Review article

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Co-evolution of early Earth environments and microbial life

Timothy W. Lyons [1,2,9] ✉, Christopher J. Tino [1,9] ✉, Gregory P. Fournier [3], Rika E. Anderson [2,4], William D. Leavitt [5,6], Kurt O. Konhauser [7] & Eva E. Stüeken [2,8]

Abstract

Two records of Earth history capture the evolution of life and its co-evolving ecosystems with interpretable fidelity: the geobiological and geochemical traces preserved in rocks and the evolutionary histories captured within genomes. The earliest vestiges of life are recognized mostly in isotopic fingerprints of specific microbial metabolisms, whereas fossils and organic biomarkers become important later. Molecular biology provides lineages that can be overlayed on geologic and geochemical records of evolving life. All these data lie within a framework of biospheric evolution that is primarily characterized by the transition from an oxygen-poor to an oxygen-rich world. In this Review, we explore the history of microbial life on Earth and the degree to which it shaped, and was shaped by, fundamental transitions in the chemical properties of the oceans, continents and atmosphere. We examine the diversity and evolution of early metabolic processes, their couplings with biogeochemical cycles and their links to the oxygenation of the early biosphere. We discuss the distinction between the beginnings of metabolisms and their subsequent proliferation and their capacity to shape surface environments on a planetary scale. The evolution of microbial life and its ecological impacts directly mirror the Earth's chemical and physical evolution through cause-and-effect relationships.

Sections

[1]Department of Earth and Planetary Sciences, University of California, Riverside, CA, USA. [2]Virtual Planetary Laboratory, University of Washington, Seattle, WA, USA. [3]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA. [4]Biology Department, Carleton College, Northfield, MN, USA. [5]Department of Earth Sciences, Dartmouth College, Hanover, NH, USA. [6]Department of Chemistry, Dartmouth College, Hanover, NH, USA. [7]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada. [8]School of Earth and Environmental Sciences, University of St Andrews, St Andrews, UK. [9]These authors contributed equally: Timothy W. Lyons, Christopher J. Tino. ✉e-mail: timothy.lyons@ucr.edu; christopher.tino@ucalgary.ca

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Introduction

The history of microbial life on the early Earth is closely linked to the history of the oceans, land and atmosphere, which is largely reflected in the evolution of planetary oxygenation and its impact on the biosphere. With the emergence and expansion of molecular oxygen (O_2) production by photosynthetic cyanobacteria and the concomitant increases in the availability of O_2, a vastly wider array of microbial niches emerged. Abundant supplies of varied oxidants and nutrients fuelled the diversification and proliferation of both aerobic and anaerobic microbial metabolisms. At the same time, microorganisms challenged or excluded by O_2 were forced to adapt to an evolving global redox landscape marked by protracted oxygenation, which progressed from surface oceans to the atmosphere and, finally, to abyssal depths over billions of years. In this Review, we provide brief updates on our understanding of this redox evolution across space and time. Microbial metabolic pathways are then mapped on this history to reveal cause-and-effect relationships with O_2 and other redox-dependent chemical ingredients essential to life.

Discussions on the rise of O_2 have focused on three main mechanisms: the evolution of oxygenic photosynthesis; the production and burial of organic matter (that is, photosynthetic biomass); and the countering effects of oxygen sinks, such as hydrogen and methane in the atmosphere, ferrous iron (Fe(II)) in the oceans and crust, and the possibility of related changes in the redox state of the mantle. There are several models that attempt to explain the so-called Great Oxidation Event (GOE), which led to permanent O_2 accumulation in the atmosphere. Importantly, it is unlikely that a single factor can account for this transition. For instance, increased biological O_2 production may have been less relevant than declining O_2 sinks. These sinks likely included first-order plate tectonic factors such as the growth and changing compositions of continental land masses and related O_2 buffering through reactions with minerals at the surface and gases released from Earth's interior[1–3].

The general timing of the GOE is well known (Fig. 1), although the specifics regarding its dynamics and duration are less certain, partially due to its occurrence likely hundreds of millions of years following the onset of cyanobacterial production of O_2 and early surface ocean oxygenation around 3 billion years ago[4,5]. A growing body of geochemical data point to transient O_2 accumulations in the oceans[3,6] and the atmosphere[7] spanning a few hundred million years before the permanent accumulation of O_2 in the atmosphere roughly 2.2 billion years ago[8], although debates remain[9–11]. This transition was likely followed by a period of elevated O_2 in the oceans and atmosphere linked to extensive organic matter burial that lasted until approximately 2.1–2.0 billion years ago[8]. The GOE was a protracted transition, rather than an event, that extended from approximately 2.5–2.4 billion to 2.1–2.0 billion years ago. A wide array of data, expressed through diverse paleoenvironmental tracers[6,8,12], suggest a complex interval of rising and falling O_2 across the GOE, particularly in the atmosphere and surface oceans. Increases in atmospheric oxygenation continued in a non-uniform fashion for another ~1.6 billion years, leading to the establishment of persistently oxygenated deep oceans roughly 360 million years ago[13,14]. These details are important to the storyline because rising but dynamic O_2 levels were accompanied by fundamental shifts in the bioavailability of diverse redox-dependent constituents on land and in the oceans, many of which were and remain central to microbial life (for example, nitrogen and phosphorus, enzymatically essential trace metals, and oxidants such as sulfate and nitrate that fuel key metabolisms).

The reconstruction of microbial evolution and its relationship to the environment − often referred to as a co-evolution because environmental change drives the patterns of life while also being shaped by important biological steps − relies on a diversity of approaches. Most notable are significant advances in geochemical analyses of the rock record and phylogenomic reconstruction of the history of the tree of life. With some exceptions of cyanobacteria[15] and, perhaps, iron oxidizers[16], fossil and organic molecular records provide little insight into the early microbial metabolisms during the Archaean, obscured in large part by the poor preservation states of the very old, often deeply buried and tectonically and metamorphically overprinted host rocks[17]. Among the major geochemical advances, isotopic fingerprints of specific metabolisms have greatly widened our view of which sorts of microorganisms were doing what and when[18,19]. When combined with genomic reconstructions and geochemical signposts for environmental evolution, they give us the possibility of delineating the origins, proliferation and ecological dominance of specific pathways, particularly when viewed within the context of a transition from a dominantly anaerobic to aerobic world.

When evaluating the phylogenomic and geochemical records of early microbial life, it is important to acknowledge the limitations of each. Molecular clocks that estimate the divergence times of microbial lineages and the presence of their respective metabolisms are a powerful tool but require careful interpretation, as many methodological biases (choices of evolutionary models, fossil calibrations and taxon sampling) can substantially impact the resulting age estimates[20,21]. Even a 'perfect' molecular clock brings inherent uncertainty, as evolutionary rates are being estimated for branches of the tree of life from statistical distributions. Fossil and stable isotopic calibrations with tight radiometric date constraints greatly aid in minimizing error[22,23], but many different rates may still be compatible with these calibrations. This is especially the case for microbial phylogenies, which generally lack direct fossil calibration and instead rely on secondary constraints such as lipid biomarker evidence, co-evolutionary histories with animals (for example, endosymbionts such as mitochondria and plastids), additional geochemical constraints and horizontal gene transfers to and from other groups that have a fossil record[20,24]. It is also important for these dates to be transparently reported, with age ranges for inferred divergence times integrated over sources of uncertainty. Even when these uncertainties are considerable, they can still help us discriminate among geochemical hypotheses, as in the case of oxygenic photosynthesis that likely evolved well before, rather than during, the GOE[20,25].

In this Review, we discuss how metabolic pathways evolved, focusing on key chemical elements associated with each pathway. The discussed biogeochemical cycles are deeply interconnected through their dependencies on the chemical species, including biomass, produced or consumed in the other cycles. All of these relationships, often involving feedback mechanisms, collectively drive and are driven by the co-evolving global environment or globally distributed local conditions.

