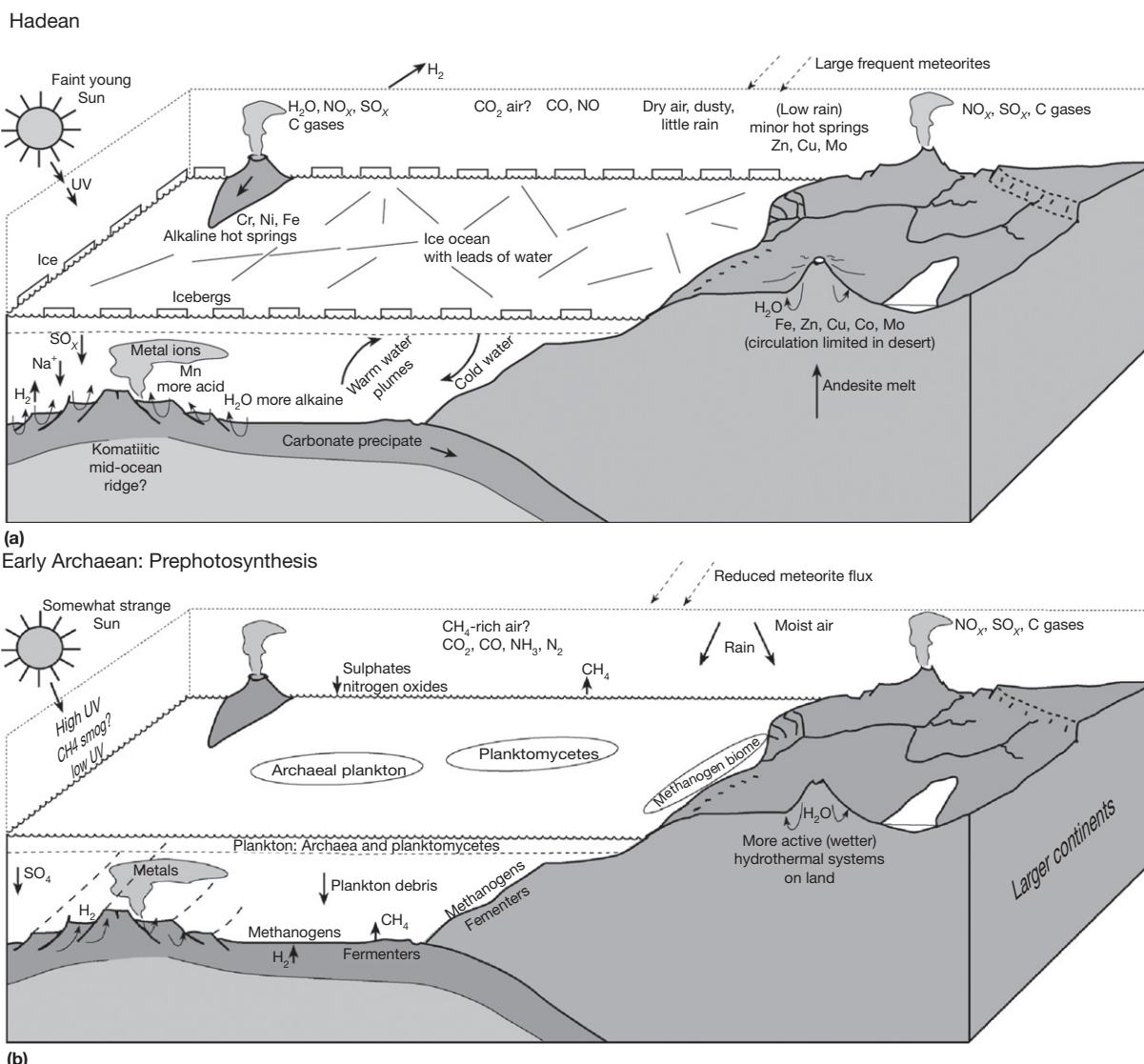
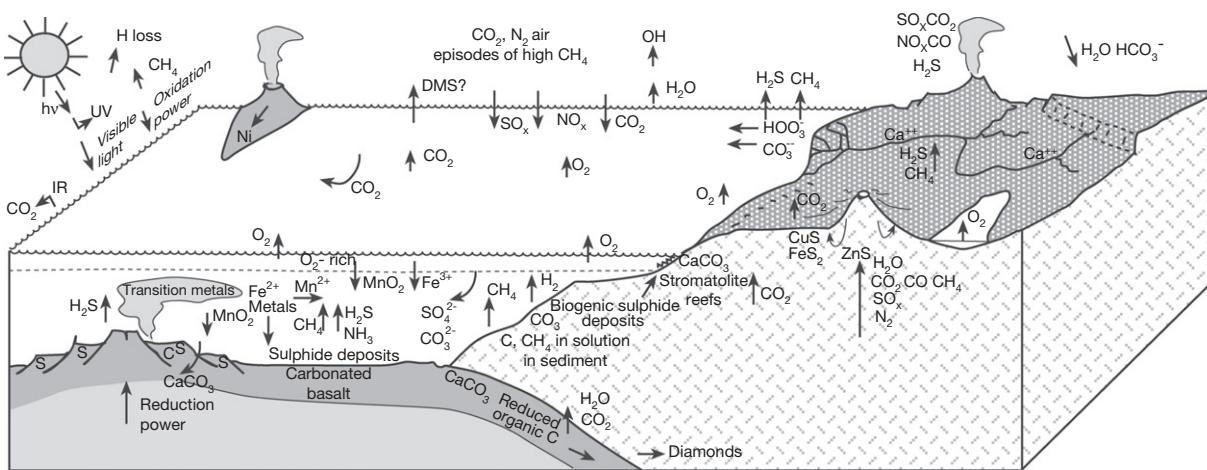
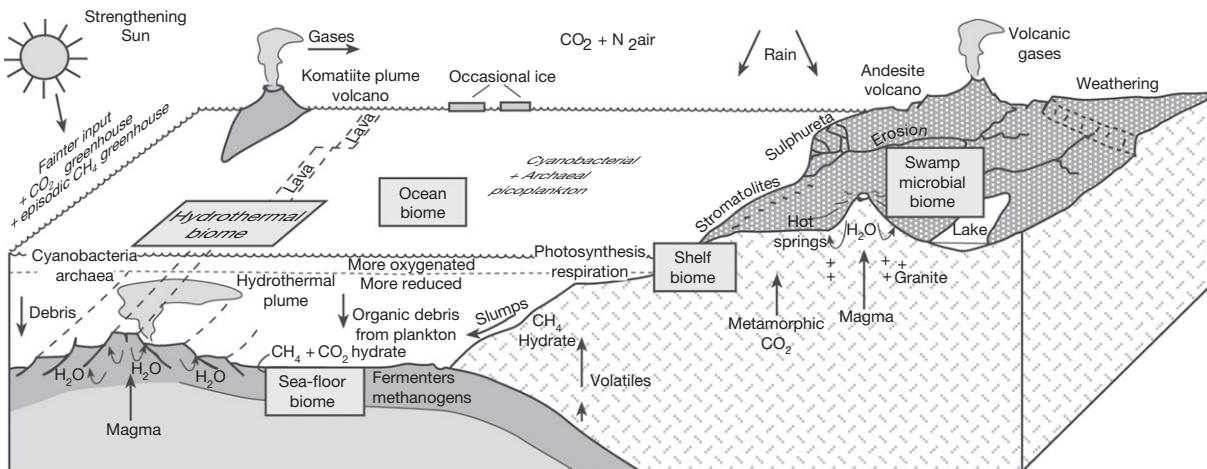


Figure 9 Model of the evolution of the planetary surface: (a) Hadean surface, possibly glacial (apart from rare very hot events after major meteorite impact); (b) early Archean surface, before the onset of photosynthetic processing of the air; and (c) late Archean surface, assuming that the major biochemical pathways had evolved and that the main groups of prokaryotes had evolved.

(Continued)

(c) Late Archaean: with oxygenic photosynthesis

**Figure 9** (Continued)

In oxygenic photosynthesis, in cyanobacteria and chloroplasts in plants, there are two linked reaction centers. One (photosystem II; PSII) is similar to that in purple bacteria. At PSII, an oxygen-evolving complex based on manganese oxide splits two water molecules into 4H^+ and dioxygen, O_2 , which is evolved as waste. The other center, PSI, is electrically connected to the PSII production of H^+ , and, with two further electrons, generates NADPH; in addition, ATP synthesis occurs on the membrane, driven by proton flow turning the ADP synthase motor. Thus, the products of light capture are NADPH and ATP.

Then in the biosynthesis reactions, the NADPH and ATP are used to capture carbon from the environment for use in biology. Three ATP and two NADPH, with two H^+ combine with a water and a CO_2 molecule to form carbohydrate. In sum, a dozen quanta of light energy are needed to incorporate one molecule of CO_2 . This process is accomplished by the enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase, or 'rubisco,' which can in effect work both ways, either capturing carbon dioxide from the air or oppositely to return it, depending on the $\text{O}_2:\text{CO}_2$ ratio it is exposed to (Lorimer, 1981; Lorimer and Andrews, 1973).

On rubisco hangs the balance of the atmosphere (Nisbet et al., 2012; Tolbert, 1994).

