8.01
The Early History of Life

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8.01.1 INTRODUCTION

8.01.1.1 Strangeness and Familiarity—The Youth of the Earth

The youth of the Earth is strange to us. Many of the most fundamental constraints on life may have been different, especially the oxidation state of the surface. Should we suddenly land on its Hadean or early Archean surface by some sci-fi accident, we would not recognize our home. Above, the sky may have been green or some other unworldly color, and above that the weak young Sun might have been unrecognizable to someone trying to identify it from its spectrum. Below, seismology would show a hot, comparatively low-viscosity interior, possibly with a magma ocean in the deeper part of the upper mantle (Drake and Righter, 2002; Nisbet and Walker, 1982), and a core that, though present, was 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, rock-forming. Of all the geochemical features that make Earth unique, the initial degassing (Genesis 2:b) and then the sustained presence of liquid water is the defining oddity of this planet. Early Earth probably also kept much of its carbon, nitrogen, and sulfur as oxide or hydride. And, after the most cataclysmic events had passed, ~4.5 Ga ago, for the most part the planet was peaceful. Even the most active volcanoes are mostly quiet; 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. Though, admittedly, green is junk light to biology, the excretion from the photosynthetic antennae, nevertheless even a green sky would have had other wavelengths also in its spectrum.

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), it was also far enough away still to be in the comfort zone (Kasting *et al.*, 1993) when the mature Sun brightened. 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, she 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).

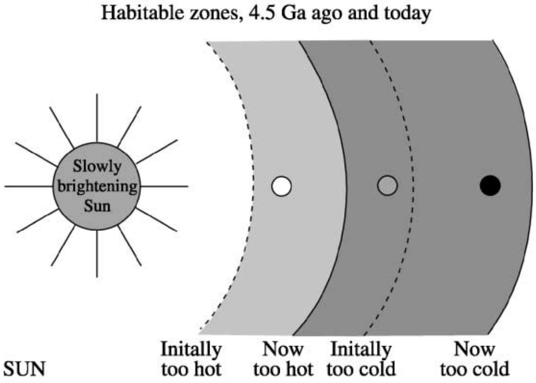


Figure 1 The habitable zone (Kasting *et al.*, 1993). Too close to the Sun, a planet's surface is too hot to be habitable; too far, it is too cold. Early in the history of the solar system, the Sun was faint and the habitable zone was relatively close; 4.5 Ga later, with a brighter Sun, planets formerly habitable are now too hot, and the habitable zone has shifted out. Note that 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).

8.01.1.2 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 the rocks, in meteorites, in what we can learn from other planets, and in solar system and stellar science. The Lucretian view of a planet, ramparts crumbling with age, may apply to Mars, but as Hutton realized, virtually all of the surface of the 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 is not renewed, relics of early life remain. Some of these relics 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 become unable to renew their surface by tectonics and volcanism. Perhaps they can also die biologically. From moons of outer planets comes 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 sun-like 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 altered in spectrum.

8.01.1.3 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.” We each start 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, and information-transfer systems, and the protein machinery of the cell all carry historical information. Every human cell lives in its own seawater, the blood—we came from a warm kindly ocean. Every oxygen-handling blood cell carries iron: we learned this trick somewhere that our 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: a massive (compared to other enzymes) RNA-based super-enzyme that in a strange way is both chicken and egg and, though much modified by evolution, is surely of the very greatest antiquity.

Modern life comes in very many forms: animals, plants, and single-celled eukaryotes in the *Eucarya* domain; prokaryotes in two great domains, *Archea* and *Bacteria* (Woese, 1987; Woese *et al.*, 1990), and *not-life* viruses. 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 our cells carries mitochondria that are descended from symbiotic purple bacteria. Plants, in addition, carry chloroplasts that are descended from partner cyanobacteria.

There is an enormous wealth of this type of information that is only just beginning to be deciphered. Indeed, deciphering the molecular record (Zuckerkandl and Pauling, 1965) may be the best route to understanding of Archean palaeontology. Geological study interacts with this, both by calibrating the 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 the rock information, 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.

8.01.1.4 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); 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 and models of the environmental settings of that life. 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 are unconstrained and can be wrong (e.g., the primaeval "soup" is geologically 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.

8.01.1.5 What Does a Planet Need to be Habitable?

Venus may have been in the right place once, and is the right size, but in the long term it was too close to the Sun. Mars may be in a tolerable place, and on occasion with liquid water (Baker, 2001; Carr, 1996), but has a small heart, almost dead of cold. Only Earth had long-term location and is large enough to keep an active interior.

What are the requirements? First, liquid water. It is difficult to imagine biology that does not include water. It may be possible (indeed, someday computers may produce some sort of water-free inorganic sentience that achieves genetic take-over from organic life) but not in Nature as we know it. Externally, the planet needs to be far enough from the Sun not to overheat, 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 progressively shift outwards as the Sun evolves and brightens. Thus, while Venus was probably within the bounds of the habitability zone early in the history of the solar system with a faint young Sun, and covered by oceans, it may today 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: some day humanity may well add water supplies from an outer solar system source and 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 non-teleological life have carried out very similar processes on Earth over 4 Ga (Lovelock and Margulis, 1974; Lovelock, 1979, 1988).

Planets also need to be geologically active to sustain life over long periods. 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 house-keeping 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 homes. But of the internally warm bodies that have a Sun-warm outer surface, only Earth and Venus are just the right size.

8.01.1.6 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 part-way up (or down) the peaks, the microbial processes link with innumerable smaller cable car systems that scatter metabolic tourists around the ecological mountain sides 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 create redox contrast between the surface of the Earth and its interior.

8.01.2 THE HADEAN (~4.56–4.0 Ga AGO)

8.01.2.1 Definition of Hadean

The Hadean is the first of the four aeons of Earth history (Nisbet, 1991). Aeons are the largest divisions of geological time: Hadean, Archean, Proterozoic, Phanerozoic. The first and last aeons are "short" (relatively, if 560 Ma can be called short); the middle two are billions of years long. The Hadean was the period of the formation of the Earth, from the first accretion of planetesimals at the start of the Hadean, to the end of the aeon, when the Earth was an ordered, settled planet, with a cool surface under oceans and atmosphere, and with a hot active interior mantle and core.

The bounds of the Hadean have never been properly defined. The birth of the Earth is the start of the Hadean, but is this the moment of the beginning of the solar system, or the moment when the first significant planetesimals collected to begin the accretion? Fortunately, this is not much more than an academic discussion—the time of formation of the oldest material in meteorites is usually taken to be representative of the start of accretion. Very roughly, 4.56 Ga is taken as the start, where 1 Ga is one thousand million (10^9) years.

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 as a working definition of the Hadean/Archean boundary. But this is unsatisfactory—a random number. The choice of the start of life as the defining moment for the boundary between the Hadean and Archean has great appeal and should surely be preferred. Fortunately, at present the best guess for the origin of life is also "somewhen around 4 Ga ago."

8.01.2.2 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. Some of the oldest objects in the solar system yet found are Ca–Al-rich inclusions in meteorites, ~4.566 Ga old (Allegre *et al.*, 1995). 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 yr (Weatherill, 1990). The core of the asteroid Vesta may have formed within only 3–4 Myr, and lavas 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 date of core formation in the Earth remains controversial but may have been as little as 30 Myr 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 took place within 29 Myr. The core of Mars may have formed as early as within 13 Myr.

The special events of this planet's accretion (Newsom and Jones, 1990; Weatherill, 1990; Ahrens, 1990; Taylor, 2001) were crucial in making Earth habitable over billions of years. Segregation of the core physically separated reduction power in the iron-rich center of the 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 most important single physical event took place roughly 4.5 Ga ago, 25–30 Myr after the birth of the solar system. At this stage, Earth was probably a substantial fraction of its present mass, with a segregated core. Sunwards of Earth, Venus and Mercury had formed; outwards, 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); an alternative model is that a Mars-sized body hit the 90%-formed Earth (Canup and Asphaug, 2001). When the impact took place, the Earth was transformed. Internally, it would have been melted, 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 the 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 day-side and cold night-side, but an even illumnation. Moreover, the night-day cycle allows a variety of photosynthetic/respiratory cycles in cells, and contributes greatly to the diversity of biota.

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, enough to cover the planet to a few tens of meters: puddle oceans (Carr, 1996). On Venus, which must have been very nearly 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 CO_2 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).

The main part of the accretion of the Earth can be considered complete by ~4.45 Ga. By this stage most of what now makes up the Earth was in place. The then much nearer Moon orbited close by. The Earth would have been molten except for a thin rocky outer carapace, possibly of broadly basaltic composition (komatiitic basalt; or even komatiite?). A large magma ocean may have persisted in the mantle for some time in the Hadean or even longer. Within the Earth, ongoing late precipitation of the core may have continued, with reaction between water in the mantle and 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 the 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).

Late Hadean Earth (say 4.2 Ga to 4 Ga ago) was thus very unusual among the inner rocky planets, in 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 extra-solar planetary systems increases.