By the end of the GOE, it is likely that the fundamental metabolisms crucial for shaping and adapting to subsequent biospheric evolution were already in place, with their time-varying, global-scale ecologic consequences evolving alongside the atmosphere and the oceans. This trajectory eventually facilitated the origins and proliferation of complex life − from unicellular eukaryotes to multicellular organisms and, eventually, animal life over a billion-year stretch beginning roughly 1.7 billion years ago[26] (see arguments for[27] and against[28,29] causal links between O_2 availability and earliest animals). For further insights into
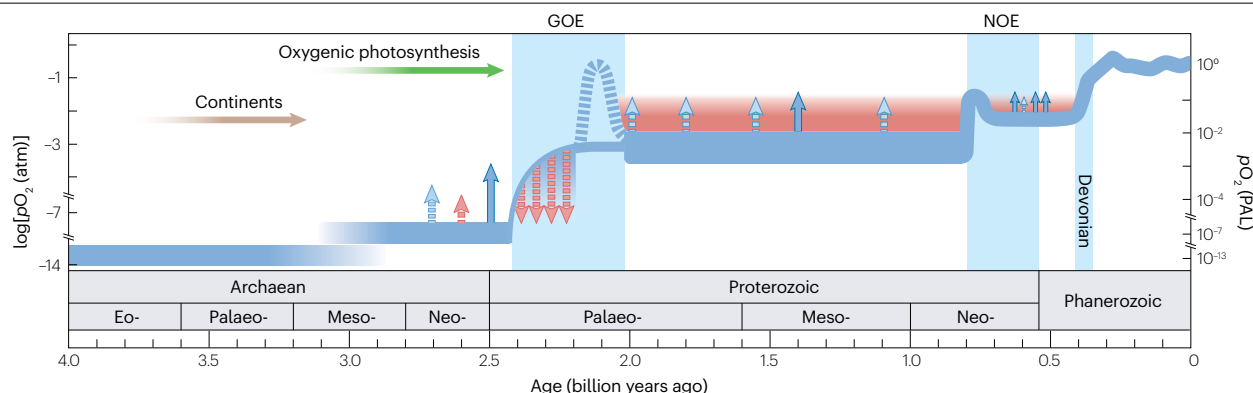
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Fig. 1 | Evolution of atmospheric oxygen content on Earth through time. The evolution of atmospheric oxygen (O_2) levels on Earth across aeons and the impact and duration of major oxygenation events. The level of O_2 is shown as the logarithm of the partial pressure of O_2 (pO_2) in atmospheres (atm) on the left y axis (log[pO_2(atm)]) and as the partial pressure of O_2 relative to the present atmospheric level (PAL) on the right y axis (pO_2[PAL]). The blue curve represents the authors' preferred model for O_2 long-term evolution. The red shaded region captures alternative estimates based on numerical simulations that allow for O_2 stability only at higher pO_2 (ref. 198). The Great Oxygenation Event (GOE; 2.5–2.4 billion to 2.1–2.0 billion years ago), the Neoproterozoic Oxygenation Event (NOE; 0.8 billion to 0.5 billion years ago) and the Devonian period (419 million to 359 million years ago) are highlighted to illustrate the most significant intervals of oxygenation (see refs. 13,14,199 for review covering the NOE through Devonian oxygenation). Solid blue arrows mark possible transient increases in pO_2 based on geochemical evidence. Events indicated by light-blue dashed arrows are more speculative. Red arrows indicate hypothetical fluctuations in O_2 and highlight the oscillatory system behaviour assumed to accompany transitions from one fundamental redox state to another, such as the GOE. Green and brown arrows represent estimates for the development of the earliest oxygenic photosynthesis and continents, respectively, and are plotted without respect to the y axes. The timings of these two major advances in Earth system evolution are not well known, and so their placements on the figure carry uncertainties.

the relationships between environmental and microbial evolution refer to Box 1.

The nitrogen cycle over Earth's history

The modern biogeochemical nitrogen cycle starts with nitrogen fixation, which is the conversion of molecular nitrogen (N_2) gas into a bioavailable form (Fig. 2). Today, only a small percentage of fixed nitrogen is derived from non-biological sources, such as lightning[30]; the vast majority is biologically generated by the enzyme nitrogenase. This enzyme generates ammonium and uses either molybdenum, iron or vanadium cofactors (molybdenum nitrogenase being the most common today)[31]. Ammonium can be enzymatically oxidized to nitrite and nitrate through nitrification metabolisms. Under low oxygen conditions, denitrifiers can reduce oxidized nitrogen (such as nitrate) to N_2. Dissimilatory nitrate reduction to ammonium (DNRA) also reduces nitrate, but it retains fixed nitrogen as ammonium and may be dominant under Fe(II)-rich (ferruginous) conditions[32,33]. Finally, anaerobic ammonium oxidation (anammox) couples ammonium and nitrite to form N_2 in low oxygen conditions and may be responsible for 30–50% of the N_2 produced in modern oceans[34]. Ammonium oxidation may also be coupled to ferric iron reduction (feammox, generating nitrate, nitrite or N_2) or sulfate reduction (sulfammox, generating N_2), but in marine settings, evidence for both processes is currently limited to a few sites[35].

The strong linkage between nitrogen speciation and oxygen availability ties the evolution of nitrogen-metabolizing organisms to Earth's redox evolution. Life's dependence on biological nitrogen fixation today might suggest that nitrogenase arose early. However, molybdenum was depleted in the Archaean ocean[36,37] as related to the low weathering flux in the O_2-lean ocean–atmosphere system. Some phylogenetic studies have indeed suggested that molybdenum nitrogenase arose as late as 1.5–2.2 billion years ago[38–41], possibly within the methanogens[40]. However, other studies have argued that it arose much earlier[42–44].

Evidence from the sedimentary rock record, which indicates the presence of biological N_2 fixation dating back at least 3.2 billion years ago[45], is consistent with the possibility of an early origin for the molybdenum-based pathway. Although oxidative weathering was essentially absent as a molybdenum source on the Archaean Earth prior to the oxygenation of the atmosphere, a combination of experiments, models and field data demonstrate that hydrothermal vents constituted a source of molybdenum to the early ocean[46] and may thus have maintained low but sufficient levels of this element for early life. Fractionated molybdenum isotope ratios from banded iron formations (BIFs) around 3.0 billion years ago[4] imply that there was at least some dissolved molybdenum in the water column at that time. Furthermore, organisms may have expressed mechanisms for scavenging molybdenum from solution as observed in modern molybdenum-depleted environments[47]. Lastly, it is important to consider that our constraints on the molybdenum demand of diazotrophs is based on cultures of modern organisms that were isolated from relatively molybdenum-rich environments[48,49]. More deeply rooted taxa that originated in environments of molybdenum scarcity may have been adapted to lower supplies of this element.

Older rocks tend to be compromised by metamorphism (that is, alteration under elevated pressure and temperature due to burial and tectonic forces). These processes can volatilize elements such as nitrogen and carbon within the rocks and result in isotopic fractionations that can limit the value of isotopic data for reconstructing primary metabolic pathways, particularly in very old rocks, yet isotopic approaches remain an important part of the conversation. Prior to the emergence of biological N_2 fixation, life may have acquired fixed nitrogen from abiotic sources such as lightning or hydrothermal fluids[50–53]. However, isotopic data for lightning products are not consistent with sedimentary $^{15}N/^{14}N$ ratio data from most of the rock record, suggesting that this source never played a major role in sustaining the biosphere[53]. Further, hydrothermal N_2 fixation has been demonstrated experimentally, but natural

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fluids are depleted in ammonium unless they recycle it from organic-rich sediments[54]. At hydrothermal temperatures of a few hundred degrees, isotopic fractionations of several per mil between N_2 and ammonium would be expected[55], which is again inconsistent with the sedimentary record of nitrogen preserved in organic-rich shales[18]. Hence, although these abiotic sources of nitrogen must have been vital for the emergence of life, they appear to have diminished in importance by the mid-Archaean when the isotopic record is less affected by metamorphic alteration. Some phylogenetic studies have suggested that vanadium and iron nitrogenases emerged much later than molybdenum nitrogenases, possibly radiating as late as the Neoproterozoic[34,43] (Fig. 1), but this step is currently not well understood.

As Earth's surface became oxygenated over time (Fig. 1), thus altering the availability of key enzymatic cofactors[56,57], other pathways within the biological nitrogen cycle emerged and diversified. Much of the evidence for nitrogen metabolism evolution comes from

Box 1

Evolving planet, evolving life

The Earth underwent dramatic environmental changes during the critical early chapters of microbial evolution, roughly 4.0–2.0 billion years ago. As life responded to those changes, metabolic footprints grew to scales that shaped the environment. The rise of molecular oxygen (O_2) is the most representative example of this, with initial oxygenic photosynthesis leading to accumulations of O_2 in the surface oceans by, perhaps, 3.0 billion years ago; this was followed by accumulation in the atmosphere — at first transiently — by roughly 2.5 billion years ago and permanently a few hundreds of millions of years later. O_2 eventually distributed throughout the deep oceans, but only over the last 10% or so of Earth's history. The early, O_2-free (anoxic) waters of the oceans were dominated by dissolved iron and, with time, hydrogen sulfide, although sulfidic waters were largely limited to ocean margins and basins with limited exchange with the open ocean. Both are supplied generously by vents on the sea floor, but bacterial hydrogen sulfide inputs increased in importance as marine sulfate levels rose in concert with rising O_2 in the oceans and atmosphere. These constituents provided substrates for microbial metabolisms and also regulated reservoirs of nutrients and micronutrients in seawater. Lower solubilities under anoxic conditions can decrease supplies of metals with important enzyme functions, such as copper, nickel and molybdenum, whereas iron oxidation by O_2 or during anoxygenic photosynthesis can lead to widespread phosphorus removal via scavenging on iron oxyhydroxide mineral products. Microbial nitrogen fixation was well underway by 3.2 billion years ago, despite low early seawater levels of molybdenum, which plays an essential enzymatic role in the process. Nutrient challenges must have been severe, but there is nonetheless ample evidence in organic-rich sedimentary rocks for substantial early primary production, likely by O_2-producing cyanobacteria.

