



How Earth's atmosphere evolved to an oxic state: A status report

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Abstract

The evolution of the Earth's atmosphere is essentially the story of atmospheric oxygen. Virtually every realm of the Earth sciences—biology, geology, geochemistry, oceanography and atmospheric science—is needed to piece together an understanding of the history of oxygen. Over the past decade, new data from these fields has shown that there were two significant increases in atmospheric O₂ levels at around 2.4–2.3 and 0.8–0.6 billion years ago, respectively. Throughout Earth history, oceanic sulfate concentrations appear to have increased in accord with greater O₂ levels, while levels of methane, a strong greenhouse gas, may have inversely mirrored O₂. Both oxic transitions occurred in eras characterized by “Snowball Earth” events and significant disturbances in the carbon cycle, perhaps associated with increases in O₂ and losses of methane. To understand what controlled the oxygenation of the atmosphere, it is necessary to determine how O₂ is consumed on geologic time scales through reaction with reductants released from the Earth's crust and mantle. There was apparently a long delay between the appearance of oxygenic photosynthesis and oxygenation of the atmosphere, and a plausible explanation is that excess reductants scavenged photosynthetic O₂ from the early atmosphere. However, a quantitative understanding of how and why O₂ became abundant on our reducing planet is still lacking. Thus, the study of the early atmosphere remains a frontier field with much to be discovered. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Abundant atmospheric O₂ distinguishes the Earth from all other planets in the solar system. Oxygen supports animals, fungi and multicellular plants, which makes Earth's surface stunningly different from that of Earth's apparently lifeless neighbors [1]. But when our planet formed, its surface must

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Table 1

Glossary

Anoxygenic photosynthesis	Photosynthesis in which O ₂ is not produced. In this process, reduced compounds (H ₂ S, S, S ₂ O ₃ ²⁻ , H ₂) and sunlight provide energy, while more oxidized sulfur compounds or water are released as byproducts.
Archean	An Eon of Earth history, before 2.5 Ga. According to the International Stratigraphy Commission, the Archean starts at the formation of the Earth. However, frequently, the Archean is taken to start at 4.0–3.9 Ga, preceded by an Hadean Eon.
Cyanobacteria	Bacteria that contain chlorophyll <i>a</i> and are capable of oxygen-producing photosynthesis (previously classified as ‘blue-green algae’).
Exosphere	The highest layer of the atmosphere. The exosphere is where collisions between molecules/atoms are so infrequent as to be negligible, while at the base of the exosphere (<i>exobase</i>) and below, frequent collisions maintain an isotropic and random Maxwellian distribution of velocities. Exospheric particles move along ballistic trajectories and some fast, upward-directed particles escape Earth’s gravitational field.
Ga	Giga Anna = 10 ⁹ years ago
Hopane	A hydrocarbon containing a molecular skeleton of five carbon rings. Found in sediments, hopanes derive from hopanoids, which are compounds of bacterial cell membranes.
Hydrogen escape	A process in which hydrogen atoms or molecules in the exosphere exceed the escape velocity of the Earth and escape Earth’s gravity.
Ma	Mega Anna = 10 ⁶ years ago
Methanogens	Microbes that generate methane (CH ₄) by their metabolism (<i>methanogenesis</i>).
Methanotrophs	Microbes capable of oxidizing methane with either sulfate or O ₂ .
Oxidation state	The degree of oxidation of an atom, molecule, compound or quantity of matter. Substances with a low oxidation state have a large number of available electrons whereas substances with a high oxidation state do not.
Oxidative weathering	A process in which O ₂ (usually dissolved in rainwater, rivers or seawater) chemically reacts with rock minerals on the continents, for example the reaction of oxygen and sulfides to produce sulfates.
Oxidizing	A process or environment in which a chemical element or ion loses electrons and is changed from a lower to a higher valence state.
Oxygenic photosynthesis	The process in which an organism uses sunlight, water and carbon dioxide to synthesize organic matter, releasing O ₂ as a waste product.
Paleosol	A buried, commonly lithified, soil horizon of the geologic past.
Phanerozoic	An Eon of Earth history, 0.542 Ga to present.
Precambrian	The part of Earth history before 0.542 Ga, composed of the Proterozoic (2.5–0.542 Ga) and Archean (before 2.5 Ga).
Proterozoic	An Eon of Earth history, 2.5 to 0.542 Ga. It is composed of three eras, the Paleoproterozoic (2.5 to 1.6 Ga), the Mesoproterozoic (1.6–1.0) and the Neoproterozoic (1.0–0.542 Ga).
Red bed	Sediments or sedimentary rock that is red or reddish-brown in color due the presence of ferric oxide materials usually coating individual grains.
Reducing	A process or environment in which a chemical element or ion gains electrons and is changed from a higher to a lower valence state.
Snowball Earth	An event in Earth history when low-latitude glaciation occurred and the whole Earth may have been covered in ice.
Steranes	Hydrocarbons with four fused carbon rings derived from sterols that have been chemically altered by diagenesis. The carbon rings are fully saturated (i.e., no carbon–carbon double bonds).
Sterols	Organic compounds containing a molecular skeleton of four fused carbon rings with an alcohol (–OH) group on part of the structure (e.g., cholesterol). Sterols are mostly found in cell membranes of eukaryotes where they give rigidity. The equivalent role in many bacteria is performed by hopanoids. Sterols are rare in bacteria, their limited occurrence probably reflecting ingestion rather than biosynthesis.
Stromatolite	A lithified, commonly laminated sedimentary structure produced as a result of the growth and metabolic activities of aquatic, bottom-dwelling communities of microorganisms.
Sulfate reduction	A process used by some bacteria to derive energy by reducing sulfate ions (SO ₄ ²⁻) to H ₂ S.

also have been devoid of life. How the complex world around us developed from lifeless beginnings presents a great interdisciplinary challenge (See Table 1 for terminology). Part of this endeavor is to understand how atmospheric composition has changed in response to the activities of organisms and how the atmosphere, in turn, has affected biological evolution.

Changes in O_2 levels define the standard history of Earth's atmosphere. Over the past decade, new data has constrained this O_2 history, models have helped our understanding, and new questions have emerged. Geochemical data now suggest that there were two major increases in O_2 . These occurred near the beginning and end of the Proterozoic eon (2.5–0.542 Ga), respectively. The first rise of O_2 occurred around 2.4–2.3 Ga, within the Paleoproterozoic era (2.5–1.6 Ga) [2]. Then, about 1.0–0.6 Ga, within the Neoproterozoic era (1.0–0.542 Ga), O_2 plausibly rose a second time [3,4]. Both O_2 increases appear in the same eras as substantial changes in the Earth's biota, geochemistry [2,5–7] and climate [8].

