

Fermor lecture: The influence of life on the face of the Earth: garnets and moving continents

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Abstract: The Hadean Earth (before *c.* 4 Ga) was abiotic, possibly steering a bumpy course between brief periods of hot inferno after meteorite impacts, and long episodes of Norse icehell. The earliest Archaean life would probably not have been planet-altering, but restricted to particular habitats. One of the first may have been hot regions around hydrothermal systems where redox contrasts between ocean water and magmatic fluids could be exploited. Molecular evidence suggests that with the evolution of anoxygenic photosynthesis, life became able to occupy wider regions, although focused in the vicinity of hydrothermal systems. Oxygenic photosynthesis by cyanobacteria allowed life fully to occupy the planet, not only forming coastal microbial mats but also possibly inhabiting the broad oceans with abundant photosynthetic bacterial picoplankton, underlain by deeper archaeal picoplankton. In the Belingwe belt, Zimbabwe, textural and isotopic evidence suggests that a complex microbial ecology existed in the late Archaean (2.7 Ga), which was essentially modern in its biochemical abilities and which sequestered into the biosphere the same fraction of primitive carbon emitted from mantle as today. To do this, by the late Archaean the biological productivity must have been significant; not necessarily as large as today, but capable of managing the global carbon budget. When this began is unknown, possibly earlier than 3.5 Ga ago. The controls on the oxidation state of the late Archaean atmosphere–ocean system are not self-evident. Although inorganic controls dominate the long-term balance, short-term biological management of the air may have been crucial. Methane may have played a major role in the pre-metazoan biosphere. The modern atmosphere is a biological construct: oxygen and its reverse, carbon dioxide, are managed by rubisco; nitrogen, its oxides and hydrides mainly by nitrifying and denitrifying bacteria, with a small input from lightning in an oxygen-rich atmosphere; and water (itself the most important greenhouse gas) by its complex interdependence with other greenhouse gases and albedo, including clouds. Earth's air is highly improbable. In controlling surface temperature a subtle interplay between organic and inorganic controls has operated, perhaps to the extent that it is invalid to ask which was the dominant factor. But there is a reasonable uniformitarian argument that life has constructed the air in the past as now, and that, within the broad constraints of the physical setting, this biologically shaped atmosphere has been the dominant control on the planet's surface temperature. In turn, the surface temperature has been one of the various controlling factors on the tectonic evolution of the planet. Thus to a significant extent life has helped shape the physical evolution of the planet.

Half-a-century ago, Sir Lewis Fermor was returning from India, where he had led the superb work of the Indian Geological Survey. Like his distinguished son, Fermor was a traveller. He took the long route, through Gondwana. While du Toit in the interwar years had gone from South Africa to the USA up South American Gondwana, Fermor returned from the land of the Gonds via Africa. In Harare, Fermor addressed one of Africa's oldest scientific societies, the Zimbabwe (then Rhodesian) Scientific Association. His topic was Garnets and moving continents (Fermor 1949). Today we would rephrase that as 'density contrast drives slab movement'.

Fermor's host was the distinguished local geologist, A. M. Macgregor, who spoke on 'The

influence of life on the face of the Earth' (Macgregor 1949). Although given far away from the intellectual centres, and published in an obscure journal, both lectures were influential. Neither lecture was polished, neither offers especially penetrating insights or solutions, but the questions they asked addressed new fields. Little more than a decade after Fermor's lecture, Harare became a focus of the palaeomagnetic work that was central to the reconstruction of Gondwana and laid some of the foundations for the acceptance of continental drift and plate tectonics. Macgregor's lecture also bore fruit: the distinguished US biogeologist Preston Cloud once commented that Macgregor had been the greatest single influence on his career.

Recently, in a review derived from a Macgregor Lecture to the Geological Society of Zimbabwe, the links between the Earth's physical evolution and the habitat of early life were explored (Nisbet & Sleep 2001): that discussion considered 'How has Earth influenced life?' For the converse Fermor Lecture it is appropriate to ask 'How has life influenced the physical development of the Earth?' Following Fermor, this review will seek to ask general questions, although not necessarily to provide answers.

This review will first examine the controls on Earth's modern atmosphere, to give a uniformitarian basis; then consider parallel worlds. Next, models of Earth evolution are built, on uniformitarian grounds; by looking at the early abiotic Earth; and by considering biogeochemical processes in the Archaean. To provide experimental constraint, the Belingwe area is examined in detail. The operation of the Archaean atmosphere is discussed; then the links between air and ocean, and the links with the mantle and interior. Lastly, the overall controls are considered.

The modern atmosphere

The starting point is the modern atmosphere (Walker & Drever 1988; Wayne 1992). Although the present may be the key to the past, it is not the same as the past. Nevertheless, it is good uniformitarian geological practice to consider the present before looking backward. The question is simple, although the answer may not be. Is the modern atmosphere a biological construct whose composition is maintained by a cybernetic set of biological feedback loops (Lovelock 1979, 1988)? If the answer is yes, was ancient air also made by biology? If so, when did biological control begin?

Dinitrogen

Nitrogen is erupted by volcanoes in a variety of oxidation states. Nitrogen oxides eventually rain out, but dinitrogen remains in the air. Dinitrogen is also emitted by a variety of nitrate reduction processes by denitrifying bacteria and also by anaerobic oxidation of ammonium with nitrate and nitrite, by planctomycetes. Thus it collects in the air. The key to the N cycle is nitrogenase, an ancient enzyme, made of two subunits, one with Fe-S and the other with Fe-Mo and S at its heart. On a massive scale, bacteria and some archaea use nitrogenase to capture and split atmospheric dinitrogen. They partition the N into all the possible oxidation states, from ammonia to nitric acid, as 'fixed' nitrogen. Then the denitrifying

bacteria capture the fixed N and return it to the air as dinitrogen. Both parts of the cycle are essential to the modern balance: if denitrifying bacteria became extinct, N would accumulate as soluble N in the soil or oceans or muds, eventually depleting the air, or, oppositely, if the nitrifying bacteria died out, N would be progressively sequestered as dinitrogen in air. Thus management of dinitrogen in the modern air is mainly a biological function.

Mainly, but not entirely; planetary atmospheres tend toward maximum entropy. Vigorous weather systems mix the air, and strong temperature gradients, pole to equator contrast, and water in liquid, vapour and probably ice phases generate lightning. In an oxygen-rich atmosphere, lightning (which is closely related to the amount of water in the air and hence the surface temperature) heats N₂ so much that it is split and then oxidized. If oxygen is absent, but CO₂ abundant, the CO₂ can supply O for N-oxides. In contrast, over a wholly abiological, anoxic Earth with an atmosphere mainly N₂, N-fixation by lightning would be less; once present, N₂ would be stable for billions of years.

In the modern oxygen-rich air, lightning N-fixation occurs on a much smaller scale than biological nitrogen fixation (today the largest source is not bacteria but humanity). Nevertheless, lightning fixation is large enough that if resupply did not occur, in a few tens to hundreds of millions of years much inorganic dinitrogen would be lost. Captured N enters the sea floor as organic nitrogen in sediment. Ammonia, in large part made by bacteria, is introduced into new oceanic plate as ammonium minerals during spilitization of basalt by hydrothermal systems (e.g. Hall 1989) and is also introduced into continental rocks by hydrothermal activity in granites (Hall & Alderton 1994). The ammonium minerals in oceanic crust return reduced N via subduction zones to the interior: it re-emerges as dinitrogen and nitrogen oxides at volcanoes. Even if denitrifying bacteria suddenly became extinct, some N₂ would, however, be reconstituted in hydrothermal circulation around volcanoes (Kasting *et al.* 1993) and returned to air.

Carbon dioxide

Oxygen and carbon dioxide are two sides of the same coin. In the modern air, the seasonal rise and fall of carbon dioxide is almost exactly reversely matched by the opposite fall and rise of the O₂/N₂ ratio: 'almost' matched, but not quite (there are very interesting second-order differences). The relationship between O₂ and CO₂ through photosynthesis and respiration (and

fire) is very clear. The biological productivity of the modern Earth, if measured in terms of carbon capture, is mostly on land. In each northern spring, the onset of plant growth draws down carbon from the air; each autumn, the carbon is released again. This cycle dominates the variation in the global distribution of carbon dioxide.

Before the arrival of humanity, the longer-term controls were burial of carbon as carbonate, as methane hydrate in sediment, as gas, as coal, or as reduced organic matter (including charcoal). Before the Devonian, fire would have been impossible, except perhaps on lightning-hit microbial peat bogs after drought.

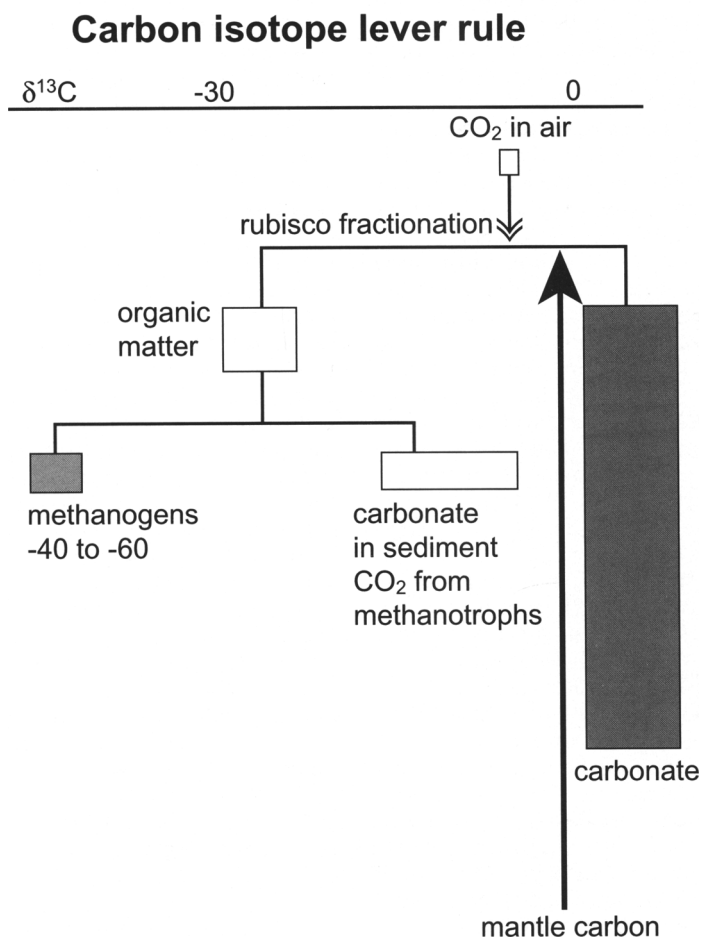


Fig. 1. Isotopic controls on carbon. The per mil scale for carbon isotope ratio ($\delta^{13}\text{C}\text{‰}$) is arbitrarily based on fossil carbonate made from sea water. Carbon from the mantle is slightly richer in carbon-12. Roughly a quarter to a fifth of the carbon is processed via rubisco, which preferentially selects carbon-12. This selection by rubisco means organic matter has $\delta^{13}\text{C}$ around -25 to -30‰ . The remaining carbon is consequently enriched in carbon-13 and precipitates as carbonate. If it is assumed that carbon emitted from the mantle source has had a ratio of about -5 to -7‰ throughout the last 4 Ga, then the dominance in the record of carbonate around 0‰ (apart from rare excursions) is circumstantial evidence that throughout this time organic matter, using rubisco, has captured a fifth to a quarter of the primary carbon coming out of the mantle, as today. Rubisco is characteristically used by bacteria in aerobic or micro-aerobic settings. The main function of rubisco is in oxygenic photosynthesis, although it is also used by purple bacteria. Thus the presence of carbonate at 0‰ for at least the past 3 Ga (own results with P. Abell from Steep Rock) and probably earlier (Schidlowski & Aharon 1992) suggests global oxygenic photosynthesis. However, this must be qualified: other microbial processes, such as carbonate precipitation via a methanotrophic path, can also produce 0‰ values in special circumstances.

Carbon emitted from the mantle has probably had $\delta^{13}\text{C}$ roughly between -5 and -7% over time, whereas carbonate carbon in sediment has been 0% ever since the Archaean, and average organic matter is about -25 to -30% (Fig. 1; Schidlowski 2002; see also Grassineau *et al.* 2002). Applying the lever rule, with the fulcrum at the -5 to -7% source, this implies that over most of the time since the Archaean (there are exceptions), for every five carbon atoms emitted to the atmosphere from the Earth's mantle, roughly four have been precipitated as carbonate, and one as organic matter (Schidlowski *et al.* 1979; Schidlowski 1988; Schidlowski & Aharon 1992). This isotopic split is the signature, written on almost every carbon compound on the planet's surface (Fig. 1), of the enzyme ribulose biphosphate carboxylase–oxygenase, or rubisco (Lorimer & Andrews 1973; Lorimer 1981). Rubisco mediates carbon capture in microaerobic or aerobic settings, in purple bacteria and cyanobacteria, and in plants. It is today the dominant link between carbon in the air and biological carbon. Rubisco preferentially accepts 'light' ^{12}C atoms from carbon dioxide and incorporates it into phosphoglyceric acid, the first step on the route to incorporation into carbohydrate: given that the carbon dioxide is abundantly available, rubisco in most plants thus selects ^{12}C sharply. The left-over 'heavy' carbon goes into carbonate.

Rubisco is an apparently 'inefficient' enzyme. In effect, it works both ways (Lorimer & Andrews 1973; Lorimer 1981; Tolbert 1994). If carbon dioxide is at high enough concentration (as it is at present), so that it is easily accessible to rubisco, then reduction power is captured photosynthetically, and carbon is added, via the Calvin cycle, to the organic carbon of the organism. On the other hand, if the carbon dioxide content of the air is low, rubisco works the opposite way, and photorespiration removes carbon from the organism and adds it to the air. The cross-over level depends on several variables (Tolbert 1994). At present atmospheric oxygen levels (where oxygen is about 21% of the air), the balance is at about 40–70 ppm carbon dioxide. The air has about 370 ppm CO_2 at present (and rising), so photosynthesis dominates. In glacial times, air had as little as 190 ppm CO_2 , and photosynthesis, although still dominant, would have been less favoured above photorespiration. Total global plant productivity would have fallen sharply. Had the air dropped below 70 ppm CO_2 , rubisco-mediated photosynthetic carbon capture would have been greatly restricted.

To escape this problem, some modern plants concentrate carbon dioxide before it is presented

to the rubisco, so that they can suppress photorespiration even if CO_2 falls as low as 5 ppm. These are the C4 plants, which appear to be adapted for a low- CO_2 glacial world. Because of the pre-concentration, the 'Rayleigh yield' of the carbon capture is much higher and thus in C4 plants the isotopic fractionation is much lower (typically $\delta^{13}\text{C}$ around -12%) than in normal photosynthesis. This adaptation appears to be limited to eucarya and only to have appeared recently, under low- CO_2 conditions during Tertiary glaciation. It is not proven from earlier glaciations, for example in the Permian. However, C4 pre-concentration seems to have evolved independently in several lines of plants; thus it must be an 'easy' modification for eukaryotes in times of low ambient CO_2 . Could C4-like processes have operated in the Archaean at times of low CO_2 ? It is an open question. Bacteria do not appear to be able to build the complex physical architecture of the concentration system: thus it is assumed that C4 fractionation was absent in earlier aeons. However, the possibility that something analogous to C4 metabolism emerged in complex microbial consortia must be considered, and would be hard to exclude in the absence of well-preserved organic structural remains.

The 'inefficiency' of rubisco determines that some carbon dioxide must remain in the air, and, conversely, that all the oxygen is not consumed. Overall, in modern organisms, the subtly switched cybernetic balance between the power-generation needs of the mitochondria in plants and animals, burning reduced carbon in oxygen to provide energy, and the photosynthetic restorative capacity of the chloroplasts, may set the daily account of planetary inputs and outputs of carbon dioxide and oxygen (Joshi & Tabita 1996).

