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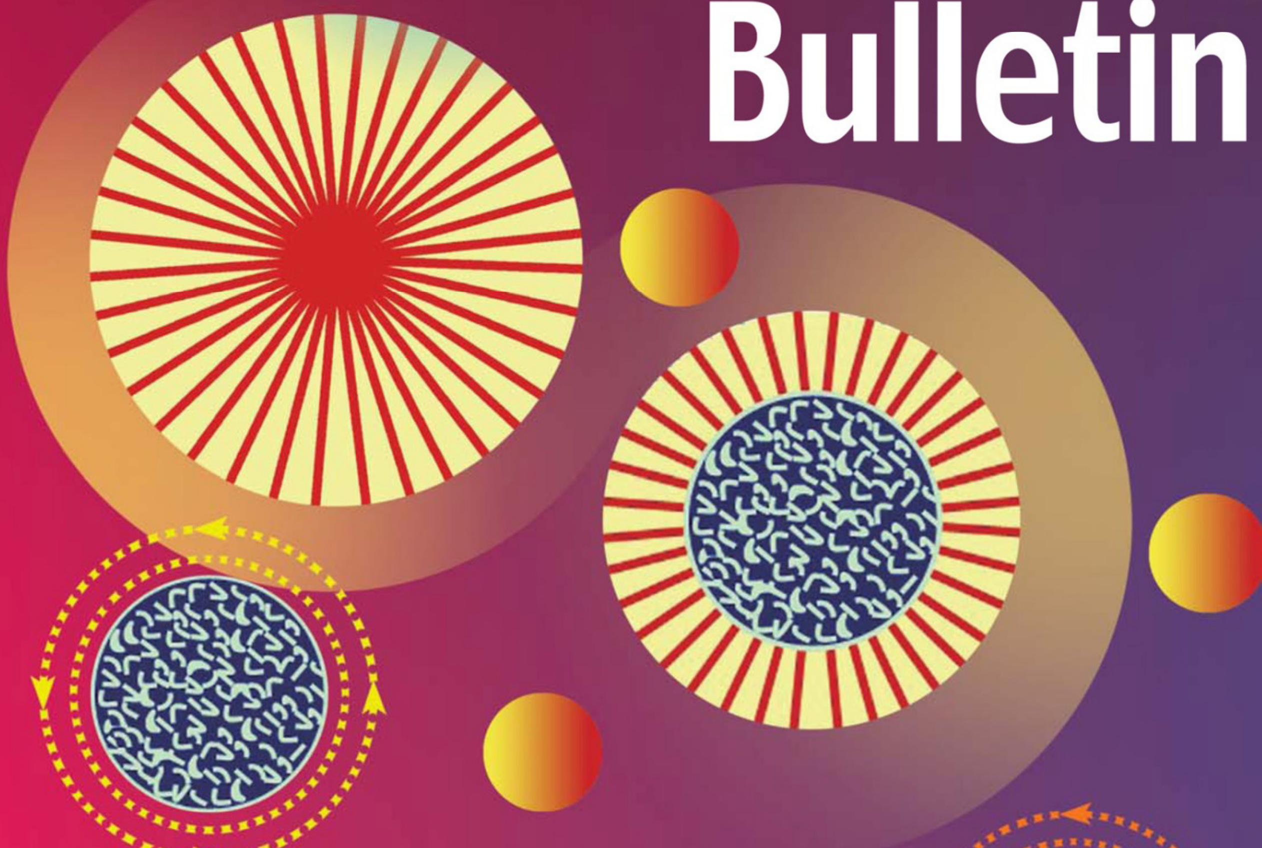

In this issue:

The evolution of the atmosphere in the Archaean and early Proterozoic

(Euan Nisbet & Mary Fowler, p. 4-13)

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Editor's note

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Euan Nisbet is Foundation Professor of Geology in the Department of Earth Sciences at Royal Holloway, University of London, UK. He studied first at the University of Zimbabwe and then Cambridge, majoring in physics and geology (1967–1970). His PhD research was at Darwin College, Cambridge, into Greek ophiolites, under the supervision of Alan Smith. With the funds of the Harkness Prize awarded by Cambridge University, he visited the University of California, Davis, during which he participated in the Penrose Conference that led to the definition of ophiolites. After this, he held a Natural Environment Research Council Research Fellowship in Oxford, studying Archean greenstone belts in his home continent, Africa, while also holding a Fellowship at Wolfson College, Oxford, and at the University of Zimbabwe. In 1977–1978 he held a Royal Society European Exchange Fellowship at the Swiss Federal Institute of Technology (ETH), Zürich, followed by a faculty post in Cambridge. In 1981 he moved to the University of Saskatchewan, Canada, becoming a Full Professor in 1986. From 1985 to 1987 he held a EWR Steacie Fellowship from NSERC Canada, presented to him by the Governor-General. Since 1992, he has been a Professor at Royal Holloway. Currently he leads the Atmospheric Methane Group at Royal Holloway, and is Leader of the Greenhouse Gas Activity in the EU's GEOmon Global Monitoring project. Formerly, he coordinated the MethMonitEUr project, studying methane in Europe and Russia. His geological work on the early Earth has been mainly in the Belingwe greenstone belt, Zimbabwe, studying komatiite volcanism, stromatolites and early microbial evolution. He is a Distinguished Fellow of the Geological Association of Canada and has given the Fermor (2000) and William Smith (2003) lectures of the Geological Society of London. Euan has published nearly 200 papers in *Nature*, *Science* and leading Earth Sciences journals, plus several books: *The Young Earth: An Introduction to Achean Geology* (1987), and, on global change, *Leaving Eden* (1991), which has been translated into Chinese and German. With Nick Arndt, he edited *Komatiites* (1982), which has also been translated into Chinese.

Mary Fowler is currently Professor of Geophysics in the Department of Earth Sciences at Royal Holloway and also Deputy Dean of Research (Science) at Royal Holloway. She studied Mathematics at Cambridge, graduating with a first in 1972, followed by a PhD in Geophysics (Darwin College, Cambridge) supervised by Drummond Matthews and Brian Kennett. She did post-doctoral research in seismology as a Royal Society European Exchange Fellow at ETH in 1977–1978. Mary's early research was on mid-ocean ridges using seismology to investigate the crustal and uppermost mantle structure of the Mid-Atlantic Ridge, as well as the study of heat flow in the Earth. From 1978 to 1992 she was primarily at home with her three young children while writing her book *The Solid Earth: An Introduction to Global Geophysics*, Cambridge University Press (1st edition in 1990, 2nd edition in 2004). This book is used worldwide at universities for undergraduate and graduate courses, and as a standard research reference. In the intervening years, Mary held various positions including Honorary Professional Research Associate (1983–1991) and then Adjunct Full Professor (1991–2001) at the University of Saskatchewan, Canada. During this time, her research interests broadened to include continental crustal structure, formation of sedimentary basins, biogeography of mid-ocean ridge vent fauna and other (paleo-) environmental problems, as well as the early history of life. In 1992, she returned to work as Lecturer at Royal Holloway, then Senior Lecturer (1998) and Professor (2003). From 2002 to 2008 she was Head of the Earth Sciences Department, where she oversaw a substantial expansion in staff and student numbers along with a broadening of research focus from mainstream geology to also include environmental/atmospheric studies in working with resource and environmental industries. With this effort, the department is now among the leading UK Earth Science departments. Mary was awarded the Geological Society of London's Prestwich medal in 1996 for her major contributions to Earth Science.