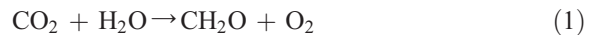
O_2 is a result of oxygenic photosynthesis, whereby organisms split H_2O and release O_2 . Oxygenic photosynthesis originated in the ancestors of cyanobacteria [9], which, long before green plants evolved, generated O_2 . Many cyanobacteria are phytoplankton—the microscopic, usually single-celled organisms floating in the surface waters of the ocean. Today, $\sim 10^{27}$ cyanobacteria constitute the most numerous phytoplankton [10] of which *Prochlorococcus* is the most numerous organism on Earth [11]. Ancestral cyanobacteria were probably just as plentiful but their effect on the atmosphere was delayed. The evidence for the earliest oxygenic photosynthesis predates detectable atmospheric O_2 by several hundred million years (Section 4.2). Consequently, how Earth's atmosphere became oxic is not simply a question of the origin of cyanobacteria. Indeed, a quantitative understanding is still lacking for how free oxygen became abundant on a planet that is overall chemically reducing. Organic carbon or its reducing equivalent balances every oxygen molecule that is produced by photosynthesis and so Earth's initially reducing environment was not easily shifted. To determine why O_2 increased requires an integrated grasp of the redox behavior of the Earth system. In

this review, we start by discussing the modern atmosphere because this enables us to lay some groundwork before turning to the ancient Earth.

2. How is oxygen regulated in modern biogeochemical cycling?

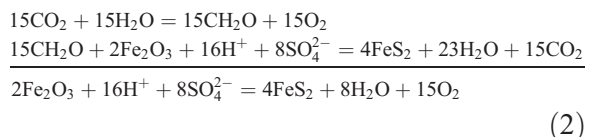
2.1. The “net” source of O_2

In oxygenic photosynthesis, the production of 1 mol of organic carbon (with average stoichiometry CH_2O) generates 1 mol of O_2 via



Respiration and decay reverse this reaction on a time scale of $\sim 10^2$ years, consuming >99% of the oxygen produced by photosynthesis. But a small fraction (0.1–0.2%) of organic carbon escapes oxidation through burial in sediments. From Eq. (1), the burial of 1 mol of organic carbon liberates 1 mol of O_2 . Such burial of organic carbon is referred to as the “net source” of O_2 , but the fate of the O_2 depends on the kinetics of the various sinks for O_2 . O_2 will not, in fact, accumulate in the atmosphere if the flux of kinetically rapid sinks exceeds the slow flux of organic burial (see Section 2.3), which is important when considering the lack of O_2 in the Archean eon (before 2.5 Ga).

The oxygen cycle is complicated by the burial of other redox-sensitive elements besides carbon. The quantitatively important elements are sulfur and iron. During weathering, O_2 dissolved in water oxidizes sulfur within continental pyrite (FeS_2), making soluble sulfate (SO_4^{2-}), which is carried by rivers to the ocean. Then, in the ocean, bacteria reduce sulfate and ferric iron (Fe^{3+}) to pyrite. The reducing power of photosynthesized organic carbon is essentially transferred to pyrite, so that pyrite buried in sediments is balanced by O_2 production [12]:



By examining the average composition of sedimentary rocks, Holland [13] estimates that organic carbon and

pyrite burial contribute fluxes of 10.0 ± 3.3 Tmol O_2 $year^{-1}$ and 7.8 ± 4.0 Tmol O_2 $year^{-1}$, respectively (where 1 Tmol = 10^{12} mol). The reduction of oxidized iron and the burial of ferrous iron ($2Fe_2O_3 = 4FeO + O_2$) also adds a minor flux of oxygen, whereas the burial of sulfate minerals in sediments removes O_2 . Summing these fluxes, the total O_2 source is 18.4 ± 7.8 Tmol O_2 $year^{-1}$ (Fig. 1).

2.2. The balance of net O_2 production and loss

Because the amount of atmospheric O_2 is relatively stable, the net source of O_2 must be balanced by losses, otherwise O_2 levels would increase or decrease. Oxidative weathering consumes $\sim 5/6$ (~ 15 Tmol $year^{-1}$) of the O_2 generated by burial of reductants, while $\sim 1/6$ (~ 3 Tmol $year^{-1}$) is consumed by reaction with reducing gases emanating from the solid Earth, noting that these proportions are highly uncertain [13]. Important reducing gases (i.e., gases that consume O_2) include H_2 , CO , CH_4 , H_2S , and SO_2 . These gases are produced in volcanism (when rocks melt) and metamorphism (when rocks are heated and/or pressurized but do not melt). Reducing gases are oxidized through photochemical reactions that sum to a net oxidation by O_2 , effectively behaving like combustion. There are uncertainties in the O_2 source and sink. For the source flux, an underlying assumption is that buried organic matter is not chemically resistant, fossil organic carbon eroded off the continents and simply reburied in a closed loop. Recent measurement of a fossil carbon flux of only

~ 0.06 Tmol C $year^{-1}$ confirms this assumption [14]. An uncertainty in the O_2 sink concerns the contribution of volcanic versus metamorphic reducing gases. Volcanic gases are commonly studied, but metamorphic fluxes are spatially extensive with uncertain global magnitude. Mass balance suggests that metamorphic fluxes could be important. For example, 0.6 wt.% of C in average sediments compared to 0.45 wt.% of C in uplifted rock exposed to weathering [13] implies that that a 0.15% difference in reductant has been lost in reactions such as $C + 2H_2O = CO_2 + 2H_2$ [15]. Given the organic burial flux of ~ 10 Tmol $year^{-1}$, a crude upper limit on today's metamorphic reducing flux due to carbon alone is $(0.15/0.6) \times 10$ Tmol = 2.5 Tmol O_2 consumption $year^{-1}$, comparable to estimates of the total reducing gas flux.