Ozone, the cold trap, and the hydrogen budget

The presence in air of free dioxygen liberated by photosynthesis, over a water ocean, and with CO_2 present, has many consequences (Warneck 1988; Wayne 1992). There is also a small volcanic source of O_2 . In the modern dioxygen-rich air, in the upper atmosphere, some singlet O is formed, which combines with dioxygen to form ozone. Singlet O drifts into the tropical lower atmosphere, where it meets water vapour, and forms hydroxyl, OH, the 'policeman' of the air (Crutzen 1987). OH is the main species responsible for attacking reduced chemicals in the air and oxidizing them. Nitrogenous gases, sulphur gases and reduced carbon gases are all removed

this way, as are methane and organic molecules. Once oxidized, they typically are converted to soluble species which are rained out into the oceans. Thus OH keeps the air 'clean' (where 'clean' is judged from the perspective of an oxygen-dependent organism).

Sunlight is absorbed when it hits ozone. This occurs on a large scale a few tens of kilometres above the Earth's surface (depending on latitude). The energy input makes the ozone warm, and it warms the rest of the air at this level. This effect, and also the various effects of the radiative budget in the air, especially the upper air, and the albedo of the surface, give the Earth's atmosphere a very odd thermal structure (Lewis & Prinn 1984) (Fig. 2).

This curious thermal structure of modern air has remarkable consequences. Liquid water, water vapour and ice coexist on the surface, in complex interchange. There is a top bound to

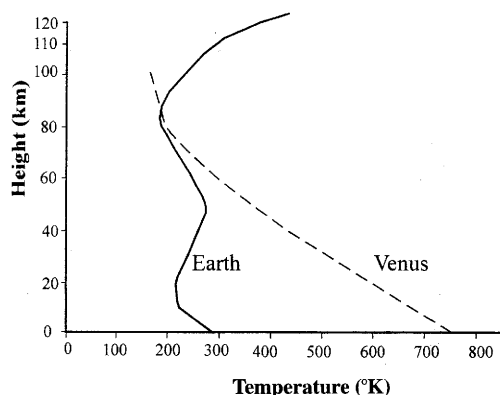


Fig. 2. Height-temperature plots for the atmospheres of modern Venus and modern Earth. On Venus, with an abiogenic atmosphere, the temperature has a straightforward lapse rate upwards until the outer bounds of the atmosphere where energetic radiation is encountered. On Earth, with an atmosphere that is biologically managed, the surface is cool: close to surface in the bottom 10–30 km (troposphere) the lapse rate upward of temperature is adiabatic; above that, the air is warmer from radiation trapped by ozone; higher yet, the air is cooler upwards; in the upmost air, interception of hard incident radiation has a strong heating effect. The cold layer in the Earth's high troposphere is here shown on average at c. 20 km above the surface, but its altitude varies with latitude from 10 km (poles) to 30 km (tropics). This layer prevents water rising higher and entering the stratosphere – hence the air above this level, the 'cold trap', is dry. Only minor amounts of water occur in the stratosphere, from the small amount that can pass the cold trap, and from methane oxidation in the higher air. From various sources (see Lewis & Prinn 1984).

this zone. At, say, 20 km altitude (less in the Arctic, more near the equator), the air is cold and thus very dry: air at -60°C can hold virtually no water, which all rains out before any air rises above this level. This is the cold trap. Above it there is little water (except the small amount that passes through the trap, plus a roughly equal amount made *in situ* high up by oxidation of methane).

If the Earth's ocean surface were to be kept hot for a sustained period, things would be very different. A hot surface would probably mean that water vapour was more abundant in the high atmosphere: the stratosphere would be moist. Without an efficient cold trap, the oceans would imperceptibly be lost as water reached the higher levels of the atmosphere, was broken by photolysis, and produced H. Any H at the top of the atmosphere is vulnerable to ejection to space, leaving matching oxidant that will eventually find its way into reaction with a surface rock.

Although little water manages to pass through the cold trap, there are other sources of hydrogen in the upper air. As mentioned above, methane emissions from the surface mix upwards from the surface, as methane has no cold trap, and in the upper air photolysis leads eventually to release of H. In addition, there is a small emission of H_2 from the surface, some of which will reach the upper part of the atmosphere however, Earth also sweeps up H and H_2 from space. Over time, net hydrogen loss must have been limited: we have kept the oceans.

Trace gases

The most important traces gases in the air are water and carbon dioxide, both closely linked to oxygen. Next is methane. Natural methane sources are almost entirely biological nowadays. In the pre-Holocene world, methane sources included methanogenic archaea (Woese 1987) living in wetland muds, in ruminants and in termites, and also vegetation fires that released rubisco-captured carbon back to the air as CH_4 , CO and CO_2 . It should be noted that in the longer run fires deplete the atmosphere-biosphere carbon supply by adding resistant charcoal to the long-term sediment store. The ocean surface biota release relatively minor amounts of methane to air in the modern world, although certain parts of the tropical ocean are significant sources (e.g. in the eastern tropical North Pacific; Sansone *et al.* 2001). Some methane may be released from organic matter in the photic zone, probably much of which is immediately oxidized

in situ to carbon dioxide. Marine plankton do, however, release large quantities of dimethyl sulphide to the air. This is broken apart in the air, where it adds not only to the supply of methane-related species, but also to the return of sulphur to the land in rain (Lovelock 1979, 1988).

There is a small non-biological source of methane, from serpentinization reactions in hydrothermal systems around volcanoes, especially mid-ocean ridge systems (Holm & Charlou 2001; Kelley *et al.* 2001). Early in the Earth's history this flux may have been greater, though still very small in comparison with modern biogenic fluxes.

Archaea recycle carbon in organic matter, reacting it with hydrogen either from other microbial sources or from volcanic processes, and the waste product is methane. On the modern Earth, possibly 1% of the plant material formed each year is remineralized via methane (Thauer 1998). This methane is isotopically light because the carbon has been twice selected, first by rubisco in photosynthesis, then in methanogenesis. The methane builds up in sediment as gas in solution, as free gas, or in hydrate. Methane is also made by thermal processes, inorganically. This methane comes from the maturation and geothermal heating of detritus rich in residual organic reduced carbon and hence is isotopically heavy. Much of the methane, from both types of source process, migrates upward to be stored in overlying sediment. In effect, the sequestration of methane in sediment much increases the leverage of available P, N, S and other biologically useful elements in managing the carbon gases of the greenhouse. The huge sedimentary stores of methane on continental shelves and slopes, which occur because the Earth is active and has density contrasts that move continents, have a major role in partitioning oxidation power into a highly oxidizing atmosphere and, the other side of the coin, a vast store of reduction power in the sediment. The present-day methane store in offshore sediment contains perhaps 10^{19} g of carbon, or more at best estimate (Kvenvolden 1988; Harvey & Huang 1995). This is tens to thousands of times as much carbon as there is in the active biosphere. These huge stores of methane are a part of the reciprocal crustal store of reduction power that matches the oxidation power stored in the O_2 of the air.

Today there is little direct CH_4 release to atmosphere from the sediment store, except in unusual events such as submarine landslips or pockmark bursts. In an oxygen-rich atmosphere, methane is removed by OH, and to a minor extent by soil methanotrophs. In the sea, unless they are large, bubbles of methane released from

sediment are oxidized by methanotrophic bacteria to carbon dioxide as the bubbles rise through the oxygenated column of sea water. In the Archaeal, if the air-ocean system had been less oxidized and methanotrophs more restricted, emissions from marine sediment would have been important.

Methane in the present atmosphere, molecule for molecule, is a much more powerful greenhouse gas than carbon dioxide (Hansen & Sato 2001). Today small changes in methane can have large climatic results. In a high-methane atmosphere, however, the incremental impact of emissions would be much less.

Of the other trace gases (e.g. N_2O , dimethyl sulphide, CH_3Cl , etc.) many are, like methane, of dominantly biological origin and are transient disequilibrium components of the air eventually oxidized, whereas others are of volcanic origin, mostly eventually rained out in some form or other.

Argon

Argon is in part a neutral basis for comparison when considering the management of the air. Atmospheric argon is not a biological product. It comes from decay of radioactive potassium in the crust and the subsequent release of the argon by erosion. Moreover, it is always a gas, whatever the temperature. Thus it is at first thought completely unconnected with the overall evolution of the air and ocean. However, erosion depends largely on water, so the argon release rate is dependent on surface temperature and water availability. The major source of K-rich material is subduction-related granitoid magmatism, which depends heavily on melting triggered by water release from subducting slabs. Moreover, the subducting slab may in some circumstances also contribute K to the melt. And on what does subduction and the formation of continental granitoids depend?: water (Campbell & Taylor 1983). Without water the K and hence the argon may have been more deeply trapped in the Earth's mantle, and less substantially released to air.

Parallel worlds

Venus

Venus has about as much carbon dioxide near its surface as Earth, but the carbon dioxide is held as gas, not bound in carbonate, so there is a massive greenhouse effect (Lewis & Prinn

1984). The thermal structure of its atmosphere is thus satisfyingly plain (Fig. 2). Light entering the atmosphere from the Sun is progressively absorbed by the carbon dioxide as it moves down to the surface, which is a gloomy place, with light winds, under perpetual clouds. The lower air, at very roughly 500°C, 90 bars, is in approximate equilibrium with the rocky ground. A rough proxy for this is the reaction between Carbon Dioxide + Wollastonite (i.e. pyroxene-like minerals) to/from Calcite + Quartz. This reaction's equilibrium lies close to the conditions on the Venusian surface. Perhaps changes in carbon dioxide precipitate a calcite snow. Upwards, the air temperature drops in the massive carbon dioxide greenhouse. Were the planet stripped of its greenhouse, it would have more or less the same temperature as a similarly greenhouse-removed Earth (Lewis & Prinn 1984): in some ways Venus seen from space is the cooler of the two planets. With its air, and the resulting greenhouse heating blanket, the surface of Venus would appear to our eyes as a dark cherry-red, as hot as a ring on a kitchen cooker.

The consequences of the thermal regime of the atmosphere permeate the planet to its core. With a surface at roughly 500°C, there is no liquid water and hence no hydrothermal cooling of newly erupted lava. There is no cold trap, and although the planet once had deep oceans it now has virtually no exterior hydrogen, except in sulphuric acid droplets in high clouds (Lewis & Prinn 1984). The high surface temperature means the transfer of heat from the interior to space is relatively inefficient compared with Earth. Compared with the Rolls-Royce radiator of sea-cooled Earth, air-cooled Venus is an old VW beetle. There can be no low-temperature metamorphic rocks. Aphroditotherms are hot, and unlikely to allow diamonds or the garnets in eclogites that so interested Fermor. Perhaps, over the aeons, the hot surface has shaped the interior regime to the extent that formation of an inner core has been hindered. Venus is not 'past-Earth': our planet has never been like this, although it may become like Venus in future. Venus is a mature, evolved stable system in equilibrium with itself: an ideal 'sustainable' world.

Mars

Mars may be an alternate 'future-Earth', but perhaps it can also be seen as a 'might-have-been' Earth. Far from the Sun, with a thin oxidized atmosphere, its surface environment is controlled by equilibrium, but also by the slow kinetics of cold (Carr 1996).

One of the most profound questions in studying the Earth's igneous and metamorphic petrology is 'why doesn't the water simply sink into the surface of the planet?' That is what happens to drizzle on a back garden, and it appears to have happened on Mars. There the original water inventory, of a few hundred metres depth if spread globally, may exist as brine aquifers in the crust, in addition to the polar ice stores. The planet is a permafrost desert. Water is present but largely inactive geologically (and of course biologically), except in rare catastrophic episodes (Carr 1996; Baker 2001).

Earth

On Earth the total water inventory, although minute compared with the planet as a whole, is much larger than on Mars, and it constantly interacts with the mantle (Walker & Drever 1988). Mid-ocean ridge crust is hydrated; carried down subduction zones, and returned. On continents, the near-surface sediments are hydrated and groundwater reservoirs are large. Volcanism at the leading edges of plates heats and metamorphoses buried or stacked sediment, so the water is returned by fluxing upwards. In effect, continents above subduction zones are 'saturated' with water. The lithospheric mantle is also effectively 'saturated', when seen on an aeon-long time scale.

The tectonic water cycle in Earth is today heavily dependent on the presence of liquid water above mid-ocean ridges. The height of the continents is controlled by the depth of the oceans (Hess 1962). If oceans froze, erosion would slow. Over time, if andesitic volcanism and continental collision continued, continents would become somewhat thicker and of smaller area, much more rugged.

Water, in liquid oceans, is what makes Earth's tectonic history different from Venus and Mars. On Earth oceanic crust and hence plate is cooled quickly by water, because the surface is close to 0°C, not 500°C as on Venus. This cooled plate thickens and becomes dense more quickly than it would on Venus. Plates fall into the asthenosphere as a steady regular process. Andesite volcanism is fluxed by water given off by subducted oceanic crust. Mars is so cold that reintroduction of water to the interior does not occur. The only volcanism in the past billion years on Mars appears to have been from deep-rooted plumes.

Neither Mars nor Venus has well-defined smoothly moving plates, thousands of kilometres long from ridge to subduction zone. Plate tectonics needs water to help cool the new plate.

Moreover, water exerts a geochemical control. Continents are built by magmatism that depends on subduction. 'No water, no granites; No oceans, no continents' (Campbell & Taylor 1983). Earth's surface geology and the geochemistry of its upper mantle depend on the presence of water that both fluxes plate geochemistry and physically controls the pressure–temperature regime of the upper mantle and crust. Without water, cool ocean floor would not exist, nor eclogitic garnets, nor the density contrasts that move continents (Fermor 1949). It is the atmosphere that makes the difference.

Apart from the initial inventory of water, many of the geological differences between Earth, Venus and Mars are a matter of the surface temperature, set by the incoming sunlight and the air's composition. Earth is the Goldilocks just-right planet: melting occurs through a subtle interaction of volatile fluxing, heat transfer from depth, and radiogenic build-up. The outward flux of volatiles carried from the mantle by rising melts, and the inward flux down subduction zones are just right, and kept that way by the maintenance of the surface thermostat by the natural greenhouse increment of its air.

A further important factor is the secular change in the Sun, which has slowly brightened over time. The hot modern sunlight needs to be managed by an oxygen-rich, low carbon dioxide atmosphere, but early Archaean sunlight was significantly fainter. If the Archaean surface was as hot as today's surface, then the Archaean atmosphere must have been better at trapping outgoing infrared radiation. Earth must have a self-adjusting thermostat (Lovelock 1979, 1988, and work by Lovelock and Watson discussed therein).

The uniformitarian argument

The surface temperature and the presence of liquid water on Earth are today consequences of the atmospheric thermal control and filtering of light that is exerted by an anomalous, dominantly biogenic, atmosphere. The uniformitarian argument would thus be: 'the present is the key to the past, hence in the past the stability of liquid water on Earth was, as today, biologically maintained – life sustains the oceans'. To this argument could come the further addendum: 'liquid water enables plate tectonics to function, subduction to operate, and andesite volcanoes to erupt'. Hence if water is sustained by life, then plate tectonics and the maintenance of continents are sustained by life. But this is only unsupported conjecture. As an alternative hypothesis it

is possible that during Earth's early history, a set of inorganic feedback loops sustaining the presence of liquid water may have accidentally been established on Earth, with consequent development of plate tectonics.

Is such thinking taking uniformitarianism too far? Perhaps; obviously the distant past was different from the present day, so the actualistic instant uniformity model (Fig. 3) does not completely apply: Earth has changed greatly over time, and the past was different. The 'coffee-pot' model has more appeal: the Earth has surely evolved through its own internal constraints, for example by dissipating heat. The cafetière (plunger) model allows periodic catastrophes, and may more nearly describe the Earth's history: part uniformitarian, part-catastrophic.