As habitats for both aerobic and anaerobic metabolisms were expanding, there were other first-order changes in the Earth system. Earth's interior was cooling, which controlled melt processes in the deep interior and the delivery of nutrients to the surface. This cooling led to decreasing nickel and increasing phosphorus inputs that may have occurred around 2.5 billion years ago. Because nickel is critical to methane-producing microorganisms, there were important implications for the early atmosphere. The early Sun was decidedly less luminous (it has brightened over time and continues to do so). Under this faint early Sun, the liquid water oceans that have been with us for more than 4 billion years demanded high greenhouse gas contents in the atmosphere to keep the surface sufficiently warm. Thus, abundant nickel in seawater before 2.5 billion years ago might have contributed to warming by stimulating microbial methane production. Carbon dioxide was also likely elevated and would, in addition to warming, have resulted in relatively low pH values in seawater (pH 6–7, compared with circa pH 8 today). Some researchers envision very warm conditions in the early oceans, although the most extreme published estimates have been controversial. It is reasonable to assume temperatures within a range of 0–50 °C. Another planetary-scale constraint was shorter day lengths, because Earth's rotational speed has diminished by up to fourfold since 4 billion years ago.

Over the same period, plate tectonic processes emerged, facilitating the early rise of continents and their eventual elevation above sea level. However, there is a wide range of opinions regarding the mechanisms and timing of these topographic milestones. With land came new habitats and new microbial possibilities. Against this backdrop of transition, increasing levels of O_2 led to oceans and underlying sediments teeming with both aerobic and anaerobic life, along with greater supplies of both oxidants and reductants. This combination increased ecosystem complexity, with additional weighty consequences. For example, the rise of biogenic oxygen increased aerobic microbial activity and sulfate. Methane decreased, in part, through the enhanced roles played by oxygen-requiring and, potentially, sulfate-requiring methanotrophic pathways. Decreasing methane beneath a still faint sun may have facilitated the dramatic climatic cooling that occurred as O_2 rose in the atmosphere between roughly 2.4 billion and 2.2 billion years ago, leading to a Snowball Earth marked by global-scale glaciation and sea-ice cover.

Not every aspect of our early planet was solely determined by the processes and products occurring on or within Earth. Impacts by asteroids and other external objects likely contributed to the origins of life on Earth and its subsequent evolution. These contributions include the delivery of organic compounds, bioessential light elements and water; initiation of hydrothermal activity; modulation of the redox state of the atmosphere and its greenhouse gas composition; and conveyance of reactive phosphorus and metal species. These 'impacts of impacts' must have been important in setting the stage for our early microbial world, but their roles in shaping the biosphere decreased in size and frequency over time.

It is a mistake to view the evolution of microbial life outside the framework of co-evolving conditions at and near the Earth's surface. Any careful assessment quickly reveals that microbial evolution has moved in tandem with the changing environments of Earth. As life's foothold continued to expand and diversify, so did its capacity to respond to, and drive, environmental change.

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phylogenetic and molecular clock analyses, which are limited in their ability to determine the precise timing of events in deep time[21,58], but nevertheless can provide broad age estimates for when specific metabolic genes arose and likely spread across the tree of life. Phylogenetic tree reconciliation has suggested that genes enabling denitrification from nitrate to nitrite arose and proliferated across the tree of life most likely after the GOE[44], which indicates increasing nitrate availability consistent with the rise of biospheric O_2. Nitrate reductase enzymes use molybdenum (Fig. 2) and may have capitalized on increased abundances of molybdenum in Neoarchaean seawater[36]. Phylogenetic reconstructions also suggest that anammox bacteria probably arose around the same time[59]. Molecular clock analyses indicate that DNRA expanded after the GOE[44], allowing organisms to gain metabolic energy while retaining fixed nitrogen in the environment. However, it appears that further denitrification of nitrite to N_2 gas, which is common today, did not radiate across the tree of life until after the late Proterozoic[44]. This trend may be the result of high abundances of ferrous
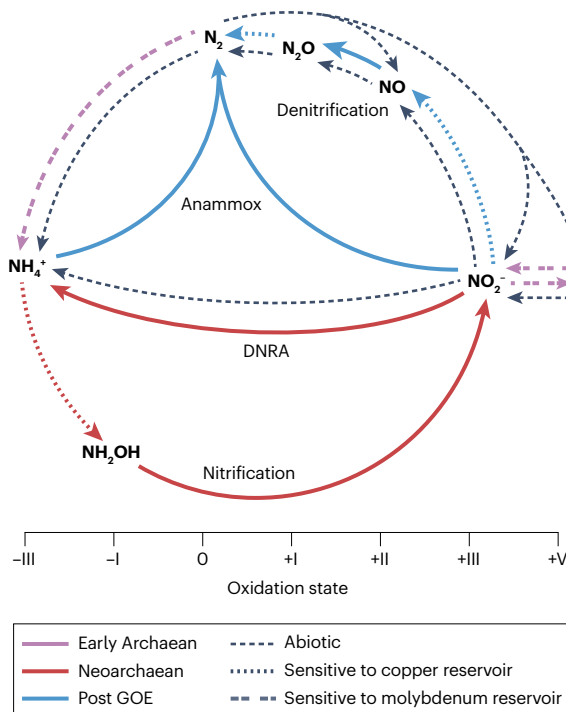

Fig. 2 | The biogeochemical nitrogen cycle on Earth. A simple representation of the interactions among different nitrogen metabolic processes and the geological intervals within which those metabolisms first expanded in terms of biogeochemical significance. Anaerobic ammonium oxidation (anammox) is a process by which microorganisms oxidize ammonium (NH_4^+) to molecular nitrogen (N_2) gas by utilizing nitrite (NO_2^-) as an electron acceptor. Nitrification is the enzymatic oxidation of ammonium to nitrite and nitrate (NO_3^-) via hydroxylamine (NH_2OH). Denitrification is the reduction of oxidized nitrogen to N_2 under low molecular oxygen (O_2) conditions. Dissimilatory nitrate reduction to ammonium (DNRA) is also an anaerobic reduction process, but it retains fixed nitrogen as ammonium rather than generating N_2. Arrows are colour-coded according to the geologic interval within which a given metabolic pathway became ecologically significant on a global scale. Nitrogen cycling is notably dependent on the oceanic molybdenum and copper reservoirs for key enzymatic cofactors, and variations in the sizes of those reservoirs may have set the tempo of a given metabolism's proliferation through time. GOE, Great Oxygenation Event.

iron in the early ocean[60,61], which could have abiotically transformed nitrite into gaseous nitric oxide and nitrous oxide and minor dissolved ammonium[62]; nitrous oxide is a potent greenhouse gas and may have impacted global climate[63]. Once ferrous iron levels decreased in the late Proterozoic deep ocean, nitrite could have accumulated and facilitated the expansion of nitrite-reducing metabolisms. Copper is required for the enzymatic conversion of nitrite to nitric oxide and nitrous oxide to N_2 (Fig. 2), signifying that global copper limitation under widespread anoxic conditions may have also delayed the expansion of these enzymatic pathways[64].

The nitrogen isotope record shows elevated $^{15}N/^{14}N$ ratios from the Neoarchaean onwards, commonly interpreted as representing the onset of denitrification to N_2 and, therefore, the appearance of nitrate in surface oceans at least transiently on the eve of the GOE[65–67]. Taken together, phylogenetic studies suggest that the onset of $^{15}N/^{14}N$ enrichment probably reflects biological denitrification from nitrate to nitrite only, followed by abiotic nitrite reduction to nitric oxide gas. Metabolic reactions finally took full control over the isotopic record as the ocean became more widely oxygenated, with a functionally modern nitrogen cycle emerging by the Neoproterozoic.