2.3. A general theoretical framework for the history of atmospheric O_2

The history of O_2 can be described generally. The rate of change of the reservoir of O_2 , R_{O_2} , in the atmosphere (in teramoles) is

$$\begin{aligned} \frac{d(R_{O_2})}{dt} &= F_{\text{source}} - F_{\text{sink}} \\ &= F_{\text{source}} - (F_{\text{volcanic}} + F_{\text{metamorphic}} + F_{\text{weathering}}) \end{aligned} \quad (3)$$

Here, F_{sink} is the removal flux of O_2 from the atmosphere (in teramoles per year) due to numerous oxi-

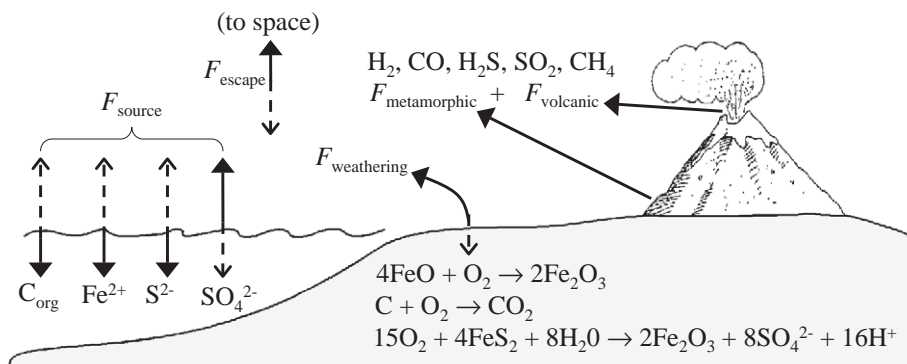


Fig. 1. Schematic diagram showing the modern fluxes of O_2 . The fluxes include metamorphic ($F_{\text{metamorphic}}$) and volcanic (F_{volcanic}) sources of reducing gases. F_{source} is the flux of burial of organic carbon, pyrite and ferrous iron that contribute equivalent oxygen into the atmosphere–ocean system. F_{escape} is the escape of hydrogen to interplanetary space and $F_{\text{weathering}}$ is the flux of reductants uplifted on continental surfaces that react with O_2 dissolved in rainwater. Solid arrows indicate flow of reductants, while dashed arrows indicate an equivalent flux of oxygen.

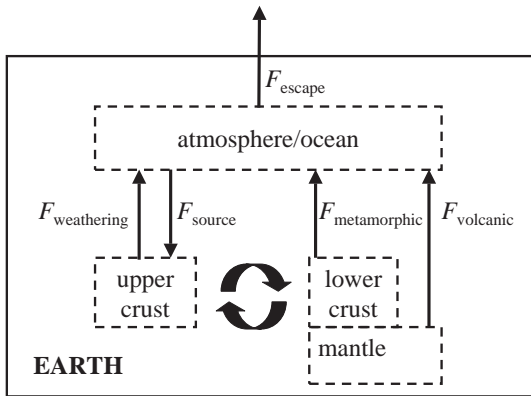


Fig. 2. A schematic diagram showing reductant fluxes that govern the oxidation state of the atmosphere, ocean and lithosphere. Curved arrows between the upper and lower crust reservoirs indicate mixing due to tectonic activity. Summing fluxes into and out of the atmosphere–ocean box gives Eq. (3).

dation reactions. F_{source} is the source flux of oxygen (in teramoles per year) due to burial of organic carbon and pyrite and the escape of hydrogen to space (Fig. 2). The sink fluxes are the reaction of O_2 with reduced volcanic gases (F_{volcanic}), reduced metamorphic gases ($F_{\text{metamorphic}}$), and reduced material on the continents ($F_{\text{weathering}}$). If R_{O_2} is in “steady-state”, F_{sink} will be close to F_{source} and $d(R_{\text{O}_2})/dt \approx 0$. Oxygen levels have changed because the terms on the right-hand side of Eq. (3) have altered over Earth history and been in imbalance in the past with $F_{\text{source}} > F_{\text{sink}}$ (see Section 6).

2.4. The stability of atmospheric O_2 and negative feedbacks

Negative feedbacks exist that prevent O_2 levels from wildly fluctuating because evidence suggests that Phanerozoic O_2 levels have been stable at 0.2 ± 0.1 bar. Animals, which require O_2 to grow and breathe, have been present throughout the Phanerozoic [16]. Also, a charcoal record extends back ~ 350 m.y., which suggests that there has been sufficient O_2 ($\sim 15\%$) to burn trees [17,18]. Yet the short residence time of O_2 in the atmosphere–ocean system means that Phanerozoic O_2 has been replaced more than 200 times. Dividing the atmosphere–ocean reservoir (3.8×10^7 Tmol O_2) by the source flux (18 Tmol O_2 year $^{-1}$) gives ~ 2 million years for the average amount of time an O_2

molecule spends in the atmosphere–ocean system (Fig. 3).

So what sets the amount of O_2 in the air? It cannot be respiration and decay. The amount of organic carbon at the Earth’s surface ($\sim 4.4 \times 10^5$ Tmol) is almost 10^2 times smaller than the atmospheric reservoir of O_2 (3.8×10^7 Tmol) so that respiration and decay can modulate no more than 1% of the total amount of atmospheric O_2 [19]. Instead, respiration and decay control the size of the small reservoir of surface organic carbon. O_2 must be regulated because an increase in O_2 hastens the consumption of O_2 and/or slows the rate of O_2 production, while a decrease of O_2 has the opposite effects. Because the oxidation of continental surfaces appears relatively complete, many researchers have favored a negative feedback on the O_2 source (organic burial) as a primary control. Evidence suggests that this feedback does not act directly, by oxidizing newly produced organic carbon and preventing its burial [20], but indirectly through the supply of nutrients. Most organic carbon is buried on oceanic continental shelves [21]. Phosphorus acts as a limiting nutrient for marine photosynthesis because its only source is from continental weathering. In the ocean, the burial of phosphorus bound to iron hydroxides becomes less efficient under anoxic conditions [22,23]. Thus a decrease of O_2 may increase phosphorus available for the production and burial of new organic matter. To counteract a rising O_2 , some have hypothesized that the forest fires would become

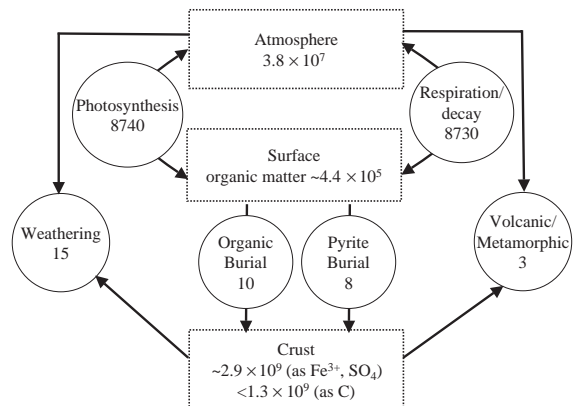


Fig. 3. Oxygen reservoirs and fluxes in the modern O_2 cycle. Primary production is from [114]. Fluxes of burial, weathering and reaction with volcanic and metamorphic gases are from [13].

more frequent, triggering an ecological shift to grassland. In the long-term cycle, trees, whose roots break up bedrock, amplify the rate of rock weathering by about an order of magnitude relative to more shallowly rooted plants [24]. Rising O_2 would thus lower the supply of marine phosphorus and the rate of organic carbon burial, the O_2 source [25]. Alternatively, Falkowski [26] argues that nitrogen can behave as the ultimate limiting nutrient and that higher O_2 leads to diminished nitrogen fixation and organic burial rates. To counter this, Tyrell [27] shows that N-fixing marine organisms (mainly cyanobacteria) can multiply to produce enough N.