The appearance of liquid water oceans was probably inevitable early in Earth's history: but was the sustained long-term stabilization of oceans preordained from the moment the Earth system was created? Or is the existence of stable oceans over 4 Ga unexpected? – Anything from mildly unlikely to quite improbable, sustained only by an unpredictable event, such as the onset of life?

Do models say anything? Is Lyellian uniformity worth considering? It is valid to assume that through the later Phanerozoic, life has controlled the composition of the air. Most likely, the air and hence the climate has been set by life at least since the appearance of rain forest in the late Devonian. Probably this has been the case since long before, ever since the dominance of oxygen over carbon dioxide, which perhaps but not certainly began in the early Proterozoic. This is only half of Earth history, but perhaps long enough, if the system is mismanaged, to lose an ocean in a greenhouse runaway, or to freeze the planet permanently. Perhaps such excursions have nearly happened, in snowballs and possibly in hot flushes also. And before the oxygen atmosphere? What of the Archaean and the Hadean?

Abiotic Earth: the Hadean

Life on this planet began possibly around 4.2–3.8 Ga ago, although there is a chance it began earlier elsewhere (see Nisbet & Sleep 2001, 2002). Before the start of life, the abiotic Earth may have undergone dramatic rapid fluctuations in its surface environment, from long periods of ice-oceans to brief moments of heat, sometimes enough to produce a rock-vapour atmosphere, after major meteorite impacts (Sleep *et al.* 2001). If life had not begun, what sort of Earth would have developed?

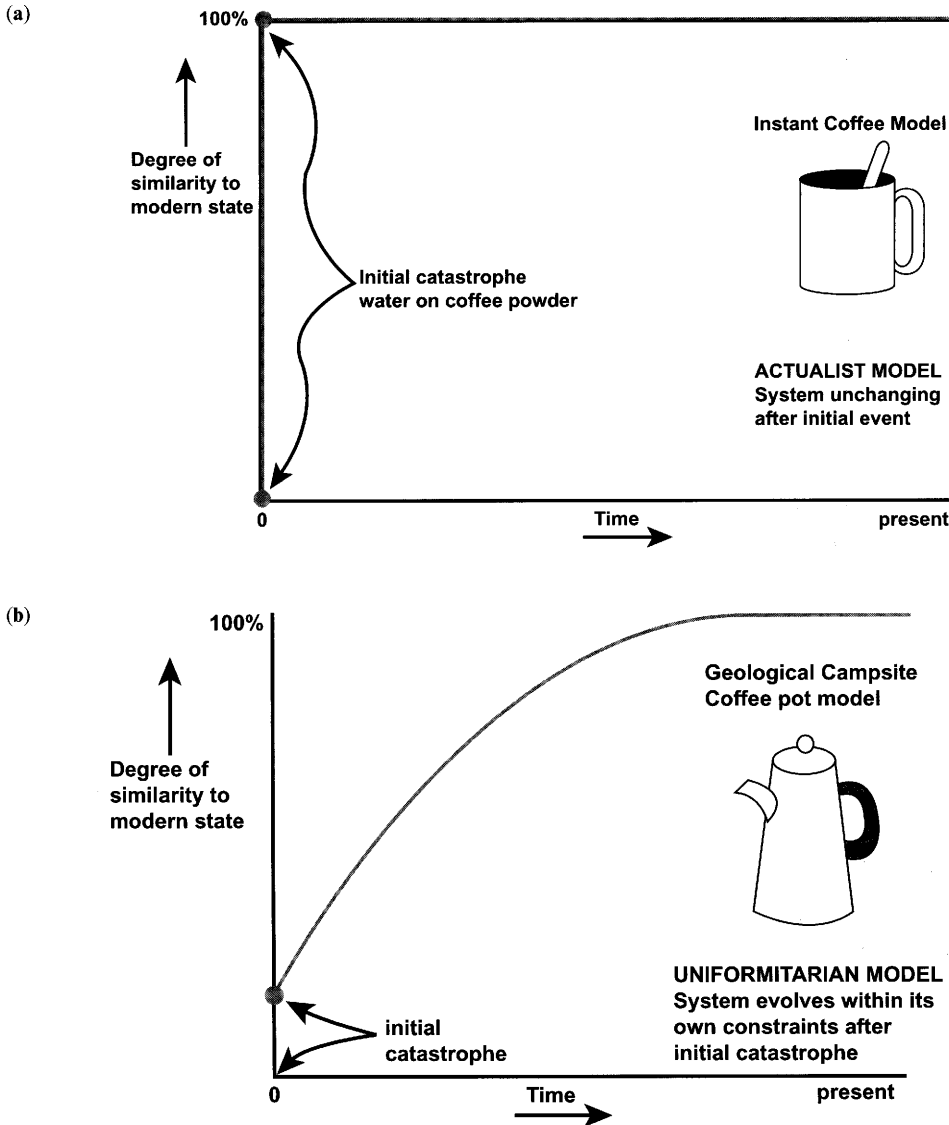


Fig. 3. Models of Earth evolution. (a) Actualistic 'Instant' model: present is the key to the past. Instant coffee, once made, changes little (apart from slow cooling). The initial event, in which hot water is poured on powder, is a catastrophe, where catastrophe is defined as sudden downwards change. It should be noted that in the view of an observer viewing from after the catastrophe, what may have been a downturn for the prior system (e.g. the dinosaurs, or King George III) is perhaps an upturn from the perspective of the later observer (e.g. a mammal, or George Bush II): an anastasis. (b) Modified uniformitarian or Zimbabwean field coffee model: once set up, the system evolves within its own constraints, as there is no external intervention once the initial catastrophe is over. Pour water into the pot, on coffee grounds, and the coffee evolves according to the internal dynamics of its system, without further external intervention. (c) Plunger or Seattle model (catastrophist model): the system evolves within its internal constraints, but is also subject to assorted catastrophes. External catastrophes include both the initial event and later the depression of the plunger. Internal catastrophes occur because of properties inherent in the system as it is created, and without external intervention. In this model, (and indeed, hidden in model (b)) there is also an internal catastrophe. When the coffee grounds become denser than the coffee-water, and turbulence reduces, the coffee grounds suddenly sink. The segregation of the core may have been an internal catastrophe; the arrival of life may also have been an inevitable internal catastrophe for abiosis, although an anastasis from our perspective.

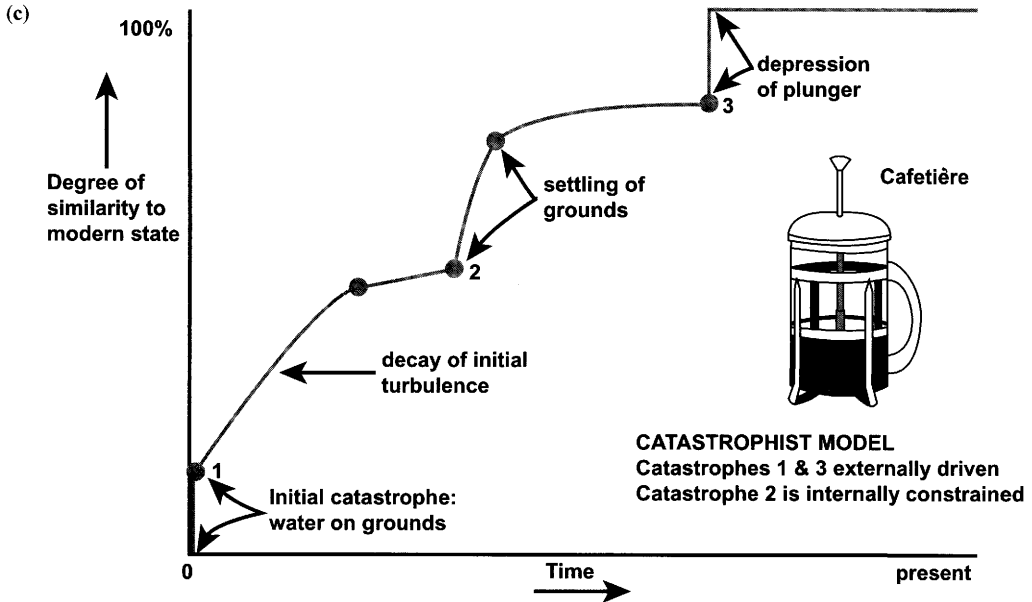


Fig. 3. (continued)

The answer is not clear. Even an abiotic planet is chaotic, unpredictable: there are too many variables. Some guesses can be made. One possibility is a Venus-like Earth. But with the faint young Sun (Sagan & Chyba 1997), an ice-ocean with a fractured frozen surface over liquid deep water (Sleep *et al.* 2001) might have persisted. If so, despite a cold surface, plate tectonics would have operated. Degassing of carbon dioxide would have been matched by carbon dioxide uptake into spilitized basalt and thence via hydrothermal water around mid-ocean ridges subducted back into the mantle. But in a snowball ice planet, with little precipitation, clastic sediment and the supply of cations by erosion would have been limited. The continents would be more rugged. Possibly the carbon dioxide would have built up in the air, causing eventually a sudden transition not to a cool ocean but instead directly to a hot moist greenhouse when the icecap melted, ocean albedo suddenly changed, and the warming water, rich in carbon dioxide, degassed. The resulting greenhouse, in extreme cases, could have led to a steam atmosphere.

As an alternate hypothesis, it is possible that an early icehouse setting could have been sustained for aeons, if the return of carbon dioxide to the mantle by carbonated oceanic crust (from ridge crest calcite, precipitated by hydrothermal

alteration around vigorous volcanoes, in carbon dioxide-rich liquid seas under ice) exceeded the degassing. On rugged polar land surfaces, carbon dioxide could have accumulated as ice. If so, an ice-capped ocean could have persisted over the aeons, perhaps eventually freezing solid under an atmosphere largely of dinitrogen. Volcanic N_2O is a strong greenhouse gas but it would have frozen out or been taken up by pools of water around volcanoes. This is a Mars-like scenario. The lack of erosion would have produced a breccia-laden ancient icy surface, broken up by meteorite impacts and occasionally resurfaced by rare meltwater events. A significant part of the ocean could have been taken back into the cold crust and upper mantle. The Earth's surface water inventory is much greater than that of Mars (Carr 1996), so the entire ocean would be unlikely to disappear, but a considerable amount could have gone.

Unlike Mars the mantle of Earth is hot enough to produce copious melt if a small amount of water is present; water fluxes melting and is driven out with the melt, to collect in the ocean-atmosphere system, where it is the most important greenhouse gas. The process is self-managing to an extent. If for some reason the surface became very cool, as time went on the cold dense surface plate would founder. This would carry down water. If so, the water in the

mantle would promote melting, increasing the rate of volcanism and carbon dioxide and water return to the surface, and dust and ash deposition on ice caps, until a degree of transient equilibrium was restored. It should be noted that volcanic heat only makes a negligible contribution to surface temperature.

As the planet ages and becomes geriatric, so much heat is conducted to the cold surface that the lithosphere becomes thicker and the upper-mantle temperature falls. The degree of melting in the mantle becomes less. Near the surface itself progressively more water can be accommodated in the fractured crust and serpentinized uppermost mantle. The oceans will thin and sink into the planet's cooling mantle. Over 4 Ga, all these factors, taken together, could have led towards a Mars-like permafrost surface over a thick cool lithosphere and a still convective deeper upper mantle, occasionally erupting plumes.

Thus Earth could have suffered an icy fate, covered by frozen carbon dioxide and water, reflecting sunlight, and slowly conducting internal heat. Perhaps, but for our planet this so far must have been unlikely except as a transient state under an early faint Sun (Sleep *et al.* 2001). The planet is still too large and too young to follow Mars and the Moon into permanent senescence. Massive meteorite impacts would have vaporized the ice, suddenly altering the albedo. Moreover, although perhaps half the heat in the planet is from the accretionary age, radioactive decay proceeds and the trapped heat would come out. Huge plume eruptions could cover the planet in dark dust and cause it to warm up and escape ice-death.

Whatever the average temperature of the planet, in the Hadean during the likely 'hot' excursions after very early major meteorite impacts Earth would have incurred substantial loss of H to space. During these events, there would have been oxidation of the atmosphere-ocean system relative to the mantle. If the surface were hot, the atmosphere's lapse rate means that water would have been present relatively high in the air. Here, after photolysis, hydrogen would be lost to space at a rate sufficient to dehydrate the planet eventually. Moreover, throughout Earth history, any episodes of methane-rich atmosphere would also have caused H loss when the high atmosphere lost hydrogen derived from methane. The D/H ratio of the modern ocean may be a record of such events (e.g. Yung *et al.* 1989). Possibly Earth has cumulatively lost the H from 1–2 km of ocean water, leaving an excess of oxygen. This excess would have been equivalent in total over a few hundred million years to 100–200 bars of oxygen (although at

any moment the actual oxygen burden of the air from H loss would be miniscule). As oxygen was released from water it would have been sequestered into the mantle by plate subduction (e.g. see Kasting 2001). The air is never in equilibrium. These small supplies of oxidation power, present as transient species in the air, may have been vital in sustaining the first living organisms, by permitting a contrast between relatively reduced hydrothermal fluids in exchange with mantle-derived lava, and ocean water in contact with slightly more oxidized air.

Did 'abiotic-Earth' steer a successful course between Hot-Scylla and Ice-Charybdis? Possibly, but it may have been a very bumpy course compared with the narrow middle route maintained today by the fine-scale management of a small greenhouse increment. Moreover, in the cross-currents of a steadily brightening Sun and a diminishing radiogenic heat flow and hence volcanic gas input, this narrow course would have needed constant correction. Was the planet steered by blind Chance and inorganic feedbacks of chemical buffers? Or did a biological 'Odysseus', guided by self-adjusting biological feed-backs, lead it? Without self-stabilizing cybernetic biological controls, could liquid oceans have been stable over a time span as long as 4 Ga?

Biogeochemical processes in the Archaean

The early settings

Life did begin: the world did not evolve inorganically. Molecular palaeontology (Zuckermandl & Pauling 1965), which infers phylogeny from nucleic acid sequences in extant modern microbial life (Fig. 4a, b) as interpreted in the light of the geological record, permits some reconstruction of the Archaean biosphere. Evidence in the rocks, including isotopic fractionation in sedimentary minerals, and relict molecules such as kerogens and oils, allows modelling of the microbial ecosystem (Brocks *et al.* 1999; Rasmussen 2000; Rasmussen & Buick 2000; Nisbet & Sleep 2001). Microbial sulphate reduction in particular is probably of great antiquity (Shen *et al.* 2001), implying that a surface supply (not necessarily in equilibrium) of oxidation power was present, to be reacted against the more reduced fluids in equilibrium with mantle-derived rock. By the late Archaean, and perhaps much earlier, this biosphere was complex enough and chemically sophisticated enough that it had the potential power to control the composition of the air. Whether it did or not is unknown: the tests are isotopic, but the controls are not well enough understood yet to be sure.