Compared with Mars and Venus in the solar system, the Earth is unique in many ways: It has (1) continents and ocean basins, (2) granitic continental crust and basaltic oceanic crust, (3) plate tectonics, (4) massive hydrosphere, (5) numerous life forms of varying sophistication, (6) the free oxygen-bearing atmosphere, and (7) advanced forms of life like ourselves sustained by the oxygen-rich atmosphere. Yet, why the Earth is so unique remains a continued quest. In this invited contribution, Euan and Mary review the state-of-the-art knowledge on the origin and evolution of Earth's atmosphere over Earth's history, which touches on and links to all the Earth's uniqueness. I trust that this paper will excite enthusiastic younger minds to participate in this quest: Why is the Earth so unique?

Invited Review

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The evolution of the atmosphere in the Archaean and early Proterozoic

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Key steps in atmospheric evolution occurred in the Archaean. The Hadean atmosphere was created by the inorganic processes of volatile accretion from space and degassing from the interior, and then modified by chemical and photochemical processes. The air was probably initially anoxic, though there may have been a supply of oxidation power as a consequence of hydrodynamic escape to space of hydrogen from water. Early subduction may have removed CO_2 and the Hadean planet may have been icy. In the Archaean, as anoxygenic and then oxygenic photosynthesis evolved, biological activity remade the atmosphere. Sedimentological evidence implies there were liquid oceans despite the faint young Sun. These oceans may have been sustained by the greenhouse warming effect of biologically-made methane. Oxygenesis in the late Archaean would have released free O_2 into the water. This would have created oxic surface waters, challenging the methane greenhouse. After the Great Oxidation Event around 2.3 to 2.4 billion years ago, the atmosphere itself became oxic, perhaps triggering a glacial crisis by cutting methane-caused greenhouse warming. By the early Proterozoic, all the key biochemical processes that maintain the modern atmosphere were probably present in the microbial community.

Archean, atmosphere evolution, photosynthesis, methane, stromatolite, Hadean

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Though the boundaries are not fully defined, Earth's history is divided into four aeons: Hadean (4.5 to ~4 Ga ago, where 1 Ga = 10^9 years, also known as a Giga-annum, Ga), Archaean (~4.0 to 2.5 Ga and the main focus of this review), Proterozoic (2.5 to 0.54 Ga) and Phanerozoic (since 0.54 Ga) (Figure 1). Recently an earliest aeon, the Chaotian, has been suggested [1]. This would cover the time during which the solar system was forming.

The Hadean is, broadly speaking, the time after the Moon-forming impact that marked the end of the main accretion of the Earth, and before the start of life and the geological record [1]. Alternately, it can be taken as the time from 4.5–4.0 Ga ago. Initially, during the Hadean, the atmosphere was entirely the product of physical and chemical processes—any volatiles from the accretion of the planet that survived or post-dated the Moon-forming impact, and probably largely from the degassing of the interior. This atmosphere would be modified by photochemical action by sunlight, and by interaction with crustal rocks and magma, both from volcanoes and following large meteorite impacts.

Most likely the dominant gases in the very earliest air were carbon gases such as CO_2 and water, whether as ice, liquid or vapour. However, if subduction of the ocean floor began early in the planet's history, a significant part of the degassed CO_2 could have been reincorporated relatively quickly (within a few hundred million years or less) into altered ocean floor volcanic rocks and then subducted into the interior (see discussion in [2]). In this case, the planet's surface may have been icy.

At some stage perhaps between 4.2 and 3.8 Ga ago, life began. Immediately, life creates organic waste. Biogenic gases would have been added to the ocean/atmosphere system, and

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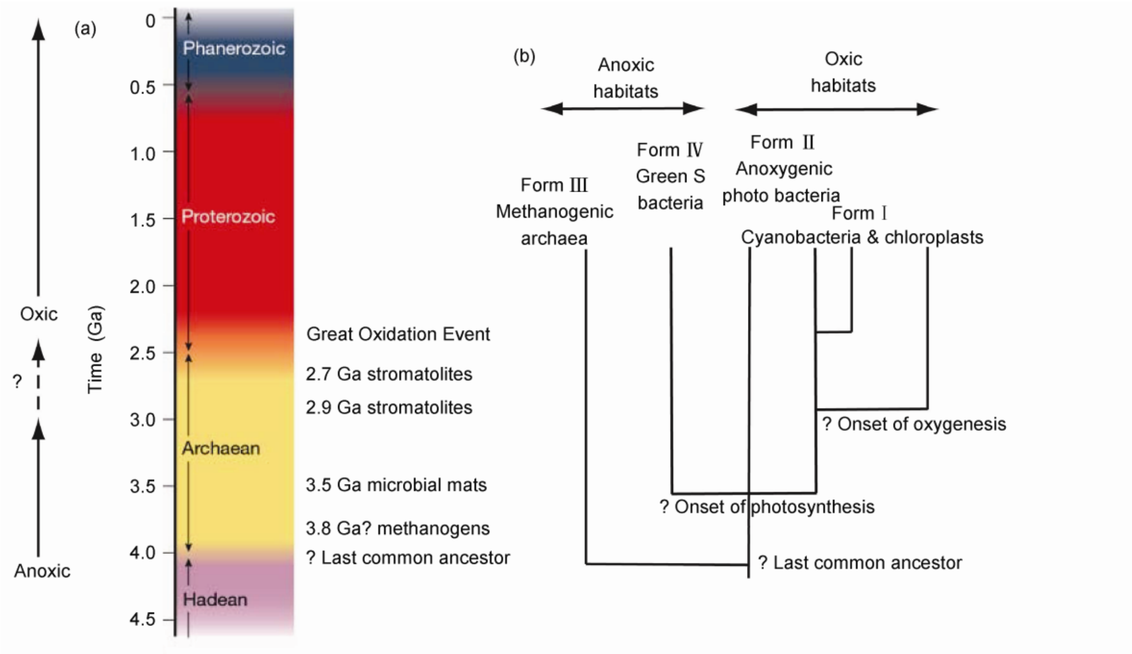

Figure 1 (a) Geological aeons (from [3]). Note that the Greek word transliterated "Archaean" in Latin and UK English is normally concatenated to "Archean" in US spelling. Both spellings are correct. (b) The forms of rubisco. Forms III, and rubisco-like protein Form IV occur in anaerobic organisms and may be older in evolutionary terms. Form II in anoxygenic bacteria and Form I in cyanobacteria and plant chloroplasts both occur in aerobic organisms. From [4].

as a result other chemical species would have formed in the air, including organic aerosols. Among the new chemical species the most interesting would have been methane, and perhaps also N_2O and maybe COS. This would have begun the first major period of biological management of the air.