Let us now examine O_2 in the ancient atmosphere.

3. How reducing was the prebiotic atmosphere?

3.1. General considerations for the composition of the prebiotic atmosphere

Walker [28] argues that before life existed the atmosphere contained mainly N_2 , with negligible O_2 , probably more CO_2 than today, and only minor levels of reducing gases such as H_2 . N_2 was likely similar to modern levels, because it would have outgassed early and does not react easily with surface rocks [29]. Many early workers favored a highly reducing prebiotic atmosphere, with gases such as hydrogen or methane as major constituents. The Oparin–Haldane theory that life originated from compounds such as abiotically synthesized amino acids in highly reducing atmospheres helped motivate this view [30]. However, such an atmosphere could only be sustained by outgassing that is far more reducing (richer in hydrogen) than modern volcanic emissions. Today's volcanic gases have a typical composition of 80–90% H_2O , 6–12% CO_2 , ~3% S gases (H_2S and SO_2 in uncertain ratio [31]), 0.6–1.5% H_2 and <0.4% CO [32], which is weakly reducing because it contains no O_2 and only small amounts of H_2 relative to H_2O . The oxidation state of volcanic gases depends on upper mantle rocks, where the gases originate. The more reducing the mantle is, the more reducing the volcanic gases. The upper mantle would have needed to contain metallic iron in order to supply sufficiently reducing gases to a highly reducing prebiotic atmosphere. But metallic iron sank into the Earth's core

within ~30 million years after the planet formed [33] (Fig. 4). Thus, the proportions of reducing versus oxidized gases from volcanism should not have changed hugely since then, although some shift is not excluded (see Section 6.2).

A recent paper [34] suggests that the early atmosphere was highly reducing because of a slower rate of hydrogen escape to space than previously thought. However, this slow escape rate stems from questionable assumptions. [34] only consider temperature-dependent hydrogen escape and assume a pure H_2 upper atmosphere, which necessarily generates a cold exosphere because neither the absorption of extreme ultraviolet by other gases nor the higher temperature of atomic ions is considered. Also, non-thermal escape processes dominate today and cannot be dismissed for early Earth.

3.2. Hydrogen and oxygen in the prebiotic atmosphere

Theory implies that abiotic O_2 fluxes on the prebiological Earth would have been swamped by hydrogen. A balance between outgassing and loss to space would have determined H_2 levels (Fig. 5). Hydrogen atoms at the top of the atmosphere escape to space. Theory, which has been verified in today's atmosphere, shows that the rate of escape of hydrogen (ϕ_{escape}) is proportional to the sum of the mixing ratio, f , of all hydrogen-bearing gases above the troposphere weighted by the number of hydrogen atoms they

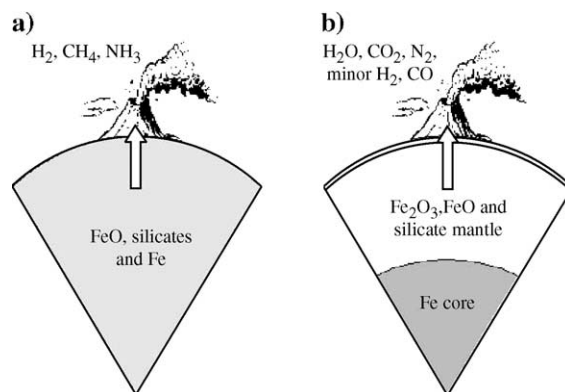


Fig. 4. (a) Reducing volcanic gases (with significant H_2 , CH_4 and NH_3) were introduced into the atmosphere before core formation, when the mantle was rich in metallic iron. (b) A weakly reducing mixture of volcanic gases has fed the atmosphere for most of Earth history, after the Earth differentiated into core, mantle and crust.

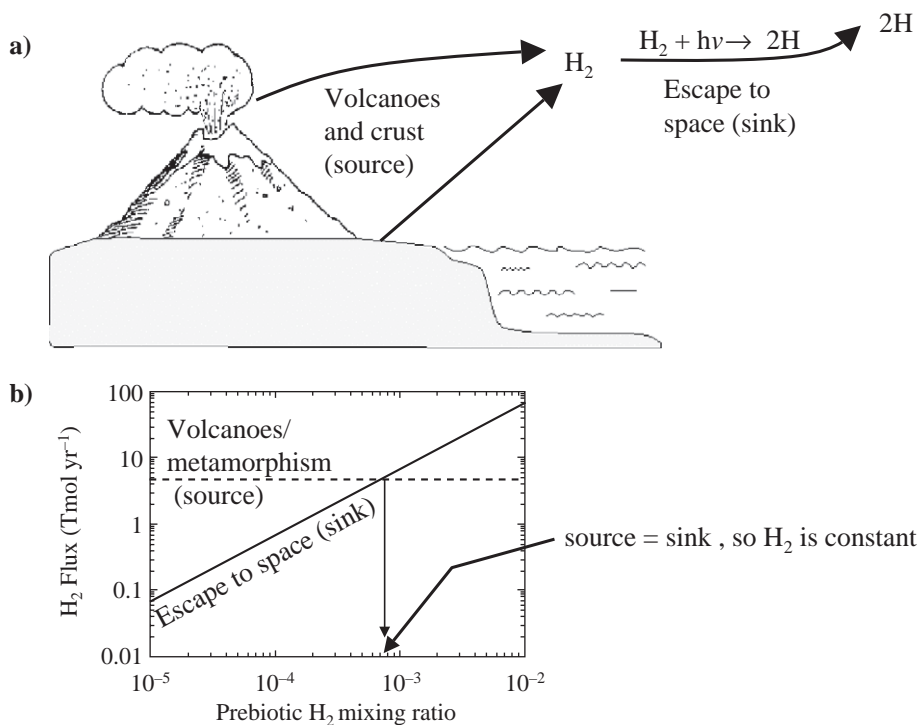


Fig. 5. Hydrogen in the Earth's prebiotic atmosphere. (a) Schematic of outgassing source and escape sink (b) how dynamic equilibrium sets the prebiotic H₂ concentration.

contain ($f_{\text{total}} = f_{\text{H}_2\text{O}} + f_{\text{H}_2} + 2f_{\text{CH}_4} \dots$). The proportionality constant is insensitive to plausible differences in structure and composition between a primitive and modern atmosphere, giving a simple equation [28]:

$$\phi_{\text{escape}} = 2.5 \times 10^{13} f_{\text{total}} (\text{H}_2 \text{ molecules cm}^{-2} \text{s}^{-1}) \quad (4)$$

The modern H₂ outgassing rate is $4.8 \pm 3.6 \text{ Tmol H}_2 \text{ year}^{-1} = 1.8 \pm 1.3 \times 10^{10} \text{ H}_2 \text{ molecules cm}^{-2} \text{s}^{-1}$ [13]. The outgassing rate may have been a few times higher on early Earth because of increased heat flow and plumes from a more radioactive interior, but to within an order of magnitude, setting the escape rate on early Earth equal to the modern outgassing rate in Eq. (4) yields an H₂ mixing ratio of $\sim 7 \times 10^{-4} \approx 0.1\%$, assuming that f_{total} was dominated by H₂ (Fig. 5b).