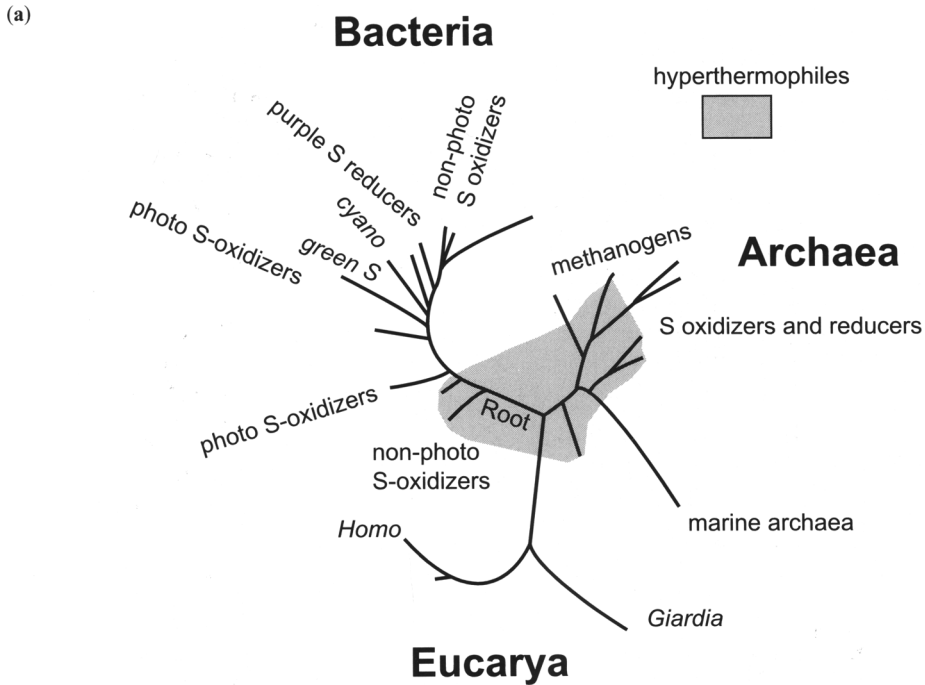


Fig. 4. (a) Evolution of microbial life: descent of major mat-forming groups. From various sources, including Barnes *et al.* (1996) and Pace (1997). The 'standard view' of the evolutionary tree (Woese 1987; but see Doolittle 1999), based on rRNA. There are three main branches to the tree: bacteria, archaea and eucarya. The most deeply rooted organisms (close to 'root') are exclusively hyperthermophile (shaded area). The implication is that earliest Archaeal organisms were exclusively hyperthermophiles, and that the branching of the tree took place in a high-temperature setting (see also Hartman & Fedorov (2002) on the antiquity of the eukaryote branch). The implication of the standard tree is that the microbial S cycle is of great antiquity. It should be noted, however, that this standard phylogenetic tree is much disputed (see discussion by Nisbet & Sleep 2001), and there is interesting evidence to suggest that mesophiles like the modern Planctomycetales were the earliest branch (Brochier & Philippe 2002). If so, the last common ancestor may not have been hyperthermophile. In the 'standard' phylogeny the first bacterial branch to escape the hyperthermophile setting includes the green non-sulphur bacteria, carrying out anoxygenic photosynthesis. Rubisco and micro-aerobic habitats may have been present at this early stage. Green S bacteria may have emerged later, and then cyanobacteria, possibly from a symbiotic combination of photosystems from purple and green bacteria, to give oxygenic photosynthesis. In the archaeal line, the evolution of mesothermophiles may have followed the start of bacterial photosynthesis, with the spread of methanogenic recyclers into mesotherm settings. In the oceans marine archaea may have appeared early, or when overlying waters first hosted photosynthetic bacterial picoplankton. **(b)** Diversification of microbial life in the Archaeal, based on the 'standard model' (Woese 1987). In the earliest Archaeal, the living community may have been restricted to hyperthermophile habitats. By the late Archaeal a diverse ecology was present in a wide variety of habitats, and capable of forming a global biosphere. This diagram assumes the last common ancestor was hyperthermophile. If, however, it was a mesophile planktonic form (e.g. Brochier & Philippe 2002), then **(b)** will refer to the evolution of only a hyperthermophile community and its descendants, whereas the eucarya line may have been mesophile.

The habitat of the last common ancestor of life is still much disputed, but there is much support from studies of rRNA for the argument that the last common ancestor was hyperthermophile (Stetter 1996), perhaps a survivor from a major impact event that heated the ocean (Gogarten-Boekels *et al.* 1995). However, the 'hyperthermophile last common ancestor' hypothesis is

not proven (Forterre 1996; Galtier *et al.* 1999). An interesting alternative hypothesis is that the last common ancestor may have been a non-hyperthermophile planktonic bacterium. This hypothesis comes from a reassessment of bacterial rRNA phylogeny using an essentially conservative approach, using the most conserved positions in rRNA (Brochier & Philippe 2002).

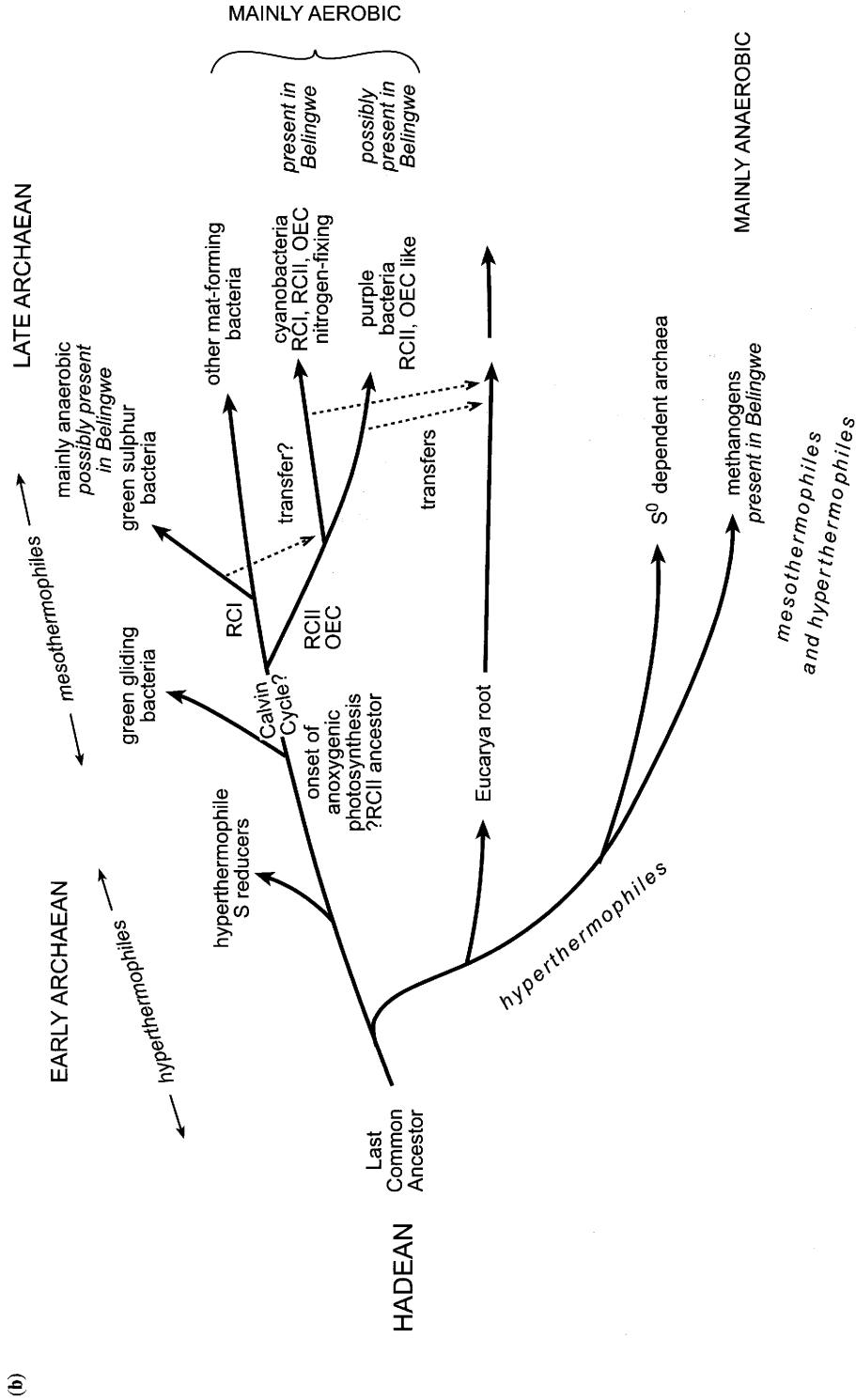


Fig 4. (continued)

The results are that the Planctomycetales emerge at the base of the bacteria as the first branching group. This is a remarkably interesting finding, if correct. Many Planctomycetales are, as their name implies, free-floating mesophiles. In stalked or budding bacteria like the Planctomycetales, cell division occurs by the formation of a daughter cell, with the mother cell retaining her identity after the division is complete. In other words, the cells are mortal, unlike most bacteria, which multiply by binary fission and are hence immortal. Moreover, these organisms, as they have polar growth, have a potential for morphological evolution that is not available to other bacteria. In many ways, these bacteria are reminiscent of eucarya, and just possibly may lie near the most ancient root of the eucarya. Among these budding bacteria, *Pirella* is chemoorganotrophic, hinting at antique habitat.

There are many but not proven arguments to suggest that, whatever the original home of life, the substantial ancestral bacterial diversification took place in a hydrothermal setting (Stetter 1996; Nisbet & Fowler 1996*a, b*). On the modern world, even on the surface of an active volcano the hydrothermal habitat is limited. Roughly 10 km³ of new oceanic crust have been produced annually on the Phanerozoic planet. Although in the early Archaean volcanic resurfacing must have been much more extensive than today, and new crust production may have been as much as 100 km³ per year, it is questionable whether the total thermodynamic power from the heat of the global hydrothermal habitat could have sustained a biosphere productive enough to alter the planet's surface environment as a whole.

Possibly the earliest habitats were thin biofilms of bacteria and archaea that existed by processing redox contrast between hydrothermal products and the external environment (sea water and atmosphere). The productivity of these early microbial mats would have been severely limited by the inorganic sources of redox power from below. Volcanic and hydrothermal processes would have ensured a small but steady supply of H₂, H₂S, CH₄ and possibly HCN from below. Nitrate (from dissolved NO₂), and sulphate are crucial. Some sulphate would have come from dissolved magmatically exhaled SO₃. Some would have been supplied by disproportionation of sulphite in seawater, the sulphite having come from magmatic SO₂. Some sulphate would have been made photochemically in air.

Microbial sulphate reduction is of great antiquity (Shen *et al.* 2001), as may be sulphur reduction by hydrogen. Sulphate chemistry gives

many microbial possibilities; for example, an extreme option is



Much, perhaps most early microbial ecology around hydrothermal systems may have been sustained by the thermodynamic contrast between sulphate supply from above (water-atmosphere) and reduction power from below (rocks and rock-interacting fluids). This primary thermodynamic power would, however, have been eked out by many recycling steps, in which reduced organic matter was multiply reprocessed. Respiration and fermentation, like burning, run the thermodynamic arrow forwards, but by recycling allow the microbial system to exploit, to the limit, the possible productivity allowed by the inorganic redox bounds of the habitat. The system is like a cuckoo clock. Light quanta wind it up, then as the pendulum's weight falls, it turns innumerable microbial cogwheels, some forwards, some backwards. Complex recycling is possible in microbial mats of sulphur bacteria (Fig. 5). Rubisco must pre-date oxygenic photosynthesis, and is probably of the greatest antiquity. It is used by aerobic or microaerobic organisms, not reducing organisms, suggesting it evolved in a setting where sulphate was present.

The knallgas reaction ($\frac{1}{2}\text{O}_2(\text{aqueous}) + \text{H}_2(\text{aq.}) = \text{H}_2\text{O}$) is used by both bacteria and archaea, some of which (Aquificales) appear to be very deeply rooted (although see the contrary view of Brochier & Philippe 2002), suggesting perhaps that hydrothermal waters carrying out-of-equilibrium O₂ (possibly from the atmosphere) and H₂ (ultimately volcanogenic) could have been important in early microbial communities. The apparent antiquity of the microbial lines using the reaction is arguably a pointer, although weak, that suggests that O₂ was widely available very early on, and that at least micro-aerobic habitats existed.

Remaking the environment

Photosynthesis (Pierson 1994) uses light to reverse the normal flow of terrestrial thermodynamics. It may have begun in purple bacteria, using bacteriochlorophyll (Xiong *et al.* 2000; Blankenship 2001). Light winds up the spring, so that an endless cycle can operate as the photosynthesizers capture reducing power, and then the other organisms, like cogs, run it down again. Oxygenic photosynthesis, aided by the start of the nitrogen cycle (which may have been nearly simultaneous), broke the bounds by capturing a new source of ordering power, and inflated the

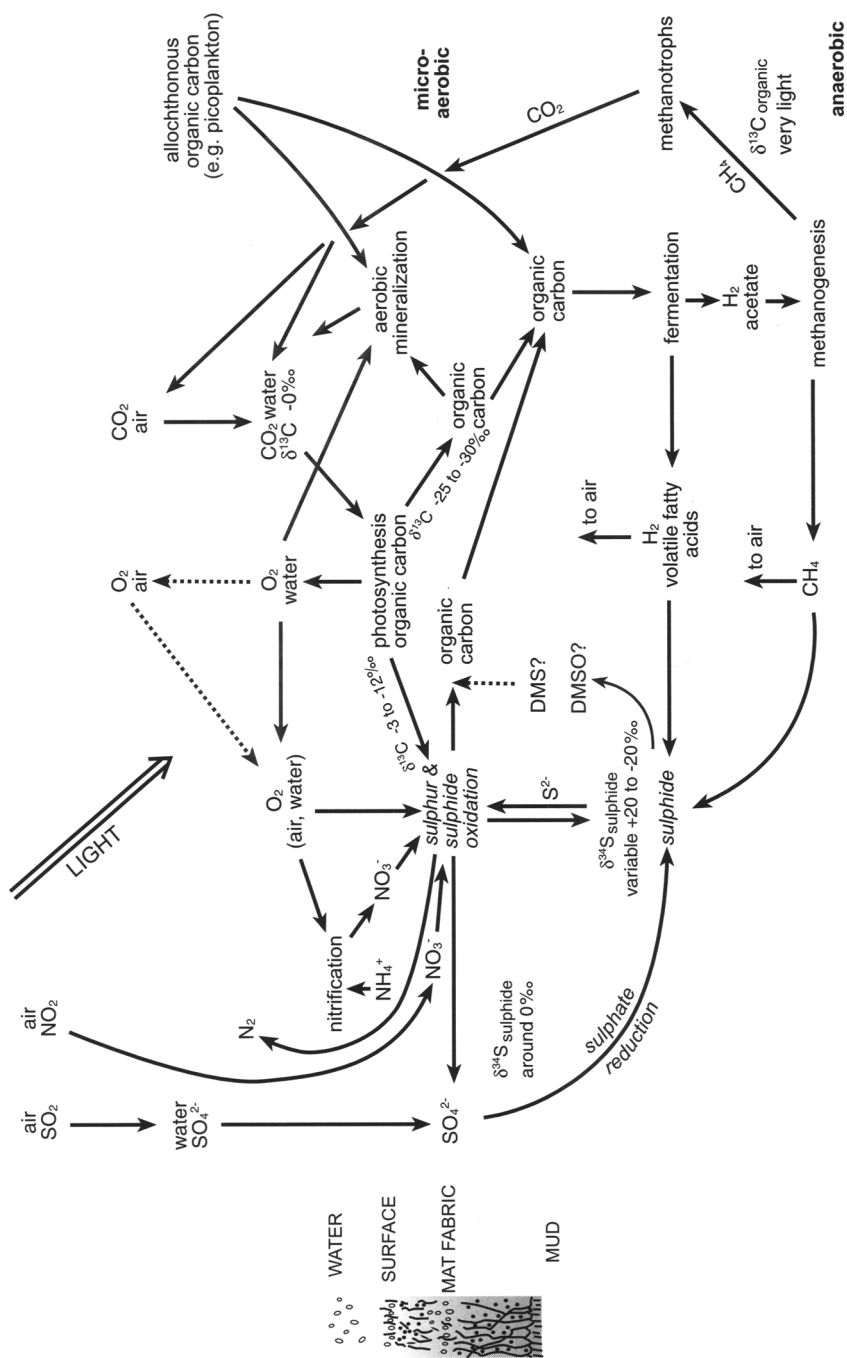


Fig. 5. Inferred biochemical pathways in an Archaean microbial mat built by sulphur bacteria. Model is based on modern mats (Fenchel & Bernard 1995). Many of these processes were probably operating in the Belingwe biota (Grassineau *et al.* 2002). Although there is direct evidence for only a few processes, for these to have operated the supporting reactions were probably present also. Thus, for example, isotopic evidence for methanotrophs suggests that fermenting bacteria were producing H_2 , a conclusion that fits with rRNA trees.

biosphere, until more subtle cation and anion supply limits were confronted.