10.1.7.2 The Rubisco Fingerprint

Geologically, photosynthesis presents several palimpsests to be searched for in the geological record. Isotopic evidence of the actions of rubisco is the most obvious target. Rubisco, which presumably must predate oxygenic photosynthesis, is the key enzyme that facilitates carbon capture during oxygenic photosynthesis. The process is very selective in the carbon atoms it accepts and leaves a distinctive C isotopic fingerprint, as light carbon-12 is selected in preference carbon-13. Hence, the organic molecules that are created are highly depleted in ^{13}C . There are several types of rubisco (Tabita et al., 2008). In oxygenic photosynthesis, rubisco operates in aerobic or microaerobic conditions, not anaerobic settings. Rubisco II is a characteristic of organisms that fix CO_2 in anoxygenic photosynthesis. It may be more ancient and is today found in deep-sea vent organisms (Elsaied and Nayonama, 2001). Other forms of

rubisco occur in anaerobic organisms. Rubisco III, for example, is found in methanogens, while rubiscolike proteins occur in a variety of anaerobes.

In studying oxygenic photosynthesis, the oxygen-evolving complex is also a target for the geologist, as it is based on manganese oxide.

More subtly, the isotopic signatures of photosynthesis in inorganic sediment are also instructive (Nisbet and Fowler, 2011; Nisbet et al., 2007a,b). Rubisco depletes the environment of ^{12}C . Hence, inorganic carbonate is enriched in ^{13}C if rubisco operates on a planetary scale. Carbon dioxide emitted from the mantle is about $\delta^{13}\text{C} \sim -5\text{\textperthousand}$ to $-7\text{\textperthousand}$, on the arbitrary Pee Dee Belemnite (PDB) scale. About a quarter to a fifth of carbon in the environment is captured by rubisco to make organic matter: kerogen (rubisco-fractionated organic matter) has about $\delta^{13}\text{C} \sim -28\text{\textperthousand}$ to $-30\text{\textperthousand}$ when fractionated by rubisco I but around $-11\text{\textperthousand}$ when fractionated by rubisco II (e.g., Guy et al., 1993; Robinson et al., 1998). Three-quarters to four-fifths is residue precipitated as carbonate at $\delta^{13}\text{C} \sim 0\text{\textperthousand}$. The presence of $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ carbonate is thus testimony that rubisco I was capturing carbon on a global scale, in aerobic conditions: this is known as the rubisco fingerprint.

10.1.7.3 The Evolutionary Chain

Respiration most probably evolved before photosynthesis (Xiong and Bauer, 2002). Each step in this chain must have a long and complex evolutionary history (Pierson, 1994) – the puzzle is similar to Darwin's puzzle – what use is half of an eye? And half of photosynthesis? The debate is vigorous and is addressed by Blankenship (2001), and Hohmann-Marriott and Blankenship (2011), and references cited therein. How did the full photosynthetic chain evolve, given that it appears at first glance that half a chain is useless? The challenge to the geologist is to identify the small steps of preadaptive advantage on which evolutionary change worked, to date those steps and to explain the way the individual links in the chain were incorporated.

There is much debate about the origin of photosynthesis and little agreement. Among the many hypotheses, Nisbet et al. (1995) suggested that photosynthesis began in organisms that were preadapted by their ability to use IR thermotaxis to detect hot sources (Figure 10). This hypothesis offers a set of small incremental steps, each immediately advantageous, each depending on accidental preadaptation that led to the very

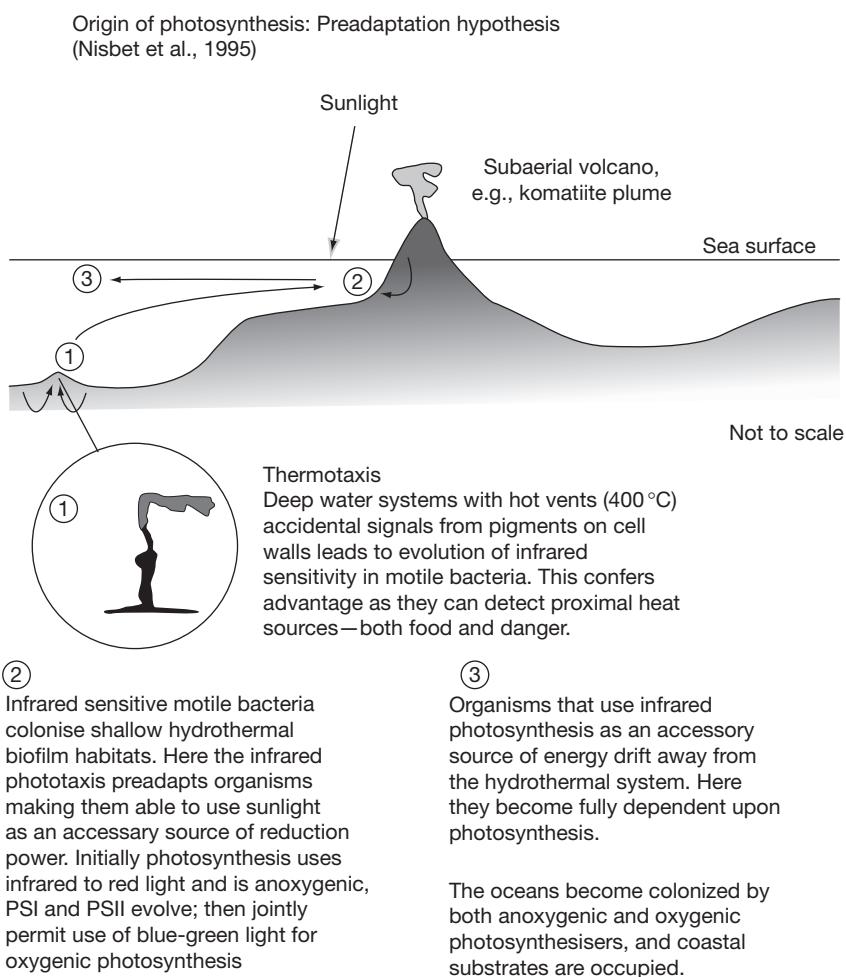


Figure 10 Possible evolutionary chain leading to photosynthesis: hypothesis of preadaptation for infrared thermotaxis. Derived from Nisbet EG, Cann JR, and van Dover CL (1995) Origins of photosynthesis. *Nature* 373: 479–480.

sophisticated electron management that occurs in photosynthesis. The steps begin with accidental IR sensitivity in cells that had pigments in their outer surfaces. Deep-water hot vents emit IR radiation at around 350–400 °C, slightly below the temperature of a hot plate on a kitchen cooker before it becomes a visible cherry red. Detection of this radiation would have been very advantageous to motile organisms, and such organisms that possessed IR detection and ability to move toward the source (or away if it became too powerful) would have gained survival advantage. Evolutionary survival would then have favored those cells that were increasingly fine-tuned to the IR. Then, in the next step, organisms that had spread to a shallow-water vent would be preadapted to use solar IR as a supplementary energy source; finally, full dependence on abundant and energetic visible light energy would follow. The hypothesis suggested by [Nisbet et al. \(1995\)](#) invokes IR phototaxis: the cells that use IR depend on bacteriochlorophyll and are anoxygenic and usually act in anaerobic settings.

However, other hypotheses have suggested that oxygenic photosynthesis came first, depending on chlorophyll, and that from chlorophyll evolved bacteriochlorophyll. Bacteriochlorophyll absorbs into the IR. Chlorophyll a is green in color, as it absorbs red and blue light and reflects green – thus green, though much loved, is waste light – the biosphere's chief excretion. If chlorophyll came first, the hypothesis of 'evolution via IR thermotaxis' would be invalid.

Which came first – bacteriochlorophyll or chlorophyll? Much of the debate centers on the long-held Granick hypothesis ([Granick, 1965](#)). The steps to the synthesis of chlorophyll being simpler, it would intuitively be expected to have come first. However, it now appears that bacteriochlorophyll predates chlorophyll ([Xiong et al., 2000](#)), refuting the Granick hypothesis, so the 'IR thermotaxis' hypothesis remains tenable.

Chlorophyll and bacteriochlorophyll are closely related, and both center around a porphyrin ring that contains a magnesium atom surrounded by four nitrogen atoms (see [Section 10.1.5.2](#) for the argument that these originated in alkaline fluids from hydrothermal systems in ultramafic lavas such as komatiites). Similar porphyrin rings lie at the heart of heme (where the central metal is iron, surrounded by 4N) and the enzyme catalase that helps split hydrogen peroxide to water and dioxygen (thereby allowing the excretion of the poison, either to the external environment or to attack neighboring cells), as well as in the cytochromes. Many of these housekeeping proteins must be of the very greatest antiquity and probably predate the LUCA. They were clearly exploited in the ancestry of photosynthesis, which may have been via evolutionary tweaking of respiratory processes. [Xiong and Bauer \(2002\)](#) concluded that cytochrome b may have been the ancestor of type II photosynthetic reaction centers.

Inorganically, linking metal with nitrogen occurs at very high pH, characteristic of alkaline hydrothermal systems ([Moller and Bau, 1993](#)), especially around ultramafic rocks such as komatiites.

10.1.7.4 Anoxygenic Photosynthesis

There is much evidence for mid-Archean life both from the Pilbara in Western Australia and from the Barberton Mountain Land in South Africa, although there has also been much controversy (e.g., [Brasier et al., 2002](#); see also [Schopf et al., 2002](#)).

As discussed earlier, in the Pilbara, the 3.43 Ga old Strelley Pool cherts ([Allwood et al., 2006, 2007](#)) describe extensive stromatolitic laminae formed as a reef in a transgressive environment with proximal hydrothermal activity, while in Barberton [Tice and Lowe \(2004\)](#) and [Westall et al. \(2006a,b\)](#) report evidence for a complex photosynthetic microbial system.