8.01.2.3 The Hadean Record

Jack Hills and Mt. Narryer, Western Australia. Some of the oldest material found on Earth consists of a few crystals of detrital zircon that are now preserved in quartzites in the Mt. Narryer and nearby Jack Hills area, Western Australia (Compston and Pidgeon, 1986, Wilde *et al.*, 2001, Halliday, 2001). The host sediment is ~3.3–3.5 Ga old, but the some of the zircons themselves are up to 4.2–4.4 Ga old (Figure 2). There are several implications of the discovery. First (also shown in many other successions) that by 3.3 Ga ago, in the mid-Archean, there was already old continental crust being eroded and redeposited by water. Second, 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 zircon 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 (Wilde *et al.*, 2001; Mojzsis *et al.*, 2001) supports the deduction that oceans of liquid water were indeed present. The zircons contain isotopically heavy oxygen: suggesting derivation from liquid surface water. This is 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 Hadean continents exist, and oceans, and were hydrothermal systems present on continental land surfaces around andesitic volcanoes, fed by water-mediated subduction?

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

Acasta Gneiss, Canada. Next oldest is the Acasta 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 km^2 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.

There is no evidence for the existence of life before 4 Ga ago. Even if a living organism had appeared, life would probably 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).

8.01.2.4 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, anywhere else that is fancied.

There are also 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* life had 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 the 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.

8.01.3 THE ARCHEAN (~4–2.5 Ga AGO)

8.01.3.1 Definition of Archean

The inter-aeon boundary between the Hadean and Archean is presently not defined (Nisbet, 1991). There are various options: (i) the date of the first life on Earth; (ii) the date of the last common ancestor; (iii) a "round" number, such as exactly 4 Ga—4,000,000,000 years ago; (iv) the oldest record of a terrestrial rock (~4 Ga ago); (v) the oldest record of a terrestrial mineral crystal (~4.3–4.4 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 can be 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 over-optimistic 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 *last common ancestor* 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 last common ancestor 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 (Sleep *et al.*, 2001; Gogarten-Boekels *et al.*, 1995).

8.01.3.2 The Archean Record

8.01.3.2.1 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 the Earth was still under heavy bombardment by meteorites (the face of the Moon, like a ravaged battlefield, dates from this time). 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 sea-floor 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 us, hydrothermal systems existed, and that they emitted methane, useful for metabolism.

There have been various claims of evidence for 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 >3,700 Ma rocks in Isua that are strongly depleted in ^{13}C relative to bulk Earth. δ^{13}C in these particles is in the range of −10‰ to −20‰, 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.

8.01.3.2.2 Barberton

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

Byerly *et al.* (1986) described probable stromatolites in the Fig Tree Group, preserved in grey-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. However, Lowe (1994) disputed this evidence and concluded that the structures were not demonstrably of biotic origin.

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 (δ^{13}C −27‰), but may be of non-Archean age. Thus the case for mid-Archean biotic material in Barberton remains open.

8.01.3.2.3 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 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 dismisses 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 material. 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 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).

Several notable pieces of evidence for early life come from Western Australia. Shen *et al.* (2001) found isotopic evidence for microbial sulfate reduction in 3.47 Ga barites from 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 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 mid-ocean ridge origin. Just possibly, some diamonds may be carbon from ancient microbial colonies (Nisbet *et al.*, 1994).

There is also evidence for the presence of methanotrophs in the ~2.8 Ga old Mount Roe palaeosol. This 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).

In the late Archean of Western Australia, there is much evidence of life, both macroscopic and microscopic. 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. Slightly younger, the 2.5 Ga Mt. McRae shale yields bitumens that contain biomolecules characteristic of cyanobacteria (Summons *et al.*, 1999). This evidence strongly supports the notion that cyanobacterial oxygenic photosynthesis was fully established.

The late Archean of Australia contains many carbonate rocks with $\delta^{13}C \sim 0‰$. This is 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 and Aharon, 1992; Schidlowski, 2002). 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 $\delta^{13}C \sim -5‰$ to $-7‰$. 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 CO_2. This carbon chosen by life is strongly selected for ^{12}C and thus has $\delta^{13}C \sim -28‰$ to $-30‰$. Thus, the residue left in the air/sea system is enriched in ^{13}C. In modern-day carbonates, $\delta^{13}C \sim 0‰$, implying by balance ($-7‰$ source, partitioning into $-28‰$ organic life and $0‰$ 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 $\delta^{13}C \sim 0‰$. Because carbon dioxide is globally mixed, the presence of carbonate with $\delta^{13}C \sim 0‰$ implies a global fractionation of carbon by oxygenic photosynthesis. This indeed is what is recorded in the late Archean.

8.01.3.2.4 Steep Rock, Ontario, and Pongola, South Africa

The evidence from the 3.0 Ga sequence at Steep Rock, Northwest Ontario, Canada, is very different (Wilks and Nisbet, 1985; Nisbet, 1987) (Figure 3). 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 recently 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 Rouch (Abell, Grassineau, and Nisbet, unpublished) 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.

The Pongola sequence in South Africa (Matthews and Scharrer, 1968; von Brunn and Hobday, 1976) also includes stromatolites above a major unconformity, and is uncannily like Steep

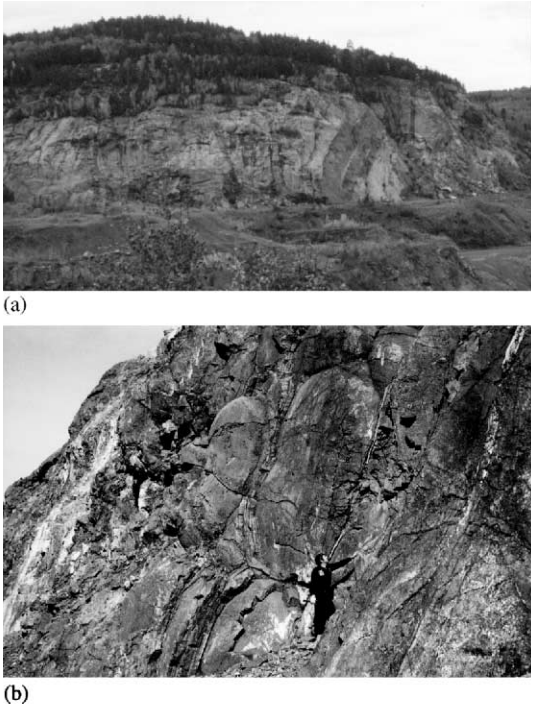


Figure 3 (a) The surface of the 3 Ga Earth, Steep Rock, NW Ontario, Canada. The hill-face is very close to a 3 Ga unconformity surface, and the rocks (granitoids and mafic dikes) exposed on the hill-face are immediately below the unconformity. Above them are assorted sediments, including thick stromatolitic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

Rock both in age and sequence: it is tantalizing to wonder if they were once contiguous before the vagaries of continental breakup and re-assembly.

8.01.3.2.5 Belingwe

The evidence for life in the sediments of the Belingwe belt, Zimbabwe, has been 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 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. 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, as well as the operation of complex sulfur fractionating processes (Grassineau *et al.*, 2001, 2002). Oil is present in some rocks (Grassineau and Nisbet, own observations). Locally associated with this stratigraphic unit are stromatolites made of calcite with $\delta^{13}C \sim 0‰$, with kerogen that contains carbon which is strongly fractionated isotopically, implying the selection of carbon by rubisco (see Section 8.01.7.2). 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) is that the complex isotopic fractionation is a record of consortia of prokaryotes, some reducing sulfate and some perhaps oxidizing sulfur, others generating methane, 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 sulfureta, 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 too have evidence for rubisco fractionation (see Section 8.01.7.2), both in kerogen carbon, and in carbonate with $\delta^{13}C \sim 0‰$.

8.01.4 THE FUNCTIONING OF THE EARTH SYSTEM IN THE ARCHEAN

8.01.4.1 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. Late Hadean and early Archean volcanism would have provided thermodynamic contrast, placing material that had equilibrated with the mantle in contact with the ocean-atmosphere system that was open at the top to space and light. In the latest Hadean and earliest Archean this contrast would have been most likely thermodynamic basis of life.