The early photosynthetic bacteria were limited in the places they could occupy (see Nisbet & Fowler 1999). There is molecular evidence (see summaries by Nisbet *et al.* 1995; Nisbet & Sleep 2001) that the first photosynthesis was anoxygenic, using bacteriochlorophylls not chlorophyll (Xiong *et al.* 2000). Most probably such life would still have been confined to the near vicinity of hydrothermal systems where there was adequate redox contrast. Supply of electron donors such as H₂, H₂S and CH₄, produced by hydrothermal processes, is necessary to sustain metabolism. It is also possible that there were enough reduced species in the global ocean to sustain anoxygenic photosynthesis in water plumes that spread far from hydrothermal sources before losing their relatively reduced state. Thus, with the initiation of anoxygenic photosynthesis, organisms may have been able to spread somewhat beyond the early hyperthermophile habitats into lower-temperature mesophile settings (Nisbet 1995; Nisbet & Fowler 1996a), subject to the availability of P and usable N.

The first organisms living by photosynthesis probably colonized the uppermost layers in microbial mats near hydrothermal systems (Nisbet & Fowler 1996b). Below them would be descendants of the earlier respirers and fermenters. The earliest possible evidence for abundant life is from Isua, Greenland, in 3.7 Ga rocks (Rosing 1999), where carbon particles in meta-turbidites appear to record biological isotopic fractionation: if so, they may be debris from plankton. It is tempting to suppose that such plankton, if they existed, were in some way distantly related to the Planctomycetales (Brochier & Philippe 2002). Possibly they were living by anoxygenic photosynthesis. In Earth's modern oceans non-photosynthetic archaeal picoplankton are widely abundant, occupying the levels in the lower photic zone (Beja 2002). Some Isua plankton may have been archaeal also. Today, planktonic archaea live in settings where oxidation and reduction power is controlled by overlying oxygenic photosynthesis by bacteria. In Isua-time, close to submarine volcanic centres, early archaeal plankton could instead have been dependent on chemical contrasts between surface waters and deeper waters influenced by hydrothermal plume sources. Possibly even archaeal methanogens reacted hydrogen (derived from hydrogen in the early air) with dissolved carbon dioxide, controlling the abundance of hydrogen in the air.

Once the planet was populated by organisms carrying out anoxygenic photosynthesis as well as others recycling the available nutrients by

respiration and fermentation, life would have begun to have a significant impact on the redox distribution of the sediment–ocean–atmosphere system. Redox segregation would here begin on a grand, planetary scale, partitioning the surface into oxidized and reduced reservoirs. Sulphate and nitrate would be ubiquitously reduced before entering the sediment; hydrogen, methane and hydrogen sulphide would be oxidized. Moreover, the increasing sophistication of life, and the evolution of siderophores, would extend to its ability to capture essential elements, such as Fe, Cu, Mo, Zn, and particularly P, sharply increasing productivity.

At some point in the mid-Archaeon oxygenic photosynthesis began (Buick 1992; Summons *et al.* 1999), allowing the evolution of complex cyanobacterial mats (Fig. 6). Nature has only once succeeded in this, in the creation of the photosystem II water-oxidizing complex. It is possible that the first O₂-evolving photoreaction centre originated in green non-sulphur bacteria, and that this was later incorporated into cyanobacteria (Dismukes *et al.* 2001). Cyanobacterial life depends on a complex partnership between both bacterial photosystems (Jordan *et al.* 2001; Kuhlbrandt 2001). Virtually all modern life depends directly or indirectly on oxygenic photosynthesis. Even in modern mid-ocean ridge hydrothermal systems, much of the life depends on sulphate, which in turn depends on the oxygen-rich ocean water created by oxygenic photosynthesis, which ensures an adequate supply of sulphate to the deep water.

An oxygenic photosynthetic ecology depends on water, carbon dioxide and light, and hence has global scope provided it can find enough usable nitrogen, phosphorus, iron, copper, etc. The moment the first oxygenic photosynthesizer evolved, a global ecosystem would have developed.

After the first appearance of cyanobacteria, presumably in microbial mats, the arrival of unicellular cyanobacterial plankton must surely have been rapid. In the modern warm tropical and subtropical oceans, cyanobacterial picoplankton are ubiquitous (Capone *et al.* 1997), supporting complex microbial consortia, and in the Archaeon they could have formed the upper 100 m layer of an open ocean biological community, which may have had great diversity (Karl 2002). Archaeal plankton would have been out-competed for occupancy of the topmost levels, but could have occupied a now more productive underlying lower layer, 100–300 m thick, dependent on the redox debris (including dissolved chemical species) from the overlying oxygenic photosynthesizers. The immediate results,

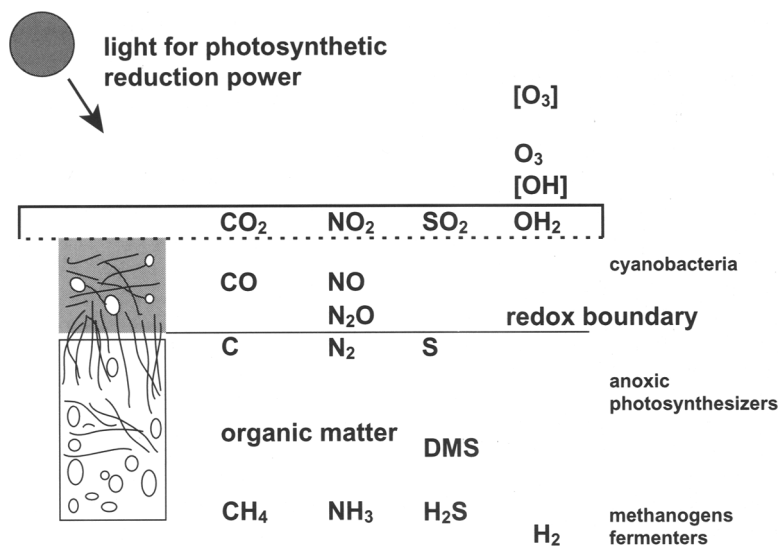


Fig. 6. Sequestration of redox power in microbial mats. An atmosphere–ocean system containing CO_2 , NO_2 and SO_2 would supply oxidation power to the water (e.g. as NO_3^- , SO_4^{2-}). Microbial mats finely focus and control the redox boundary, so that it becomes a sharp plane rather than a diffuse zone. Above the boundary, rubisco-using bacteria, both photosynthetic and non-photosynthetic, provide reduced organic matter. Below the redox transition, anaerobic microbes recycle the oxidation power, returning chemical species such as CH_4 , H_2S and NH_3 to the upper levels. The deeper levels of the mud become a long-term store of reduction power (e.g. methane-rich sediment), sequestered from the atmosphere and inaccessible to it until recycled by large-scale geological processes such as subduction.

possibly as an event around 3.5–3.0 Ga ago, would have been a global crisis. They would have included massive release of dioxygen, massive nitrogen fixation of nitrogen, and biological control of the carbon and sulphur gases in the air.

Cyanobacterial plankton have a major role in modern nitrogen fixation (Capone *et al.* 1997; Zehr *et al.* 2001), a role they presumably also had in the late Archaean (Nisbet & Sleep 2001). Without this, nitrogen supply would have presented a problem (Kasting & Siefert 2001; Navarro-Gonzalez *et al.* 2001). In air rich in carbon dioxide, lightning would have fixed nitrogen and supplied NO_x to early life. If enhanced organic productivity meant a decline in carbon dioxide content and, from methanogenic recycling, an increase in methane content of the air, there could have been a marked reduction in supply of fixed nitrogen. Life would rapidly consume its resource base of accessible N. Biological nitrogen fixation may have been an evolutionary response. This is a plausible hypothesis, but the crisis may have happened much earlier. Nitrogen fixation may be very ancient, pre-dating the last common ancestor (Line 2002). Possibly nitrogenase may be of great antiquity, and may have first evolved in a microbial mat

to handle redox excesses. Perhaps, being available, it was then pressed into service to solve a N-shortage crisis.

There is another knock-on problem with oxygenic photosynthesis. Nitrogenase is very sensitive to dioxygen. One solution is a physical partition, to create a small space where an 'older' pre-oxygen condition can be preserved, despite being in an aerobic habitat. A key part of the apparatus in many cyanobacteria is the heterocyst, a walled-off microhabitat where very oxygen-sensitive nitrogenase can be protected.

The waste disposal from the Mn–oxygen evolving complex, in supporting the nitrogen cycle, is also worth considering. As planktonic cyanobacteria bloomed, the MnO_2 detritus would have become a global carpet on the ocean floor. In modern marine muds, with an infall of MnO_2 , anoxic nitrate production during Mn reduction allows coupled sedimentary nitrification–denitrification cycles to occur. These 'nitrificata' link the nitrogen, manganese and sulphur cycles (Hulth *et al.* 1999), and would have been much promoted when cyanobacteria using Mn–oxygen evolving complexes first became ubiquitous in the oceans and first began to supply abundant MnO_2 debris to the sea bed.

The Belingwe case study

The 2.7 Ga old Belingwe Greenstone Belt, Zimbabwe, gives an insight into the state of life in the late Archaean (Nisbet & Sleep 2001; Grassineau *et al.* 2002). Several sedimentary facies contain clear evidence of microbial activity, and these have been studied using high-resolution small sample isotopic techniques (Grassineau *et al.* 2001, 2002). The results give a picture of a complex and interlinked microbial biosphere. Three distinct microbial bio-facies types can be distinguished in the sediment.

(1) The carbonate horizons of the Cheshire and Manjeri Formations contain extensive well-preserved stromatolites. These were formed in shallow or intertidal waters, as demonstrated by interbedded ripple-marked and mud-cracked silts. Texturally, the limestones show many indications of organic activity and gas release structures (Martin *et al.* 1980). The simplest uniformitarian explanation is that the structures were built by cyanobacteria. Isotopically, carbon from kerogen in the stromatolites typically has $\delta^{13}\text{C} = -25$ to -30% . This implies but does not prove fractionation by rubisco of carbon captured from the atmosphere–ocean system. Carbonate in Cheshire limestones is typically close to 0‰, suggesting that carbon in the atmosphere–ocean system was modulated by rubisco and dominated by oxygenic photosynthesis on a planetary scale (Fig. 1) at least by this date. It should be noted that the *c.* 3 Ga Steep Rock stromatolites are similar (work by Abell, Grassineau and Nisbet).

(2) Shales tell a rather different story (Grassineau *et al.* 2001, 2002). The Manjeri Formation shales, which are very well-preserved intertidal ripple-marked deposits and shallow sub-tidal deposits, include sulphide stringers that show great S isotopic fractionation (at least for the Archaean). Rare carbonate samples from Cheshire shales show $\delta^{13}\text{C}$ significantly lighter than 0‰. Organic carbon in these rocks ranges widely. The simplest, although not the only interpretation of the facies analysis and C and S isotopic results is that anoxygenic photosynthesis was occurring, that sulphuretum-cycling was operating, and in addition, methanotrophy recycled carbon and, presumably to support the methanogens, fermenting bacteria were producing hydrogen. A community of anoxygenic photosynthesizers, respirers and fermenters may have been using light to operate a complex cycle involving sulphate reduction to sulphide and eventually H_2S , producing reduced organic matter that was eventually recycled by methanogens and methanotrophs in a microbial mat. How-

ever, it should be noted that this is speculation; in particular, there is no clear evidence for anoxygenic photosynthesis, only inference.

(3) Rocks from the Jimmy Member of the Manjeri Formation record a different facies. They may have been laid down below wave base and include very finely laminated carbon–sulphide layers (Grassineau *et al.* 2001). They are in very close stratigraphic proximity to submarine volcanic rocks, including pillow lavas of komatiitic basalt. There is strong rare earth element (REE) geochemical evidence for proximal hydrothermal influence. The carbon isotopes in the C–S layers show either rubisco fractionation or in many cases more extreme fractionation, presumably by methanogens. The S isotopes are also highly fractionated, both heavy and light, implying complex S cycling processes. As the rocks are thought to have formed below the wave base (some preserve finely laminated fragments), they may record a deep-water microbial community around a hydrothermal system. This microbial community may have cycled C and S between oxidation states, using sulphate from sea water and possibly reduced (rubisco-fractionated?) organic debris from planktonic life above.

Collectively (Fig. 7), the exceptionally well-preserved Belingwe material shows in its various bio-facies evidence for a complex interlinked biosphere at 2.7 Ga. In coastal waters, oxygenic photosynthesis by cyanobacterial stromatolites occurred. If cyanobacteria existed in stromatolites they surely existed also as free-living plankton, on a global scale. The evidence for anoxygenic photosynthesizers is weak: permissive, not proof. It is consistent with most models of microbial evolution: if cyanobacteria were present, then anoxygenic photosynthesizers probably preceded them. Collectively, if the cyanobacteria were productive enough to influence the global C isotope budget (as is implied by the $\delta^{13}\text{C}$ of 0‰ in carbonate), they would have necessarily produced dioxygen on a globally significant scale. Methanogens operated too in stromatolites, recycling organic debris, and probably archaeal plankton lived in deeper waters.