Hydrogen exerts a control on oxygen through a net reaction.



Abiotic O₂ arises only from the photolysis of water vapor and associated escape of hydrogen to space.

By itself, photolysis of H₂O or CO₂ does not provide a net source of O₂ because the photolysis products recombine. The rate of O₂ production from H₂O photolysis and hydrogen escape would have been $\sim 0.01 \text{ Tmol O}_2 \text{ year}^{-1}$ [35]. Thus, the volcanic flux of hydrogen would have overwhelmed the O₂ source by a factor of $\sim 10^2$. Under these circumstances, oxygen attains only $\sim 10^{-13}$ bar partial pressure [36].

4. How did the arrival of life affect the early atmosphere?

4.1. The effect of early life on atmospheric chemistry and climate

The coexistence of reducing and oxidized gases in the prebiotic atmosphere would have provided untapped chemical energy. At some point, life must have evolved to exploit this. Methanogens are modern microbes that exploit redox disequi-

librium by combining H_2 and CO_2 to make methane:



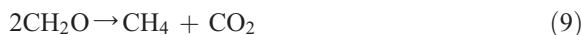
In the laboratory, methanogens draw down H_2 to produce methane until they reach a thermodynamic limit at $\sim 0.01\%$ H_2 [37]. Methanogens are strictly anaerobic with a tendency toward thermophily, which suggests that they are evolutionarily ancient [38]; also remnant organic molecules and carbon isotopes suggest methanogens were present in the Archean [39,40]. Thus, methanogens likely would have converted atmospheric H_2 into methane, with H_2 dropping from 0.1% to 0.01% (Fig. 6a) [37,41]. CO_2 levels would have decreased as a consequence. CH_4 is a powerful greenhouse gas, and the warming associated with elevated CH_4 would have diminished CO_2 in temperature-dependent weathering, where CO_2 dissolved in rainwater reacts with continental silicates [42].

Anoxygenic photosynthesis would have also affected H_2 and CH_4 (Fig. 6b). This type of photosyn-

thesis does not release O_2 but sulfur compounds or water [43], e.g.,



An organism using a metabolism such as Eq. (8) can flourish at lower H_2 concentrations than methanogens. Thus, the evolution of anoxygenic photosynthesis, perhaps before 3.5 Ga [44], would have depressed atmospheric H_2 levels even more than the advent of methanogens. Also, photosynthesized organic matter would likely have been fermented to produce higher levels of CH_4 (Fig. 6b) via the overall metabolic pathway



In the steady state, the influx of reductants would be balanced by an equal outflux. As a consequence, the supply of reductants, such as H_2 or H_2S , from geological sources would have restricted the productivity of early life.

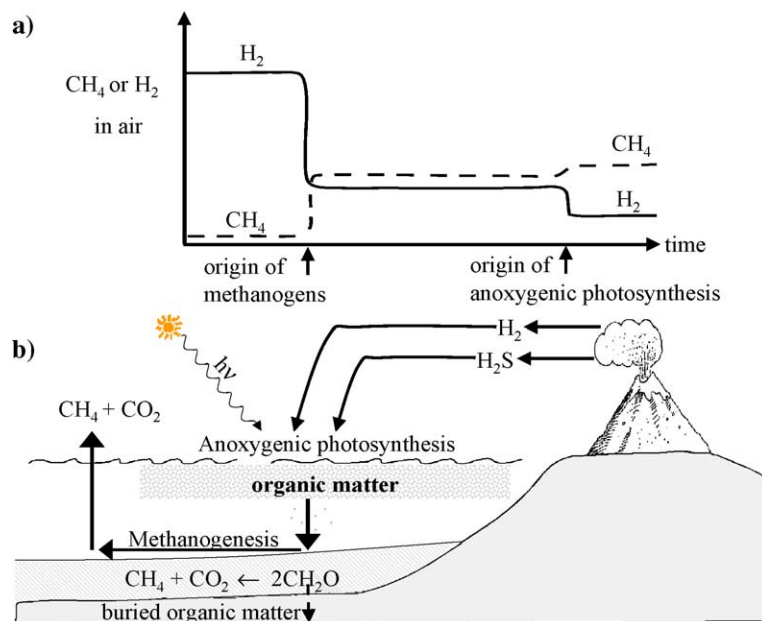


Fig. 6. Schematic showing the effect of organisms on the early atmosphere before the origin of oxygenic photosynthesis. For the sake of argument, this graph assumes methanogens evolved before anoxygenic photosynthesis, but this is uncertain.

4.2. When did oxygenic photosynthesis appear?

Oxygenic photosynthesis extracts hydrogen from ubiquitous water and enabled life to overcome its dependency on geothermal sources of reducing gases (needed to reduce CO_2 to organic matter). Consequently, productivity was no longer limited by reductants but by nutrients, e.g., phosphorus [27,45].