Early Archean volcanism was probably largely basaltic or komatiitic, but perhaps with some

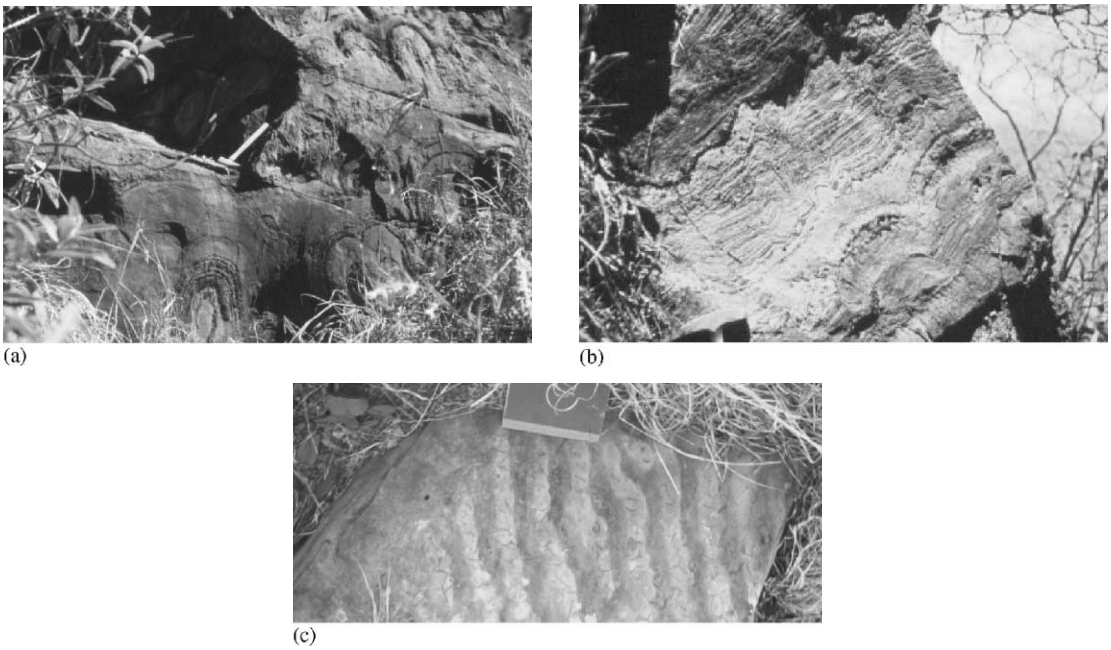


Figure 4 Stromatolitic limestone, Cheshire Formation, Belingwe belt, Zimbabwe (2.6–2.7 Ga old): (a) outcrop surface—structures occur on a variety of scales, from microscopic to metre relief; (b) detail of one outcrop (from Nisbet, 1987); and (c) shallow-water shale associated with Cheshire stromatolites.

andesitic and alkaline centers. The mantle may have been somewhat hotter than today (Nisbet *et al.*, 1993), and thus the primary melt at mid-ocean ridges 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 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 and the existence of 4 Ga gneiss provide evidence for the existence of continental crust, but this may have been of limited areal extent. Significantly, by the early Archean there had probably been inadequate time for deep continental lithosphere to develop, yet by 2.7 Ga, 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.

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 biological host environments.

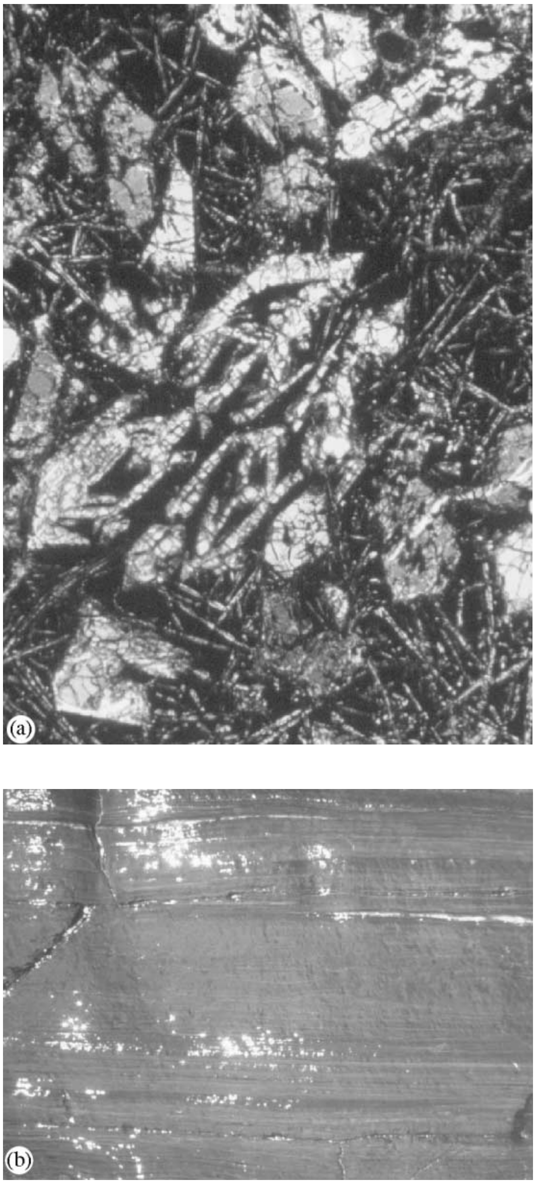


Figure 5 (a) Thin section of 2.7 Ga komatiite lava, Reliance Fm, Belingwe belt, Zimbabwe. About 6.5 mm across photo. Olivine crystals set in fine grained to once-glassy groundmass. For details see Nisbet *et al.* (1987). Photo W. E. Cameron. (b) Alternating iron-rich and carbon-rich shales. White bands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

8.01.4.2 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 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 mid-ocean ridge 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 CO_2 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 spilitization reactions, and hence providing calcium for *in situ* precipitation in oceanic crust.

Before significant thicknesses of lithosphere had cooled over large areas, the subduction may have been limited, and hence the return of carbonate-held carbon dioxide to air, via subduction volcanoes, would have been hindered in the earliest Hadean: by late Hadean subduction should have become the general fate of old oceanic plate. 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. The crustal Urey cycle buffers carbon dioxide in the air. In the Urey cycle, if global warming occurs, silicate weathering is speeded up, more calcium, magnesium, 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 mid-ocean ridges 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.

To return now to the carbon dioxide question, early in Earth's history, 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). 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 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 (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 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 CO_2 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. 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; and locations in ice; and in warm water (Nisbet and Sleep, 2001a,b).

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 H_2 would have been generated. Likely terrestrial sources of redox contrast included: hydrogen emitted from serpentinization reactions when water reached hot ultramafic rock; 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; as well as the contrast between water and magmatic hydrogen. Meteorites would have provided reduced iron and carbon particles. Hot iron, falling in to 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 late Hadean Earth offered these on a plate.

8.01.5 LIFE: EARLY SETTING AND IMPACT ON THE ENVIRONMENT

8.01.5.1 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, yet 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 ability, 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 can in principle reproduce and thus increase the scale of the disequilibrium, while 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, 1959), noted the characteristics of modern hydrothermal systems: abiotic formation of hydrocarbons may occur today in mid-ocean ridge systems (Holm and Charlou, 2001). An interesting variant is the idea of "genetic take-over" (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, that 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 (Figure 6).

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, it is not discussed why the men were green, or why they were men: pan-oo would be perhaps more likely than pan-sperm.