It is possible that mats existing by sulphur-based redox cycling were global in distribution, both in shallow-water muds and in deeper water, driven by the availability of sulphate (in part derived from oxidation power from cyanobacteria), organic carbon, and in shallow settings, light. The Jimmy Member may tell a deep-water story. Here the ecology may have been in part dependent on the abundant hydrothermal nutrients from the underlying volcanic rocks, and in part on the debris and the sulphate that came

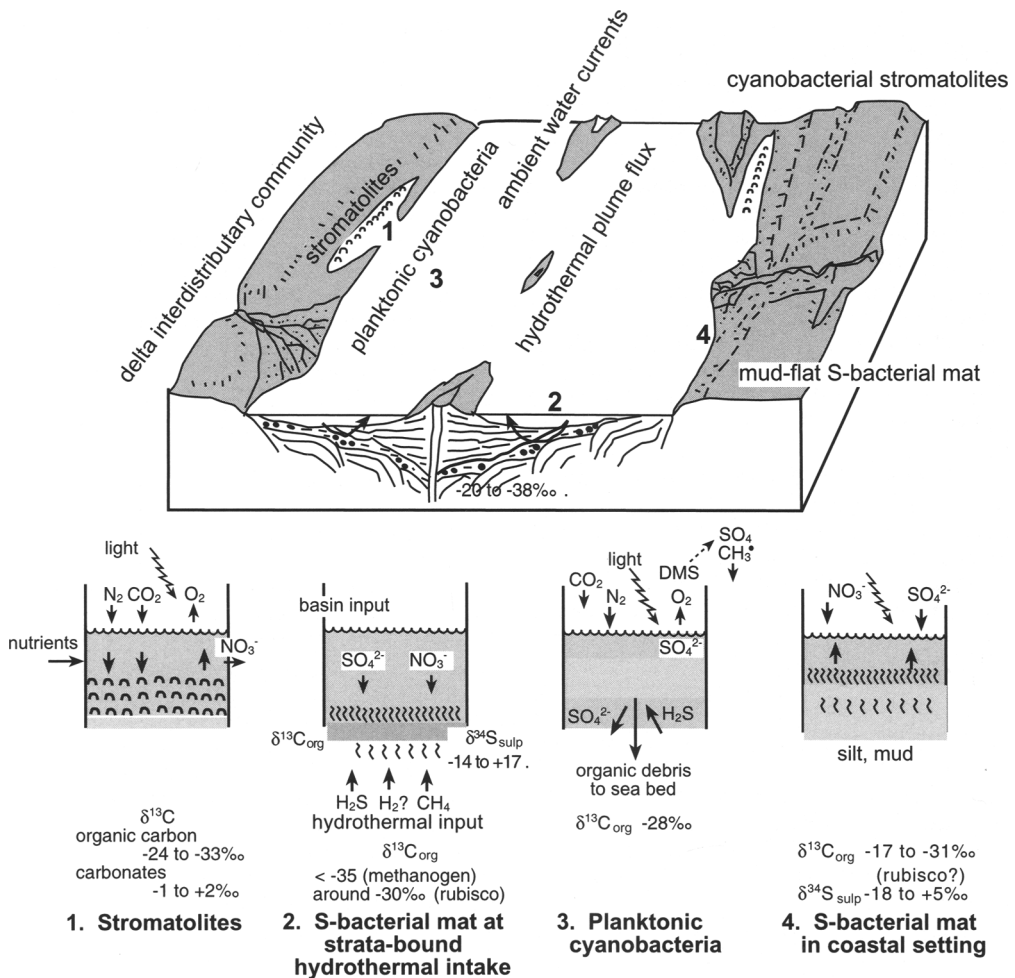


Fig. 7. Inferred generalized photosynthetic microbial mat consortia in an Archaean rift sea floor, inferred from carbon and sulphur isotopic results in the Spring Valley, Shavi, and Jimmy Members of the Manjeri Formation, and the Cheshire Formation (see Grassineau *et al.* 2002). General palaeoenvironment is reconstructed from sedimentary facies in typical greenstone belts (see summary by Nisbet 1987). Model assumes metabolic pathways from isotopic results and assumes that metabolic processes inferred from rRNA metabolic phylogeny (Woese 1987; Pace 1997) were extant. See also Nisbet & Sleep (2001). It should be noted that the palaeogeographical reconstruction shown here is a generalization, not specific to Belingwe, but drawing from the array of settings studied.

in from the light-driven planktonic communities in the upper layers of water above.

The various facies record microbial ecologies that have close parallels today. A plant can be seen as a community of chloroplasts and mitochondria; a microbial mat in a purpose-built house. The chloroplast is a cyanobacterium, whereas a mitochondrion is a purple bacterium. A land animal is an assemblage of mitochondria able to leave the seas in a walk-around space suit.

Animal digestions include archaeal recyclers: to a methanogen a cow or a termite is simply a handy life support system.

Both cyanobacteria and purple bacteria appear to have been present as the basic drivers of the Belingwe ecology, and archaeal recyclers were probably present also. It thus would be logical to expect many similarities between Belingwean and modern biochemical cycles. The most obvious difference is the absence of environment-altering

multicelled eukaryotes (e.g. worms) capable of digging into mud, churning sediment, and pumping water and fluids through redox boundaries. This would have gravely limited the productivity of the sea-floor mud biome as recycling would have been restricted. Many primary nutrients, such as accessible metals and phosphorus, would have been buried permanently after one pass through the biosphere, whereas today with eukaryote recycling they may be reused many times before being lost to the tectonic cycle.

Controls on the Late Archaean atmosphere

The implication of the isotopic evidence from late Archaean successions such as Belingwe supports the view from molecular biology that if cyanobacteria existed, a very diverse array of organisms had already evolved (Fig. 4). This diverse community would have necessitated a complex global microbial ecology (Nisbet 1995), and if so, it was probably managing the redox budget and the C, S and N (and probably Fe^{2+}) budgets of the ocean-atmosphere system on a global scale by the late Archaean. Just possibly, carbon and sulphur were managed isotopically on a global scale as early as mid-Archaean. Given the evidence for microbial control of C such as the carbonates with $\delta^{13}\text{C}$ c. 0‰, the atmosphere was probably a biological construct in the late Archaean. The further implication is that by the late Archaean, the global surface temperature was modulated by biological processes.

The air is not a simple linear system. There are many feedbacks, giving an atmosphere that appears stable when viewed over the time scale, say, of human evolution. However, even though the air has stabilities, it may have longer-term instabilities, or else bistable or multistable states. How was redox power managed? Models can help.

The bathtub model

The atmosphere is the global reservoir of redox power. The level of oxidant in the air is not set by the various fluxes, but by the switches that control input and output gates. Consider a bathtub. Within wide limits, in a bathtub, the level of water is not set by the flow of water out of the tap, but by whether the plug is in or not. If the plug is in, even a dripping tap will eventually fill the tub so that it spills from the overflow. There is no obvious relationship between tap flow and height of water in the tub. Instead, the level of the reservoir is set by an external physical factor, the height of the over-

flow hole. If the plug is not in, even the flow from a tap full-on will put only a minimal amount of water in the tub.

The bathtub analogy can be used to consider many aspects of sequestration on the Earth. The most obvious problem, the storage of water in the oceans rather than the mantle, has already been discussed above. A similar problem is the sequestration of oxygen in the air. In the late Archaean Earth, the photosynthetic cause of the flow of oxygen production through the 'tap' was presumably in cyanobacterial mats and global cyanobacterial plankton. This view is based on the evidence for the presence of cyanobacteria (Buick 1992). Bacteria spread very rapidly and once cyanobacteria had evolved they would have occupied every available niche very quickly. Just as rabbits filled Australia within a few decades, so cyanobacteria would spread globally within a very few years of their first evolution. If they are present in one place, they will be present planet-wide.

There is no particular *a priori* reason to suspect that oxygen production was any different from that in the modern ocean, except that there may have been constraints imposed by different availabilities of key nutrients such as phosphorus (Bjerrum & Canfield 2002). Today, the availability of fixed nitrogen may constrain productivity on geological time scales (Falkowski 1997), but in the Archaean phosphorus removal by adsorption on iron oxides could have reduced P availability, significantly reducing productivity compared with today.

Even today cyanobacterial picoplankton are ubiquitous in the ocean. In the late Archaean, resources nowadays used by multicelled eukaryotes would be available for microbial plankton. In the later Archaean, when continental land masses were present, abundant aeolian dust would have provided nutrient for ocean plankton blooms. There may also have been some land production of oxygen from photosynthetic microbial mats growing in damp or swampy areas. In the Archaean, the 'plugholes' that removed dioxygen were dominantly microbial oxidation of reduced organic debris and photorespiration, and, on a longer timescale, flow precipitation of oxidized minerals. This oxygen removal and carbon dioxide return would have matched the photosynthetic oxygen production and net carbon capture (after allowing for methane emission), or the system would have quickly sequestered all its carbon. Broadly, for both carbon dioxide and oxygen, obverse and reverse, the two fluxes of production and removal must be equal, if the oxygen and carbon dioxide levels in the air are stable. Wrapped around this rapid biological

cycling of carbon, on a slower time scale, is an outer nested geological carbon cycle, so that any slow carbon burial and crustal storage must be matched by carbon return from volcanoes.

But this applies to the fluxes. The size of the oxidation reservoir in the air (as opposed to the flux) is not necessarily coupled to the flux. In some cases, linkage occurs. For example, if the concentration build-up promotes the oxygen removal process by planktonic oxygen-consuming light harvesting (e.g. see Karl 2002), then controls of chemical equilibrium and kinetics may operate. However, many biological processes are very insensitive to such crude chemical controls, as the cell wall is a powerful barrier. Thus heterocysts protect nitrogenase, which is very oxygen-sensitive, in cyanobacteria. Nitrogen fixation is decoupled from external oxidation state and even in a modern oxygen-rich atmosphere, nitrogenase operates very successfully.

The speed of biological control and recycling of critical nutrients is much faster than the slow action of erosional supply and removal of cations. Thus the dioxygen balance level is not set by an inorganic buffering reaction, nor by a flux rate, but is a plane in O_2 - CO_2 - T space defined by the competing modes of action of rubisco (see Lorimer & Andrews 1973; Lorimer 1981; Tolbert 1994; Joshi & Tabita 1996), and by biological management and sequestration of crucial elements such as phosphorus.

Oxidation of the surface by methane loss and carbon subduction

Photosynthetically gathered reducing power, collected by bacteria, accumulates as reduced organic matter in sediments. From this, methane and other reduced products are generated by archaea after various processes of microbial fermentation. There are many steps, but finally the fermentation products such as acetate and ethanol are themselves utilized until two ends of anoxic fermentation are reached: isotopically light methane, and isotopically heavy bicarbonate or carbon dioxide. Methane is thus one end member of the full photosynthetic process: $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$. Other reduced remains include dihydrogen, hydrogen sulphide and ammonia. In the modern world (for example, in the cover of a landfill), these reduced products in turn are reacted by bacteria such as methanotrophs and microbial sulphate reducers, against the opposite waste product, the oxidant stored in the air.

Cyanobacterial mats in modern hypersaline environments also release significant quantities

of CH_4 . This flux is probably related to H_2 -based alteration of the redox potential within the mats (Hoehler *et al.* 2001). In the Archaean the flux of CH_4 from mats and emissions from muds where methanotrophs were recycling organic matter from plankton would have supplied methane to the air, and hence to the upper air. However, marine microbial consortia of archaea and sulphate-reducing bacteria would probably have been active, carrying out anaerobic oxidation of methane by sulphate reduction. (e.g. Boetius *et al.* 2000).

In a biologically active planet, microbial activity focuses on redox boundaries (Fig. 6). This enhances the effectiveness of the interaction between oxidant and reductant, and leads to massive sequestration of reducing power as buried reduced biomass. On the surface and near-surface, reservoirs of oxidant and reductant can be sequestered very efficiently. This sequestration is short term (plate-tectonic lifetime of around 100–200 Ma) compared with the history of the Earth, but it is a continuous process and so in effect the sequestration is permanent.

On the modern Earth, near-surface stores of reduction power include coal and oil, gas, and vast reserves of methane in and below hydrate caps, as well as disseminated kerogen and charcoal. The total store of reduced carbon near the surface is many orders of magnitude larger than the total held in the air and living biosphere. Even in Archaean rocks, carbon-rich strata are common. Some Belingwe rocks, for instance, are extremely rich in organic carbon and leave oily sheens on the saw-water when cut. Archaean oil is known to survive (Dutkeiwicz *et al.* 1998; Summons *et al.* 1999; Rasmussen & Buick 2000). Equilibrium was clearly not attained: indeed, the biology may have acted to increase the disequilibrium, sequestering redox power into separate reservoirs and hence deepening the bathtub by moving the overflow upwards.

In the modern atmosphere, free methane is oxidized within about a decade by OH, derived from water vapour attacked by O which in turn is derived from ozone and dioxygen. If the Archaean atmosphere were reducing and if it had lower O_2 , biologically released methane would have lasted far longer in the air. If abundant, atmospheric methane would have been a powerful greenhouse gas.

There is no cold trap for methane, and thus it would have been abundant in the high Archaean atmosphere. Here it would have been decomposed by UV radiation, releasing hydrogen. Some of this hydrogen would have diffused to the top of the atmosphere and would have been lost to space. There would also have been significant

microbial H₂ in the air and hence H loss to space (e.g. Catling *et al.* 2001). Over time, the Earth could have lost substantial hydrogen and hence substantial water (the original source of the hydrogen in the methane), leaving residual oxygen.

A parallel geological sequestration may have been going on. There is strong evidence that early microbial communities lived in hydrothermal systems (Rasmussen 2000). Such microbial communities would have lived on mid-ocean ridge systems. The reduced carbon in the organisms would have been buried by lavas and eventually subducted. Much of this carbon would be returned to the surface as carbon dioxide within the vigorous Archaean plate cycle in, say, 100 Ma to 1 Ga. However, in part the carbon would have been converted to graphite and then into diamond (Nisbet *et al.* 1994) when the ocean floor was subducted. Some of this diamond would have been underplated under continent, or else permanently removed from the Earth's surface (the 'exosphere') by return to the deep mantle. Loss of reduced carbon to the depths is, in effect, supply of oxygen to the surface because the C was ultimately derived by splitting CO₂. Similarly, subduction of reduced sulphur (Alt & Shanks 1998) effectively oxidizes the surface atmosphere–ocean system.

Cumulatively, over an aeon, the total impact of H loss to space and C return to the mantle would be relative oxidation of the surface and reduction of the interior. However, if iron oxides were being precipitated in sediment, and then subducted, this process would return oxidation power to the interior. To accomplish both carbon return to the interior and iron oxide return, subduction deep into the mantle is necessary, rather than shallow subduction of relatively hot plate. Thus, to return to Fermor's point, the density contrast that drives subduction, which comes from cooling by liquid water, plays a role in maintaining the oxidation regime of the surface.

Walkerworld

In 'normal' times the air is more oxidized than fresh volcanic rock, and also more oxidized than the sediment column, which is enriched in reduced organic matter. Before the onset of global photosynthesis this contrast with the sediment may have been very different (Walker 1987), especially if methane were abundantly released (Hayes 1994).

In 'Walkerworld' conditions, an 'upside-down' biosphere occurs. The waste oxidant is held in the sediment and the air contains the reducing power. To sustain a Walkerworld, emissions into

air of methane, hydrogen, etc. from decay must exceed burial of reductant and hence must exceed photosynthetic emissions of waste oxidant and any inorganic production of oxidant by hydrogen loss to space. These events, if they occurred at all, must be abnormal because the primary wastes of oxygenic photosynthesis are gaseous dioxygen, which tends to escape upwards, and the primary reduced waste, organic matter, which tends to be buried downwards, ensuring an up–down partition, and thus the main steady flux to the air has been oxidant ever since planktonic oxygenic photosynthesis began. Even in a biosphere depending on anoxygenic photosynthesis, the buried organic waste is reduced.

But there is no obvious intrinsic reason why the air cannot for a brief period (geologically speaking) become so rich in methane that the system is inverted, with a reduced atmosphere and a relatively oxidized sedimentary mass. Today a vast reducing biosphere exists in sediment under oxidized skies yet with trace methane in the air, whose lifetime is determined by kinetics. Then the reverse could have been true, especially before the onset of oxygenic photosynthesis, when the output of gaseous oxidation power to the air was less. The air could have been methane rich, with trace oxygen.

If huge quantities of methane are suddenly released from geological stores (for a modern analogue, one can imagine a giant slump releasing several tens of gigatons of methane from hydrate in sediment of a large delta, or a sudden large plume-head intrusion into the giant permafrost-hosted Siberian gas fields), then the onset of methano-dominant events could occur. The microbial ecosystems would invert, and methane release would dominate the air, with carbon dioxide, not methane, being the gas stored in the sediment pile. The geological record may bear witness to such events in major C-isotopic excursions.

Given the absence of eukaryote reworking of muds, it would perhaps have been easier to sustain an inverted ecology in the Archaean than today. In some ways, the deep-water environment of the modern Black Sea is today a Walkerworld, with ambient reduced species in the water above more oxidized sediments (and the chilling possibility that one day the water body will overturn, releasing its gases to air). It is possible that in the Precambrian major events took place with methane as the dominant carbon gas (Hayes 1994). Inversion is, ultimately, arguably unstable as the reduced organic matter settles downwards, so the natural order is reduced below, oxidized above, but Walkerworld events may have been sustained for long periods.