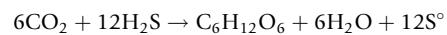
Anoxygenic photosynthesis is carried out by a wide range of bacteria. The chief groups are green sulfur bacteria, such as *Chlorobium* (which do not use rubisco); green nonsulfur bacteria, such as *Chloroflexus*; purple sulfur bacteria, such as *Thiospirillum*; and purple nonsulfur bacteria, such as *Rhodobacter*. The purple bacteria (proteobacteria) are classified by 16S rRNA study into several major evolutionary groups ([Woese, 1987; Wu et al., 2009](#)).

Green sulfur bacteria are strict anaerobes and obligate phototrophs, using hydrogen sulfide, hydrogen, or elemental sulfur, and are unable to respire in the dark. Some have gas vesicles that allow them to float up and down in lakes, adjusting their level with the movement of the redox boundary. Green nonsulfur bacteria are thermophiles, and *Chloroflexus* is typically found as gliding bacteria in mats in hot springs. Purple sulfur bacteria are strict anaerobes, oxidizing hydrogen sulfide to sulfur and often eventually to sulfate. They typically inhabit deeper, anaerobic, parts of the photic layer of lakes, where IR light penetrates. Purple nonsulfur bacteria (many of which are nonphototrophic) are very flexible in life. Normally anaerobic photosynthesizers that use organic molecules as electron acceptors and carbon sources, some species can also oxidize low (nontoxic) levels of sulfide to sulfate. In the dark, most purple nonsulfur bacteria can grow in aerobic or micro-aerobic conditions.

The linking characteristic between these groups is the use of various types of bacteriochlorophyll in a single stage process, involving either photosynthetic reaction center II (e.g., purple bacteria) or photosynthetic reaction center I (e.g., green sulfur bacteria). This photosynthetic process uses electron donors, such as H₂, H₂S, S, or organic matter, and does not, as a consequence, evolve waste oxygen. Many green and purple bacteria can grow phototrophically using H₂ as the sole electron donor and CO₂ as the carbon source, using hydrogenase (a nickel enzyme) for CO₂ reduction.

The two photosystems are structurally related, and [Xiong et al. \(2000\)](#) concluded from a study of sequence information in photosynthesis genes that green sulfur and green nonsulfur bacteria are each other's most closely related groups. Phototrophic purple bacteria use the Calvin cycle and utilize rubisco, with its characteristic (and geologically identifiable) strong fractionation of carbon. Green bacteria, however, do it differently and do not produce the same isotopic signature: *Chlorobium* uses the reverse citric acid cycle, and *Chloroflexus* uses the hydroxypropionate pathway. Geologically, these should be distinguishable in the kerogen record from rubisco-captured carbon.

When the first photosynthetic sulfur-compound oxidizers appeared, the development of full sulfureta would have been possible. Sulfate reducers would take sulfate from the external environment and eventually produce H₂S. Then the photosynthetic oxidizers would reverse the steps, for example,



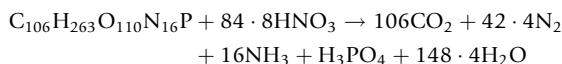
depositing the sulfur either outside the cells (as in phototrophic green bacteria) or inside them (in most of the purple bacteria). This is a trail the geologist can hunt.

The isotopic evidence of [Shen et al. \(2001, 2009\)](#) and [Bontognali et al. \(2012\)](#) suggests bacterial sulfur processing, whether by microbial elemental sulfur disproportionation or by sulfate reduction, is very old and is probably at least 3.5 Ga old. Whether a full sulfur cycle, including microbial S oxidation, was present in the early- to mid-Archean is unknown. The evidence is not inconsistent with a full sulfur cycle but does not prove it. The wider fractionation observed in 2.7 Ga material by [Grassineau et al. \(2002\)](#) (which also includes carbon isotope support) is very suggestive of a full S cycle. [Grassineau et al. \(2002\)](#) reported abundant evidence for highly fractionated carbon in kerogen, the signature of rubisco. Such evidence suggests either the presence of cyanobacteria or anoxygenic photosynthesizers: by extrapolation, this implies the presence of bacteria capable of oxidizing sulfur compounds.

Once anoxygenic photosynthesis had evolved, the planet would have become widely habitable and the biosphere much more productive. Tidal and shallow-water environments around the globe would have been immediately occupied by life. Sulfureta would have cycled sulfur, derived from oceanic volcanogenic sulfate, between the upper more oxidized layers of mats and the lower H₂S-rich layers, creating a complex microbial mat habitat.

Plankton today are very diverse, including Archaea, Bacteria, and Eukaryotes ([Beja et al., 2002; Wu et al., 2009](#)). It is very likely that anoxygenic photosynthesizers would rapidly have spread as plankton, limited only by the availability of reducing chemicals. It is possible to imagine a microbial biosphere dependent on anoxygenic photosynthesis, with widespread abundance of oxidized sulfur and nitrogen chemical species in the uppermost few tens of meters of the sea above an anoxic deeper mass of the seas and oceans. At this stage, the oceanic biomes may have been stratified with anoxygenic purple, green photosynthesizers and planctomycetes ([Fuerst, 1995](#)), which may be an ancient prephotosynthetic branch of the bacteria ([Brochier and Philippe, 2002](#)), as discussed earlier, although their similarities to eukaryotes may simply be a product of convergent evolution ([McInerney et al., 2011](#)).

Complex global-scale nitrogen cycles would also have become possible at this stage. The modern nitrogen cycle is dominated by bacteria. Some bacteria such as *Pseudomonas* release N₂. Many purple and green bacteria can fix nitrogen, using the Fe-Mo enzyme nitrogenase. Anoxic nitrification can occur, coupled with manganese reduction ([Hulth et al., 1999](#)), in suboxic mud (e.g. [Froelich et al., 1979](#)), with evolution of N₂ to the air by denitrification.



The planctomycetes, if presumed ancient, are also capable of emitting N₂ by anammox reaction of NH₃ with NO₂. In the reverse direction, supplying nitrogen from the air, the inorganic sources are mainly volcanoes and lightning. But this source could have been restricted (e.g., see [Navarro-Gonzalez et al., 2001](#)). A nitrogen cycle may have become possible very early on, some species emitting gaseous nitrogen, others

capturing nitrogen from air/ocean. Nitrogen fixation may be closely connected with hydrogen emission: in reducing N₂ to NH₃, eight electrons are consumed, six for producing 2NH₃, and two to make H₂: hydrogen production and nitrogen fixation appear closely linked. Possibly, nitrogenase originally evolved to manage ammonia in close association with methanogenesis using H₂.

With the evolution of the anoxygenic bacteria, the global-scale biosphere would have been greatly enriched. It would have been capable of cycling sulfur, carbon, and nitrogen on a global scale and presumably with fluxes that were on a much greater scale than the inorganic volcanogenic fluxes – over a geologically brief time, bacterial emissions would thus have used photosynthetic energy to reconstruct the atmosphere. From this date also the N₂ cycle has been dominantly biological-produced and consumed by organisms.

10.1.7.5 Oxygenic Photosynthesis

The development of oxygenic photosynthesis created the modern biosphere. Most likely, oxygenic photosynthesis came after the development of photosynthetic reaction system II in purple bacteria and reaction system I in green sulfur bacteria. The use of ubiquitous ingredients, water, carbon dioxide, and light, to capture carbon into life was the final metabolic step that made the entire planet habitable by life. The waste product was simply dumped – indeed, it may originally have been a deliberate toxic by-product in toxin warfare between cyanobacteria and their neighbours.

There are many notions about how photosynthesis evolved (e.g., [Blankenship, 2001, 2010](#)). All photosystems are basically alike and must have had a common origin ([Blankenship, 2010; Jordan et al., 2001; Kuhlbrandt, 2001](#)). Helio bacteria, which are anoxygenic phototrophs living in tropical soils utilize a modified form, bacteriochlorophyll g, that is related to cyanobacterial chlorophyll a. It has been suggested they may be the microbial branch with the photosynthetic genes, which are most closely related to the ancestral cyanobacteria ([Xiong et al., 2000](#)).

Perhaps a primitive reaction system evolved first, in the mutation that produced the common ancestor of the purple bacteria, then a further mutation led to the ancestor of the green sulfur bacteria and of the heliobacteria. It is possible that the first O₂-evolving photoreaction center originated in green nonsulfur bacteria, and that this was later incorporated into cyanobacteria ([Dismukes et al., 2001](#)). Then to speculate further, possibly the two lines formed a symbiotic partnership across a redox boundary and eventually became so close that the genes for PSI and PSII were incorporated into the cell. Another possibility is that, following the development of photosynthesis in the purple bacteria, transfer of Mg-tetrapyrrole genes occurred to the line leading to the cyanobacteria, which together with gene duplication, produced the cyanobacterial reaction center II in the ancestral cyanobacterium ([Xiong and Bauer, 2002](#)). The puzzle remains open.