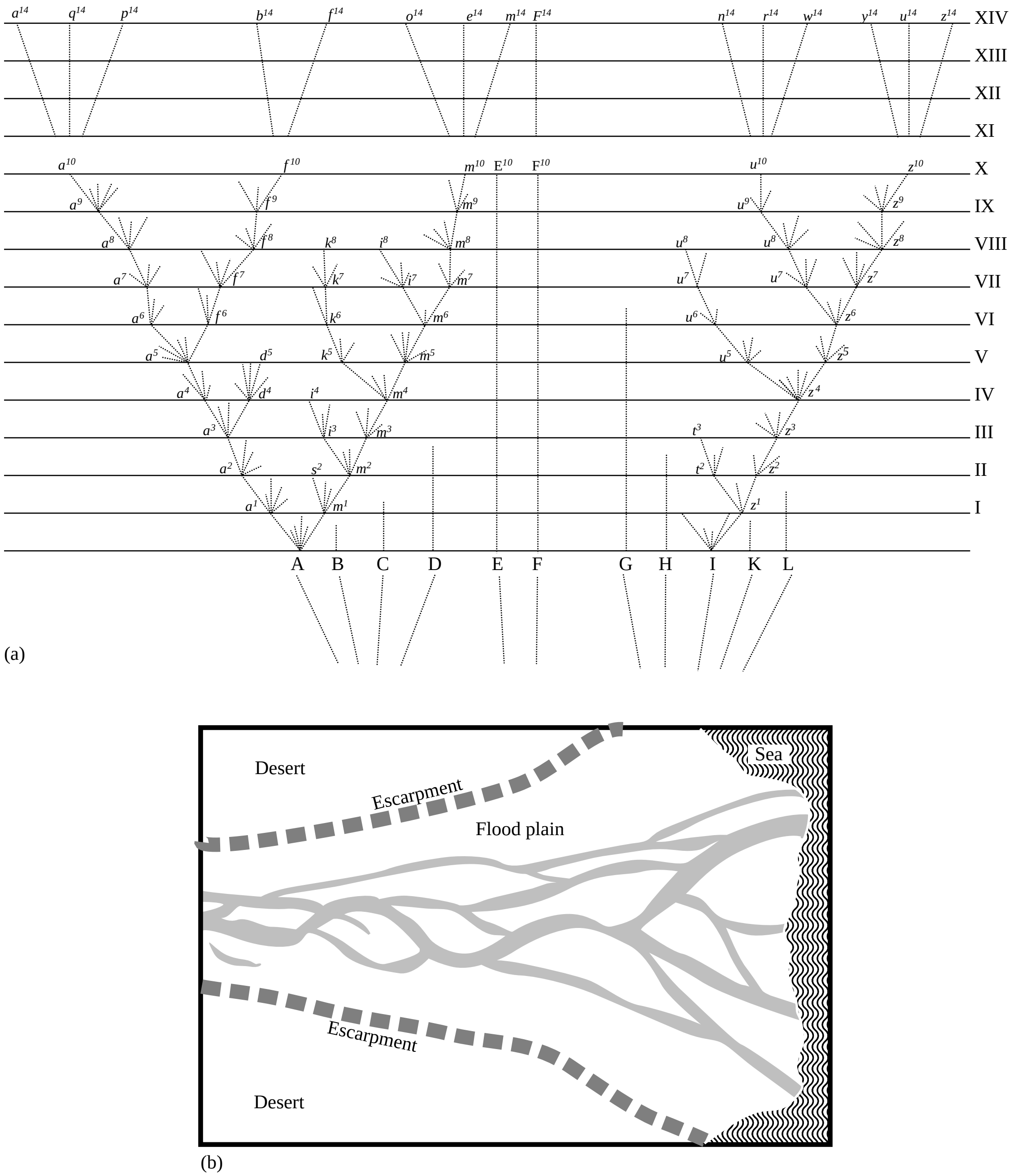
8.01.5.2 RNA World

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 propagate; 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 pre-adapted to life in the open environment, away from the rock vesicle. But this is a notion—many other notions have equal or greater validity.

Geologically, some inferences can be made. The setting of the first life to use nucleic acids would presumably have had abundant local phosphate sources and accessible phosphorus, as well as sugars and nitrogen bases. Here the evidence of the existence of komatiite plumes and the antiquity of continents is just possibly relevant. Alkali volcanism is a feature of plume volcanoes (e.g., Mauna Kea in Hawaii). Carbonatite volcanism and associated very unusual rocks (such as phosphatites) occur today mainly on ancient continental crust. 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–melt 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 would have occurred around the widespread



(a)

(b)

Figure 6 Models of the descent of life: (a) after Darwin's single illustration in Origin of Species (chapter IV) (Darwin, 1859, 1872) and (b) braided delta model, assuming large-scale lateral gene transfers and boundaries of nonviability.

cooling ultramafic rocks, such as the enormous komatiite flows that would have issued from komatiitic plume volcanoes, and also at distal sites near early mid-ocean ridges (themselves possibly fed by komatiitic basalt liquid). These hydrothermal systems would emit high-pH hot fluids. Here ammoniacal hydrothermal systems (Hall, 1989, Hall and Alderton, 1994) would probably have occurred. Under such high-pH conditions metal atoms (e.g., iron, 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: haem with iron and four nitrogens; chlorophyll with magnesium surrounded by four nitrogens.

8.01.5.3 The Last Common Ancestor

The *last* common ancestor 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.

The *last* common ancestor 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 last common ancestor. This last ancestor would have been a DNA-based organism, already complex, with many of the 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 last common ancestor. The majority view is that the root was a prokaryote, more bacterial than anything else, from which diverged the sister domains of Archea and Eucarya (Woese, 1987) (Figure 7). In this view, complex eukaryotes evolved from simple prokaryotes. This interpretation also leads to the inference that the last common ancestor was a hyperthermophile, living in hot conditions (>85 °C) probably in close proximity to a hydrothermal system (Stetter, 1996; Nisbet and Fowler, 1996a,b; Miyazaki *et al.*, 2001). In standard microbial phylogenies (e.g., Woese, 1987; Barnes *et al.*, 1996; Pace, 1997), the most deeply rooted organisms all appear to live in high-temperature settings. This view makes abundant geological sense, as the diversity and fluctuation of chemical settings in hydrothermal systems offers 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. Moreover, heat shock proteins are integral to protein shaping, suggesting the speculation that heat shock was a general problem for early life (Figure 8).

However, the argument in favor of a mesophile last common ancestor is equally strong (Forterre, 1995; Forterre and Philippe, 1999; Galtier *et al.*, 1999). Heat is a threat to life: it cooks it, and cells have heat-shock proteins 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., Stetter, 1996; Nisbet and Fowler, 1996a) 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.

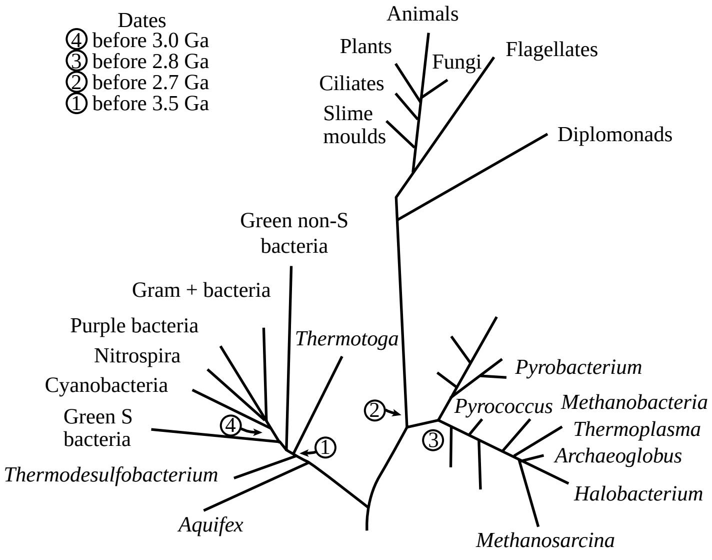


Figure 7 Model of the descent of life following the "standard" model of Woese (1987), as calibrated by the geological evidence (source Shen *et al.*, 2001, and other evidence). See Figure 11 for alternative model.

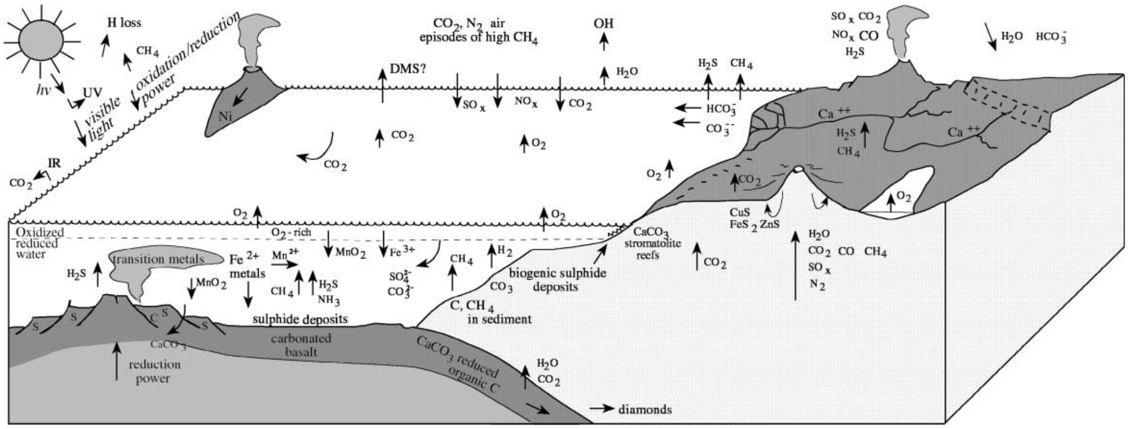


Figure 8 Sources of disequilibrium—possible geochemical (redox) resources for life in the early to mid-Archean.

An analogy would be the comparison between geometrically complex early multiple-winged aircraft such as Sopwith biplanes of the 1914–1918 era, the streamlined Hawker Hurricane monoplanes of the Battle of Britain with protruding propellers and tail wheel, and the Hawker Harrier still today in service: all built under the direction of Thomas Sopwith. These airplanes simplified in shape as they became more powerful and internally complex. 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 brother-in-law of author J. D. Salinger: close relations, utterly different careers.

Derivation of molecular phylogeny from rRNA suffers from various mathematical pitfalls, especially the difficulty of dealing with branches of the tree of life that evolve especially rapidly. Any model that assumes uniform rates of evolution will make these branches appear inaccurately ancient. 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), 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 (i) shared ancestry between the lines, rather than (ii) lateral transfer of information between contemporary but unrelated lines, is not easy. 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) point 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.

In this view, the eukaryotes may well preserve some very primitive characteristics that are not seen in prokaryotes. Glansdorff (2000) reappraised claims for lateral gene transfer and concluded that the extent of transfer was overemphasized; moreover, Glansdorff inferred that the last common ancestor was probably nonthermophilic and perhaps a protoeukaryote, from which the thermophilic archaea may have been the first divergent branch.