Pavlov *et al.* (2001) have constructed a plausible history to explain carbon isotope excursions and then major changes in the early Proterozoic atmosphere as the product of a Walkerworld. In this view, the pre-biotic atmosphere was kept warm by high CO₂, with which a significant amount of H₂ coexisted. With the onset of life, methanogens rapidly began to use the H₂ to produce CH₄. In this view, the early C isotope record does not reflect oxygenic photosynthesis but rather methanogenesis. By *c.* 2.8 Ga ago, however, Pavlov *et al.* (2001) have suggested that oxygenic photosynthesis began and increased the supply of organic matter and hence of CH₄ and an associated hydrocarbon haze. At this stage, sulphate-reducing bacteria, exploiting the increase in oceanic sulphate after the onset of oxygenic photosynthesis, either outcompeted for the H₂ supply or converted CH₄ back to CO₂ (e.g. see Boetius *et al.* 2000), causing a decrease in atmospheric methane. In turn, the loss of the greenhouse warming at the collapse of the Walkerworld initiated a massive glaciation at *c.* 2.3 Ga. Eventually, the response led to the oxygen-rich air.

Building a biosphere

A possible sequence of events can be deduced.

Life before photosynthesis

From the origin of life to the evolution of the first cell capable of anoxygenic photosynthesis (say from between 4–3.8 Ga and 3.8–3.5 Ga), oxidation power was provided by bicarbonate and by oxidized sulphur and nitrogen compounds, especially sulphate and nitrate. Elemental sulphur, as sulphur vapour, may also have been important (Kasting *et al.* 1989), acting as a shield in the atmosphere to protect against UV radiation and as a supply for sulphur-metabolizing microbial life. On the sea floor, life would have sequestered reduced matter in sediment mainly by burial of organic matter and sulphide precipitation. Organic carbon would have been further recycled by archaeal generation of methane in the deeper parts of microbial mats. Part of this methane would in turn have been reoxidized by methanotrophic bacteria, but some would have escaped to air.

Today, much of the methane that is produced by methanogens is stored in the muds and clays of the mature sediments of the continental slope, where massive reserves build up. In the early Archaean, perhaps with far less continental sur-

face, mature sediments would have been much less common. If methane escape from sediment were easy, Walkerworld conditions (methane, not carbon dioxide, in a 'negative' bathtub) could have been favoured, with the build-up of a reduced atmosphere and a relatively oxidized sediment, possibly rich in precipitated elemental sulphur and sulphate. If methane were more abundant than carbon dioxide it may have created a methane-rich smog that was analogous in function to the modern ozone layer (Love-lock 1988).

Anoxygenic photosynthesis

After the evolution of anoxygenic and before the arrival of oxygenic photosynthesis (say 3.8–3.5 Ga to 3.5–3.3 Ga) (see also Rosing 1999; Brasier *et al.* 2002), molecular oxygen production from inorganic sources and from biological emissions would have been small, but the added redox power and productivity of microbial mats would have been nevertheless considerable. Consequently, large amounts of reduced organic matter would have built up in sediment, and, though methane emissions from sediment would have increased, so would have the bulk sequestration of reduction power out of the ocean-atmosphere and into the crust. Possibly methane emissions from methanogens were large enough to be a crucial component of the atmospheric greenhouse, able to sustain a warm surface (Pavlov *et al.* 2000)

Oxygenic photosynthesis

When oxygenic photosynthesis began, whenever this was, the spread of uniquely advantaged cyanobacteria blooms across the planet would have been explosive: an 'Andromeda event' (to recall the Fred Hoyle fiction in which genetically manipulated microbial life suddenly challenged the atmosphere), instantaneously altering the air. Cyanobacterial mats are potent physical separators of oxidant and reductant. Reduced muds would be separated from oxidized surface by the leathery septa of microbial mats. Release of waste oxygen would have been a sudden consequence of the arrival of cyanobacteria, catastrophic to the previous surface ecology. The oxygen level in the bathtub (Fig. 8) would have deepened instantly. Biological sequestration of redox power would have become global, wherever fluid flow occurred into and out of the sediment. But, as argued above, it is not the flux that controls the depth. In the bathtub of a microbial world it is not obvious where or how the overflow level was set.

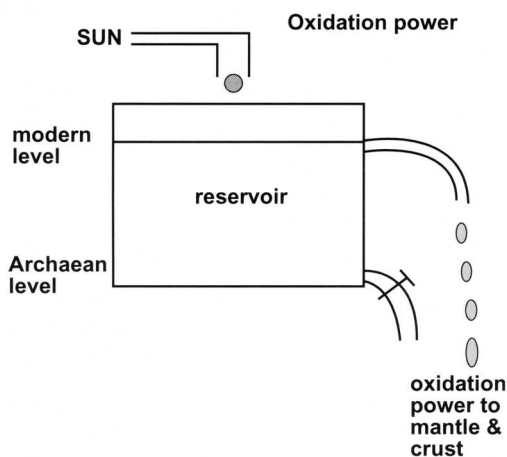


Fig. 8. The bathtub model. The level of the water in the bath is not controlled by the flow from the tap (unless it is huge) but rather by the levels of the output pipes. With the plug in, even an inflow that is just dripping will eventually fill the bath to the overflow level; if the plug is out the bath will start to fill only when the flow from the tap is greater than the capacity of the plughole. If the atmosphere is compared with the bathtub, with the water content analogous to the atmospheric burden of, say, oxygen or carbon dioxide, then the short-term inflow and outflow gates are set by the subtle response of rubisco to CO_2 and O_2 mixing ratios (Lorimer & Andrews, 1973; Lorimer 1981), as managed by chloroplasts and mitochondria and by similar cyanobacteria and purple bacteria in the Archaean. There may be bistable modes, either with low CO_2 and high O_2 as now, with rubisco acting one way, or with high CO_2 and low O_2 in the Archaean. These immediate molecular controls act in a world where the dominant long-term controls are the large-scale inorganic redox stores and geochemical controls (e.g. Lasaga & Ohmoto 2002), for example, iron oxidation, and there are also medium-term organic controls (e.g. wildfire on the modern Earth; microbial blooms and subsequent rapid sinking of reduced organic material in the pre-metazoan planet). Which time scale of control is responsible for setting the atmospheric burden is not obvious, but short-term biological controls, by their ability to sequester redox power (see Figs 5 and 6), may be dominant.

The rise of oxygen

The oxygen burden of the Archaean air (the 'level in the bathtub' Fig. 8) remains an unsettled controversy. Much opinion (e.g. Kasting 1993; Holland 1999) holds that oxygen levels rose sharply in a sudden event that took place in a short time, somewhere around 1.8–2.4 Ga ago. Much evidence, such as the need for reduced

settings to transport iron, implies that free dioxygen was virtually absent (Holland 1999), except as a short-lived biologically sustained trace gas (just as 1.8 ppm methane is present in today's oxygen-rich air, with a lifetime around a decade).

Kump *et al.* (2001) accepted that the initial rise in O_2 levels occurred at some time between 1.8 and 2.4 Ga ago. They suggested that this rise was abrupt, and followed a major period of magmatism, produced by mantle overturn and/or mantle plume activity. In contrast, Catling *et al.* (2001) have suggested that the transition from low to high dioxygen burden in the atmosphere was a consequence of hydrogen escape into space as a result of high methane concentrations in the Late Archaean–early Proterozoic air. The methane could have been produced biologically (Pavlov *et al.* 2000) by methanogens acting on carbon captured by photosynthesis, to give atmospheric methane concentrations of 0.1% or more. In the high atmosphere, photolysis of methane would produce hydrogen, leading to steady escape of H. This escape of H to space would slowly oxidize the whole Earth, building up oxygen inventories and increasingly enhancing the kinetic stability of atmospheric O_2 , while also slowly reducing the volume of water in the oceans. Atmospheric O_2 would be scavenged in the early reducing environment, by oxidation of crust, but eventually the net photosynthetic production of oxygen would exceed the input of reduced gases to the air, and this would cause irreversible oxygenation of the air.

Kasting (2001) pointed out that serpentinization of new sea floor also produces reduced species, such as H_2 when water is the oxidant, and methane when CO_2 is present. In this process, Fe_3O_4 is produced. Possibly these two processes together sequestered enough oxygen that through the Archaean aeon the atmospheric oxygen was suppressed. Then, when the net photosynthetic flux of oxygen became larger than the flux of reduced gases, the oxygen level suddenly rose. In terms of the bathtub analogy (Fig. 8), the plug would be put in, and the level in the tub would suddenly rise until the new rubisco-controlled overflow operated.

Farquhar *et al.* (2000) investigated mass-independent fractionation in sulphur isotopes from across the period when oxygen levels are thought to have risen. They found a major change somewhere between 2090 and 2450 Ma ago. In rocks older than this, gas-phase atmospheric reactions may have influenced the sulphur cycle, playing a role in determining the oxidation state of sulphur. This would imply that atmospheric oxygen had low partial pressures, and microbial oxidation and reduction of sulphur were

minimal. These results are of great interest, but have been disputed (see questions by Ohmoto *et al.*, and the response by Farquhar *et al.* (Ohmoto *et al.* 2001)). It is also not clear how the work is reconciled with the implications of the large fractionation in ^{34}S observed by Grassineau *et al.* (2001, 2002), in 2.7 Ga material.

With the rise in oxygen would come an increase in ozone and a fall in UV irradiation of the surface (Cockell 2000). Possibly this more benign setting played a role in the onset of eukaryote and metazoan diversification.

The opposite view has been championed by Ohmoto (1997) on the basis of isotopic evidence, interpreted as suggesting relatively high oxygen levels. There is a reasonable case that oxygen levels in the Archaean were higher than thought in orthodox opinion.

Phillips *et al.* (2001) discussed the central evidence on which the 'reduced' model of the Archaean atmosphere is based. This evidence includes the composition of detrital gold grains, inferred detrital uraninite, inferred detrital pyrite, and inferred palaeosols, especially in the Witwatersrand succession. In a careful detailed review, Phillips *et al.* concluded that the geological evidence for a reducing atmosphere remains ambiguous. In particular, post-depositional processes may need far more examination. Phillips *et al.* pointed out that some of the mineralogical and field evidence can be interpreted as supporting an oxidized Archaean atmosphere.

There are many pitfalls here. For example (own observations), in the Steep Rock succession of NW Ontario, which is old with abundant stromatolites (Wilks & Nisbet 1985), mining operations about 1100 ft (*c.* 300–350 m) underground produced 'buckshot ore', a pisolitic laterite iron ore that clearly implied oxygen-rich conditions. However, A. de Barros Machado (pers. comm.) pointed out termite-made features in the ore, and further investigation in the open pit (E.G.N. and R. Bernatchez) produced a small outcrop of the ore, rich in woody fragments. Obviously, wood and termites are not Archaean. Most likely, the ore had been made by Cretaceous or Tertiary termites that had tunnelled down 500 m from the pre-glacial palaeosurface to the contemporary water table, bringing down wood and oxygen. The location 1100 ft. underground in 3 Ga rocks had led to the wrong but obvious assumption that the oxidation of the ore was Archaean; it was not.

Nevertheless, although some arguments for Archaean redbeds can be questioned, Phillips *et al.* (2001) have a powerful case. The question 'was the Archaean atmosphere reducing' must be regarded as still unsettled.

The evolution of the eucarya

The eucarya may be of very great antiquity (Hartman & Fedorov 2002) even though their geological record is only as far back as possibly 2.7 Ga (Brocks *et al.* 1999). The possible antiquity of the budding bacteria such as Planctomycetales (Brochier & Philippe 2001) is of great interest here, as it immediately suggests a root stock for the eucarya. The date of incorporation of chloroplasts into the eukaryote cell is not clear, but may have been late Archaean. Whether or not the arrival of the eukaryotes was involved in the rise of oxygen is an open and fascinating question.

Eukaryotes can be regarded as 'microbial-mats-in-a-single-cell'. They incorporate both oxygen production from the chloroplasts (included cyanobacteria) and oxygen removal in the mitochondria (included purple bacteria). The earliest eukaryotes would not necessarily have had any more impact than their individual component parts, as it would have been likely that cyanobacteria and purple bacteria lived in close symbiosis before the arrival of the eukaryotes. Yet the dinoflagellate is a fearsome whip with which to beat the planet: there may have been large changes. There appears to be an intracellular switch controlling oxygen levels in the eukaryote cell (Joshi & Tabita 1996), and this switch would probably have had global impact.

Biological controls, acting rapidly, and sequestering redox power into reservoirs, can override the background inorganic chemical controls. For example, Fe^{2+} can be carried in biological organisms, which have captured it from hydrothermal water reducing settings, into oxidized environments, isolated by biological membranes. The debate about the oxidation state of the sea remains open, and it is possible that, like the modern Black Sea, the top of the Archaean ocean may have been oxidizing as a result of widespread cyanobacteria picoplankton, whereas deeper levels were reducing because of the high rates of settling of reduced organic debris. With the arrival of multicelled organisms in the Proterozoic it became possible to pump more water through microbial mats: worms move fluids and rearrange reservoirs of reduction power. The sequestration became intense.

Links between the Archaean atmosphere and the ocean: biology and temperature

The atmosphere controls the planet. The effective temperature of the modern Earth (the temperature without the greenhouse warming of the

air) is about -18°C . The greenhouse warming of $+33^{\circ}\text{C}$ ensures an actual average temperature around 15°C and thus oceans are liquid. The main greenhouse gas is water vapour. The CO_2 and CH_4 have a multiplier effect. If the carbon greenhouse gases are absent, not only is there less water vapour in the air but more of the polar region is white from ice; thus more sunlight is reflected and the water-caused greenhouse declines; which makes the planet cooler yet, and so on: there is a risk of global glaciation. In the early Archaean the Sun was somewhat fainter (Sagan & Chyba 1997), and atmospheric oxygen was probably insignificant. The fainter Sun means that to sustain liquid oceans a more powerful greenhouse may have operated.

Biology-absent planet

What would have controlled surface temperature? Imagine first the snowball risk to an Earth-like but biology-absent planet in the Archaean: the risk that the ocean surface would freeze. Carbon dioxide might eventually freeze at the poles, and an icebox runaway would follow. In the long term, the situation would right itself if the planet were positioned in the Sun's habitable zone. Eventually either a huge volcanic eruption or a meteorite impact would generate enough dust to change albedo. Carbon gases and nitrogen gases would have progressively degassed from volcanoes, and a sudden warming could follow.

The opposite risk is an 'oven', a greenhouse runaway, in which a primary carbon dioxide greenhouse is added to by other gases: indeed, this risk is very present as a planet rights itself from a snowball. Imagine a very large plume eruption, that contributes huge amounts of carbon, sulphur and nitrogen gases to the air and injects huge amounts of dust to the stratosphere. The ocean initially cools under the dust, but soon warms as the dust settles. The carbon dioxide can only be removed on an abiological planet as dry ice or by precipitation; this demands the presence of adequate Ca^{2+} . But if the plume emissions are very large, the weathering that supplies Ca may be too slow in supplying cations, so that precipitation cannot keep up with emissions, despite the acidity of the rain. In this case huge quantities of water can be evaporated, creating a steam atmosphere. In the absence of a temperature inversion at the cold trap, water reaches the high atmosphere and hydrogen is lost to space. Eventually, the Ca supply from weathering precipitates the carbon dioxide, which can then return to the mantle by subduction and normality returns. But there is a risk that such events,

repeated too often in the Archaean, could dehydrate the planet.

Biology-present planet

Consider now a biological planet. Imagine it entering a snowball phase for some reason. Methane would accumulate as the photosynthetic biosphere died and sediment was filled with organic debris. Methanogens would create vast unstable reservoirs of methane held in clathrates. Eventually this would emerge to air, probably catastrophically (in terms of geological time); there it would be a powerful greenhouse gas, and as warming occurred methane would be released by hydrates and carbon dioxide would be released massively from the oceans: one hypothesis for the escape from the snowball. The biological planet could probably 'right' itself earlier, after a less prolonged snowball, than an abiological planet.