The iron and manganese cycles over Earth's history

Iron is the most abundant element on Earth and the fourth most abundant in the crust. It exists in a range of oxidation states, but in the biosphere the most common are ferrous iron (Fe(II)) and ferric iron (Fe(III)). Redox transformations between these two states galvanize several microbial metabolisms[68–70] (Fig. 3). Chemolithoautotrophic bacteria can utilize the energy associated with Fe(II) oxidation under low pH or at low oxygen concentrations at circumneutral pH, and this type of oxidation usually occurs with O_2 or nitrate as the electron acceptor. Light energy can also facilitate Fe(II) oxidation via anoxygenic photosynthesis (photoferrotrophy). Resultant Fe(III) from either pathway can feed into dissimilatory iron reduction (DIR), which is the anaerobic microbial respiration of biomass coupled to Fe(III) reduction. DIR microorganisms tend to expel Fe(II) into the environment, leading to the precipitation of Fe(II)-bearing minerals (for example, sulfides, phosphates, carbonates); these phases represent key geochemical records.

For 2 billion years (from 3.8 billion to 1.8 billion years ago), vast quantities of iron-rich sediments were deposited on the sea floor as iron formations, including BIFs. These rocks are composed of iron-rich and silica-rich layers and signify that the Archaean–Palaeoproterozoic oceans were Fe(II)-rich. This Fe(II) provided an abundant energy source for microorganisms capable of oxidizing it. The resulting Fe(III) phases (for example, ferrihydrite), often attributed to photoferrotrophy[71], are needed for the formation of BIF, and thus it has been suggested that this metabolism was operating as early as 3.8 billion years ago[72]. Given the relatively high concentrations of dissolved Fe(II) in Archaean seawater (micromolar versus only nanomolar today), these phototrophs could have inhabited much of the upper water column overlying continental shelves[73]. The consequent Fe(III) would have been deposited as sedimentary precursors of BIF[74], which have experienced heavy burial overprints (for example, mineral transformations) since deposition. Those sediments would have been an ideal environment for DIR bacteria to oxidize the sedimented biomass, leading to the observed organic-lean nature of BIFs[75]. The coupling of carbon and iron isotopes in the Archaean rock record supports this notion[76,77]. Moreover, DIR requires simple substrates as electron donors[78] (such as molecular hydrogen (H_2), acetate, lactate and methane), indicating the presence of fermenting bacteria and methanogens – the microorganisms responsible for

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producing these substrates – during that time[79,80]. Iron(III) phases may also have avoided DIR. It has been demonstrated that in certain photoferrotrophic experimental cultures, ferrihydrite does not attach to cell surfaces, suggesting a general lack of co-deposition of ferrihydrite and biomass[81]. Therefore, biomass resulting from photoferrotrophy may have remained separated from sediments involved in BIF formation and could have instead contributed to the production of biogenic methane rather than DIR. This methane could have helped stabilize the Earth's climate under a less intense young Sun.

In the Neoarchaean, life for photoferrotrophs would have become challenging for several reasons[82]. First, by acquiring traits such as filamentous growth and motility[83,84], cyanobacteria gained the ability to colonize shallow waters fringing the continents, which led initially to the formation of oxygen oases[5,85] and ultimately facilitated the GOE[84]. Second, the juxtaposition of dissolved Fe(II) and O_2 would have triggered abiotic iron oxidation and created opportunities for competing microaerophilic chemolithoautotrophs to thrive at the interface between upwelling ferruginous waters and oxygenated photic zones (that is, from the ocean surface to depths at which light energy is no longer available for life, at approximately 100–200 m)[86,87] (Fig. 3). Last, the presence of O_2 might have elevated the ecological relevance of metabolisms such as nitrate-dependent Fe(II) oxidation[88,89].

An expansion of microbial sulfate reduction (MSR) coincident with the GOE[19] and, more specifically, the hydrogen sulfide produced from it, would have titrated large amounts of dissolved Fe(II) from seawater[90]. Thus, approximately 2.4 billion years ago marks a fundamental step up in the interaction between the iron and sulfur cycles within the ocean. This timing is nearly coincident with the relative lack of BIF deposits until 1.9 billion years ago (only between 5% and 15% of all BIFs were deposited between roughly 2.4 billion and 1.9 billion years ago)[91], although low-O_2 oceans generally dominated by Fe(II) persisted through the Proterozoic and into the Palaeozoic[60,61]. During the late Mesoproterozoic to early Neoproterozoic, the spread of planktonic cyanobacteria throughout the ocean's photic zone[25] may have allowed microaerophilic Fe(II) oxidizers to dominate along the redoxcline (that is, the depths over which water chemistry transitions from oxidizing to reducing, typically as a result of decreasing O_2)[87]. Once the deep ocean became oxygenated in the Phanerozoic, hydrothermally derived Fe(II) would have precipitated around submarine vents as it does today[92]. Marine iron cycling would, consequently, have been confined to something near its current state: existing almost exclusively as DIR within sediments, leading to extremely low Fe(II) concentrations in the water column.

The evolution of the iron cycle is partly mirrored by manganese[93,94], which is of paramount significance to our understanding of the ancient biosphere. Iron and manganese have travelled similar paths in terms of their abundance in the oceans through time. They are both insoluble under oxic conditions, and their oxide forms are relatively energetic electron acceptors for respiration, falling above and below sulfate reduction and denitrification, respectively, on the redox ladder. However, unlike every other element discussed in this Review, manganese has only one stable isotope, making it impossible to track the advent and proliferation of specific redox steps through diagnostic isotope signatures. As is the case for most systems during the Archaean, fossil records (organic molecular and/or morphological) offer little solace.

The nature and cycling of manganese oxides are an active area of debate. However, the extensive oxidation of Mn(II) to Mn(III) and Mn(IV), along with the associated ore resources, is widely included when compiling evidence for the GOE[95]. Implicit in these arguments
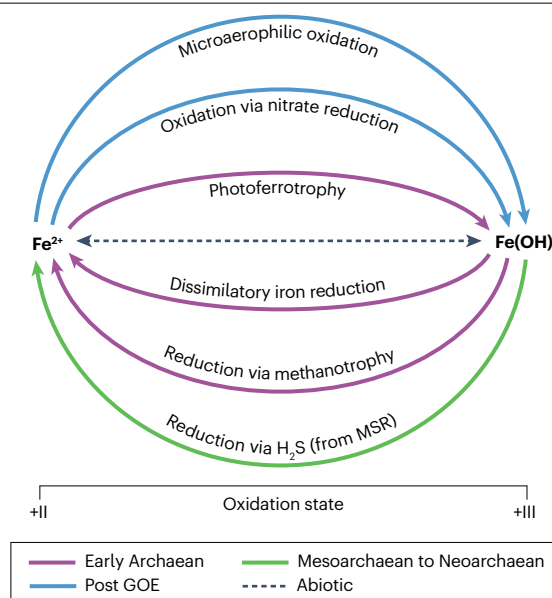

Fig. 3 | The biogeochemical iron cycle on Earth. A simple representation of the different iron metabolic processes and the geological intervals within which those metabolisms first expanded in terms of biogeochemical significance. Arrows are colour-coded according to the geologic interval within which a given metabolic pathway became ecologically significant on a global scale. Although oceanic iron is present in only two oxidation states – ferrous iron (Fe^{2+}) and ferric hydroxide ($Fe(OH)_3$) – a wide variety of metabolisms are known to leverage this limited range. Iron is oxidized by chemolithoautotrophic bacteria at low oxygen concentrations (microaerophilic oxidation). Such oxidation can also occur using nitrate as the electron acceptor (oxidation via nitrate reduction). Photoferrotrophy is the oxidation of reduced iron via anoxygenic photosynthesis. Resultant oxidized iron from any of the above pathways can be reduced during the anaerobic respiration of biomass (dissimilatory iron reduction (DIR)). Reduction of oxidized iron can also occur using methane (reduction via methanotrophy) or sulfide (reduction via hydrogen sulfide (H_2S)) as the electron donor. In this way, shifts in the dominant pathways of iron cycling are intimately linked to selective environmental and/or evolutionary pressures, including the rise of oxygenic photosynthesis approximately 3.0 billion years ago and subsequent accumulations of nitrate and H_2S in the Proterozoic ocean. GOE, Great Oxidation Event; MSR, microbial sulfate reduction.

is the requirement for O_2 to drive the microbial manganese oxidation, which leads to the formation of manganese oxide. This scenario differs substantially from the oxide-producing phototrophic pathway for iron, which occurs in the absence of O_2. This distinction is essential for unravelling Earth's early history. However, this long-held assumption about manganese oxide formation has been recently challenged by assertions of oxidation linked to anoxygenic photosynthesis in the absence of O_2 (refs. 96,97).

The presence of manganese oxides provides the mechanistic underpinning for multiple geochemical proxies that are used for tracking atmospheric oxygenation through time (Fig. 1), and whether O_2 is required for manganese oxide formation is a foundational question for those approaches. The proxy relationships in question include a direct connection between manganese oxides and chromium[98] isotope fractionation, which can provide an O_2 palaeobarometer for the ancient atmosphere[99,100]. Interactions with manganese oxides can also yield molybdenum[101] and thallium[102] isotope fractionations, which

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help constrain the evolving O_2 landscape in ancient oceans[103,104] and shed light on the beginnings of oxygenic photosynthesis as far back as 3.0 billion years ago[4].