A second great change then took place. The evolution of oxygenic photosynthesis produced quantities of oxygen as a waste product, dangerous to much of the life extant in the Archaean. Eventually the air became oxic with the waste oxygen. This was the Great Oxidation Event, which took place in the early Proterozoic aeon about 2.3–2.4 billion years ago (see [5] for a history of oxygen in the air). Since then, free oxygen has been present in the air. As an indirect result, methane has become a trace species. Waste that is dangerous to microbial life presents an opportunity for other cells. Throughout the Phanerozoic, the oxygen content has been high enough to sustain animal life. Today, the air is one-fifth oxygen and four-fifths nitrogen, both biogenic.

(i) Management of the air. The air today is made and managed by life: life has furnished its own home. Unlike the other major geochemical reservoirs, the atmosphere is small, fragile, quickly and easily changed. Over the aeons, life has so modified the products of volcanic degassing that the atmosphere has become a biological construction, managed by living organisms. The modern air, excepting the argon, is made and controlled by biochemical reactions that first evolved in Archaean bacteria and archaea. This sets the surface conditions of the planet and influences the evolution of the interior.

The major gas in the air, dinitrogen, N_2, is emitted by diverse bacteria, including both the anammox planctomycetes (which may be very ancient) and the denitrifying bacteria. On the natural (pre-industrial) world their output was probably equally balanced by uptake during nitrogen fixation, so the N_2 content was stable. Most nitrogen fixation is biological, but N_2 is also fixed by lightning: this flux depends on the water vapour content of the air, which in turn depends on the greenhouse gases. Achieving a balance between nitrogen fixation and emission sets the mass of nitrogen in the atmosphere, and hence the pressure of the air, which influences greenhouse warming. The nitrifying and denitrifying reactions are probably very old. Nitrous oxide, a potent greenhouse gas, is also part of the nitrogen cycle. The distribution of nitrogen between atmosphere, the earth's crust, and the planetary interior is not well constrained. Goldblatt et al. [6] estimated that the continental crust contains 1×10^{18}–2×10^{18} kg N, much of which it may have collected since ~2.7 Ga ago. The mantle may contain more.

Oxygenic photosynthesis may have evolved 2.9 billion years ago or earlier [7,8], from prior anoxygenic photosynthesisers [9]. The first oxygen-emitter must have been an ancestral cyanobacterial cell, distantly related to the very diverse array of modern cyanobacteria. Diversification was likely very rapid in the late Archaean (2.9 to 2.5 billion years ago) [3]. Some of the early cyanobacteria probably lived as "stromatolites" (layered sediments made by biofilms), while other cells probably quickly evolved to fill the niche for free-living plankton. Chloroplasts in modern algae and plants are descended from early cyanobacteria that were symbiotic with ancestral eukaryote cells. Just as astronauts can walk on the Moon in space suits, so the cyanobacteria within plants are wearing "land-suits", and thereby can even occupy the desert places of the continents.

Biological respiration consumes oxygen to produce CO_2. The oxygen content of the air represents the balancing level between photosynthetic emission and respiratory uptake. The carbon dioxide uptake is the obverse side of the coin: CO_2 is given out by respiration and fixed by photosynthesis, while emission of equivalent moles of oxygen is the reverse. Most of the fixed carbon in organic matter is quickly respired again, but some of the C is sedimented as organic debris into seabed mud. In the organic-rich mud deposit, available oxidation power is quickly consumed. Methane, which is arguably the most interesting of the greenhouse gases, is emitted by methanogenic archaea, which thereby return the organically fixed carbon to air. Hence their productivity is indirectly linked to the amount of respiration and photosynthesis. In the modern world, some of the emitted methane is destroyed in the upper layers of the sediment by anaerobic microbial oxidation. Other methane is oxidised aerobically in the topmost mud. Methane bubbles passing upwards in water are today microbially oxidised by methanotrophs. For methane that does enter the air, the atmospheric oxidation power wins. Atmospheric methane is destroyed by OH (which is created from water in the oxygen-rich air by photolysis), and is also taken up by methanotrophic bacteria in soil.

In the air, only argon is abiotic, emitted by radioactive decay of crustal rocks. Yet even the argon emission is indirectly controlled by water, as it is liberated by erosion of potassium-rich rocks, themselves created in magmatic events, many of which depended on subduction of oceanic water.

The total mass of the atmosphere is small – 1 kg cm^{-2} of surface area. This means that atmospheric composition can easily be altered by biogeochemical or volcanic processes, acting over a few tens of millions of years. In the Archaean geological record, where a million years is as a moment, atmospheric change is not gradual. Isotopic data suggest change comes relatively abruptly, a shifting of the gears on the geochemical engine. The controlling mode of operation can change suddenly and catastrophically. Swift change is not only an Archaean phenomenon. It has happened in the past twenty thousand years in the glacial-interglacial changes and in the great warming event on the Palaeocene-Eocene boundary 55 million years ago, which may have been driven by methane emissions (e.g. see [10]). Further back in the past, the Earth has been through great cold crises ("snowball Earth events"), for example in the late Precambrian 600–700 million years ago. Even more major was the reconstruction of the entire atmosphere in the Great Oxidation Event, 2.3–2.4 billion years ago [5].

(ii) Rubisco and Nitrogenase. Two families of enzymes manage the atmosphere: these are the rubiscos and the nitrogenases. The atmospheric greenhouse is mainly the product of gases managed by these enzymes.

Rubisco is of great antiquity [11], and nitrogenase probably also. Rubisco (ribulose 1,5-bisphosphate carboxylase/ oxygenase), as its name implies, can work either way, to capture C into life from CO_2 in the air (and thereby permit oxygen emission), or to assist in its respiration out of life into the atmosphere (and thereby permit oxygen-burning).

There are several forms of rubisco and rubisco-like-proteins [10]. Form I enables oxygenic photosynthesis. It oc- curs in cyanobacteria and chloroplasts in algae and plants, and may have evolved about 2.9 billion years ago [8]. Rubisco's Form II occurs in aerobic anoxygenic photosynthetic bacteria. Form III is found in anaerobic organisms, both bacteria and archaea such as methanogens, while Rubisco-like proteins (Form IV) occur in anaerobic bacteria.