Conceivably, if the last common ancestor were mesophile, the majority of bacteria (except perhaps planctomycetes (Brochier and Philippe, 2002)) may descend from an early mesophile prokaryote, perhaps via a genetically streamlined descendant that occupied a hyperthermophile setting. Archea too may descend from the last common ancester via a streamlined cell that had evolved to inhabit hyperthermophile settings. In contrast, the Eucarya may be directly descended from a mesophile, as may the planctomycetes.

A possible geological scenario for this process may be that the last common ancestor lived on the warm (~40 °C) but not hot periphery of a 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 near 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, 2002), and there are cells preserved in ice that has crystallized from Lake Vostok, the great ancient lake under the Antarctic ice cap. Just possibly, early relatives of the planctomycetes, a bacterial branch which may be of the greatest antiquity, may have been distributed in the glacial oceans, and would have been subject to freezing in thick ice cap, and thus preferentially likely to survive a global heating event after a meteorite impact.

8.01.5.4 A Hyperthermophile Heritage?

Whatever the setting of the last common ancestor, there are many aspects of modern cells that have a possible or likely hyperthermophile origin. 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)).

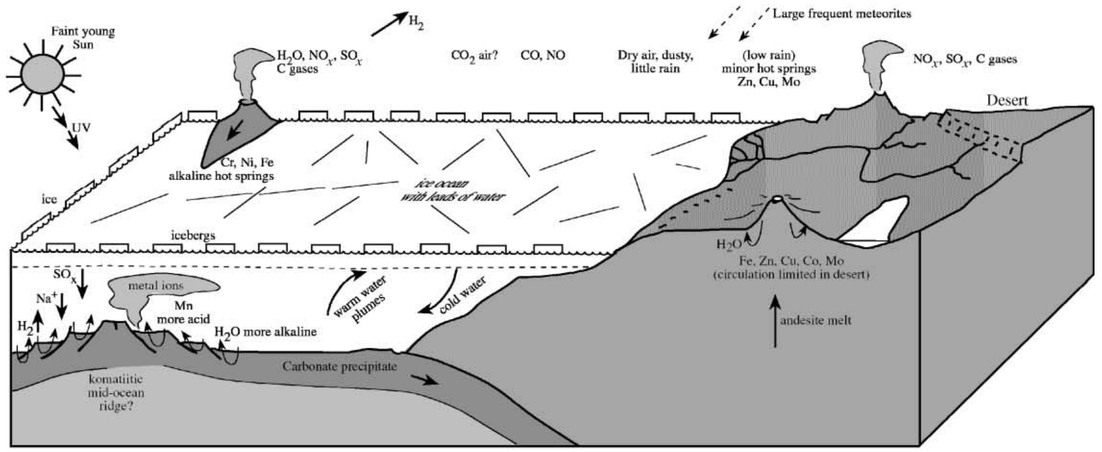
Candidates for biochemical processes or molecules with hyperthermophile origins include the heat shock proteins, and the metal enzymes (Nisbet and Fowler, 1996b). Heat-shock proteins are ubiquitous in all domains of life. They help repair damage after heat shock, but more generally they help to shape new protein molecules so they can carry out their proper functions. The heat-shock proteins 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, heat-shock proteins may indeed descend from an original function evolved to enable life to enter hyperthermophile settings around hot-water vents.

Like the heat-shock proteins, 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 housekeeping 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. 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 F_{430} of methanogens and hydrogenase contain nickel. Consequently, nickel is essential to methanogens. 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 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 (see Section 8.01.6.5) (Figure 9). It is interesting to wonder if the cytochromes, methanogens, and the nitrogen cycle all first evolved on the flanks of komatiite volcanoes.

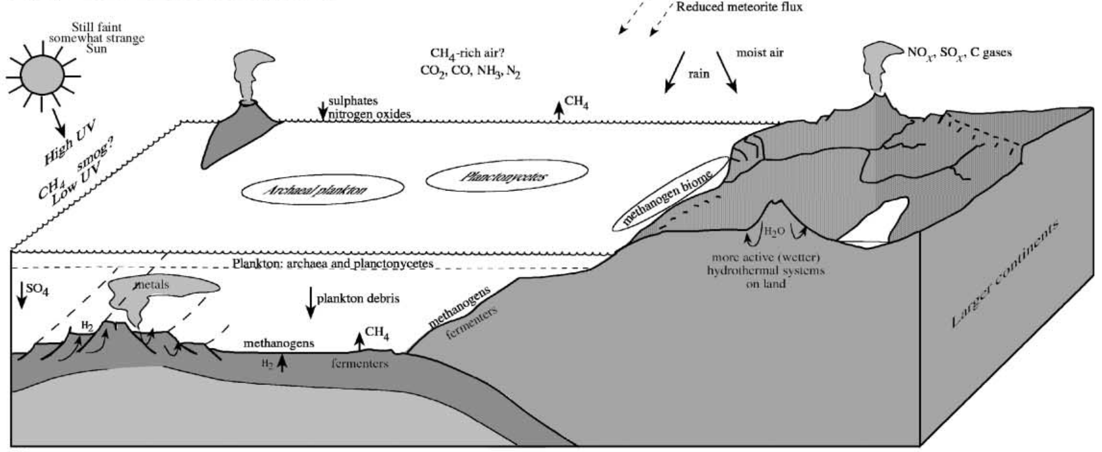
Today, metals are scavenged from water by extremely sophisticated biochemical processes (Morel and Price, 2003). Thus, seawater can have very low ambient levels of metal ions. Early Archean seawater would likely have been much richer in trace metals. But given that early organisms presumably had very 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 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 last common ancestor was not hyperthermophile but lived

Hadean



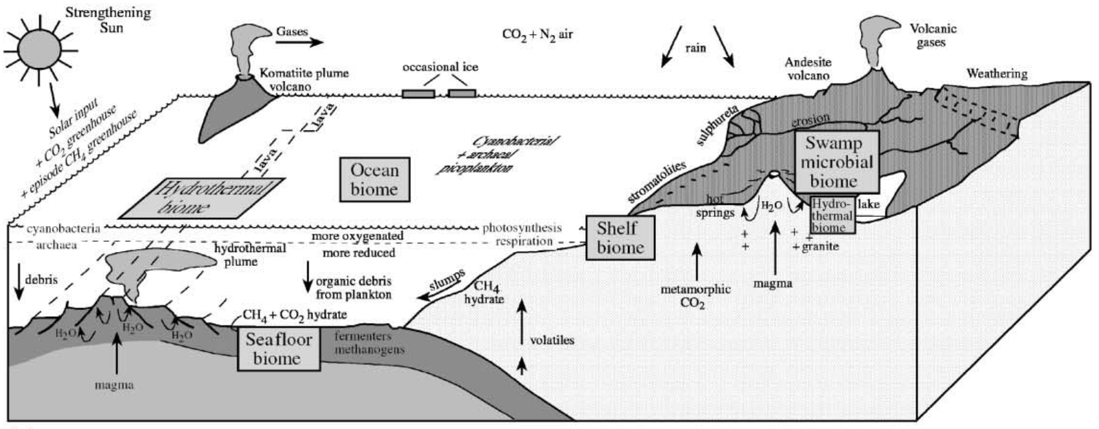
(a)

Early Archean: prephotosynthesis



(b)

Late Archean: with oxgenic photosynthesis



(c)

Figure 9 Model of the evolution of the planetary surface: (a) Hadean surface, possibly glacial (apart from rare very hot events after major meteorite impacts); (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.

in somewhat cooler conditions, from it came volcano-hosted hyperthermophile ancestral lines, living in and around hydrothermal systems, that led to the Archeal domain and perhaps also to most bacteria (excluding perhaps the planctomycetes). 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.

8.01.5.5 Metabolic Strategies

It is likely that the oldest organisms were not photosynthetic (see discussion in Nisbet *et al.*, 1995; Nisbet and Sleep, 2001). 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, 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, H_2, and perhaps NH_3 would have been present also. The chief source of reduction power would be hydrothermal exchange with magma, providing reduced sulfur species, H_2, methane, CO, and ammonia.

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 (Stevens and McKinley, 1995; Kaiser, 1995) produces molecular hydrogen when circulating groundwater reacts with ferromagnesian minerals (FeO silicate), producing iron oxide (e.g., Fe_2O_3) 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:

$$\tfrac{1}{2}O_2(\text{aqueous}) + H_2(\text{aqueous}) \rightarrow H_2O$$

Others reduce sulfur:

$$S + H_2(\text{aqueous}) \rightarrow H_2S(\text{aqueous})$$

Methanogenesis (Thauer, 1998) is another process that involves H_2; in this,

$$CO_2(\text{aqueous}) + 4H_2(\text{aqueous}) \rightarrow CH_4(\text{aqueous}) + 2H_2O$$

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

$$CH_4 + SO_4^{-} \rightarrow HCO_3^{-} + HS^{-} + H_2O$$

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

$$NO_2^{-} + NH_4^{+} \rightarrow N_2 + 2H_2O$$

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 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.