Recent data shows that the atmospheric oxidation transition occurred at ~ 2.4 – 2.3 Ga [2], while oxygenic

photosynthesizers existed long before that [39]. Microfossils [46,47], stromatolites (fossilized remains of microbial communities) [48,49], and carbon and sulfur isotopes [50,51] all indicate global microbial life in the mid-Archean [44]. Specific evidence for oxygenic photosynthesizers comes from biomarkers, which are remnants of organic molecules diagnostic of particular organisms. At 2.7 Ga, 2- α -methylhopane biomarkers derived from oxygenic photosynthetic cyanobacteria and steranes derived

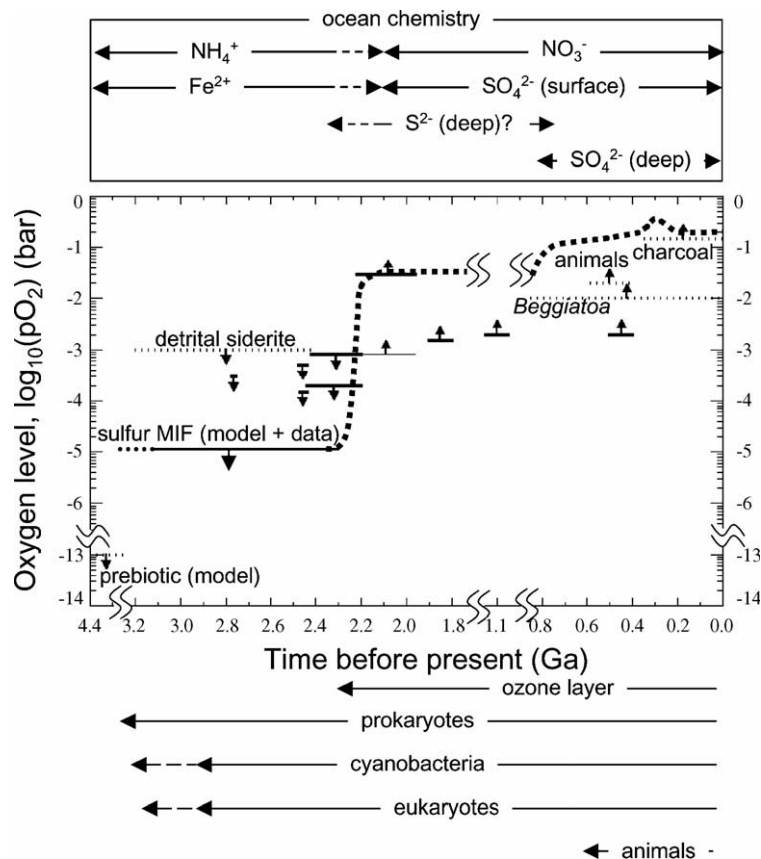


Fig. 7. The history of O_2 , where the thick dashed line shows a possible evolutionary path that satisfies biogeochemical data. Dotted horizontal lines show the duration of biogeochemical constraints, such as the occurrence of detrital siderite (FeCO_3) in ancient riverbeds. Downward-pointing arrows indicate upper bounds on the partial pressure of oxygen ($p\text{O}_2$), whereas upward-pointing arrows indicate lower bounds. Unlabelled solid horizontal lines indicate the occurrence of particular paleosols, with the length of each line showing the uncertainty in the age of each paleosol. Inferences of $p\text{O}_2$ from paleosols are taken from [58]. An upper bound on the level of $p\text{O}_2$ in the prebiotic atmosphere at c. 4.4 Ga (shortly after the Earth had differentiated into a core, mantle and crust) is based on photochemical calculations. MIF is “mass-independent isotope fractionation”, which in sulfur is caused by photochemistry in an O_2 -poor atmosphere. The $p\text{O}_2$ level inferred from MIF observed in pre-2.4 Ga sulfur isotopes is based on the photochemical model results of [70]. Biological lower limits on $p\text{O}_2$ are based on the O_2 requirements of: (1) the marine sulfur-oxidizing bacterium, *Beggiatoa* [3]; (2) animals that appear after 0.59 Ga [115]; (3) charcoal production in the geologic record. A “bump” in the oxygen curve around ~ 300 Ma, in the Carboniferous, is based on the interpretation of Phanerozoic carbon and sulfur isotope data by [116].

from eukaryotic sterols are present [39,52,53]. Sterols require O_2 in their biosynthesis, so that eukaryotes presumably lived in proximity to O_2 producers. The only alternative is sterol biosynthesis without O_2 in a metabolic pathway that has since vanished, but no genetic evidence supports this. Sterols are also found in some planctomycetes, which are evolutionary ancient bacteria [54,55], indirectly suggesting an early origin for O_2 producers. Stromatolites from a 2.7 Ga lake are consistent with the presence of oxygenic photosynthesis because the lake lacked sulfate and hydrothermal reductants needed for anoxygenic photosynthesis, while the stromatolites display a photosynthetic habit [56]. Analysis of lead isotopes has also been interpreted to infer that oxygenic photosynthesis existed even as early as 3.7 Ga [57]. Isotopes of carbon in sedimentary organic carbon and carbonates back to 3.5 Ga are permissive of oxygenic photosynthetic fractionation, although anoxygenic photosynthesis is a possible alternative [50]. In summary, the data presents the puzzle that oxygenic photosynthesis existed at least 0.3 b.y., and perhaps >1 b.y., before the initial rise of O_2 . Section 6 presents suggested solutions to this paradox.

5. What is the evidence for the Paleoproterozoic rise of O_2 and its effect?

5.1. Geochemical evidence

5.1.1. Evidence from continental environments

Paleosols, detrital grains and red beds suggest very low levels of O_2 before ~2.4 Ga. Well-preserved paleosols (lithified soils) provide estimates of the oxygen partial pressure (pO_2) based on iron and rare-earth element geochemistry (reviewed by [58]) (Fig. 7). Iron was leached from soils before the ~2.4 Ga oxic transition but not afterwards because anoxic rainwater flushes soluble ferrous iron (Fe^{2+}) through a soil, whereas oxygenated rainwater produces insoluble and immobile ferric iron (Fe^{3+}). Cerium (Ce^{3+} and Ce^{4+}) can be used similarly [59]. Other evidence comes from detrital grains, which are sedimentary minerals that never completely dissolve in weathering. Detrital grains in pre-2.4 Ga riverbeds commonly contain reduced

minerals that would only survive at low pO_2 [60]. Grains of pyrite (FeS_2), uraninite (UO_2) and siderite ($FeCO_3$) place upper bounds on Archean pO_2 of ~0.1, ~0.01 and ~0.001 bar, respectively. The roundness of such grains shows that they were transported long distances in aerated waters. A further constraint is the appearance of Proterozoic continental redbeds. Redbeds are sedimentary sandstones derived from windblown or river-transported particles coated with red-colored iron oxides, usually hematite (Fe_2O_3), which formed after atmospheric oxygenation [61,62].

5.1.2. Evidence from marine environments

Banded Iron Formations (BIFs) appear from the start of the geologic record but decline in abundance through the Paleoproterozoic and disappear after ~1.8 Ga, consistent with redox change. BIFs are laminated marine sedimentary deposits that contain iron-rich and iron-poor (usually silica-rich) layers. Trace and rare earth element patterns in BIFs indicate hydrothermal input of ferrous iron, which would have remained in solution if deep waters of the Archean ocean were anoxic [63,64]. Fe^{2+} is hypothesized to have been transported to shallow continental shelves where oxidation precipitated ferric iron. BIFs' presence for ~0.5 b.y. after the rise of O_2 has been used to argue that the deep ocean was not oxygenated until 1.8 Ga [65]. Recently, Canfield [4] suggested that the deep ocean remained anoxic until the Neoproterozoic, with Fe^{2+} being removed by the precipitation of pyrite derived from sulfate reducing bacteria (Section 7).