Nitrogenase occurs in nitrogen-fixing bacteria and archaea and is the key enzyme in nitrogen fixation from N_2 in air into life. It ranks among the most abundant proteins in the biosphere. Nitrogenase consists of two proteins, an iron protein and an iron-molybdenum protein. It is very sensitive to molecular oxygen, which can irreversibly inactivate it. Nitrogen fixation is metabolically very expensive and very costly in hard-to-acquire elements like iron. Yet, like rubisco, nitrogenase appears to be very inefficient.

(iii) Greenhouse warming. Over time, the Sun steadily brightens as it ages (e.g. see [2]). It was much fainter in the Archaean than now. Even today, under a strong old Sun, the Earth verges on glaciation. Yet sedimentary deposits occur throughout the geological record, showing that liquid water oceans have existed throughout the past 4 billion years, except possibly in rare "snowball" events. One possibility is that this record implies that to sustain liquid oceans, the natural greenhouse warming effect of the air was larger in the past, and that this warming increment has been reduced over time, so maintaining a steady surface environment by compensating for the increase in solar insolation. Another possibility discussed further below, is that albedo was different.

1 The Hadean atmosphere

The end of the proposed Chaotian aeon can be taken as the time of the great Moon-forming impact [1,12], when the proto-Earth was struck by a planet about the size of Mars, roughly 4.5 Ga ago. The impact probably melted the entire planetary mantle, and ejected a vast debris of splatter, some of which formed the Moon, though much fell back to Earth. It also may have removed much of a deep primaeval inventory of volatiles, then replaced by secondary degassing by volcanism from the molten interior.

The impact spun and tilted the Earth, imparting the angular momentum that today, after billions of years of tidal dissipation, gives us a 24-h day and clearly defined winter and summer seasons. Both the day/night cycle and the seasonality are key factors in the habitability of the planet, giving equable temperatures to all longitudes and most latitudes, and a small pole-to-equator thermal gradient. In short, the impact 4.5 billion years ago determines the length of day, weather, tides, phases of the Moon and eclipses in 2011.

At the start of the Hadean, the early Earth was bombarded by planetesimals up to several hundred kilometres in diameter. Sleep et al. [13] pointed out that under the weak early Hadean Sun, Earth's surface may have been icy, except immediately after great impact heating or volcanic events. The oldest material known on Earth is in zircon crystals from Western Australia, preserved as detritus in younger sediment. These crystals are up to 4.3 to 4.4 Ga old, and must have formed in very early continental material [14]. Magmas containing zircons typically form as a consequence of subduction (i.e. cold dense oceanic plate falling back into the planetary mantle). The oxygen isotope geochemistry of the very old zircons implies that the surface was covered in cool water oceans [15]. For very long periods the planetary surface may have been frozen water ice, losing heat to space. Deep under the ice and insulated by it, warm water would have existed above the many active volcanic vents, fed with hot highly magnesian lava from the molten mantle.

At intervals of millions to hundreds of million years in the Hadean, one or more great impacts would have occurred, when the Earth was hit by bodies say, 200–300 km in diameter. If such a body did hit the planet, the energy from the impact and resultant volcanism would be capable of vaporising the entire surface water inventory [13] by heating the water to 350°C or more (when the whole ocean boils, air pressure rises to 350 bars). After such events, for a few thousand years the air would be steam, then it would condense to a brief liquid ocean phase, then return to ice. Smaller impacts, by bodies of 100–200 km, would be capable of heating the ocean to 100°C or more, sterilising any early life. Thus any surface life that evolved at this time would not last long – it would be killed in the freeze-fry cycle. Sometime between about 4.2 and 3.6 Ga ago, the bombardment ran out of ammunition [16]. In the period from 4.4 to 3.8 Ga ago, one possibility is that there may have been only few or no giant impacts and Earth may have been comparatively peaceful. Indeed, impacts could have been beneficial in stirring up hydrothermal processing. If so, the origin of life could have taken place at any time between 4.4 and 3.85 Ga. If the first life existed in the crevices of deep hydrothermal systems, then it may have been protected from all but the very largest impacts. Ryder found no justification for the claim that life originated as late as 3.85 Ga in response to the end of hostile impact conditions. Since then, though large impacts have occurred, the Earth's water has not been sterilised.

2 Early to mid-Archaean life: anoxygenic photosynthesis

The oldest rock on Earth (as distinct from relict crystals after erosion and redeposition) is arguably (there are other claims) the Acasta gneiss, from NW Canada [17]. This is roughly 4 Ga old, latest Hadean.

The oldest large-scale rock suite, formed around 3.8 to 3.6 Ga ago, is the Isua Greenstone belt, in what is now west Greenland. A "greenstone belt" is a collection of rocks typically around 30–50 km long and 10–20 km across, sometimes much larger, that formed on the Earth's surface and which still recognisably retains features of its original character. All old rocks are metamorphosed, but greenstone belts have relatively low-grade metamorphism (i.e. heated to say no more than a few hundred centigrade, so that many of their minerals are green in colour) and deformation has not destroyed original textures. In the Isua belt, a wide range of original features such as sedimentary and volcanic textures can be recognised. Although there are other examples of very old, highly metamorphosed material, Isua is the oldest major area on the Earth's surface that has been well preserved.

Though there are other claims, it is in Isua that the earliest presumptive evidence for life on Earth is found. Some rocks contain carbon dust that is highly fractionated isotopically, rich in ^{12}C [18]. Such fractionation is characteristic of biological processes. It is possible that this dust could have been made abiotically in space before falling to Earth, but this is very unlikely, given the abundance of the carbon and the sedimentological facies. The simpler explanation is that it comes from dead plankton. In other Isua rocks, sulphur isotopes [19] also suggest biological activity. Sulphate reduction may date from this time and pyrite is present. Methanogenesis, which leaves a record of highly fractionated C isotopes, may also be very old.

In general, early Archaean life may have existed in the proximity of submarine hydrothermal systems at the rock/water interface. Here magmatic chemical species, derived from the somewhat more reduced mantle of the planet, came into contact with the somewhat more oxidised chemistry of the ocean/atmosphere system. At the top of the atmosphere, hydrogen loss to space may have provided net oxidation power, and lightning could have fixed nitrogen. The date of the earliest photosynthesis is unknown. It seems likely that the first photosynthetic organisms were anoxic, using H_2, H_2S or CH_4, or FeO for example.

The mid-Archaean record comes mainly from the Barberton Mountain Land in South Africa, and the Pilbara in Western Australia. A wide variety of organo-sedimentary rocks has been described. Though most interpretations are controversial, it is very likely that microbial life was abundant. In the Pilbara, the 3.45 Ga Strelley Pool Chert has well-preserved, widespread, long-lived stromatolites (characteristic laminated textures, often built by microbial consortia) in a reef laid down in a lake [20], in an anoxic setting. Evidence for photosynthetic microbial mats 3.4 Ga ago also occurs in the Barberton belt, South Africa [21].