8.01.6 THE EARLY BIOMES

8.01.6.1 Location of Early Biomes

Replication of the last common ancestor would lead to mutation: in turn, mutation would create accidental pre-adaptation to life in diverse new habitats. Whatever the habitat of the last common ancestor, 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. Examples include: hydrothermal high-temperature (>85 °C) settings; moderate thermophile settings (~40 °C) on the fringes of hot areas, or in cooler, probably more alkaline springs; very cool (~0 °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.

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.

8.01.6.2 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. In particular, 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 palaeontology (Woese, 1987; Barnes *et al.*, 1996; Pace, 1997) have value. Possibly they also predate the methane oxidizing archaea. These 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. 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.

Methanogenesis on a scale large enough to affect the atmosphere would have been possible if the hydrogen supply from inorganic and organic sources (and hence methanogenesis) had been adequate: given the likely abundance of ultramafic rock near the surface, 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, then much of the methane formed by the first methanogens would have been emitted directly to atmosphere. In the dry air on a cold glacial planet, this methane might rapidly overwhelm the OH. Over a few tens of millennia, the atmospheric methane burden would build up and have a major greenhouse impact (see Pavlov *et al.*, 2000), until enough ice melted to permit OH in air and thus control the methane.

Methane may have played a crucial role in allowing the early Earth to be habitable (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 ultraviolet 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) pointed out that in the early Archean, biogenic methane may have saved the Earth from permanent glaciation. On the modern Earth, on a 20 yr 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 sediment, would be expected to invoke high methane concentrations (10^2–10^3 ppmv—compared to modern air with less than 2 ppmv CH_4 and ~375 ppmv of CO_2). 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 O_2 at any particular time.

Methanogenesis may have had the interesting consequence of triggering the evolution of nitrogen fixation (Navarro-Gonzalez *et al.*, 2001; Kasting and Siefert, 2001). On an early planet with CO_2 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 CO_2 levels declined and CH_4 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.* suggested, may have come 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 N_2 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) points 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 some day be seen as the greatest peril of global climate change: not the greenhouse.

8.01.6.3 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 H_2, H_2S, and probably CH_4. 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 the 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 input from transient chemical species formed in the air. The solar radiation, acting on an atmosphere containing water vapor, would likely have produced OH, and probably some O_2. 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, H_2 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 gypsy-like cells that were perpetually seeking a new home as the old one was exhausted.

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 $\sim$1,000 m depth, where pelagic crenarchaeota are abundant (Karner *et al.*, 2001). In the early Archean, there may have been a significant boundary between deeper, more reduced water, and shallower water in sunlight. This boundary, as it shifted diurnally, would provide a fluctuating redox contrast for organisms that could exploit it. For example, the planctomycetes, form macroscopic aggregates ($>$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 the greatest antiquity.

Most intriguing of all, they are bacteria that have babies.

8.01.6.4 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 last common ancestor, fairly early in Earth's history, came the occupation of a diversity of habitats. 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, was probably well established and diversified by the mid-Archean.

The geological evidence for the presence of sulfur-processing microbial life and for methanogens goes back at least as far as the late Archean, and probably earlier. Rocks containing highly fractionated sulfur isotopes, closely spatially associated with highly fractionated carbon, are known from many 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).

Strong evidence for Archean methanogens comes from highly fractionated carbon isotopes. As mentioned above, these have been found in 2.7 Ga material from Belingwe (Grassineau *et al.*, in press), and also from similarly aged rocks in Australia (Rye and Holland, 2000).

Standard rRNA molecular phylogeny (Woese, 1987; Barnes *et al.*, 1996; Stetter, 1996; Pace, 1997) implies the antiquity of hyperthermophile organisms. Though there has been much dispute about the rRNA interpretation, there is some consensus that, whether or not it is the very most ancient, life around hot-water vents is certainly of great antiquity. The implication is that by mid-Archean, hyperthermophile habitats around hot vents were populated by microbial mats, and the waters around hot vents were occupied by free-swimming cells. 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, a target for investigation by the geologist. Though there is controversy about sulfur isotope fractionation (Farquhar *et al.*, 2000), the strong fractionation of $\delta^{34}S$ seen in the best-preserved Archean organo-sedimentary rocks can only be biological. Sulphate reducers are probably very old, present 3.5 Ga ago in the early Archean (Shen *et al.*, 2001), 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 setting. 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.

8.01.7 THE EVOLUTION OF PHOTOSYNTHESIS

8.01.7.1 The Chain of Photosynthesis

Photosynthesis is the source of the redox power that allowed life to escape from the very restricted early settings where inorganic redox contrast existed, and occupy the planet. Without access to light energy, life would have been permanently restricted to a few narrow 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). 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), as well as 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.

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, PSI, is electrically connected to the PSII production of H^+, and, with two further electrons, generates NADPH; in addition, ADP 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 $O_2:CO_2$ ratio it is exposed to (Lorimer and Andrews, 1973, Lorimer, 1981). On rubisco hangs the balance of the atmosphere (Tolbert, 1994).

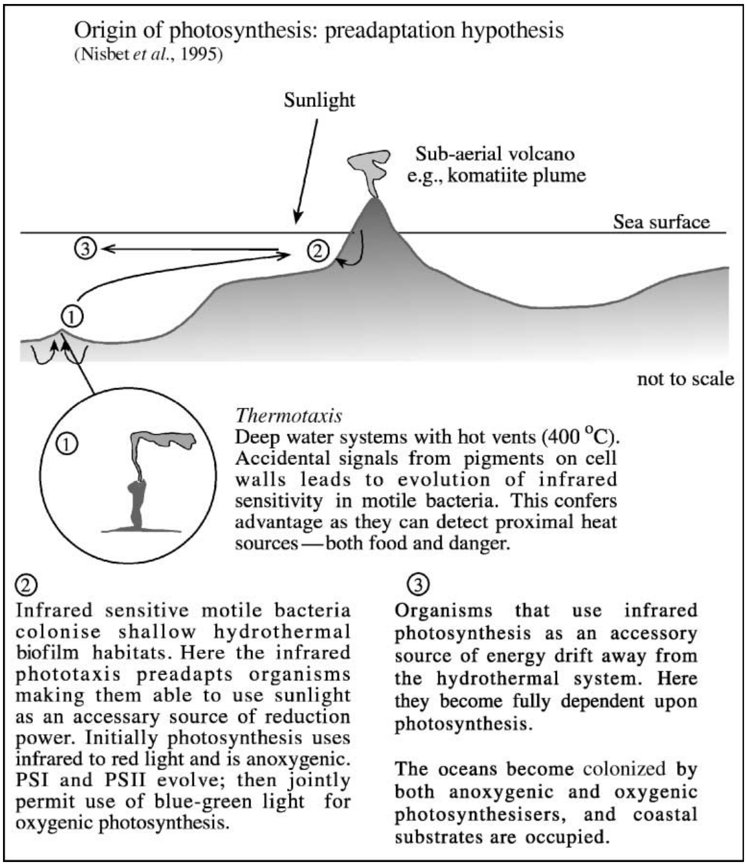
8.01.7.2 The Rubisco Fingerprint

Geologically, photosynthesis presents several quarries to be hunted down in the geological record. The distinctive isotopic fingerprint of rubisco, which presumably must predate oxygenic photosynthesis, is the most obvious target—it is very selective in the carbon atoms it accepts and hence the organic molecules it creates are highly depleted in ^{13}C. There are two main types of rubisco. Rubisco I is used in oxygenic photosynthesis, it operates in aerobic or microaerobic conditions, not anaerobic settings. Rubisco II is characteristic of organisms that fix CO_2 anaerobically. It may be more ancient, and is today found in deep-sea rent organisms (Elsaied and Nagunama, 2001). The oxygen-evolving complex is also a target for the geologist, as it is based on manganese oxide, as are the transition metal isotopes that are likely to have been fractionated by capture in key enzymes.

More subtly, the isotopic signatures of photosynthesis in inorganic sediment are also valuable. 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 $\delta^{13}C-5‰$ to $-7‰$, on the arbitrary 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 $\delta^{13}C\sim-28‰$ to $-30‰$ when fractionated by rubisco I, but around $-11‰$ 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 $\delta^{13}C\sim0‰$. The presence of $\delta^{13}C\sim0‰$ carbonate is thus testimony that rubisco I was capturing carbon on a global scale, in aerobic conditions: this is known as the rubisco fingerprint.

8.01.7.3 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 references cited therein. How did the full chain evolve, given that half a chain is useless? The challenge to the geologist is to identify the small steps of pre-adaptive advantage on which evolutionary change worked, to date those steps, and to explain the way the individual links in the chain were incorporated.



Thermotaxis
Deep water systems with hot vents (400 °C). Accidental signals from pigments on cell walls leads to evolution of infrared sensitivity in motile bacteria. This confers advantage as they can detect proximal heat sources—both food and danger.