Isotopes of carbon, sulfur and iron in marine sediments also indicate major change in the Paleoproterozoic. Photosynthesis concentrates ^{12}C into organic matter, leaving inorganic carbonate relatively enriched in ^{13}C . Isotopic compositions are expressed as $\delta^{13}C$, a measure of $^{13}C/^{12}C$ in a sample relative to that in a limestone standard ($\delta^{13}C = [(^{13}C/^{12}C)_{\text{sample}} / (^{13}C/^{12}C)_{\text{standard}} - 1] \times 1000$, in parts per thousand (‰)). From ~3.5 Ga, sedimentary organic carbon is found to be ~30‰ (3%) lighter than marine carbonates with mean $\delta^{13}C \approx 0‰$. The difference reflects biological fractionation. Carbon entering the atmosphere–ocean system from volcanism, metamorphism and weathering has $\delta^{13}C_{\text{in}} \approx -6‰$. On time scales greater than $\sim 10^5$ years, the residence time of carbon

in the ocean, the same mixture of isotopes entering the atmosphere–ocean system must exit, implying,

$$\delta_{13}\text{C}_{\text{in}} = f_{\text{carb}}\delta_{13}\text{C}_{\text{carb}} + f_{\text{org}}\delta_{13}\text{C}_{\text{org}} \quad (10)$$

Here, f_{carb} is the fraction of carbon buried as carbonate with isotopic composition $\delta_{13}\text{C}_{\text{carb}}$, and f_{org} is the fraction buried as organic carbon with $\delta_{13}\text{C}_{\text{org}}$. Solving Eq. (10) with the observed $\delta_{13}\text{C}$ values gives $f_{\text{org}} \approx 0.2$. Thus, over geologic time, $\sim 20\%$ of the carbon in CO_2 entering the ocean–atmosphere system has exited as buried organic carbon and $\sim 80\%$ as carbonate [50]. Very positive $\delta_{13}\text{C}_{\text{carb}}$ excursions (Fig. 8) occur in the Paleoproterozoic, the same era as the rise of O_2 , and are possibly associated with enhanced organic burial (Section 6.2.1). The sulfur isotope record indicates that while there was <0.2 mM sulfate in the Archean oceans, sulfate levels increased in the Proterozoic [65]. For concentrations exceeding ~ 0.05 – 0.2 mM, sulfate reducing bacteria preferentially use ^{32}S rather than ^{34}S , producing sulfides that are enriched in ^{32}S relative to co-existing seawater sulfate [65]. Sulfides with significant ^{32}S enrichment only become widespread after 2.3 Ga, suggesting more

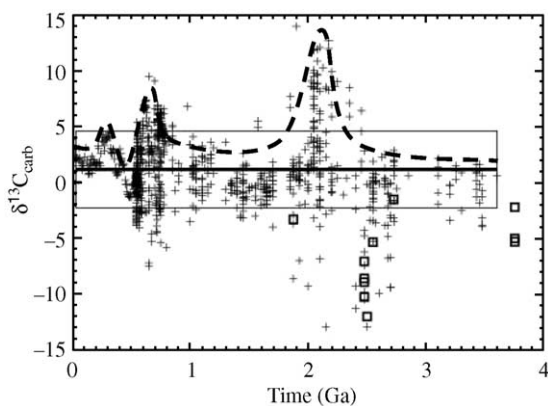


Fig. 8. The carbon isotope record of $\delta_{13}\text{C}$ in marine carbonates. The horizontal line is the average of all values (neglecting those from banded iron formations (square symbols)) and the surrounding rectangular box extends to one standard deviation. The dashed line is a sketch indicating how the Paleoproterozoic and Neoproterozoic were times of unusually isotopically heavy carbonates. Isotopically light carbonates between 2.7–2.4 Ga are likely due to carbonates derived from respired organic matter, which is particularly true of banded iron formations [117]. The Precambrian carbon isotope data is from R. Buick (unpublished), modified from [118] by additional literature and improved radiometric dating. Phanerozoic carbon isotope data is from [87].

available sulfate and hence oxygen [66]. Changes in iron isotopes also provide evidence for an oxic transition [67]. When iron precipitates as iron oxide, ^{56}Fe is sequestered relative to more weakly bonding ^{54}Fe , which leaves $\text{Fe}^{2+}(\text{aq})$ isotopically light. Negative $\delta^{56}\text{Fe}$ in pyrites before ~ 2.3 Ga suggests an anoxic deep ocean, rich in $\text{Fe}^{2+}(\text{aq})$, with fractionating loss of iron to BIFs.

A small minority claims that the model of a Paleoproterozoic rise of O_2 is incorrect [68]. For the rest of the community, however, new mass-independently fractionated sulfur isotope data essentially prove a rise of O_2 at 2.4–2.3 Ga when considered in concert with all the above evidence [2,69]. Isotope fractionation is generally “mass dependent” and approximately proportional to the mass difference between isotopes. Photochemistry can produce “mass-independent fractionation” (MIF) where isotopes are still fractionated by mass, but relative abundances deviate from simple proportionality. In the modern atmosphere, volcanic sulfur volatiles are oxidized to sulfate, which dissolves in rainwater and produces isotopically uniform oceanic sulfate. An anoxic atmosphere has two differences. Firstly, the lack of a stratospheric ozone layer allows shortwave ultraviolet to penetrate the troposphere and produce MIF during photolysis (e.g., $\text{SO}_2 + h\nu = \text{SO} + \text{O}$ and $\text{SO} + h\nu = \text{S} + \text{O}$). Secondly, if $p\text{O}_2 < 10^{-5}$ bar, sulfur compounds exit the atmosphere in a range of oxidation states, allowing MIF to be preserved in sediments [70–72]. Sulfur isotopes from a wide variety of depositional settings show MIF prior to ~ 2.4 Ga, but not afterwards.

5.2. What were the consequences of the rise of O_2 for atmospheric chemistry and climate?

Atmospheric O_2 and CH_4 annihilate each other. Consequently, for an anoxic Archean atmosphere, photochemical models simulate 10^2 – 10^3 ppmv CH_4 [70], compared to ~ 1.75 ppmv today [73], if given a global methane source ranging 10–100% of today’s flux. The early sun was 25–30% fainter than today and so the atmosphere must have had more greenhouse gas to prevent Earth from being globally frozen [74]. Abundant methane can provide such greenhouse warming [75]. A rise in O_2 would promote the rapid destruction of the methane, cooling the Earth by a few

tens of °C, which could explain the ~2.4 Ga Paleoproterozoic “Snowball Earth” [75]. Oxygen also has another important repercussion. Ozone (O₃) derives from O₂. Once O₂ rose to ~1% of the current atmospheric level, an effective stratospheric ozone screen for ultraviolet radiation emerged (Fig. 7), shielding the surface biosphere.