Although it is possible that oxygenesis dates back as far as Isua times [22], but see also [8], much of the 3.5 to 3.0 Ga old mid-Archaean evidence suggests anoxic conditions, with a CO_2-rich atmosphere [23]. This is consistent with the suggestion that anoxygenic photosynthesis came before oxygenic [9]. The presence of sedimentary sulphides that show mass independent fractionation of Sulphur-33 strongly implies there was no oxygen in the early to mid-Archaean air [24].

Most likely, the top layers of mid-Archaean biological communities were dominated by anoxygenic photosynthetic bacteria using the enzyme Rubisco II. It is possible that a full microbial sulphur cycle operated, with both sulphate reduction and photosynthetic sulphide oxidation. However, though isotopic evidence suggests sulphate reduction was abundant [19], the return process is more difficult to prove as isotopic fractionation is small.

The mid-Archaean geological record includes widespread sediments laid down by liquid water. It is possible that the climate was very warm (70°C) [25] though there is no consensus on this. Whatever the temperature of the ocean, it was liquid. Given that the Archaean Sun, in which less dense hydrogen was more abundant than now, was fainter than today, the maintenance of warm temperatures implies there must have been a powerful atmospheric greenhouse. This would most likely have been sustained by both methane and CO_2, emitted by biological sources (i.e. methanogens). Carbon isotope evidence for fractionation by methan- ogenic archaea (e.g. see [8]) supports this contention, strongly suggesting the presence of methanogens and hence methane emission. If the atmosphere were anoxic, then the methane would have had a long lifetime in the air and would have accumulated.

3 Late Archean life: oxygenesis

Around 2.9 Ga ago, quite different rocks appeared. These were large microbial carbonate reefs, not greatly different from modern examples extant today in places like Shark Bay, Australia. They occur as "stromatolites" (sedimentary structures built by microbial consortia) at Steep Rock in Canada (Figure 2), where the reef is kilometres long [26], in the Pongola Belt in South Africa [27], and at Mushandike in Zimbabwe [28]. All three sequences are, coincidentally, dated as over 2.83 Ga old: the rounding of ~2.9 Ga, approximating the likely age, is used here for convenience.

In these examples, the reef material is sedimentary carbonate, including abundant limestone, and has formed in shallow marine settings, implying the water was not markedly acid, and by implication that the CO_2 level in the air was modest. There is evidence from Mo and Fe isotopes that the water was locally oxic, not anoxic [29], and S-33 evidence also suggests oxic episodes in the Archaean [30]. Carbon isotopes in organic matter in the rocks strongly suggest capture from the atmosphere by Rubisco I—using cyanobacteria: the start of oxygenic photosynthesis [8].

Here lies a problem. The high organic productivity that must have sustained the reefs would have extracted carbon dioxide from the air. Release of oxygen into the air would have supported photochemical reactions that led to the destruction of methane in the air. Both processes would have reduced the greenhouse warming, risking glaciation. Indeed, in the Pongola succession, and in other rocks in South Africa, there is possible evidence of glaciation at this time. If oxygenic photosynthesis by cyanobacteria evolved around 2.9 Ga ago [8], its onset may have been associated with the first signs of glaciation in these 2.9 Ga rocks in southern Africa.

Around 2.7 Ga ago, at a time of massive volcanism around the world (and hence CO_2 release from lavas), there

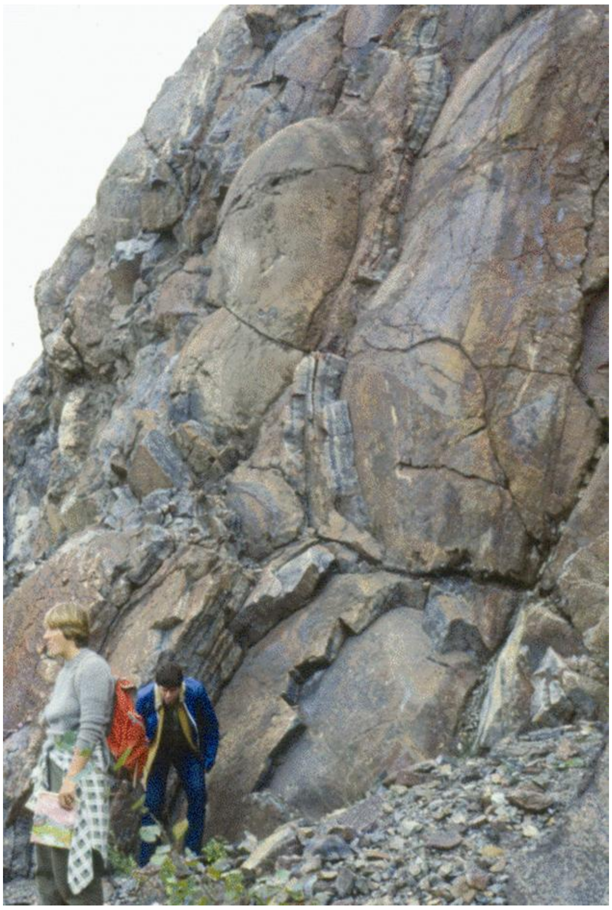

Figure 2 Stromatolites, Steep Rock Lake, NW Ontario, Canada. These >2.8 Ga stromatolites are laid down unconformably on basement. The carbonate unit is hundreds of metres thick and >10 km long, perhaps the oldest preserved carbonate reef.

is abundant record of stromatolitic limestones. In particular, the 2.7 Ga record shows a wide array of Australian examples as well as the Belingwe stromatolites in Zimbabwe (Figure 3) [8]. The Belingwe rocks include a wide variety of shallow-water sands, shales and limestones, in two separate successions. The 2.7 Ga Manjeri Formation includes small-scale limestone reefs, while the ~2.65 Ga old Cheshire Formation has luxuriant stromatolite growth in very shallow-water and evaporitic lagoons.

Carbon isotopes from the Belingwe carbonates are most simply explained as the product of oxygenic photosynthesis [8,31]. Carbon isotopes are usually expressed in a delta notation, denoting difference from a carbonate standard in per mil (per thousand) units (‰), where the standard is 0. In these terms, $\delta^{13}C_{carbonate}$ values in the Cheshire carbonates are tightly clustered around +0.2‰±0.3‰ and $\delta^{13}C_{organic\ matter}$ –28.6‰±3.3‰. Modern carbonates and organic carbon captured into cells by oxygenic photosynthesis have very similar partitioning of carbon isotopes, and the implication is that organic carbon in the Belingwe rocks was captured from the ocean/atmosphere system by the same processes as today, in consortia sustained by oxygenic photosynthesis. This inference is supported by Mo isotopes, which strongly suggest the water was locally oxic, at least in the Belingwe lagoons [29] and capable of mobilizing Mo during terrestrial weathering. In contrast, shales in the Belingwe rocks appear to have been laid down in anoxic settings (like much modern pond mud) and have much more fractionated carbon, with $\delta^{13}C_{organic\ matter}$ as low as –45‰. This extreme fractionation is typically a sign of methanogenic carbon.