The evolution of the cyanobacteria and in particular the development of the various forms of the enzyme rubisco ([Figure 11](#)) massively changed the ability of the biosphere by harvesting sunlight and using it to sequester reduced chemical species from the waste oxidation power dumped into the air. These cells would be able, in a single cell, to photosynthesize with the

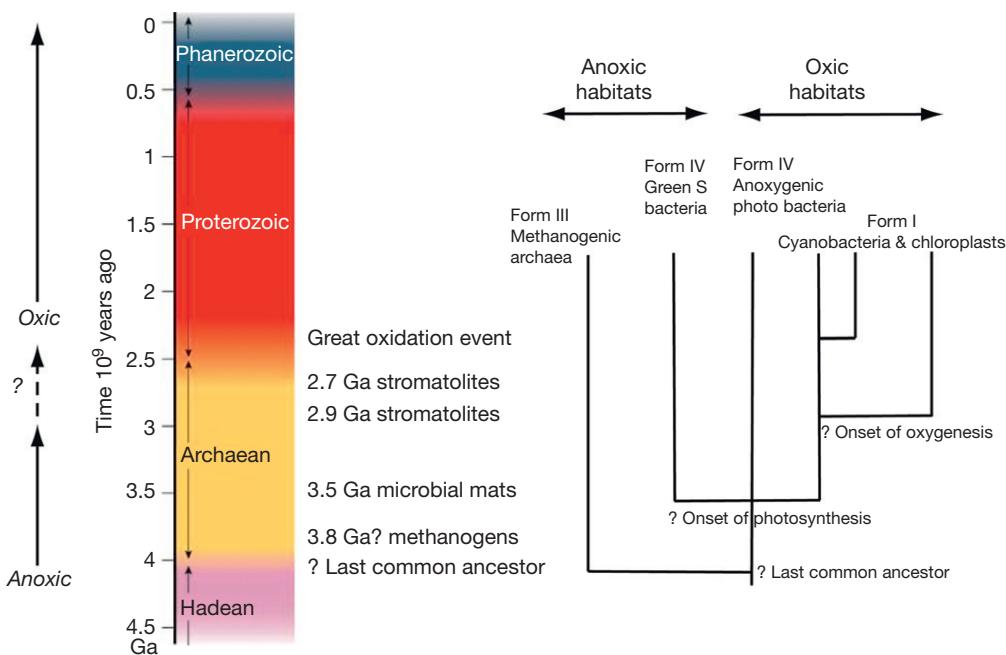


Figure 11 (left) Geological aeons. Note that the Greek word ἀρχαῖ (e.g., in St. John's gospel, 1.1), transliterated 'Archæ' in Latin and thus leading in UK English to Archæ-an, or Archaean, is normally concatenated to 'Archean' in US spelling. All three spellings are correct. (right) The forms of rubisco. Forms III, and rubisco-like protein Form IV occur in anaerobic organisms and may be older in evolutionary terms. Form II in anoxygenic bacteria and Form I in cyanobacteria and plant chloroplasts both occur in aerobic organisms. Modified from Nisbet EG and Fowler CMR (2011) The Evolution of the Atmosphere in the Archean and early Proterozoic. *Chinese Science Bulletin* 55: 1–10; Nisbet EG and Sleep NH (2001) The habitat and nature of early life. *Nature* 409: 1083–1091.

most available of ingredients, water, light, and air, to fix nitrogen (e.g., Zehr et al., 2001) and even to grow anaerobically if need be.

When did this occur? There is a strong evidence for oxygenic photosynthesis in the late Archean. Anbar et al. (2007) describe strong evidence in the Mt. McRae shales in Western Australia for a 'whiff' of oxygen being present, while Buick (2008) pointed out that as early as 2.7 Ga ago, both stromatolites and biomarkers from evaporative lake sediments, which were deficient in exogenous reducing power, strongly imply that oxygenic cyanobacteria were present.

Perhaps the key signature (see Section 10.1.7.2) is in the $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ isotopic signature of rubisco I in carbonate rocks (Nisbet, 2002; Nisbet et al., 2007a; Schidlowski, 1988, 2002; Schidlowski and Aharon, 1992). This is the modern fingerprint imposed by the chloroplast, still a member of the cyanobacterial line. Carbon dioxide in the atmosphere and the ocean is well mixed. For the $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ fingerprint to occur, carbon dioxide must have been managed by rubisco I on a global scale. The only process that could perform this is photosynthesis. Although purple bacteria use rubisco, arguably only oxygenic photosynthesis can drive the Calvin cycle to capture carbon dioxide on a scale large enough to create the isotopic signature.

The evidence for the $\delta^{13}\text{C} \sim 0\text{\textperthousand}$ signature is strong around 2.7 Ga (e.g., Grassineau et al., 2002). Buick (1992, 2008), for example, in the 2.7 Ga Tumbiana formation in Western Australia, presented strong textural evidence for oxygenic photosynthesis in stromatolites growing in shallow lakes. Similarly, the c.3 Ga Steep Rock carbonates have $\delta^{13}\text{C}$ not far from 0‰ (Nisbet et al., 2007a).

10.1.7.6 Archean Oxygen

By 2.7 Ga ago, the modern carbon cycle was in operation: the oxygen production must have been considerable, even though much evidence, such as that from the $\Delta^{33}\text{S}$ record in sediments, suggest that the ocean/atmosphere system taken as a whole was not oxic (Figure 12; Canfield, 2005; Farquhar and Wing, 2003; Farquhar et al., 2000, 2007). This opinion is based on the claim, from comparison of sulfur isotopes, that so-called 'mass independent' fractionation occurred as a result of gas-phase photochemical reactions, particularly photolysis of SO_2 . Such fractionation would be much more likely to occur in a low- O_2 atmosphere in which sulfur was present in a variety of oxidation states.

If oxygenesis were taking place, as the C isotope evidence and much other geochemical evidence implies (e.g., Siebert et al., 2005), why did oxygen not build up in the air? For contrasting views on this vexed problem, see Holland (1999) and Ohmoto (1997). Catling et al. (2001) and Catling and Claire (2005) argued persuasively for a high-methane atmosphere or Earth would have frozen over. Towe (2002), commenting on Catling et al. (2001), presented strong arguments that it would be very difficult for the Earth system to scavenge back the free dioxygen released by the cyanobacteria and argued equally persuasively for a low- O_2 but oxic atmosphere in the late Archean. Catling et al. in response (see Towe, 2002), with somewhat different assumptions, defended the methane-rich model of the air, though agreeing that local high- O_2 'oases' (presumably water masses rich in dissolved oxygen) and high- O_2 events could occur, just as today methane

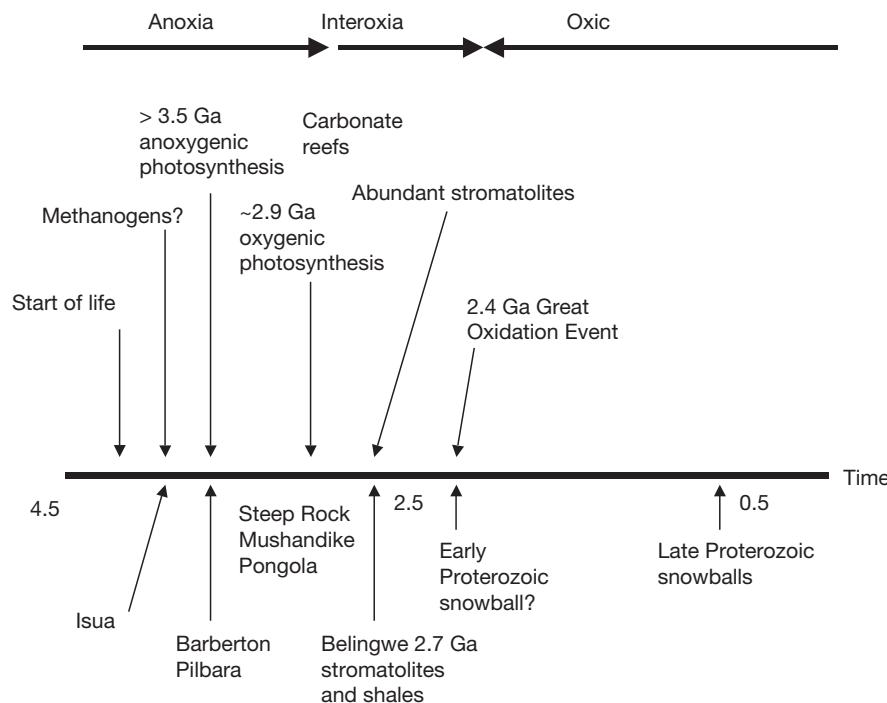


Figure 12 Simplified event chart to show the possible history of oxygen in the air. Modified from Nisbet EG and Fowler CMR (2011) The Evolution of the Atmosphere in the Archean and early Proterozoic. *Chinese Science Bulletin* 55: 1–10.

accumulates in swamps despite the O_2 -rich air. Although the $\Delta^{33}S$ record strongly implies widely anoxic environments in the late Archean, Phillips et al. (2001), in a careful review of the actual rock evidence based on much field knowledge, consider that some of the mineralogical and field evidence can be interpreted as supporting an oxidized Archean atmosphere but conclude that the geological evidence for a reducing atmosphere remains ambiguous. In particular, postdepositional processes may need far more examination. Similar conclusions can be drawn from the rocks of Steep Rock and Belingwe.

Holland (1999, 2009) pointed out that sometime between about 2.5 and 2 Ga ago, free oxygen appeared in Earth's atmosphere. This 'Great Oxidation Event' radically and forever altered the path of biological evolution. The evidence for the change is strong (Canfield, 2005). Kasting (2001) argues in support of the view of Farquhar et al. (2000) (but see also Ohmoto et al., 2001) that sulfur isotope fractionation changed around 2.3 Ga. Thus, the claim that fractionation changed around 2.3 Ga ago can be seen as supporting the notion that there was a substantial rise in O_2 around this time. This, however, raises the question: if cyanobacterial oxygen production had been sufficient to create the rubisco fingerprint in carbonates as early as 2.7–3.0 Ga ago, why did the rise of free O_2 only occur 400–700 My later?