Taken together, manganese oxide-dependent proxies have played a crucial role in elucidating early oxygenation on Earth[27]. Importantly, whether O_2 is required to drive microbial oxidation of manganese becomes less critical when we consider how easily manganese oxides redissolve in the presence of dissolved Fe(II) and hydrogen sulfide[94,105]. Regardless of the manganese oxide formation mechanism, it is reasonable to suspect that O_2 must have been present at all depths (that is, extending to the sea floor) at some relatively shallow locations in order for manganese oxides to avoid dissolution and settle in ancient sediments, thereby preserving the diagnostic isotope fingerprints of molybdenum and thallium. Additionally, this process would have facilitated the shuttling of various oxides and adsorbed metals to the sea floor[94].

The sulfur cycle over Earth's history

Similar to the early iron cycle, the sulfur cycle on the early Earth was kick-started by volcanic outgassing and hydrothermal vent circulation[106]. These sources were later overwhelmed by sulfate derived from continental weathering once O_2 rose in the atmosphere. Volcanogenic sulfur is primarily sulfur dioxide gas, which can be oxidized to sulfite and sulfate through gas-phase and aqueous-phase reactions in the ocean, in the atmosphere and on land[107]. Deep-marine hydrothermal vents deliver sulfide and lesser amounts of various reduced and oxidized sulfur phases[108]. Sulfate is currently the second most abundant oxidant available to life, but it was a minor constituent over most of Earth's history[109]. At geologically low temperatures (below 120 °C), the reduction of sulfate to sulfide is facilitated by a subset of bacteria and Archaea[106,110,111] This process is termed MSR and is often powered by organic carbon respiration, and thus interweaves Earth's sulfur and carbon cycles. This linkage is strengthened by the utilization of sulfate as an electron acceptor during the anaerobic oxidation of methane, which drives more than 90% of modern oceanic methane consumption[112]. Altogether, MSR in marine sediments accounts for up to half of all organic matter oxidation today[113], with associated genes found in widespread environments across the planet[114]. Resultant sulfide can react with iron to form sulfide minerals (for example, pyrite), effectively removing sulfur, iron and electrons from active biogeochemical processes and coupling the sulfur and iron cycles[106,115]. Sulfide itself is also an electron source for anoxygenic phototrophs and a diverse range of chemotrophs that oxidize it using various electron acceptors (for example, O_2 and nitrate)[111,116,117]. Mineral and/or dissolved sulfide may be oxidized directly back to sulfate, although this process more often stops along the way at intermediates such as polysulfide, elemental sulfur, thionates or sulfite, which themselves participate in biotic and abiotic oxidation, reduction and disproportionation reactions[113,118,119]. An additional, essential sink for reduced sulfur is its association with organic matter, either through primary assimilation or later incorporation during the burial of organic remains.

The evolution of the sulfur cycle is intricately linked to the global transitions in the Earth's surface oxidation state over time (Fig. 4), with particular emphasis on the dynamic history of oceanic sulfate. The earliest lines of geochemical evidence for sulfur metabolism(s) are from the Palaeoarchaean (from 3.6 billion to 3.2 billion years ago)[120–122], an interval during which sulfate concentrations are thought to have been between 5 and 200 μM (as compared with 28 mM today)[123,124], and the relative roles of sulfate and sulfite in these early metabolisms remains an open question. Indeed, genomics-based studies suggest that the *dsr* genes responsible for either reducing or oxidizing sulfite

arose early[125]. The reductive form is thought to have arisen first, followed by the oxidative form[126–129]. Consequently, dissimilatory sulfite/thionate reduction appears to have been among the first sulfur metabolisms to develop[128,130,131]. The major source of sulfite would likely have been dissolution of volcanogenic sulfur dioxide gas in water. Consistent with these genomic data and estimates pointing to a small Archaean sulfur reservoir in seawater[132], sulfur isotope variation in Archaean sediments is small and apparently dominated by abiotic atmospheric processes[133], with some overprinting resulting from intermediate sulfur metabolisms carrying minimal fractionation signals[19,134–136]. Pre-GOE anoxygenic photosynthesis using sulfide cannot be dismissed given genomic evidence for the antiquity of the relevant photosynthetic reaction centres[137], but the Fe(II)-rich Archaean ocean would have precluded appreciable sulfide accumulation and, by extension, the ecological relevance of this metabolism in marine systems. The stem lineage of the earliest ancestors to extant anoxygenic sulfur phototrophs dates to the Palaeoproterozoic, thus separating their origin from any hypothetical Archaean lineage[137]. Importantly, traces of Archaean lineages could have been lost through extinctions.

After the advent of oxygenic photosynthesis and the subsequent GOE, sulfate transport to the ocean increased due to the oxidative weathering of sulfide minerals such as pyrite exposed on continents[68], signifying the initiation of Earth's 'Middle Age' sulfur cycle (Palaeoproterozoic to Mesoproterozoic, from 2.5 billion to 1.0 billion years ago)[19,134,138]. Whether this shift resulted in persistent, elevated oceanic sulfate concentrations (more than 1 mM) is a matter of active debate; however, the increased sulfur isotope variation within Proterozoic samples has been attributed to permanently increased sulfate concentrations[19]. It has been argued that these early signals were heavily influenced by geochemical parameters within the early diagenetic burial environment[139,140], whereas other work has suggested they are best explained by the onset or expansion of oxidative sulfur cycling[109]. In any case, the wider range of thermodynamically favourable reactions likely expanded the importance of the microbial sulfur cycle in the Proterozoic, coincident with a time when both the oxidants (O_2, nitrate) and the reductants (hydrogen sulfide, elemental sulfur) utilized by modern chemotrophic and phototrophic sulfur oxidizers and disproportionators became more widely available in shallow seas. This step paved the way for the evolution of thiosulfate oxidation and reduction via the *sox* pathway. Indeed, genomic evidence supports the emergence of this pathway after the GOE[125,141]. Regardless of the specific metabolic processes involved, the number of favourable redox couples involving sulfur greatly expanded across the Archaean–Proterozoic transition, driven by increasing O_2 levels in the atmosphere and surface oceans. Perhaps paradoxically, this permitted a broad expansion of anaerobic metabolic niches within marine sediments, as oxidative power was effectively transferred from atmospheric oxygen to sulfate widely available for MSR.

The Neoproterozoic Oxidation Event (NOE), and with it a concomitant increase in sulfate, marked the onset of a sulfur cycle encompassing all the microbial processes operating in the present day[19,142]. Despite the further expansion of oxygen and sulfate reservoirs within the Earth's surface environment over the last approximately 0.6 billion years (perhaps related to tectonics[115,132] and plant and animal expansion[143,144]), the microbial sulfur metabolisms most consequential to global biogeochemistry over Earth's history have largely been in operation for 2–3 billion years. One exception is the microbial production of organic sulfur compounds such as dimethylsulfoniopropionate (DMSP), which play a role in cloud nucleation. Phylogenomic analyses indicate that the cycling of organic sulfur compounds may not have

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emerged until approximately 1.5 billion years ago[125]. The distribution of these metabolisms in current environments is largely dictated by oxygen availability, which is widespread, pushing many of the anaerobic and, presumably, more ancient metabolisms into anoxic refugia such as sediment layers and restricted marine basins.

Methane and the Archaean biosphere

In today's biosphere, carbon metabolisms provide a link between the organic and inorganic phases of the carbon cycle. Many of these metabolisms are anaerobic, either respiring organic carbon using various electron acceptors or degrading organic compounds through fermentation. Although these reactions yield less chemical energy than aerobic respiration, they power much of the microbial biosphere, particularly when multiple electron acceptors (for example, sulfate and nitrate) are abundant. Of these anaerobic metabolisms, one of the most unusual, yet pervasive, is methanogenesis − respiration that uses carbon itself as a terminal electron acceptor, reducing various carbon compounds to methane.

The primary energy-generating step of methanogenesis is the final one, which involves the reduction of a methyl group bound to coenzyme M (methyl-CoM) to methane, coupled to heterodisulfide reduction and the synthesis of ATP. These reactions are catalysed by the N^5-methyl-H$_4$SPT:coenzyme M methyltransferase (Mtr) and methyl-coenzyme M reductase (Mcr) complexes. There are multiple distinct pathways for generating methane via methyl-CoM from different classes of carbon compounds[145–147]. Hydrogenotrophic methanogenesis is the most elaborate, involving the stepwise reduction of carbon dioxide via single carbon intermediates bound to cofactors. The resulting methyl group is transferred to coenzyme M (CoM), with reducing power provided by H$_2$ or organic compounds such as formate. Methanogenesis can also occur from methylated compounds (for example, methylamines), which involve a different set of enzymes and corrinoid cofactors that enable the methyl group transfer to CoM. Finally, acetoclastic methanogenesis obtains a methyl group from acetate via an acetyl-CoA intermediate, which is cleaved by the carbon monoxide dehydrogenase complex into carbon dioxide and a methyl group.