On a biologically active planet, the feedback controls are faster, to counteract both freezing and heating. In an ice age, biology responds by reducing carbon consumption and then recycling carbon as methane and carbon dioxide. In a hot-house, biology runs rampant, removing carbon by organic capture and precipitation of carbon. This too depends on essential elements, such as Fe, Cu, Zn, Mo and especially P, but the supply is regulated by weathering rates, themselves controlled by biological carbon cycling. Biology is a multiplier, using recycling to extract more carbon management power from the available store of cations than inorganic chemistry. The presence of biological control speeds the return of the planet to 'normality'. Yet the dehydration risk remains, this time via methane partition into the top of the air and subsequent loss of H.

The state of the mantle and crust

Assume a planet in which the upper mantle has about 0.2% water, and the composition is broadly peridotitic, with heat production as on Earth. The geotherm depends on the vertical distribution of the heat production in the interior and on the surface temperature, and on the heat transfer controls. The surface temperature is maintained by the radiative balance of the atmosphere and any greenhouse increment, and is only indirectly dependent on interior processes. If the state of the atmosphere means that the surface is cold, say -100°C to -200°C , then the lithosphere will be thick. The top of the mantle adiabat will be forced to cool. The deeper mantle will thus store heat until melting extracts it as

plumes. Conduction will carry the heat away over the aeons (depending on how large the planet is), but more quickly than if the surface had been kept warm by the air's greenhouse blanket. If the planet is small the cold and moderately wet mantle will freeze into inactivity.

In the opposite case, consider a Venus-like planet with surface temperature forced by greenhouse blanketing to remain at 500°C. The geotherm will intersect the mantle solidus at shallow depth. Melt will be very efficiently extracted from the topmost levels of the mantle, and with melt will come heat production elements and volatiles, especially water. The crust will be dry, especially deeper than a few kilometres, and will largely be pyroxene-dominated granulite. There will be no return of water to the interior as there is no cold dense wet crust: no muds, no clays, no eclogite, no mud-derived garnets in moving continents. Instead, hydrogen from water photolysis in the high atmosphere will be lost to space.

The extent of the crust will depend on whether a buried mantle ocean, in which dunite floats over denser ultramafic magma, develops in the lower part of the upper mantle. If a mantle magma shell is present, water will be retained in the mantle melt. If a magma shell is not present, melt will rise carrying water, so that the mantle is eventually entirely dehydrated as water is extracted and lost to space. Even if a magma ocean is present, the long-spaced catastrophic overturns of cold dense surface and resulting massive eruptions will lose water to space. The surface and interior will be strongly oxidized by residual oxygen. Although the mantle is so hot, it will be dry after a few billion years.

On a Goldilocks planet the surface temperature is just right. Where volcanism occurs, water is ejected from the interior, but is held under the cold trap until it can be returned to new crust via hydrothermal systems. Old plate is dense and falls in; the water returns to the interior. Much of this water fluxes melt and is returned at andesitic volcanoes. A small amount is retained by plate entering the deep mantle. This intake is controlled by the ambient temperature and in effect the system becomes self-fluxing. If it is locally too hot, abundant melt production removes water and heat. As the planet cools, andesitic melt production falls and the cooler deep mantle accepts more water, to allow melt production to continue at mid-ocean ridges. All this depends on a surface temperature that allows rehydration and cooling of the new plate.

The Earth lies in the habitable zone, the right distance from its star (Kasting *et al.* 1993). But the Sun's output both varies and is steadily brightening. How wide is the allowable range of

the Goldilocks temperature window, that allows liquid oceans to be sustained for thousands of millions of years? The upper limit is probably around 70–100°C. Above that, the ocean goes. The lower limit of the window is perhaps a little below 0°C as an equatorial temperature. Below this, there would be less rehydration of new plate, except locally around active volcanism where heat would melt ice and permit hydrothermal systems. The ice-laden planet would be white, and would cool. If it became very cool and carbon dioxide precipitated on high polar continents, the temperature would drop further. Only methane emission could allow an escape from this, but on an abiological planet there would be no massive source.

Thus the Goldilocks window is probably between 0°C and 100°C, or less. This surface temperature also may have influence on the permissible depth of the oceans. Kasting & Holm (1992) have argued persuasively that the depth and hence volume of the oceans is actually controlled by the depth at which the critical pressure for sea water occurs. If mid-ocean ridge axes are at this depth, this optimizes convective heat transport and thus hydrothermal circulation into the new crust. Consequently, the crust is hydrated efficiently, and water is subducted and fluxes the plate system, in a self-stabilizing regime (Kasting & Holm 1992). If this is correct, a surface at, say, 15°C, would imply oceans in which mid-ocean ridges were 2.5 km deep (250 bars pressure) and hence about 3.5 km deep on average in a plate system where ocean depth is determined by the cooling of the plate. Although brief excursions beyond these bounds are possible, indeed likely, the planet must stay in this regime over aeons, despite a brightening Sun, and despite the stochastic occurrence of 'accidents' such as plume eruption and meteorite impacts.

Recapitulation: managing the surface temperature

We exist: therefore the planet has never been dehydrated and there has been liquid water somewhere on the planet's surface ever since life began.

Two questions can be asked:

(1) Could inorganic chemical feedbacks have succeeded, alone, in maintaining planetary temperature?

(2) Did Archaean biology manage the planetary surface temperature?

Before addressing these questions, it should be pointed out that biological and inorganic processes are not independent. They act on the same

planet: thus both must contribute jointly to planetary maintenance today, and presumably acted jointly in the past.

The Solar System is not stable, neither is our planet. Both are chaotic, in which luck may allow a certain degree of stasis. Thus orbital collisions occur until there are few bodies left, and interactions become so infrequent that the large planets seem to have attained stability in orbit. On a planet, geochemistry and heat production sort themselves out until the structure of the planet and its tectonic behaviour seem stable. But neither orbits nor tectonics are truly stable. Catastrophic events can and will occur that can upset the system. Planets collide. The Earth has precipitated a core, probably frozen a magma ocean, and will eventually freeze and be still. To stabilize the surface of a planet such that life can exist for 4 Ga surely needs restorative feedbacks, and perhaps luck also.

The inorganic model

Powerful inorganic feedbacks do exist. If a volcanic event degasses huge amounts of carbon dioxide (e.g. eruption of a major plume head), then the air will become warmer and hence wetter, and more acid. Weathering will become more intense; bicarbonate will flow off the land and eventually carbonate will be deposited in sediment and in new oceanic plate, to return the carbon dioxide to the deep continental crust and to the mantle. But this process depends on the availability of exposed land to be weathered, on the rate of erosion, and on the rate of plate motion. Weathering reaches only a certain depth:

after the surface and the rock accessible to groundwater have been attacked, the flow of cations is limited. It is possible to imagine a huge plume eruption in which a massive carbon dioxide greenhouse builds up, such that the oceans degas and a global steam greenhouse would exist. Eventually this would subside as carbonate precipitated, but the event could be long-lived.

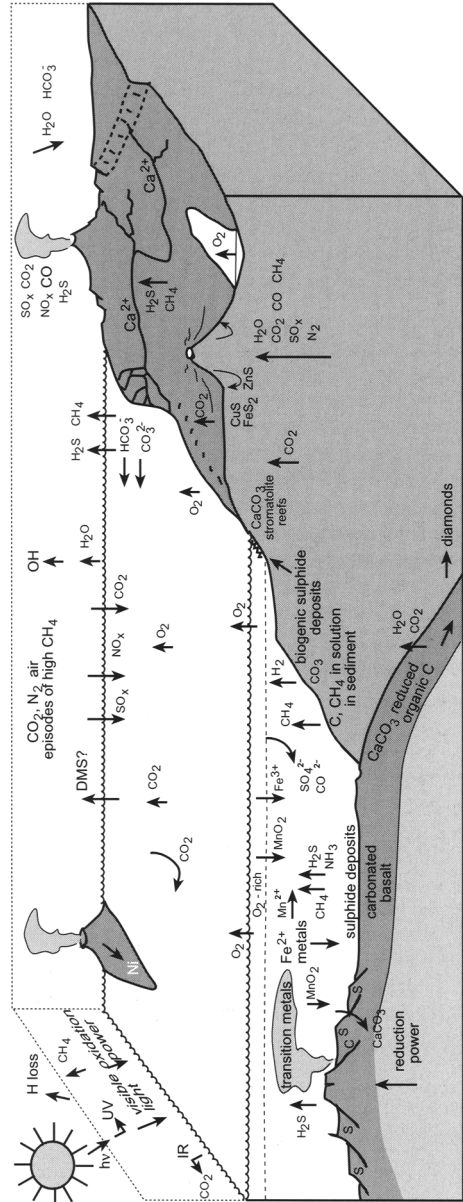
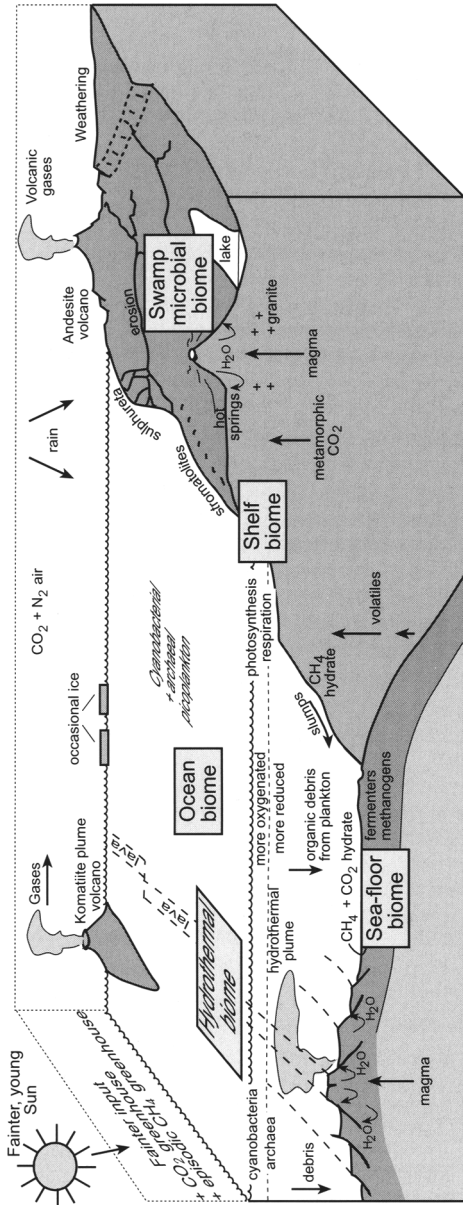
Conversely, if too much carbonate is withdrawn by tectonics, by subduction or precipitation, then the ocean freezes. Weathering ceases. Carbon dioxide precipitation stops and the gas builds up in the air until part of the ocean melts and degasses more carbon dioxide, and the world switches from total glaciation to partial glaciation. Indeed, intuitively an inorganic world might be expected to see-saw between these two states, with rare excursions into a plume-driven moist greenhouse state.

Despite the abundant evidence for huge plume events, such as the immense Bushveld event, the anthropic principle implies that the whole Earth has not experienced $\gg 100^\circ\text{C}$ greenhouse conditions as long as life has existed. Since then, there have always been parts of the Earth below about 100°C , and since the evolution of mesophiles there have been parts of the Earth below about 40°C . Possibly the plume events have simply been too small to disrupt global climate beyond habitability. Or possibly life itself has played a hand.

The organic model

The powerful organic feedbacks allow a much more sophisticated greenhouse control. More

Fig. 9. Controls on the Archaean atmosphere. Top: major components of the atmosphere–biosphere–ocean system in the Archaean. The major inputs come from below (magma and volatiles) and above (light energy, meteorite infall, and removal of H to space). The various biomes and inorganic processes on the surface move and sequester the inputs, adding them to the various inventories that constitute the memory of the system. The ocean is assumed to be at least as deep as at present and possibly deeper; the atmospheric pressure may be comparable to that today. The possibility of a deeper ancient ocean arises because today there is probably a net water loss by deep subduction that is slightly greater than the net gain from deep magmatism, as volatile intake acts to flux mantle melt in compensation for secular cooling of the planet. The assumption of a comparable old atmospheric pressure (i.e. *c.* 1 bar) is very weakly founded, based on the assumption that nitrification–denitrification by bacteria was broadly subject to the same dynamics as today. The CO_2 partial pressure of the Archaean air is difficult to assess intuitively, as greenhouse constraints (the sedimentary record implies mostly unfrozen oceans) include methane (e.g. Pavlov *et al.* 2000; Catling *et al.* 2001). Bottom: chemical exchanges between parts of the system. The magnitudes of organic fluxes depend on limiting constraints (e.g. availability of fixed N and especially supply of available phosphorus; Bjerrum & Canfield 2002). The surface of the ocean (top 100 m) may have been oxygen-rich, from the waste oxygen released by cyanobacterial photosynthesis in picoplankton. Deeper levels of the ocean, like the modern Black Sea, may have been mildly to strongly reducing, and kept so by the influx of reduced organic debris from the photosynthetic layer (but note there would also have been a transient frequent influx of sulphate and MnO_2). At the bottom of the ocean, sulphide deposits probably formed by microbial reduction of sulphate (e.g. see Grassineau *et al.* 2002). Deeper water would have contained reduced iron species in solution, from hydrothermal vents. Where deep water rich in Fe^{2+} reached the shallow levels in upwellings, blooms of photoferrotophs would be likely.



levers are available to control atmospheric water (the main greenhouse gas): in addition to carbon dioxide, methane, nitrous oxide, and albedo change can also be influential. Carbon dioxide management still depends on chemistry, but in addition to calcium, carbon can be deposited as organic matter, which in effect is controlled by access to phosphorus and iron. Thus the potential for greenhouse reduction by carbon removal can be greater, especially after a major outgassing, which will also increase P and Fe availability, increasing biological productivity.

Carbon removed by organic processes is not necessarily shipped to the mantle. Much is deposited as organic matter in sediment, where it is converted in part to methane by methanogens. This is, in effect, a delayed positive feedback: archaea in sediment convert organic matter to methane, and emitted methane can drive sharp strong greenhouse events. Thus any over-removal of carbon by life is ultimately self-correcting.

The real world

Both the inorganic model and the organic model are thought-experiments. The real world is neither. Life, garnets and moving continents are all interdependent. For 4 Ga both have been operating subtly in tandem. Life has shaped the planet; so have inorganic processes. In stabilizing not ice nor steam, but liquid water, on the surface, the combination of life and inorganic processes (Fig. 9) in the Archaean together shaped the planet. The two factors together have sustained plate tectonics by sustaining a cool surface and allowing the reintroduction of water to the interior. Over the aeons they have set the temperature of the top of the mantle adiabat and hence the overall temperature and melting state of the mantle, and thereby its composition. Over 4 Ga it is even arguable that their influence reaches to the precipitation of the inner core, via the adiabat.

Sir Lewis Fermor, half a century ago, considered garnets. In many ways they symbolize crustal material; they also form the richness of the mantle. He rightly recognized the importance of density contrast in driving continental drift, and wondered if garnet formation could help drive movement. He was correct in thinking of density contrast, and of downward recycling of crust, although we now know that the main density drive of subduction is the cooling of the entire lithospheric slab, not just the mafic crust. This cooling would not occur but for the maintenance of the cool surface by the ocean–

atmosphere system. Moreover, the recycling of volatiles from the crustal part of the slab as it converts to eclogite is vital in sustaining the continents. Many crustal garnets, those formed from metamorphism of muddy sediment, could exist only on a planet that has continents and erosion. The whole Earth system, garnets, moving continents, and even the mantle adiabat and the modern core temperature, all depends on the sustained existence of the cool wet surface. Is this the result of the influence of life on the face of the Earth? Or accident?

It is probably not a quantifiable question to ask which factor, life or inorganic chance, has been in the driving seat. Both operate. But if any one factor has been central it is the agent that controls the air. Is that agent life?

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