The antiquity of cyanobacteria remains a puzzle but the geological evidence discussed above (Sections 10.1.3.2.4 and 8.01.3.2.5) very strongly suggests that cyanobacteria probably long antedate the Great Oxidation Event. Cyanobacteria are extremely diverse and include both unicellular and multicellular filamentous forms, including forms that irreversibly differentiate in function. Schirmeister et al. (2013) used a data set of RNA sequences to infer that cyanobacteria originated well

before the rise in atmospheric oxygen, and that it was the evolution of multicellularity that came with the rise in oxygen in the Great Oxidation Event. The implications of the Catling et al. (2001), Catling and Claire (2005), and Haqq-Misra et al. (2008) suggestion that the air had high methane concentrations (>0.1%) in the late Archean are worth further comment. If so, then consequently, as methane mixed into the stratosphere and upward through the mesosphere, the Earth would have lost much hydrogen through the thermosphere at the top of the atmosphere. Loss of hydrogen from biologically produced methane equates to surplus of oxygen. This would have produced a substantial net accumulation of oxygen, consumed by oxidation of crust and perhaps by the creation of an upside-down biosphere (Walker, 1987), in which the sediment was more oxidized than the water or air above. The debate continues.

By the late Archean and early Proterozoic production of the key gases in the atmosphere was by complex biologically dominated processes capable, although with rare snowball accidents, of maintaining equable conditions across the aeons. An enormously complex system evolved that over time, balances inputs and outputs, manages positive and negative feedbacks, and has long memory through its large segregated inventories of redox power (e.g., broadly oxidizing air and ocean, storage of reduction power in sediment; Figure 13).

10.1.8 Mud-Stirrers: Origin and Impact of the Eucarya

10.1.8.1 The Ancestry of the Eucarya

The origin of the Eucarya remains a deep mystery. Some (e.g., Forterre, 1995, 1996) would place it very early indeed; yet it

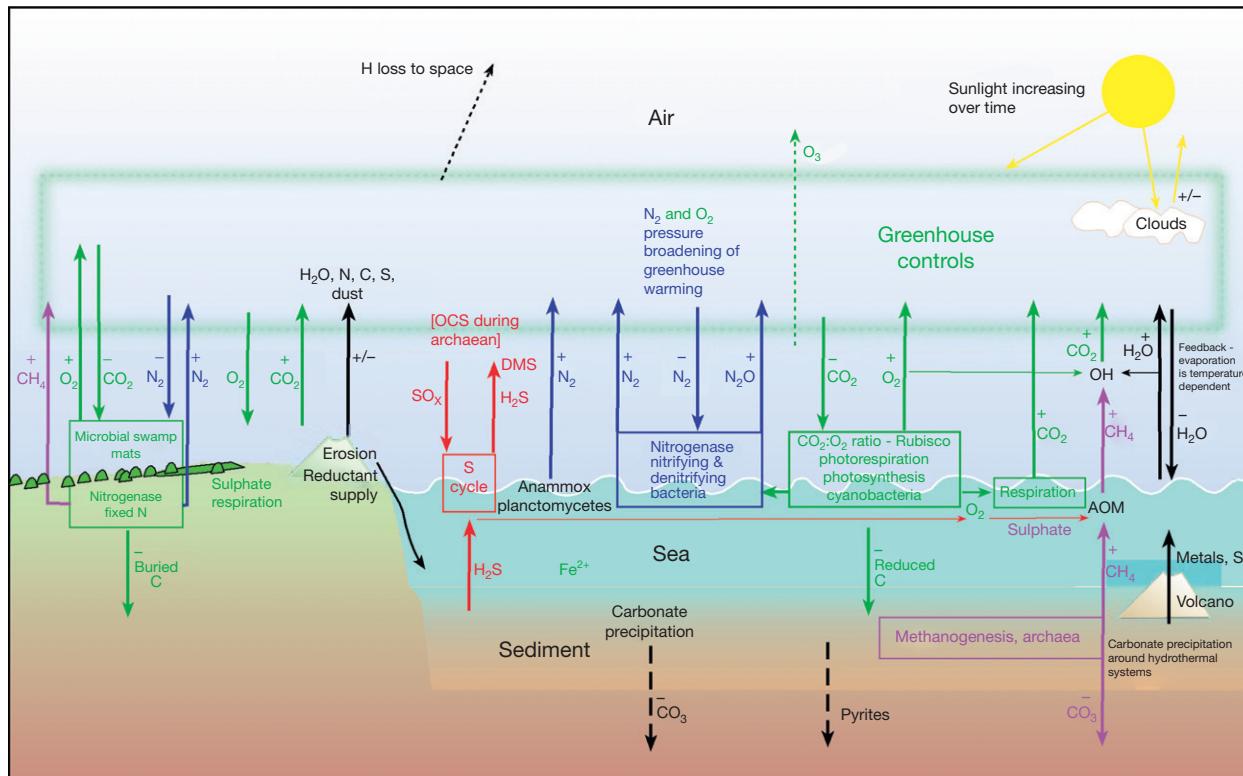


Figure 13 Reservoirs and fluxes in the atmosphere/ocean/sediment system showing biological controls on atmospheric composition, pressure, and temperature. Positive and negative temperature forcing is shown by + and – symbols. Green shading on land represents photosynthetic life. Abbreviations: AOM – anaerobic methane oxidation and AIR – natural mix, now mainly N₂ and O₂, but prior to the Great Oxidation Event ~2.4 Ga ago anoxic and richer in CO₂ and CH₄; other letters are chemical species. (Reproduced with permission from Nisbet et al. (2012); modified from Nisbet et al. (2012)).

has also been ascribed to a time as recently as 850 Ma ago, in the later Proterozoic (Cavalier-Smith, 2002). Wang et al. (2011) studied protein folds and, using molecular clock methods, built phylogenies and timelines. They concluded that aerobic metabolism emerged about 2.9 Ga ago and for the next 400 Ma expanded, until the Great Oxidation Event. They suggest that the arrival of oxygen triggered a diversification of life.

The geological evidence for Archean eukaryotes can be dealt with swiftly. Javaux et al. (2010) found large microfossils in 3.2 Ga old estuarine sediments in the Moodies Group of the Barberton belt, South Africa, and suggested they may have been eukaryotic. However, the interpretation remains controversial: for example, they may have been giant S bacteria. Brocks et al. (1999) found organic molecules (sterols) in the Archean sediment that they ascribed to the presence of eukaryotes. This is permissive but not necessarily persuasive evidence, as some bacteria (e.g., methanotrophs, planctomycetes) may leave similar molecular records; moreover, contamination could have occurred. Thus the interpretation by Brocks et al. (1999) had been strongly contested (Cavalier-Smith, 2002; Rasmussen et al., 2008). In particular, Rasmussen et al. (2008) concluded there was no evidence for eukaryotes prior to the Proterozoic. Nevertheless, it is just plausible that in specific oxygen-rich settings, the Archean eukaryotes did, indeed, occur.

It is very likely that all eukaryotes share a single last eukaryote common ancestor (LECA) (Koonin, 2010a,b). The molecular evidence for the descent and radiation of the eukaryotes (Hartman and Fedorov, 2002; Keeling and Palmer, 2008; Knoll, 2011; Koonin, 2010a,b; Poole and Neumann, 2011; Rogozin et al., 2009; Walker et al., 2011; Yoon et al., 2008) remains controversial (see Section 10.1.6.3). Most models (Pace, 1997; Woese, 1987) suggest an ancestral line among the archaea, with massive transfers and symbioses from the bacteria. Poole and Neumann (2011) discuss how this could have occurred. Perhaps the early archaea and bacteria diverged from a hyperthermophile last common ancestor. Then, a sequence of symbiotic events took place between a stem-cell line among the archaea that developed partnership with symbiotic purple bacteria (e.g., Grey et al., 1999). The result was the first eukaryote cell, with the mitochondria derived (e.g., Bui et al., 1996) from within the α -proteobacteria.

Even eukaryotes, such as the microsporidia, that are no longer capable of aerobic respiration still have relict mitochondrial proteins (Embley and Martin, 2006; Roger and Silberman, 2002; Williams et al., 2002). Simple eukaryotes that today do not have mitochondria (e.g., some parasites) appear to have once had them and then lost them; moreover, mitochondria and hydrogenosomes (distinctive hydrogen-producing organelles in some amitochondrial organisms) appear to have had

a common ancestor (Bui et al., 1996). Thus the ancestral eukaryote was probably a very complex cell (Koonin, 2010a, 2010b), which possessed mitochondria; and the amitochondrial eukaryotes then lost them. In the ‘hydrogen hypothesis’ (Martin and Muller, 1998), the symbiosis is seen as the end product of a tight physical association between anaerobic archaea and heterotrophic proteobacteria capable of producing molecular H₂ through anaerobic fermentation. In another version of the close-association idea, anaerobic archaea may have evolved the ability to survive in oxidizing settings by incorporating respiring proteobacteria (Vellai and Vida, 1999).

Rogozin et al. (2009) and Koonin (2010a,b) concluded that the LECA was indeed a very complex organism, with a remarkably wide array of genes in a highly complex genome. It is possible that a single symbiogenic event led to the incorporation of the mitochondrion and the formation of the first eukaryote cell, with the cell nucleus evolving in defence against intron invasion (Koonin, 2010b).