There is ample other evidence of complex Archaean life. Brocks et al. [32] found a wide variety of molecular fossils in bitumens extracted from 2.7 to 2.5 Ga old shales in the Fortescue Group, Pilbara, Australia. If the bitumens are indeed Archaean in age (and not contamination: there is controversy on this point), then hopanes imply bacteria were present. In particular, 2α-methylhopanes are evidence for cyanobacteria and hence possibly oxygenic photosynthesis [33]. The ^{33}S evidence from the ~2.7 Ga record is complex, but also implies episodes in which oxygen was abundant. For example, this S isotope evidence has been reported in 2.76 Ga lake sediments in the Pilbara, Australia [30].

The dating of the onset of oxygenic photosynthesis is controversial. Kopp et al. [34] put the evolution of oxygenesis much later, at ~2.3 Ga ago, at the time of a great glaciation. Canfield [5], in a comprehensive and careful review of the debate about the start of oxygenesis, suggests a date of 2.7 Ga, possibly earlier, while there is also possible evidence for early oxygenic cyanobacteria [33]. Weighing the diverse evidence, Nisbet et al. [8] preferred a date of ~2.9 Ga ago (Figure 4), though there is the possibility that it is even older. Note that Ohmoto et al. [30] argue for an early start of oxygenesis, which Rosing and Frei place possibly even in the earliest Archaean [22].

Whether or not oxygen was present in the air of 2.9 Ga and 2.7 Ga ago, there is however consensus on one point, that after about 2.3 Ga ago, the air has been oxic. Sometime around 2.3 to 2.4 Ga ago, the O_2 content of the air increased strongly and permanently. This has been termed the Great Oxidation Event [5]. Since then, the atmosphere and the uppermost layers of the sea have contained free O_2.

4 Models of the Archaean air

Models of the Archaean atmosphere are as diverse as the, often contradictory, evidence on which they are based. Figure 4 shows a schematic (and speculative) synopsis of the oxication history of the air [4]. There are some general (though not wholly accepted) points of agreement. Nisbet et al. [8] considered that prior to about 3 Ga ago, the geochemical evidence from sediments implies the air was probably anoxic [11]; after 2.3 Ga ago it has been oxic. In the intervening period, between 2.9 and 2.4 Ga ago, oxygenic photosynthesis appears to have been active and free oxygen may have been present in surface waters, but not in the air. Given the low solubility of O_2, the water would have saturated easily.

The greenhouse gas limits are critical to this debate. The modern pre-anthropogenic Earth had from 250–300 parts

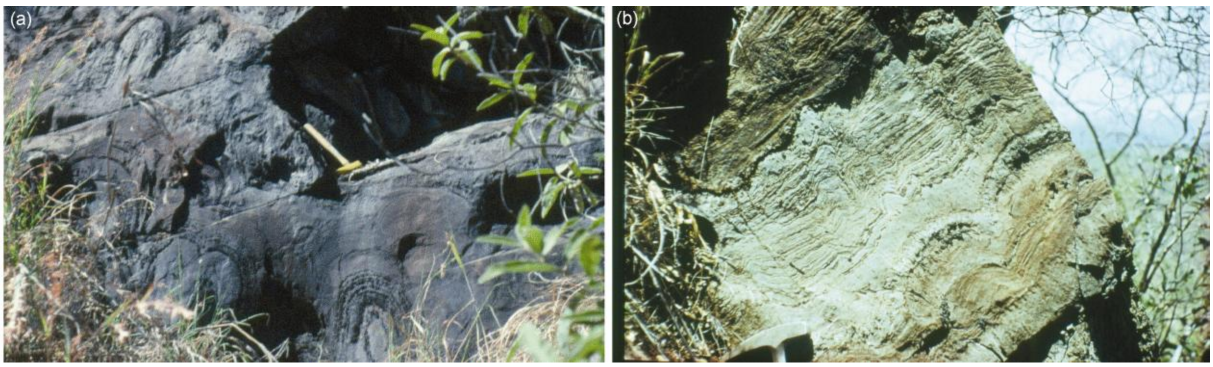

Figure 3 Stromatolites, >2.6 Ga old, in the Cheshire Fm., Belingwe Greenstone belt, Zimbabwe. (a) Outcrop; (b) detail. These shallow-water deposits are very well preserved and show a wide variety of forms. They outcrop along a strike length of kilometers.

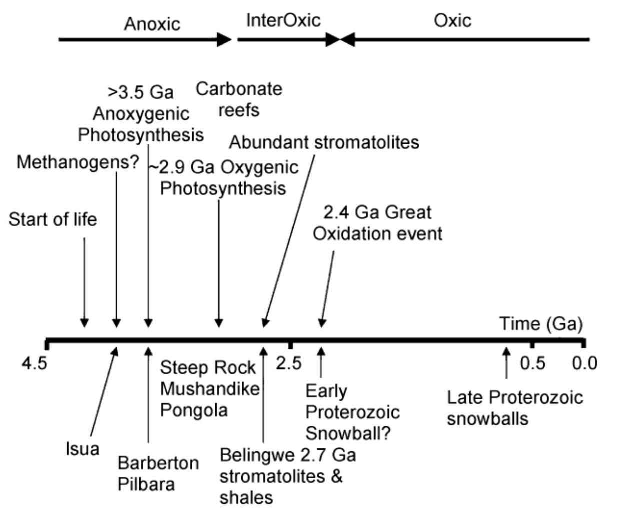

Figure 4 Simplified event chart to show the possible history of oxygen in the air.

per million of pre-industrial CO_2 and ~1 ppm of pre-industrial CH_4. These two carbon gases induce evaporation of the main greenhouse gases, water vapour, so that the global temperature is raised from about –18°C to +15°C. Today the greenhouse warming increment of the natural (pre-anthropogenic) air is about 33 K.

In the early Archaean with a much fainter Sun, this increment must have been higher. To maintain a greenhouse warming strong enough to support liquid oceans in Isua (3.8 Ga) times, the air probably had abundant CO_2 and perhaps (even so early), other biologically managed gases. The most obvious of these is methane, which Lovelock [35] suggested played a major role in planetary management, once life had begun. On the modern Earth, with abundant CO_2 in the air but little methane, the incremental impact of adding a molecule of methane to the air is much greater than a molecule of CO_2, in terms of blocking the infra-red sky and trapping heat in the atmosphere/ocean system. In the Archaean, with more methane present, this disparity in warming power may have been less, but nevertheless significant.