The simpler forms of methanogenesis (acetoclastic and corrinoid-dependent) have narrow taxonomic distributions and are only found in two orders within Euryarchaeota (Methanosarcinales and Methanomassiliicoccales)[146], suggesting that they evolved more recently within these groups. By comparison, the hydrogenotrophic pathway is found across all but one order of methanogens and appears to be ancestral[146]. The simplest organic methanogenic cofactors are found in the methyl reduction step (CoM and coenzyme B) conserved across all three pathways, suggesting that powering respiratory chains from reducing methyl groups may nevertheless be the most ancient step in the pathway.

Counter-intuitively, the primordial process of reducing carbon dioxide to methane requires many steps. A correspondingly large number of genes encoding proteins for several enzymes and the biosynthesis of highly specialized cofactors enables thermodynamic exploits that overcome unfavourable steps in reducing carbon dioxide. The overall reaction is narrowly favourable (−34 to −40 kJ mol^{-1}, depending on the reductant), providing sufficient energy for growth in environments where other metabolisms appear precluded[148]. The acetoclastic and corrinoid-dependent pathways are substantially more straightforward and show similarly low energy yields but have the additional constraint of being limited by the availability of those specific organic compounds.
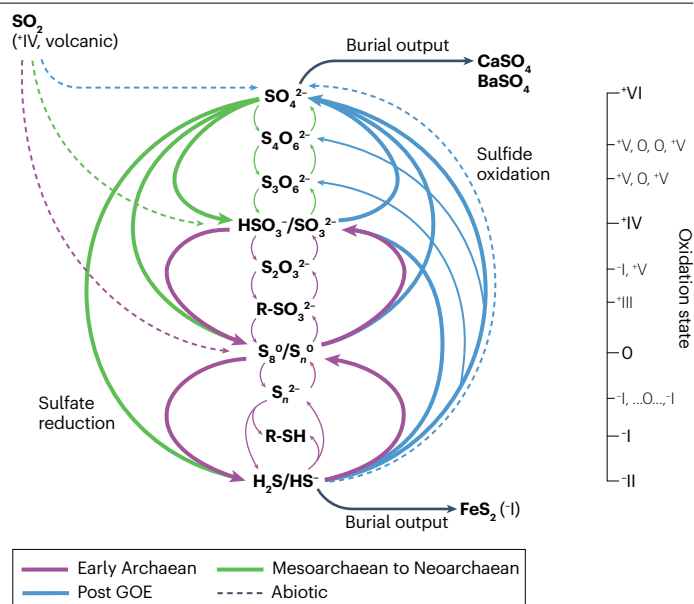

Fig. 4 | The biogeochemical sulfur cycle on Earth. The different metabolic processes involved in the sulfur cycle and the geological intervals within which those metabolisms first expanded in terms of biogeochemical significance. Sulfur is notable for its large range of oxidation states. Sulfate reduction (specifically microbial sulfate reduction) is the process by which sulfate (SO$_4$$^{2-}$) is converted to sulfide during the anaerobic respiration of organic matter. Resultant hydrogen sulfide (H$_2$S) can be an electron source for anoxygenic phototrophs and chemotrophs that oxidize it using various electron acceptors (for example, molecular oxygen (O$_2$) and nitrate). Sulfide oxidation can proceed directly to sulfate, although this more often occurs via intermediates such as polysulfide (S$_n$$^{2-}$), elemental sulfur (S$_n$^{0}), thionates (S$_nO_m$), sulfite (SO$_3$$^{2-}$), thiols (R-SH) and sulfonates (R-SO$_3$$^{2-}$). All these intermediates participate in biotic and abiotic oxidation, reduction and disproportionation reactions. Pathways involving intermediate valence sulfur species are indicated by thin arrows. Burial output arrows signify that sulfide can react with iron to form sulfide minerals such as pyrite (FeS$_2$), whereas sulfate can react with calcium or barium to form minerals such as gypsum and anhydrite (CaSO$_4$ ± 2H$_2$O) or barite (BaSO$_4$), respectively. Sulfur dioxide (SO$_2$) gas is primarily produced by volcanoes and can be converted into bioavailable forms through gas-phase and aqueous-phase reactions in the ocean, in the atmosphere and on land. Dashed arrows refer to pathways that do not require life. Arrows are colour-coded according to the geologic interval within which a given metabolic pathway became ecologically significant on a global scale. The Great Oxygenation Event (GOE) spurred the global-scale relevance of the full oxidative suite of metabolisms.

Phylogenomics and geochemical studies both point to hydrogenotrophic methanogenesis via methyl group reduction being one of the most ancient metabolisms, tracing its ancestry back to (at least) the deepest diversification of Euryarchaeota[146], likely more than 3.6 billion years ago[149]. Geochemical evidence supporting this age is provided by isotopically light methane found within fluid inclusions from the 3.46 billion year-old Dresser Formation (a geologic formation in Western Australia)[150], although abiotic sources for this methane and its isotopic signature have also been proposed[151]. This estimate, however, is consistent with hypotheses proposing a 'methane greenhouse'[152] as part of the solution to the faint young Sun paradox. Specifically, atmospheric methane would have helped maintain liquid

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oceans on the surface of the early Earth despite the less luminous sun[153,154]. Yet the presence of a particular metabolic pathway does not necessarily imply ecological prevalence or significant impacts on the atmosphere. Further, abiotic pathways of methane production must also be considered[155].

Much of the current microbial methane production on Earth depends on compounds generated by a productive photosynthetic biosphere, which may not have evolved until roughly 3.0 billion years ago[4,14,20]. Most of the carbon dioxide, acetate and methylated compounds encountered by methanogens are fermentative waste products from a reservoir of biomass[148]. Even H_2 for the hydrogenotrophic pathway is produced biotically through the same fermentative microbial metabolisms that produce acetate and carbon dioxide within anaerobic systems (acetogenesis and acidogenesis)[156,157], although abiotic H_2 sources and temporal patterns in their fluxes must be considered[158]. Therefore, a methane-rich Archaean biosphere requires one of two conditions. The first is a highly productive biosphere producing sufficient biomass that is fermented rather than remineralized via respiration. This scenario may have had to wait until oxygenic photosynthesis originated at circa 3.0 billion years ago[1,4] to overcome a productivity threshold. It also implies that heterotrophic fermentative metabolisms pre-date methanogenesis, which would place them among the most primordial dissimilatory carbon metabolisms. The second plausible condition for methanogenesis requires abundant abiotic sources of H_2. Importantly, abiotic H_2 and methane can be produced in large amounts[159] by geochemical interactions between water and rocks, such as serpentinization[160], which may have been more prevalent on the early Earth.

The abiotic generation of both H_2 and methane is modulated by diverse controlling factors, including the dynamics of large-scale tectonic processes and ocean composition through time[158]. Other possible abiotic controls include evolving mantle redox and even large impacts that can stimulate transient production and atmospheric accumulation of methane[161]. Yet abiotic methane production is viewed by some to be 'sluggish' (ref. [162]) and quantitatively less impactful than its biological counterpoints[163], implying that appreciable atmospheric accumulation likely required methanogenesis. Such accumulations could support major climate variability, with global-scale[164] glaciation (that is, Snowball Earth[164]) being a likely consequence of declining methane with rising atmospheric oxygen at the GOE. An important topic of research is the degree to which methane could be a biosignature gas in the atmospheres of exoplanets, recognizing that whereas some level of O_2 in the atmosphere is deleterious to methane, ozone ultraviolet shielding attributable to increasing O_2 can reduce photochemical destruction[165]. Finally, the purported substantial methane abundance during the Archaean, followed by a subsequent decrease, has been attributed to the progressive decline in marine levels of nickel[166], an essential enzymatic cofactor in methanogenesis. In this context, first-order solid Earth processes are invoked, specifically our planetary cooling history manifested in the changing compositions of volcanic rocks[166].

Ultimately, there is no direct evidence of a long-lived methanic greenhouse on the early Earth[167]. However, there are both direct and indirect contextual observations suggesting high concentrations of methane (potentially producing organic hazes such as those on Titan, Saturn's largest moon[168]) in the Archaean atmosphere. Direct suggestions include carbon isotope signals in late Archaean carbonate rocks consistent with pervasive methanotrophy[106,169], and it is reasonable to speculate that vanishingly low O_2 and sulfate throughout the Archaean would have more generally favoured methane production and accumulation. Today, microbial pathways oxidize nearly all methane produced in sediments via aerobic or anaerobic pathways, including syntrophic coupling to sulfate reduction[23,170,171].