② Infrared sensitive motile bacteria colonise shallow hydrothermal biofilm habitats. Here the infrared phototaxis preadapts organisms making them able to use sunlight as an accessary source of reduction power. Initially photosynthesis uses infrared to red light and is anoxygenic. PSI and PSII evolve; then jointly permit use of blue-green light for oxygenic photosynthesis.

③ Organisms that use infrared photosynthesis as an accessory source of energy drift away from the hydrothermal system. Here they become fully dependent upon photosynthesis.

The oceans become colonized by both anoxygenic and oxygenic photosynthesisers, and coastal substrates are occupied.

Figure 10 Possible evolutionary chain leading to photosynthesis: hypothesis of pre-adaptation for infrared thermotaxis (Nisbet *et al.*, 1995).

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 pre-adapted 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 pre-adaptation that led to the very 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 the ability to move towards 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 finer-tuned to the IR. Then, in the next step, organisms that had spread to a shallow-water vent would be pre-adapted 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 suggest 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. Recent work supports the notion 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 an magnesium atom surrounded by four nitrogen atoms (see Section 8.01.5.2 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 haem (where the central metal is iron) 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 must be of the very greatest antiquity and probably predate the last common ancestor. 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.

8.01.7.4 Anoxygenic Photosynthesis

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 (e.g., *Rhodobacter*). The purple bacteria (proteobacteria) are classified by 16S rRNA study into several major evolutionary groups (Woese, 1987). 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 dark, most purple nonsulfur bacteria can grow in aerobic or microaerobic 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 H_2, H_2S, S, or organic matter, and does not, as a consequence, evolve waste oxygen. Many green and purple bacteria can grow phototrophically using H_2 as the sole electron donor and CO_2 as the carbon source, using hydrogenase (a nickel enzyme) for CO_2 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* the hydroxyproprionate pathway. Geologically, these should be distinguishable in the kerogen record from rubisco-captured carbon.

When the first photosynthetic sulfur-compound oxidizers first appeared, the development of full sulfureta would have been possible. Sulfate reducers would take sulfate from the external environment and eventually produce H_2S. Then the photosynthetic oxidizers would reverse the steps, e.g.,

$$6CO_2 + 12H_2S \rightarrow C_6H_{12}O_6 + 6H_2O + 12S^0$$

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) 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 H_2S-rich layers, creating a complex microbial mat habitat.

Plankton today are very diverse, including archaea, bacteria, and eukaryotes (Beja *et al.*, 2002). 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 and green photosynthesizers, as well as planctomycetes (Fuerst, 1995), which may be a very ancient prephotosynthetic branch of the bacteria (Brochier and Philippe, 2002), as discussed earlier.

Complex global-scale nitrogen cycles would also have become possible at this stage. The planctomycetes, if presumed ancient, are capable of emitting N_2 by reacting NH_3 with NO_2. 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). The modern nitrogen cycle is dominated by bacteria. Some bacteria such as *Pseudomonas* release N_2. 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). 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 N_2 to NH_3, eight electrons are consumed, six for producing $2NH_3$ and two to make H_2: hydrogen production and nitrogen fixation appear closely linked. Possibly nitrogenase originally evolved to manage ammonia in close association with methanogenesis using H_2.

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 N_2 has been a biological product in the main, produced and consumed by organisms.

8.01.7.5 Oxygenic Photosynthesis

The development of oxygenic photosynthesis created the modern biosphere. 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 neighbors. Cyanobacteria achieve this by a multicomponent system. Most likely (though not if the Granick hypothesis is correct), oxygenic photosynthesis came *after* the development of photosynthetic reaction system II in purple bacteria and reaction system I in green sulfur bacteria (Nisbet and Fowler, 1999).

There are many notions about how oxygenic photosynthesis evolved (e.g., Blankenship, 2001; Nisbet and Fowler, 1999). All photosystems are basically alike and must have had a common origin (Jordan *et al.*, 2001; Kuhlbrandt, 2001). Heliobacteria, which are anoxygenic phototrophs living in tropical soils, utilize a modified form, bacteriochlorophyll *g*, that is related to cyanobacterial chlorophyll *a*. They may be the microbial branch with the photosynthetic genes, which are most closely related to the ancestral cyanobacteria (Xiong *et al.*, 2000). Perhaps the photosynthetic reaction system in green gliding bacteria, such as *Chloroflexus*, is ancestral to both. What of the host cell, apart from the photosynthetic process? One possibility is that the cyanobacterial cells themselves are chimaera, created by genetic transfer (perhaps lunch) between close-living or symbiotic purple and heliobacteria. This would imply that purple bacteria evolved before cyanobacteria. 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 O_2-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 occurred, plus gene duplication, to produce the cyanobacterial reaction center II in the ancestral cyanobacterium (Xiong and Bauer, 2002). The puzzle remains open.

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

Nitrogen supply is a key limitation on productivity (Falkowski, 1997). Cyanobacteria 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. 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. 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.

When did this occur? The key signature (see Section 8.01.7.2) is in the $\delta^{13}C \sim 0‰$ isotopic signature of rubisco I in carbonate rocks (Schidlowski and Aharon, 1992; Schidlowski, 1988, 2002; Nisbert, 2002). This is the modern fingerprint imposed by the chloroplast, still a member of the cyanobacterial line. Carbon dioxide in the atmosphere and ocean is well mixed. For the $\delta^{13}C \sim 0‰$ 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 photosythesis can drive the Calvin cycle to capture carbon dioxide on a scale large enough to create the isotopic signature.

The evidence for the $\delta^{13}C \sim 0‰$ signature is strong around 2.7 Ga (e.g., Grassineau *et al.*, 2002). Buick (1992) in the 2.7 Ga Tumbiana formation in Western Australia presents strong textural evidence for oxygenic photosynthesis in stromatolites growing in shallow lakes. However, older evidence for oxygenic photosynthesis is problematic. The ca. 3 Ga Steep Rock carbonates have $\delta^{13}C$ not far from 0‰ (Abell, Grassineau and Nisbet, unpublished), but in older material there is strong controversy (e.g., Brasier *et al.*, 2002; see also Schopf *et al.*, 2002).

8.01.7.6 Archean Oxygen

By 2.7 Ga ago, the modern carbon cycle was in operation: the oxygen production must have been considerable. Did it build up in the air? For contrasting views on this vexed problem, see Holland (1999) and Ohmoto (1997). Catling *et al.* (2001) argue 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 accumulates in swamps despite the O_2-rich air. 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.

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. 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. 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 Myr later?

The implications of the Catling *et al.* (2001) suggestion that the air had high methane concentrations (>0.1%) in the late Archean are worth further thought. If so, then consequently, as methane mixed into the stratosphere and upwards 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.

8.01.8 MUD-STIRRERS: ORIGIN AND IMPACT OF THE EUCARYA

8.01.8.1 The Ancestry of the Eucarya

The origin of the *Eucarya* remains deep mystery. Some (e.g., Forterre, 1995, 1996) would place it very early indeed; yet it has also been ascribed to a time as recently as 850 Ma ago, in the later Proterozoic (Cavalier- Smith, 2002).

The geological evidence for Archean eukaryotes can be dealt with swiftly. Brocks *et al.* (1999) found organic molecules (sterols) in 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; thus the interpretation by Brocks *et al.* (1999) is contested (Cavalier-Smith, 2002). Nevertheless, the simplest interpretation is that this is a just-plausible record of Archean eukaryotes.

The molecular evidence for the descent of the eukaryotes (Hartman and Fedorov, 2002) is deeply controversial (see Section 8.01.6.3). Standard models (Woese, 1987) suggest an ancestral line among the Archea, with massive transfers and symbioses from the bacteria. The standard model (e.g., see summaries in Pace (1997); Nisbet and Fowler, 1996a,b) is that 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 partnerships with symbiotic purple and cyanobacteria, either in separate events, or in a single moment of fusion. This produced the eukaryote cell, with the mitochondria derived (Bui *et al.*, 1996 from within the α-proteobacteria such as *Rickettsia*. The other great acquisition of the eukaryotes, the chloroplast, is clearly related to the cyanobacteria (Figure 11).

Much discussion followed on the timing of the event or events, especially as some eukaryotes lack mitochondria. Could they be more primitive? At first it was thought so, but recently it has become clear that even eukaryotes, such as the microsporidae, that are no longer capable of aerobic respiration still have relict mitochondrial proteins (Williams *et al.*, 2002; Roger and Silberman, 2002). The ancestral eukaryote did probably possess mitochondria, and the amitochondrial eukaryotes lost them. Even 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 it appears that the ancestors of all modern eukaryotes diverged after the mitochondrion symbiosis. Likewise, animals may have descended from an ancestral photosynthesizer by loss of the chloroplast.