Whatever the explanation of the stem eukaryote, the eukaryote mitochondria and chloroplasts are best explained as being derived from symbiont bacteria. Explanations of the mitochondrial symbiosis mostly invoke an early Archean stem that incorporated a bacterial symbiont. Although far back in the early Archean, Penny and Poole (1999) suggested that the LUCA may have been a mesophile with many features of the eukaryote genome. It appears that the ancestors of all modern eukaryotes descend from the last eukaryote common ancestor (LECA) and diverged after the mitochondrion symbiosis. At many stages in their evolution, each of the three domains gave and received genetic material with the other two lines so that major innovations were acquired by sharing between all three domains. The ‘tree of life’ is like a braided delta.

As for the antiquity of LECA, there is no consensus. Those who support a eukaryotelike last common ancestor, of course, propose that the eukaryotes date to the early archean. It is not improbable to those who consider that the eukaryotes were the last domain to appear that Eukaryotes first evolved in the late Archean. There is, however, little support in the rock record for the hypothesis of a ‘very late’ origin of both the archaea and eukaryotes proposed by Cavalier-Smith (2002), especially as the evidence for early methanogens is strong (Grassineau et al., 2002; Rye and Holland, 2000). However, a Proterozoic origin of the eukaryotes is not yet excluded, as the sterols found by Brocks et al. (1999) could be of prokaryote origin.

The other great acquisition of the eukaryotes, the chloroplast, is clearly related to the cyanobacteria. Chloroplasts may have been acquired at the same time as the mitochondrion or much later. Some lines of dinoflagellates appear to have had multiple gains and losses of plastids (Saldarriaya et al., 2001), although perhaps from a single ancient endosymbiotic origin (Fast et al., 2001). Although the acquisition of organelles into eukaryotes by incorporation of free-living bacteria appears to be extremely uncommon, Nowack and Grossman (2012) studied an amoeba, *Paulinella chromatophora*, in which the photosynthetic organelles are only recently established, probably in the Cenozoic (last ~60 Ma). The symbiont’s genome is still large compared with most plastid genomes, but it has been significantly reduced by gene transport into the nucleus. The

shift in genetic control is occurring and ongoing with evolution (Waller, 2012).

10.1.8.2 The Last Eukaryote Common Ancestor: Possible Settings for the Eukaryote Endosymbiotic Event

LECA appears to have had a very complex genome, including fully established organelles (Koonin, 2010a,b). What was the purpose of symbiosis? And in LECA were the organelles, mitochondrion, and chloroplast incorporated simultaneously or sequentially? The answers are not known. Today there are several major supergroups of eukaryotes (Knoll, 2011; Marron et al., 2012; Walker et al., 2011). These include the unikonts (e.g., fungi and animals), the excavates (e.g., euglenids and diplomonads), and the plants, rhizaria (e.g., foraminifera), and alveolates (e.g., dinoflagellates; Figure 15). It may be that there was a ‘big bang’ in evolution when an original LECA eukaryote parent, uniquely advantaged after creation by the endosymbiosis of an α -proteobacterium and an ancestral archaeon, then bloomed and very rapidly produced diverse photosynthetic and nonphotosynthetic lineages all probably originating in this event. It is not clear whether all modern eukaryotes are descended from organisms that possessed chloroplasts. Some have multiply acquired and lost chloroplasts. Perhaps ‘big bang’ metazoa descended from an ancestral photosynthesizer by loss of the chloroplast (Figure 14).

Geologically, where did LECA live? Possibly it may have been a distal inhabitant of a subaerial hydrothermal system or a planktonic form. The same hypotheses apply. A possible environmental setting of symbiosis is a microbial mat community in which a complex community of cells is clustered in close proximity across a redox boundary, cycling and recycling redox power (Nisbet, 2002; Nisbet and Fowler, 1999). The aerobic top of the mat would include photosynthetic cyanobacteria, above photosynthesizing purple bacteria. There would be a very sharply focused redox boundary. Below would be the green photosynthetic bacteria and at the base, the methanogens and the hydrogen producers. In the Archean, such prokaryotic mats would be limited to some extent by diffusion gradients, in the absence of multicelled organisms like worms capable of physical movement of fluid on a large scale. However, microbes are motile and, moreover, they can move fluid, so the thickness of the mat would be substantial compared to the dimensions of a single cell, despite lack of physical power.

In such a setting, there is great benefit from being very close to the redox boundary between aerobic and anaerobic conditions, where the greatest thermodynamic power is to be had. Any cluster of cells that straddled this boundary or incorporated it within itself would possess great advantage. To some extent, some cyanobacteria already do so within their cell, as they include heterocysts, which protect nitrogenase, which enzyme needs to function within the cell in anaerobic conditions despite the emission of molecular oxygen from the cell during photosynthesis. Any cluster of cells that carried out oxygenic photosynthesis and yet managed to control redox levels by respiration also would be greatly advantaged. Oxygen is dangerous, and mitochondria may have evolved to manage it (Abele, 2002). There would be much advantage to a

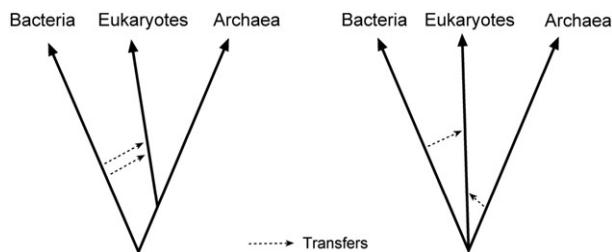


Figure 14 Two models of eukaryote evolution. Left diagram shows eukaryotes as a derived group emerging from the Archaea, with lateral transfer of genetic material (chloroplast; mitochondria) from bacteria. Right diagram shows alternate view that all three domains emerged separately from a common ancestor, with transfers into the eukaryotes from both Archaea and Bacteria.

symbiotic association, located just above the redox boundary, of a host cell that linked cyanobacteria and purple bacteria alternately providing useful redox waste to each.

Photosynthesis by a symbiont cyanobacterium would produce reactive oxygen species in the fluid. The buildup of oxidation power in the near environment would be a nuisance to the cyanobacterium, as its rubisco would begin to work in reverse. Thus, it would have to wait until the oxygen diffused away before continuing photosynthesis. Moreover, the oxygen would be damaging to the nearby symbiont cell. However, if nearby, on the redox boundary, there were an α -proteobacterium, this would mop up the excess oxidation power immediately, allowing the cyanobacterium to keep photosynthesizing. Thus, the host cell would be protected, the rubisco in the cyanobacterium would operate, and the respiring α -proteobacterium would flourish. Such an arrangement is beneficial to all, thus it is tempting to imagine that both symbiotic incorporations took place by single lucky improbable accident. Arguably, however, it is more likely that initially only one partner was incorporated and then the second.

10.1.8.3 Water and Mud Stirring – Consequences

Eukaryote cells have a significant advantage in that they can grow large. They can also be multicelled. Multicelled eukaryotes have some unique advantages and some disadvantages. The disadvantage is that they evolve by Darwinian evolution. Genetic change can only occur when parent organisms have a number of different offspring, some of which are better suited than others to the environment in which they find themselves: these are more likely to survive and in turn have offspring, so natural selection chooses the genes most suited. Failures are discarded. Nature is vicious. Tennyson, who was Darwin's fellow student and fellow science enthusiast under the tutelage of William Whewell (who coined the term 'scientist'), put this paradox first:

Who trusted God was love indeed
And love Creation's final law
Tho' Nature, red in tooth and claw
With ravine, shriek'd against his creed.

Tennyson. In memoriam 56 (1849)

Only females reproduce, so the ability to 'bloom' is slightly restricted. For single-celled eukaryotes, rapidly passing through the generations, the evolutionary process of adapting to a

changed environment (e.g., the arrival of a virus) can be quick and population recovery fast, but for an elephant that lives for decades or a tree that lasts for centuries, adaptation can be slow, and the population can be brought dangerously near extinction before it can respond to the new challenge.

Human cultures evolve as bacteria do, by horizontally swapping information among living individuals. This is a rapid and highly advantageous method of adaptation. Most readers of this (except Scots) are likely to wear some variety of lower undergarment, but the habit is only a few generations old; prior to that it was thought unclean. The change was non-Darwinian. Human families who did not wear such attire a few lifetimes ago did not become extinct by failing to find mates and reproduce – instead they mysteriously acquired the habit from contemporaries by a hidden process of mother-to-mother horizontal subjeans transfer. Eukaryotes do, to some extent, adopt such quasi-Lamarkian evolution in the immune system. This has an extraordinarily bacterial-like ability to learn in life – perhaps it alone has ensured the domain's survival in the face of viral challenge and microbial attack.

An advantage of the eukaryotes is that they can mix genomes over long distances (males wander) and also create striking cellular architecture and thereby link together colonies of cells so that they form a single unit with distributed tasks. This may have had major consequences in the Proterozoic when multicelled eukaryotes became capable of moving water and stirring mud (Figure 15). Bacteria do this to some extent but only slightly. By stirring mud and water, the eukaryotes expand the range of the biosphere. The bacterial biosphere is at most only a few millimeters thick – the growing biofilm in a microbial mat. The physical structure of a prokaryote mat may include a debris layer a meter or more thick, but most of the action is close to the redox boundary. In contrast, eukaryotes can move redox power up and down and widen the environment – they become capable of more reducing power, more photosynthesis – limited only by nutrients such as iron. Eventually, they even become able to send roots down into the soil and rock to extract the nutrient, or in humans, to dig for potash to put on fields, or to fix nitrogen directly.

The expansion of the productivity of the biosphere by the eukaryotes must have begun slowly, but it probably started in late Archean. Around 2300 Ma, much evidence suggests (but does not conclusively prove: see Section 10.1.7.6) that oxygen levels rose sharply. Possibly the eukaryotes were beginning to muscle the world.