In summary, methanogenesis was operating early in Earth's history, but its impact on the ancient biosphere is highly contingent on both microbial metabolisms and geologic processes, especially the balance of organic carbon respiration versus fermentation and/or the abiotic production of H_2. The potential for sulfate-dependent and, perhaps, iron-dependent anaerobic methane oxidation prior to the GOE is poorly understood at present. Therefore, the planetary-scale impact of methane in the Archaean remains an open question.

Conclusion and future perspectives

A central message of this Review is that all of Earth's biogeochemical cycles are inextricably linked across spatio-temporal scales, spanning from the smallest local environments to the overarching umbrella of the biosphere. The largest scale is defined by an ocean–atmosphere system that evolved from being essentially devoid of O_2 for the first half of its history to the pervasively oxic world we know today. This transition occurred through progressive ventilation over roughly 2 billion years. The couplings between life and its environments over time are highlighted in Fig. 5. There is no better example of this cause and effect than the beginnings of oxygenic photosynthesis and the subsequent origins and ecological expansion of metabolisms dependent on both oxygen and oxidants, as well as greatly expanded reservoirs of reduced organic matter.

Many models (reviewed elsewhere[1,172]) have been proposed to explain the balance between O_2 sources and sinks from roughly 3.0–2.4 billion years ago. This pre-GOE interval marks a conspicuous delay in oxygen's reshaping of the biosphere. Thus, oxygen teaches us that there is a need to draw a clear distinction between the beginnings of a metabolic process versus its subsequent proliferation and capacity to shape surface environments on a planetary scale. The ecological consequences of these changes, including the alteration of complex feedbacks, become broad and even irreversible, along with the widening spatial distributions of the participating organisms. This is the distinction between metabolisms being permissive versus pervasive, and this relationship changes over time. For example, ecological impact is likely to vary, rising and falling in magnitude, such as the putative heyday of methanogens in a low-sulfate, low-O_2 world prior to the GOE.

Equally important was the rise of continents (Fig. 1) for their likely roles as oxygen sinks moving towards and past the GOE (reviewed elsewhere[1]). Simultaneously, there was a corresponding expansion of ecological niches in terrestrial settings, including freshwater systems, as land masses eventually became more common and rose above sea level per the predictions of the tectonic models (although the precise timing of continental growth and emergence is still debated[173]). Oxidative weathering of continents is a source of diverse chemical species to the oceans, including sulfur, trace metals and phosphorus. Cycling and recycling of phosphorus to and within the oceans is largely a story of weathering, first on the sea floor[174,175] and then, with time, on the continents. Indeed, the beginnings of oxygenic photosynthesis may have occurred on land[176,177], begging the question[82] of how and when it spread to the oceans, although early marine origins or contributions remain a possibility. Stable isotope (molybdenum, iron) and radiogenic isotope (uranium–thorium–lead) data suggest O_2 production and accumulation in the surface oceans along continental margins by at least 3.2 billion[178] or 3.0 billion years ago[4]. Whether any or all of the above theories tie to the emergence of modern-style plate tectonics and rising continents in roughly the same time window is an essential
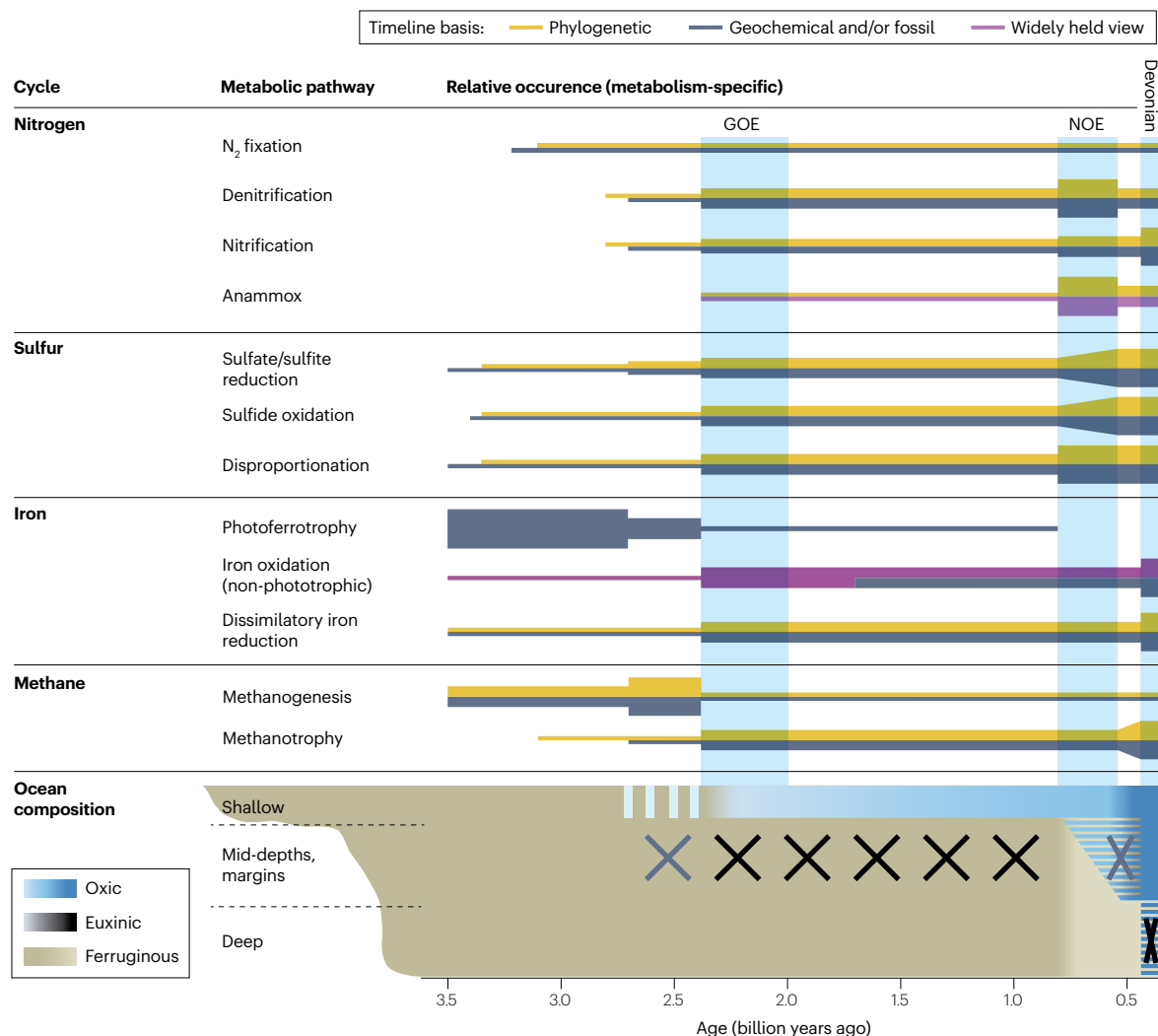
Fig. 5 | Co-evolution of oceans and microbial pathways on Earth through time. Each element cycle — nitrogen, sulfur, iron and methane — their metabolic pathways and the relative occurrence of each metabolic process according to specific analyses. Specifically, the start of each colour-coded line coincides with the earliest phylogenomic estimate (yellow); geochemical, geological and/or fossil evidence (dark grey), such as distributions of iron formations; or widely held view based on indirect evidence for a given metabolic pathway (purple), such as environmental favourability (for example, low sulfate (SO_4^{2-}) and oxygen (O_2) favouring methane accumulation). The lines continue for as long as a metabolism is considered to maintain ecological relevance. The global-scale ecological impact of a metabolism through time is qualitatively tracked by the total combined thickness of all lines for that pathway, with the thinnest state representing the baseline and the thickest representing the maximum level of ecological impact, provided a pathway is thought to have been dynamic through time. In each case, thickness is derived from a combination of geochemical evidence (for example, magnitudes of isotopic variation for the sulfur isotope system), changes in phylogenetic distribution and/or indirect evidence for favourable or deleterious conditions based on prevailing views of broader biospheric evolution. Each assessment is metabolism-specific (that is, made independent of other metabolisms), although the ecological expansion or contraction of a given pathway is inextricably linked to the evolution of other pathways and, more broadly, the oxidation state of the entire biosphere. Note the strong, expected correspondence between these trends and major steps in biospheric oxygenation in the Great Oxygenation Event (GOE), the Neoproterozoic Oxygenation Event (NOE) and the Devonian period. Changes in ocean composition over time are represented at the bottom of the figure. Relative concentrations of given seawater constituents — oxygen (oxic), sulfide (euxinic) and ferrous iron (Fe(II); ferruginous) — at different ocean depths (shallow waters, mid-depths (particularly along continental margins) and the deep ocean) are represented qualitatively by shading, with highest concentrations (and likely spatial and temporal persistence) depicted in darker tones. Euxinic 'X' shapes indicate that sulfide accumulations were limited in extent, temporally variable and strongest along productive continental margins, particularly during the Proterozoic (from 2.5 billion to 0.5 billion years ago). Alternating blue and green lines within the Neoarchean (from 2.8 billion to 2.5 billion years ago) represent transient oxygenation of shallow waters leading up to the GOE. Horizontal, pale green lines in the Phanerozoic represent the complex history and still-developing understanding of ferruginous conditions below shallow oxygenated waters during the Palaeozoic, marking the transition from dominantly iron-rich waters in the Proterozoic to mostly oxygenated waters later in the Palaeozoic[13]. Anammox, anaerobic ammonium oxidation; N_2, molecular nitrogen.