Whatever the explanation of the stem eukaryote, the eukaryote organelles, both mitochondria and chloroplasts, are best explained as symbiont bacteria. Explanations of the mitochondrial symbiosis mostly invoke an early Archean stem that incorporated a bacterial symbiont. One explanation of the mitochondrion is that the origin of the mitochondrion was simultaneous with the origin of the eukaryote nucleus (Grey *et al.*, 1999). In the “hydrogen hypothesis” (Martin and Muller, 1998), the symbiosis is seen as the end product of a tight physical association between anaerobic

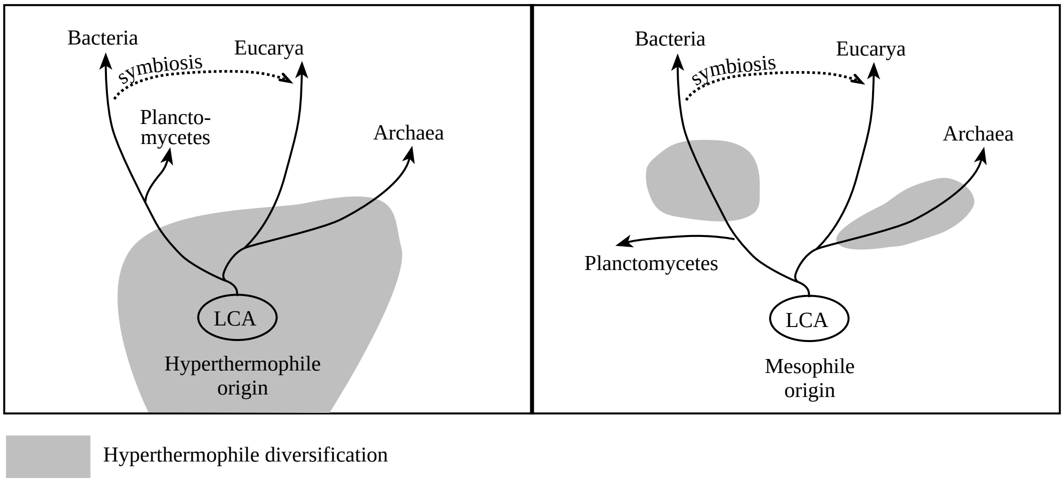


Figure 11 Standard and alternative models of eukaryote evolution (see Figure 7) (with thanks to J. Fuerst). Alternative model assumes a last common ancestor that was mesophile, and that the divergence of the planctomycetes was very ancient (see Brochier and Philippe, 2002).

archaea and heterotrophic proteobacteria capable of producing molecular H_2 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).

In contrast, Penny and Poole (1999) suggested that the last universal common ancestor may have been a mesophile with many features of the eukaryote genome, and the first distinct eukaryote may thus also have been mesophile—a distal inhabitant of a hydrothermal system, or a planktonic form.

However, if the "eukaryote-like" view of the last common ancestor (Forterre and Philippe, 1999; Glansdorff, 2000) is correct, then the sequence of events may have been greatly different. In this view, an ancient common ancestor may have been a fairly complex organism, living in mesophile conditions, possibly some hundreds of meters distal to a shallow hydrothermal system, in water between, say, 35–45 °C (blood-temperature, optimal for DNA-based life), perhaps in water with pH around 7 or more alkaline (to account for the cytochromes).

From this, in Forterre's thermoreduction hypothesis (1995), came several lines of descendants. Some became colonists of much hotter environments. Of these lines, some necessarily streamlined both their genomes and their physiology, in order to survive, while others, also with reduced physiology, developed heat shock proteins to correct damage. This led to the distinct domains, the *Bacteria* and *Archea*. In contrast, other descendants retained the complex more primitive physiology—biplanes or triplanes, as opposed to prokaryote monoplanes. This third line became the *Eucarya*. This third line may share some characteristics with the planctomycetes (Fuerst, 1995; Lindsay *et al.*, 2001).

At some stage in this hypothesis came the key acquisition by the ancestor of the modern *Eucarya* of the mitochondrion. Possibly: (i) this was very early—perhaps not so much an acquisition as a primitive characteristic; alternately (ii) it may have been a later product of a symbiosis between a mesophile eukaryote stem-organism directly descended from a mesophile eukaryote-like last common ancestor and a proteobacterium that had evolved from a line that had passed through a hyperthermophile bottleneck; or, (iii) it could have been a later product of a symbiosis between two organisms that had both been through a hyperthermophile stage, an achaea-like host and a proteobacterial symbiont.

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 (Saldarriga *et al.*, 2001), although perhaps from a single ancient endosymbiotic origin (Fast *et al.*, 2001). The same hypotheses apply. It is not clear whether all modern eukaryotes are descended from organisms that possessed chloroplasts, but the hypothesis is attractive. Some have multiply acquired and lost chloroplasts.

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.

As for the antiquity of the *Eucarya* there is no consensus. Those who support a eukaryote-like last common ancestor, of course, propose that the eukaryotes date to the very start of the Archean and end of the Hadean. It is not improbable to those who consider that the *Eucarya* were the last domain to appear, that Eukaryotes first evolved in the Archean aeon. 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.* (1994) could be of prokaryote origin.

8.01.8.2 Possible Settings for the Eukaryote Endosymbiotic Event

What was the purpose of symbiosis? And were the organelles incorporated simultaneously or sequentially? The answers are not known, but an argument can be made that simultaneous acquisition of both organelles took place, as they in effect balance.

The most likely setting of symbiosis is a microbial mat community, in which a complex community of cells is clustered across a redox boundary, cycling and recycling redox power (Nisbet and Fowler, 1999; Nisbet, 2002). 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 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 incorporations took place by single lucky improbable accident. Arguably, however, it is more likely that initially only one partner was incorporated, then the second.

8.01.8.3 Water and Mud Stirring—Consequences

Multi-celled 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. Only females reproduce, so the ability to "bloom" is slightly restricted by one generation time. 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 swapping genetic 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 undergarment, but the habit is only a few generations old: prior to that it was thought unclean. The change was non-Darwinian. Those human families (probably most) who did not wear such attire a few lifetimes ago did not become extinct—they mysteriously acquired the habit from contemporaries by a hidden process of cultural infection. 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.

The advantages of the eukaryotes are 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 major consequences in the Proterozoic when multicelled eukaryotes became capable of moving water and stirring mud. 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 2,300 Ma, much evidence suggests (but does not conclusively prove: see Section 8.01.8.6) that oxygen levels rose sharply. Possibly the eukaryotes were beginning to muscle the world.

8.01.9 THE BREATH OF LIFE: THE IMPACT OF LIFE ON THE OCEAN/ATMOSPHERE SYSTEM

8.01.9.1 The Breath of Life

The modern atmosphere is the breath of life—a biological construction. 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 ~33 °C to the temperature (Lewis and Prinn, 1984). Without the atmosphere, the temperature of the planet would be ~−18 °C; with the atmosphere it is a pleasant +15 °C. But is the control pure inorganic chance, or is it somehow implemented because the Earth, uniquely, is inhabited? And when did the control begin?

8.01.9.2 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 fundamental control remains very controversial. One argument that may be made 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. The debate remains open.

8.01.9.3 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 nitrifying bacteria (lifetime in air ~10–100 Ma). Nitrogen is emitted to the air by guilds of denitrifying bacteria (e.g., *Pseudomonas*, *Bacillus*), which reduce nitrate to N_2 as an alternative respiration process in anaerobic settings when oxygen is absent. This raises the inference that this process may be very old, and could have evolved before oxygenic photosynthesis, predating the time of abundant oxygen supply. As argued above (Section 8.01.6.3), the anammox process may also be of great antiquity, perhaps long predating oxygenic photosynthesis.

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 reduced to the nitrogen oxides and ammonia emitted by volcanoes and hydrothermal systems. Nitrogen fixation reverses this, and is carried out by cyanobactria, 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. Given the clear evidence for cyanobacteria (albeit bound in mats) in the Archean (Summons *et al.*, 1999), it is reasonable to assume that cyanobacterial plankton were presumably ubiquitous in the Archean oceanic photic zone. Thus, there is a reasonable presumption that in the Archean the dinitrogen atmospheric burden was organically fluxed.

8.01.9.4 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 and water, as well as dinitrogen), but also substantial methane and probably ammonia emissions occurred, that 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 at the Archean–Proterozoic transition (Hayes, 1994). For example, this could occur after massive release of geological methane stores (e.g., see Kvenvolden, 1988; Harvey and Huang, 1995).

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 Archean "Walkerworld" events may have occurred, when the biosphere was inverted: relatively reducing air and 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.

8.01.9.5 Sulfur

The oxidation states of sulfur may have been the core tool by which life bootstrapped its way to a global biosphere (Kasting *et al.*, 1989; Kasting, 1993, 2001). 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, 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.

8.01.10 FEEDBACK FROM THE BIOSPHERE TO THE PHYSICAL STATE OF THE PLANET

The planet shapes life, but life also shapes the planet (Nisbet, 2002). 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 and Margulis, 1974; Lovelock, 1979, 1988).

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) as well as 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 the Earth.

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