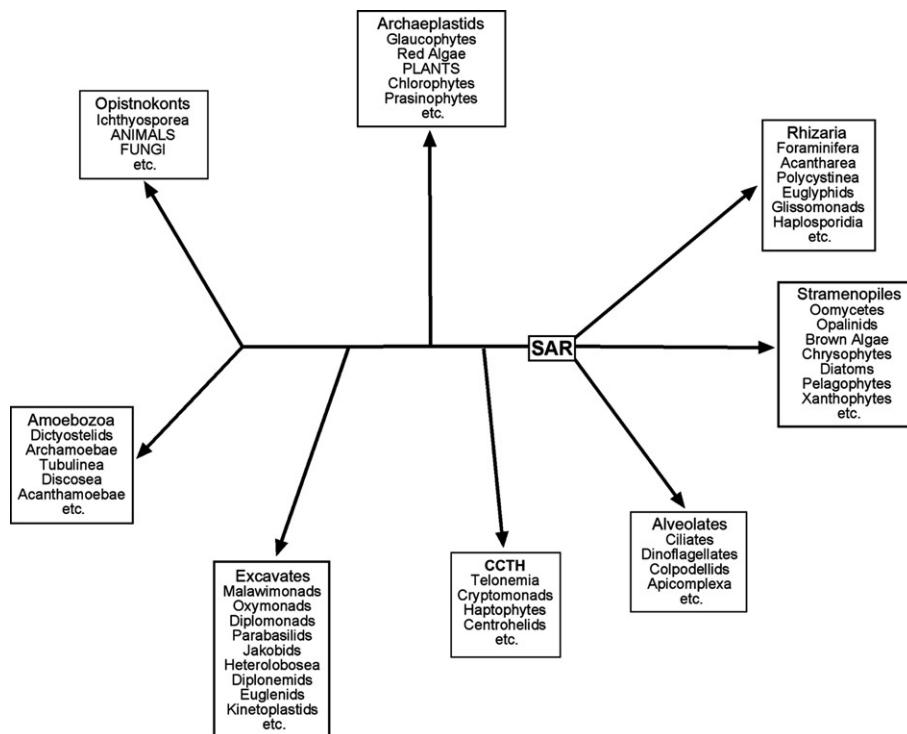


Figure 15 The major eukaryote supergroups. These share a last eukaryote common ancestor (LECA), but their descent and interrelationship remains uncertain. With each supergroup some examples of key lineages are shown: there are many others. SAR supergroup includes Stramenopiles, Alveolates, and Rhizaria. Eukaryote tree is unrooted. From [Walker et al. \(2011\)](#).

10.1.9 The breath of Life: The Impact of Life on the Ocean/Atmosphere System

10.1.9.1 The Breath of Life

The modern atmosphere is the breath of life – a biological construction ([Nisbet et al., 2012](#)). Excepting the argon, the balance of the exosphere is entirely fluxed by life: the gases are emitted and taken up by living organisms. This does not necessarily mean that life manages the air, as life may simply be fast-tracking inorganic processes that would happen anyway, but there is also the possibility that life is maintaining thermodynamic disequilibrium (e.g., the sharp contrast between reducing sediment and oxidizing air; or on an even finer scale, the kinetically improbable presence of ammonia and methane in oxygen-rich lower tropospheric air).

The controls on the atmosphere's operation ([Walker, 1977](#)) are complex and poorly understood yet have been robust enough to keep the planet habitable over 4 Ga. The greenhouse effect adds $\sim 33^{\circ}\text{C}$ to the temperature ([Lewis and Prinn, 1984](#)). Without the atmosphere, the temperature of the planet would be $\sim -18^{\circ}\text{C}$; with the atmosphere it is a pleasant $+15^{\circ}\text{C}$. But is the control pure inorganic chance, or is it somehow implemented because Earth, uniquely, is inhabited by life ([Nisbet et al., 2012](#))? And when did the control begin?

[Kharecha et al. \(2005\)](#) and [Haqq-Misra et al. \(2008\)](#) investigated the controls on surface temperature. As detailed earlier, the geological evidence for surface temperature is very controversial ([Knauth and Lowe, 2003; Knauth, 2005; Robert and Chaussidon, 2006; Blake et al., 2010](#)). [Haqq-Misra et al. \(2008\)](#), correcting an earlier error in calculation, showed that

an atmosphere rich in both CO_2 and CH_4 , as well as water vapor could have produced equable late Archean conditions under a fainter Sun. Much of this warming probably came from relatively high CO_2 (within the constraints of the geological evidence) and consequent evaporation of water vapor, which is a potent greenhouse gas. CH_4 may have played a supplementary but vital role. Removal of the CH_4 could have triggered a glaciation. [Konhauser et al. \(2009\)](#) suggested exactly this took place; that when the vast late Archean outpouring of komatiite and basalt lava flow ceased, the consequent shortage of biologically accessible nickel induced a nickel famine. In turn, because Ni enzymes are essential in methanogenesis, this would cut the supply of CH_4 to the atmosphere, inducing global cooling ([Figure 16](#)).

10.1.9.2 Oxygen and Carbon Dioxide

Since the Archean, the oxygen that has been emitted into the atmospheric reserve by the oxygen-evolving complex as the waste product of oxygenic photosynthesis has been taken up again by respiration. The carbon is the other side of this coin: it is stored for the most part in the biosphere and crustal reserves, forming a well of reduction power that matches the surficial oxidation power, with just enough carbon dioxide is sustained in the air to allow rubisco to operate in balance ([Tolbert, 1994](#)). There are complex inorganic controls and buffers in the carbon dioxide content of the air, and the partitioning of carbon between air/water and surface/crust ([Walker, 1994](#)), but the extent to which biological processes exert the

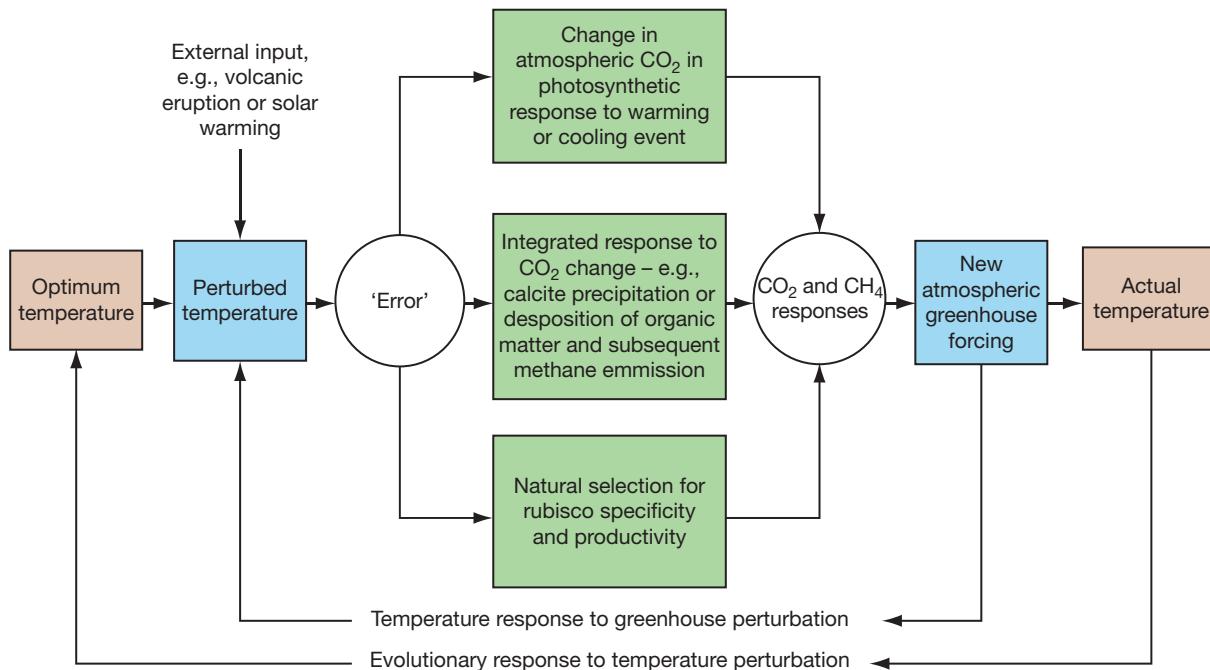


Figure 16 Possible feedback controls in atmospheric regulation, modeled on a PID controller. Diagram illustrates the way natural selection, acting on rubisco specificity, can manage the surface temperature. Reproduced from Nisbet EG, Fowler CMR, and Nisbet RER (2012) The regulation of the atmosphere: A hypothesis. *Solid Earth* 3: 1–10.

fundamental control remains very controversial. One argument that may be made is that the most basic control may lie within the cell itself, in within-cell controls (Joshi and Tabita, 1996). The control in photosynthetic cells would lie in the balance between chloroplasts and mitochondria in eukaryote cells. There would be strong evolutionary feedback, as natural selection operated both on individual cells and on the prosperity and survival of whole biomes. The debate remains open (Nisbet et al., 2012).

10.1.9.3 Nitrogen and Fixed Nitrogen

Dinitrogen, like dioxygen and carbon, is almost entirely a biological product: there is roughly 3.8×10^{21} g presently in air, and each year $\sim 3 \times 10^{14}$ g are added and subtracted from this reservoir by denitrifying and nitrogen-fixing bacteria (lifetime in air $\sim 10\text{--}100$ Ma). Nitrogen is emitted to the air by guilds of denitrifying bacteria (e.g., *Pseudomonas* and *Bacillus*), which reduce nitrate to N₂ as an alternative respiration process in anaerobic settings when oxygen is absent. This raises the inference that this process may be very old and may have evolved before oxygenic photosynthesis, predating the time of abundant oxygen supply. As argued earlier (Section 10.1.6.3), the anammox process may also be of great antiquity, perhaps long predating oxygenic photosynthesis.