Rosing et al. [36] pointed out that the ubiquitous presence of mixed-valence Fe (II-III) oxides in the mineralogy of Archaean sediments is difficult to reconcile with the hypothesis of high concentrations of greenhouse gases in the Archaean air. Their suggested way out of this puzzle is that the albedo of the young planet, with small land areas and large oceans may have been lower than now, especially if there were few dust particles and biological aerosols to nucleate clouds. A low-albedo early Earth may have been able to sustain liquid water on its surface, even under the fainter Sun. A higher pressure, with consequent pressure-broade- ning of the greenhouse warming, may also have contributed to keeping the planet warm.

On the late Hadean Earth there would have been some abiotic methane production, made by water-rock-CO_2 reactions around volcanic vents. It is possible that the small amount of methane observed on Mars was made this way and then stored in clathrates, to be released by seasonal warming. But the main source of Earth's methane is biological: reprocessing of biological debris by methanogenic archaea. Today the atmospheric methane budget is almost entirely made by biological sources, either directly or from fires, or from stored methane produced by maturation of carbon rich deposits. Much of the output is directly from methanogenic archaea, either in wetlands or shallow natural gas. Other sources are geological, from geothermal heating of organic matter, but these too recycle organic debris. Methane's lifetime in the air today is about a decade, before the C atom is oxidised to CO_2 and becomes much less potent as a warmer.

In the anoxic Archaean air, methane's lifetime could have been orders of magnitude greater, with the consequence that its atmospheric burden could have built up from sources not greatly larger than today. Once biological carbon capture had begun (for instance by sulphate reduction), geothermal processing of the sedimentary build-up of organic debris would have provided an abundant methane source. Carbon isotope evidence suggests methanogenic archaea, which produce debris very depleted in ^{13}C, are very ancient [19]. Once they evolved, recycling of organic debris into methane would have become much more rapid and important than via slow geological maturation. This would have had a strong warming impact.

A productive ecosystem probably existed 3.4 Ga ago [21]. If so, this would likely have been based on anoxygenic photosynthesis under an atmosphere that was oxygen-free. Kharecha et al. [37] modelled such a system, and found that although methane production may have been between a third and 2.5 times modern emission, the atmospheric concentrations of methane in the anoxic early to mid-Archaean air could have been very high, from 100 ppm to as much as 35000 ppm (3.5%) (Compare this with ~1 ppm in the pre-industrial modern air). Thus the air 3.4 Ga ago may have had high enough greenhouse gas burdens to sustain a warm surface climate, possibly even warmer than today (some suggestions are that the surface temperature was 50–70°C). Moreover, if the methane/CO_2 ratio were high, an atmospheric smog could have developed that blocked incoming ultraviolet light, protecting life on the planetary surface.

By the period between 2.9 Ga ago, and 2.7 Ga ago, a highly productive global ecology may have been established. Figure 5, modified from [35], is a speculative reconstruction of the history of the air, and Figure 6, from [4] shows possible processes in the late Archaean atmosphere. Most of the major biochemical reactions that manage the modern atmosphere were present in the microbial ecology. The air was warm enough to sustain stromatolite reefs of carbonate rock (including limestones) and abundant other water-laid

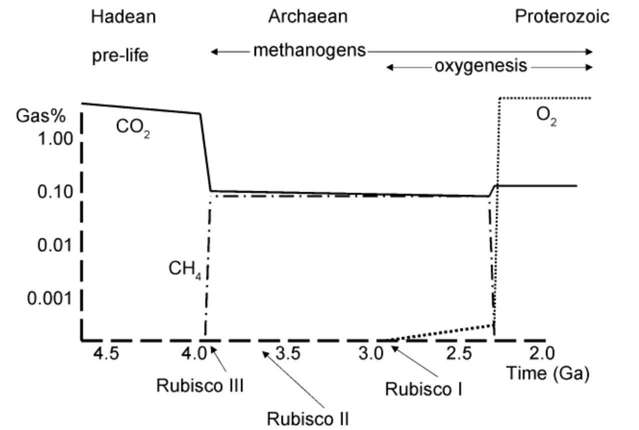

Figure 5 Possible evolutionary history of the air (modified from [35] in [4]).

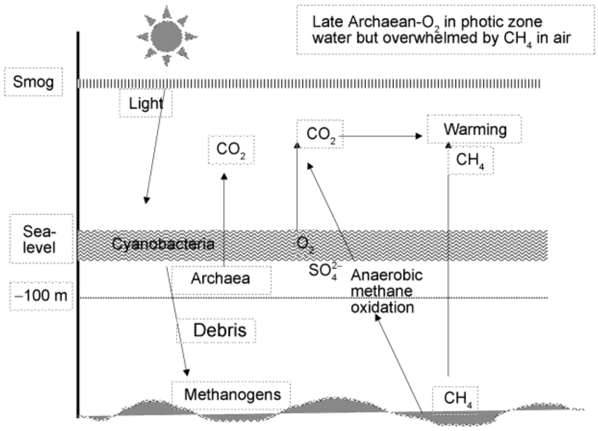

Figure 6 Possible processes in the late Archaean atmosphere. From [4].

deposits. The presence of limestone in the stromatolites suggests water pH was not especially acid, implying modest CO_2 abundance in the air (and probably therefore a methane increment to the greenhouse). In anoxic upwelling waters anoxygenic photoautotrophic bacteria may have catalyzed Fe(II) oxidation to form Fe deposits. Figure 7, from [3] shows a synopsis of the conditions.

The evolution of oxygenesis would have challenged this. Free oxygen in the air will eventually reduce the methane lifetime. That cuts the temperature. In short, oxygen emission risks glaciation and shut down of organic productivity. This may have been the cause of the apparent glaciation around 2.9 Ga ago, and also a large scale glacial event about the time of the Great Oxidation Event, ~2.3–2.4 Ga ago [4]. This was the birth of the modern oxygen rich air. During the Proterozoic, eukaryote respirers became widespread as plankton. Near the end of the Proterozoic, the greenhouse crashed and major glaciations occurred ("snowball Earth" events). At this stage, the oxygen burden rose further and animal life evolved.

The specificity of Form I rubisco for CO_2 appears to be exquisitely tuned to its task [38,39] and may be the key control on the $O_2:CO_2$ ratio of the modern air. Thus rubisco, via the biological productivity that depends on its catalysis, directly controls atmospheric CO_2. This implies that rubisco I is the primary control on the modern atmospheric greenhouse. The second C greenhouse gas, methane, is a product of anaerobic rubisco III methanogens. These in turn rely on recycling the biological debris that falls to the sea-bed mud and underlying sediment. Most of this debris includes carbon fixed by the productivity of Rubisco I oxygenic photosynthesisers. Finally, the third major biological greenhouse gas, N_2O, depends on the N cycle and hence nitrogenase. Nitrogenase has been described as evolutionarily crippled, inefficient, yet it is interesting to speculate whether it may also be tuned as finely to its task as rubisco may be.