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and lingering question complicated by landmass constraints that are poorly known and highly controversial (reviewed elsewhere[179]).

Nutrient cycling has also been mechanistically linked to progressively oxidizing conditions, including early throttles on phosphate availability[180], as well as the evolving balance of nitrification and denitrification and the expanded ecological impact of biological nitrogen fixation[18,45]. The expansion of diazotrophy gives us a wonderful, albeit somewhat enigmatic, example of the importance of redox-sensitive trace metals as cofactors in the catalytic actions of many enzymes. Early nitrogen data from marine sediments point to molybdenum as the critical ingredient[45] (Fig. 2) despite its hypothesized scarcity in the early anoxic ocean[37]. This surprise is elevated by the far greater abundance of $Fe(II)$ in those waters (Fig. 5) in combination with the existence of an iron-based alternative nitrogenase that does not require molybdenum. The answer may lie with advantages thought to come with molybdenum through its more favourable electron transfer stoichiometry. Recent work[181] has demonstrated that molybdenum nitrogenase has a greater affinity for N_2 than the vanadium and iron alternatives. Then, as the atmosphere and, eventually, the oceans accumulated O_2, the sources and sinks for molybdenum in oceans concomitantly grew and shrank, respectively, setting the stage for increased molybdenum-requiring diazotrophy. Another example of evolutionary innovations under specific conditions that fortuitously benefited from subsequent broader environmental change is the development of antioxidant enzymes hundreds of millions of years before the earliest accumulation of O_2 in the oceans[182,183]. In this case, production of reactive oxygen species (ROS) and O_2 through geological (abiological) processes[182,183] may have triggered an innovation that would be beneficial later on. On the flip side, iron has a critical role in chemical catalysis and energy production within phytoplankton today, in part through enzymatic functions, yet it occurs in vanishingly small amounts in modern O_2-rich seawater, suggesting the persistence of pathways that once thrived in the ancient $Fe(II)$-rich oceans. Other well-known relationships between metal distributions and the biospheric footprint of a particular metabolism include waning nickel in the oceans and its enzymatic importance in methanogenesis and the role of copper in nitrogen cycling[64,166]. In general, there often appears to be little correlation between the availability of a metal ion and whether it is used in essential metabolic pathways. This disconnect is a testament to how efficiently organisms can scavenge metals and hold on to that capacity and the related evolutionary advantages even in the face of environmental change. Indeed, studies exploring the relationships among evolving biospheric oxygenation and metal supplies in the oceans are important and ongoing[56,184–186], and all this work is now informed in unprecedented ways by a growing understanding of how ocean redox and related chemical compositions have changed over time (Fig. 5).

The balance between dissolved $Fe(II)$ and hydrogen sulfide in the early oceans carries important implications for anoxygenic photosynthetic pathways, including the strong possibility of those evolving prior to oxygenic photosynthesis[187–189]. We can infer little to no sulfide in the early oceans because the absence of oxygen meant low sulfate delivery from the continents and there was strong titration of sulfide by the abundant $Fe(II)$. Such settings allow us to speculate on consistent conditions favouring photosynthetic $Fe(II)$ (and possibly manganese) oxidation in the oceans prior to, and perhaps beyond, when local sulfide accumulations may have started (from ~2.7 billion to 2.5 billion years ago)[165,190,191]. We might thus hypothesize that sulfide oxidation became widespread in Archaean terrestrial environments, whereas photoferrotrophy dominated in the oceans. The origins and

ecological impacts of anaerobic oxidation of methane via a syntrophic consortium of methanotrophic archaea and sulfate-reducing bacteria further place evolving redox-dependent supplies of oceanic sulfate among the critical environmental factors, in this case for methane cycling and therefore climate[165]. Studies of anaerobic oxidation of methane, along with anammox[59,192] among others, have filled important gaps in our understandings of oxidative cycling without O_2 in the local setting.

Another essential consideration is the degree to which pathways are spread across different groups of microorganisms, highlighting the importance of enzymes over taxa[193] (for example, N_2 fixation that may have originated within Archaea and eventually spread to cyanobacteria[56]). The large diversity of pathways and participants in sulfate reduction and denitrification stand out as additional examples[56]. Thus, as metabolic pathways evolve, the ecological advantages they bring may prompt shifts in the key microbial players against a backdrop of co-evolving environments. In other words, we should ask which taxonomic groups dominated a specific metabolism at a given time and how these groups may have shifted in phase with changes in the environment. A similar question could be asked of an enzyme's evolution. For instance, a recent study[194] showed that amongst cyanobacteria, superoxide dismutase enzymes used copper and zinc as cofactors in the Archaean, but by the Paleoproterozoic they were capable of using iron, nickel and manganese instead. Furthermore, this theme leads to the inference that many important biogeochemical processes in the past may have been performed by different groups of microorganisms compared with what we observe today, either because of extinction or shifting metabolic traits.

Through all of the volumes of related research lies one unmistakable problem: we know almost nothing about the size of the Archaean biosphere, although upper bounds arising from nutrient limitations have been suggested[180,195], and relatively large biomass production may have emerged for the first time with the early stages of oxygenic photosynthesis[1]. Remaining questions centre on the time-varying magnitude of H_2-based and iron-based biological production, particularly in the oceans, and their controls on metabolic, taxonomic and ecological diversity. Nested within these impacts is the role of heterotrophy as a gateway to metabolic innovation, whereby accumulating degradation products may have driven an ever-expanding suite of other metabolic opportunities, including for chemoautotrophs. Additionally, considerable uncertainties persist regarding the evolutionary timeline of exoenzymes utilized by heterotrophs. These enzymes play a crucial role in breaking down large external molecules into smaller substrates directly useable by the cell[196]. The timing of this evolution is important, because in an ocean devoid of exoenzymes, heterotrophic microorganisms would have limited access to organic matter. Consequently, a substantial portion of dead phytoplankton biomass would have traversed the water column, settling on the sea floor without being efficiently utilized.

The clearest message we hope to convey through Fig. 5 is that the advent of a given metabolism does not necessarily walk hand in hand with the timeline for its significant ecological impact. The implication is that phylogenomic trees might tip us off to the beginnings of metabolisms before the environmental signatures of those reactions are detectable as isotopic fingerprints preserved in rocks. This disconnection partially reflects the patchiness of the early rock record, the degree to which abiotic pathways can yield similar isotopic expressions and the unfortunate reality that alteration of host rocks often confounds the geochemical story. It is worth noting, however, that

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there is often strong agreement between genomic predictions and geochemical records, with oxygenic photosynthesis emerging as one of the most prominent examples. Despite ongoing uncertainties and debates, we can argue for a general agreement between independent molecular clock analyses for the earliest O_2-producing cyanobacteria and geochemical arguments for accumulation in coastal regions on newly emerging continents roughly 3.0 billion years ago[4,20]. These shallow settings are similar to where light-bathed microbial mats thrive today. It also seems clear that the capacity of the early Earth to buffer O_2 production, both biotically and abiotically, drove the apparent time gap between the beginnings of biological O_2 production and related accumulation in surface ocean niches and much later persistent global-scale oxygenation.

The history of microbial life marched in step with the history of the oceans, land and atmosphere, and our understanding remains limited by how much we still do not know about the environments of the early Earth. Further challenges come with recognizing what we can or cannot learn through studies of modern biogeochemical cycles. Although much remains to be uncovered, the efforts made in recent years to bridge early life with its environments have substantially advanced our understanding of the early states of habitability of our planet. We have now reached a point where estimates of early atmospheres on Earth are being used as templates in the exploration for microbial biosignatures in gases surrounding exoplanets[197].

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Author contributions

T.W.L., C.J.T. and E.E.S. contributed to all aspects of the manuscript. G.P.F., R.E.A., W.D.L. and K.O.K. contributed to the research and compilation of materials for the article, to meaningful discussions and to initial drafting of at least one section and corresponding figure within the article.

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