Canfield et al. (2010) pointed out that with the evolution of anoxygenic photosynthesis, it is possible that chemical stratification developed in the global ocean, with ammonium accumulating deep in the oceans. In the deep photic zone, intense productivity would have occurred, removing both NH₄⁺ and Fe²⁺. It is possible, with abundant ammonia in deep water,

that ammonium zeolites were important in low-grade metamorphic alteration of seafloor basalts and thus later subduction of ocean floor.

The nitrogen cycle has a controlling role on the carbon dioxide/oxygen cycle (Falkowski, 1997). Were all fixed nitrogen to be evolved as dinitrogen, the biosphere would rapidly be limited to subsistence on the nitrogen oxides and ammonia emitted by volcanoes and hydrothermal systems. Nitrogen fixation reverses this and is carried out by cyanobacteria, by free-living bacteria such as *Azotobacter* and *Clostridium*, by archaea such as *Methanococcus*, and (perhaps since late Palaeozoic) by plant symbionts. Fixation is very expensive energetically, requiring a large ATP price. At least six electrons and 12 ATP are required to fix one dinitrogen molecule. The use of nitrogen fixation by cyanobacteria is especially interesting geologically, as cyanobacterial picoplankton are very important today and presumably were from the geological moment the cyanobacteria evolved. It is reasonable to assume that cyanobacterial plankton were ubiquitous in the late Archean oceanic photic zone. Thus, there is a reasonable presumption that in the Archean the dinitrogen atmospheric burden was organically fluxed.

Nitrogen supply is a key limitation on productivity (Falkowski, 1997). It is possible that the ancestral cyanobacterium was a thermophile that did not fix nitrogen (Shi and Falkowski, 2008), although later cyanobacteria likely did fix nitrogen. This is a process that needs low oxygen tension in heterocysts, yet the cyanobacteria can also use the oxygen-evolving complex to excrete waste oxygen. Shi and Falkowski (2008) suggested that N₂ fixation in cyanobacteria occurred at some time in the late Archean or early Proterozoic, via horizontal gene transfer, possibly during a supply crisis in fixed nitrogen. They suggested that the accumulation of

a small concentration of oxygen, produced by oxygenic photosynthesis, led to massive denitrification of the upper ocean and a loss of fixed inorganic nitrogen for growth of marine photoautotrophs. In the crisis, natural selection would favor transfer of the ability to fix nitrogen from a heterotrophic prokaryote to a cyanobacterium.

The formation of nitrate from ammonium needs molecular oxygen ([Falkowski, 1997](#)): it is reasonable to suppose that this could not have evolved until oxygenic photosynthesis appeared. But, conversely, productive oxygenic photosynthesis could not have become global unless there was a good supply of biologically accessible nitrogen. In oxic environments, siderophores facilitate iron nutrition, by forming strong complexes with Fe^{3+} . The evolution of precursors to siderophores, presumably at the time of the development of the first oxidation oases, would have been a necessary prior event before life could occupy an oxidized ocean. Cyanobacterial plankton still today occupy the tropical oceans in vast numbers ([Capone et al., 1997](#)), and the chloroplast in a modern plant is in effect a cyanobacterium in a space suit. Given that respiration today is still carried out by mitochondria, which are in effect proteobacteria also in space suits, the modern cycle of life had begun.

10.1.9.4 Methane

Of the lesser gases, methane is the most interesting. Today, the natural methane sources are primarily archaea, but operating in eukaryote hosts (e.g., archaea symbiotically cooperating with plants in wetland, termite stomachs, cows, and sheep). In the Archean, methane was probably managed by complex microbial communities, comparable to those in modern oceans ([Boetius et al., 2000](#)). [Walker's \(1987\)](#) surprising hypothesis that the Archean biosphere at times may have been inverted, with a relatively reducing atmosphere and a relatively oxidizing sediment is not as absurd as it seems. Today the oxygen-rich air is sustained by photosynthesis. Prior to oxygenic photosynthesis, the air would have contained relatively oxidized species (carbon dioxide, water, and dinitrogen), but also substantial methane and probably ammonia emissions occurred, which would have had multiyear atmospheric lifetimes. In the continental slope sediments, huge methane hydrate reserves would have built up, as they do today ([Kvenvolden, 1988](#)). In these circumstances, episodes of major atmospheric methane burden could occur, as perhaps happened in the late Archean ([Hayes, 1994](#)). For example, this could occur after massive release of geological methane stores (e.g., see [Kvenvolden, 1988; Harvey and Huang, 1995](#)). However, [Konhauser et al. \(2009\)](#) pointed out the likelihood of a subsequent catastrophe – glaciation caused by a nickel famine.

Today, a large part of the biosphere is reducing – much of the soft sediment. It is possible, especially if methanotrophy were absent or ineffective in the absence of abundant oxidant, that the Archean ‘Walkerworld’ events may have occurred when the biosphere was inverted, with relatively reducing air and relatively oxidizing sediment. Once such an event was established, it might be stable for long periods, until reversed by the combined impact of volcanic degassing of carbon dioxide and nitrogen oxides and of methanotrophy. With methane, other reduced gases such as ammonia would build up in the air, reversing the nitrogen cycle also.

10.1.9.5 Sulfur and Biology

The oxidation states of sulfur may have been the core tool by which life bootstrapped its way to a global biosphere ([Kasting, 1993, 2001; Kasting et al., 1989](#)). Sulfur offers a wide range, from H_2S through HS and sulfur to the oxidized species up to SO_3 (H_2SO_4). Moreover, dimethyl-sulfide is two methyls linked with one sulfur.

For bacteria living close to a redox boundary, sulfur is a marvellous reservoir. Should conditions become reducing, they can tap it and make H_2S . Conversely, if conditions become strongly oxidizing, they can make SO_x species. Thus, if the bacteria can sequester sulfur, rather as in a piggy bank saved for a needful day, it becomes a redox currency. Even better, sulfur-bearing chemical species are common components of hydrothermal fluids –readily available!

In the inorganic world, sulfur would have been available in a variety of oxidation states. Even in a reduced atmosphere, transient SO_x would have been present from volcanic sources supplemented by interaction between sulfur-bearing aerosols and oxidants produced by photolytic chemistry in the early UV flux or from escape of hydrogen to space. Reduced sulfur species would have been widely available in lavas and volcanic vents. Thus, for the early organisms, shuffling sulfur between various oxidation states would have been the best way of exploiting redox ratchets. When anoxygenic photosynthesis started, a full sulfuretum cycle would have been possible in sediments, fluxing sulfur endlessly up and down to capture a living from oxidizing decaying organic matter or reducing available oxidant.

Once abundant oxygenic photosynthesis began, the sulfureta would have become much more productive, and sulfur would have become the chief currency of redox transactions on the bottom. Finally as in most piggy banks, the contents are lost, buried in the mass of reduced sediment as pyrite or sulfide mineral or even as sulfur, eventually to return via the plate cycle to the volcanoes or groundwater as oxidized sulfur.

10.1.10 Feedback from the Biosphere to the Physical State of the Planet

The planet shapes life, but life also shapes the planet ([Nisbet, 2002; Nisbet et al., 2012](#)). The maintenance of surface temperature is managed by the air, hence, as life controls the composition of the air and the atmospheric greenhouse, then life sets the surface temperature ([Lovelock, 1979, 1988; Lovelock and Margulis, 1974](#)).

What would be the nature of the air if life did not exist? If for the past 4 Ga, life had not captured carbon and sequestered it, and cycled nitrogen back from soluble compounds, returning it as atmospheric dinitrogen, and evolved oxygen and hence permitted ozone to form in the stratosphere, what would the atmosphere be? It is almost impossible to say. Reasonable guesses include a nitrogen–carbon dioxide atmosphere, or perhaps a nitrogen atmosphere over ice, with the carbon dioxide removed as carbonate after volcanic paroxysm. One possibility is that over time, the air would have evolved as Venus’s air may have evolved, first as a steam greenhouse, then, after hydrogen loss, to a dry, hot carbon

dioxide greenhouse over a dehydrated planet. Alternately, the surface could have become very cold and icy. This would have interesting consequences, as it may have changed the operation of the erosional cycle and the plate system, perhaps leading to periods of long quiescence followed by volcanic resurfacing. The persistence of oceans of liquid water is closely interwoven with the long-term history of the continents and oceans (Hess, 1962), and the controls on water depth may be linked to the physical properties of water (Kasting and Holm, 1992) and to the nature of the atmosphere and its greenhouse impact. In an inanimate planet, whether or not liquid water would have persisted for as long as 4 Ga is a moot point. If it had disappeared, would Earth have had plate tectonics? Perhaps not: perhaps the life has shaped the face of Earth.

Acknowledgments

Thanks to the community of Archean field geologists in Zimbabwe and Canada for many years of discussions, especially Mike Bickle and Tony Martin, Jim Wilson, John Orpen, Tim Broderick, and Tom Blenkinsop; to Freeman Dyson, Jim Kasting, Jim Lovelock, Dave Schwartzman, Norm Sleep, Crispin Tickell, Kevin Zahnle, and especially our daughter Ellen for much thought; and to the late Preston Cloud, Teddy Bullard, Harold Jeffreys, and Drum Matthews for tuition and insight on these matters. Many thanks also to David Karl for his very helpful comments and thoughtful insight.

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