The biological control on the greenhouse goes further. For a molecule of CO_2, CH_4 or N_2, the radiative forcing power and hence the Global Warming Potential depends in part on the ambient pressure. Pressure is set by the N_2 burden that is mainly maintained by microbial nitrogen fixation, with a minor input also from lightning. Thus there is a feedback between nitrogenase and the greenhouse. Goldblatt et al. [6] assumed a rate of transfer of nitrogen from the ocean crust and sediments to the mantle (subduction minus volcanism) of about 7.5×10^8 kg a^{-1}, 2×10^{18} kg N would have been subducted to the mantle since 2.7 Ga. Subduction rates in the past may well have been higher, so this may represent a lower bound. Thus the atmospheric nitrogen inventory in the late Archean may have been much higher than the present amount [6]. A higher pressure would have enhanced the warming impact of the greenhouse gases, thereby stabilizing the climate.

Finally, water vapour, the most important greenhouse gas, responds to warming by the other gases. Without this natural greenhouse warming, the temperature of the Earth's surface would be around –18°C. Water is part of the original chemical inventory of most planetary bodies, but its common phase on the planet's surface – as "rock" (ice), liquid, or gas, or even completely lost to space, depends on the surface temperature. Thus although water is the major greenhouse gas, it is those feedbacks involving the organically produced gases, CO_2, CH_4 and N_2O, that manage the abundance of water vapour in the modern air.

On the modern Earth, Rubisco I's molecular specificity [38] is matched on a macro-scale by compensation controls [40]. If there is more CO_2 in the air than the compensation limit, and other resources are adequate, then carbon is taken up by photosynthetic cells. Conversely, if there is more O_2 than the barrier limit, then it is too disadvantageous to carry out photosynthesis, which is overwhelmed by photorespiration, and net photosynthetic growth ends. There is as yet no full understanding of how the molecular specificity exerted by rubisco is expressed at the macroscopic and global levels via the compensation controls on O_2 and CO_2.

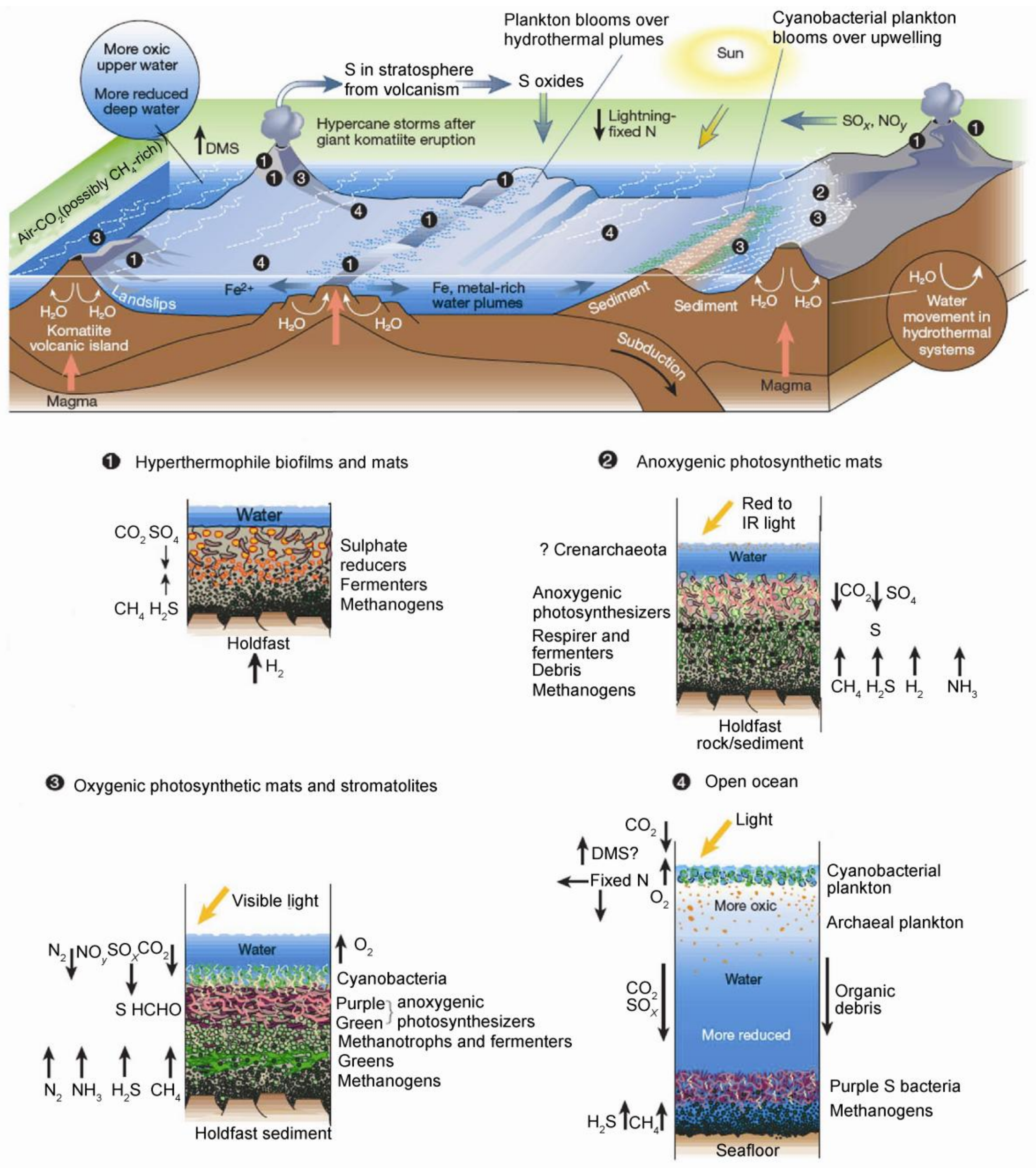

Figure 7 Synopsis of the late Archaean environment. Main diagrasm: general setting. Inset columns: local micro-habitats in microbial mats located in settings indicated by numbers in main diagram. Modified from [3].

The causes of the Great Oxidation Event are much debated [5], and it may have been accompanied by a decline in the amount of the UV-shielding molecule OCS in the air, which would have previously played an important supporting role in maintaining the clement surface conditions [41] under the faint young Sun. There is no consensus, however, on why the atmosphere changed so radically in the Event. Perhaps the Earth system may be bi-stable, with both anoxic and oxic stable states [42]. Yet the primary biochemical reactions of methanogenesis, photosynthesis, and respiration, as well as nitrogen fixation, are very ancient and were likely present in the Archaean. Our modern oxic world is based on that ancient anoxic Archaean ecology.

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