6. Explaining the rise of O₂ and the oxidation of the surface of the Earth

6.1. What defines an oxic versus anoxic atmosphere?

An oxidizing atmosphere is poor in hydrogen-bearing reducing gases whereas a reducing atmosphere is not. Even a small excess of hydrogen tips the balance. For example, an atmosphere with a steady-state abundance of ~0.1% H₂ (or equivalently, 0.05% CH₄) will be anoxic.

An atmosphere becomes anoxic if the flux of rapidly reactive reductants, principally reducing gases, exceeds the net flux of O₂. To be exact, an atmospheric oxygenation parameter, K_{oxy} , can be defined as follows,

$$K_{\text{oxy}} = \frac{F_{\text{source}}}{F_{\text{Rsink}}} = \frac{F_{\text{source}}}{F_{\text{metamorphic}} + F_{\text{volcanic}}} \quad (11)$$

where F_{source} (in teramoles per year) is the net flux of O₂ due to burial of reductants and F_{Rsink} is the flux of metamorphic and volcanic reductants, expressed as Tmol O₂ year⁻¹ consumed (Figs. 1, 2). F_{Rsink} mostly consists of hydrogen-bearing gases and, conceptually, even hydrothermal reducing cations behave as effective H₂ through schematic reactions such as $2\text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 4\text{H}^+ + \text{H}_2$. When $K_{\text{oxy}} < 1$, an atmosphere has very low O₂; when $K_{\text{oxy}} > 1$, an atmosphere is O₂-rich. Today, $K_{\text{oxy}} \sim 6$ because F_{Rsink} is ~1/6 of the O₂ source flux (Section 2). As a consequence, F_{source} is mostly balanced by losses to oxidative weathering, which permits a high concentration of O₂. If in the past $K_{\text{oxy}} < 1$, the atmosphere would have been redox-dominated by hydrogen-rich species even if organic burial and associated O₂ production were exactly the same as today.

Another aspect of anoxic atmospheres is that the rate that hydrogen escapes to space (see Eq. (4)) can cause significant oxidation of the Earth over time.

Terrestrial hydrogen originates within water, hydrated silicates, or hydrocarbons. So when hydrogen escapes, matter left behind has been oxidized to balance the reduction of hydrogen from its original bound form to elemental hydrogen in space. It is immaterial whether the hydrogen is transported upwards through the upper atmosphere within CH₄, H₂, H₂O or some other H-bearing “vector”. For example, when hydrogen emanates from volcanoes and subsequently escapes to space, the upper mantle is oxidized through schematic reactions such as $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2 = \text{Fe}_3\text{O}_4 + 2\text{H}(\uparrow \text{space})$. Similarly, when hydrogen derives from metamorphic gases, the crust is oxidized.

6.2. Theories for the rise of O₂

Understanding the history of O₂ involves explaining why there was a delay of 0.3–1 billion years between the earliest oxygenic photosynthesis and the rise of O₂ (Section 4.2). For O₂ to rise, either the O₂ source (F_{source}) increased or the O₂ sink (F_{Rsink}) decreased.

6.2.1. Theories for an increasing flux of O₂

Some have argued that O₂ rose because the rate of organic carbon burial (O₂ production) increased, either as a pulse or long-term trend.

6.2.1.1. Paleoproterozoic pulse of organic carbon burial. At 2.3–2.1 Ga, many marine carbonates are unusually depleted in ¹²C [6,7]. This can be explained if there was a large pulse of burial of organic carbon: a ¹²C-enriched flux to sediments. The burial pulse could generate the equivalent of 12–22 times the present atmospheric O₂ inventory, which some have interpreted as causing the rise of O₂ [76]. However, the residence time of O₂ is only ~2 million years, even today (Section 2). So a pulse of organic burial should merely cause a parallel O₂ pulse. O₂ would return to its previously low levels once burial and oxidation of previously buried carbon had re-equilibrated. Another problem is timing. The oxic transition occurred before 2.3 Ga [2], and since the Paleoproterozoic organic burial pulse follows the rise of O₂, it cannot be its cause. Instead, perhaps the pulse is an effect of O₂. One speculation is that increased oxidative weathering produced copious sulfuric acid

(the reverse of Eq. (2)), which dissolved rocks more efficiently during weathering [77], releasing phosphorus that stimulated photosynthesis and organic burial. Perhaps organic burial slowly returned to normal rates because available phosphorus was diminished by adsorption onto iron oxides in oxygenated waters [13].

6.2.1.2. Secular increase of organic carbon burial. A long-term increase in organic carbon burial rates relative to O_2 sinks would lead to a rise of O_2 . Godderis and Veizer [78] follow the suggestion that growth of continental shelves increased organic burial [79], and present a model showing how an assumed continental growth curve is paralleled by a growth of O_2 . In their model, O_2 levels are tied to phosphorus delivery, which, in turn, is set proportional to continental area, so that the correspondence of continental growth and O_2 curves is an assumed foregone conclusion. Of course, large continents with substantial internal drainage would not necessarily deliver more phosphorus to the oceans. Bjerrum and Canfield [80] suggest that early phosphate delivery was limited by adsorption onto iron oxides and that a secular increase in organic burial rates overcame this. Specifically, if ^{12}C -depleted carbonate were precipitated during enhanced ancient hydrothermal weathering then Archean organic burial rates could have been lower [81]. However, this is perhaps difficult to reconcile with the average sedimentary organic carbon content of ~0.5 wt.% throughout geologic time [64]. Des Marais et al [82] suggest a secular increase in organic carbon burial rates based on boxcar averaging of carbon isotopic data from 2.6 Ga onwards. However, the selection of this particular start-date is biased by organic matter anomalously enriched in ^{12}C , perhaps caused by an era of abundant methanotrophs, which are organisms that oxidize methane and incorporate its ^{12}C -enriched carbon [40,83]. More recent data are interpreted as general stasis in carbon isotopes and a series of complex fluctuations in the Paleoproterozoic [6,7] and Neoproterozoic [5] (Fig. 8), which may be linked to “Snowball Earth” events [84,85].

6.2.2. Theories for a decreasing sink of O_2

A conservative interpretation of the carbon isotope record (Fig. 8) is that it indicates no secular trend in organic burial rates. Carbon isotopes show that the Mesoproterozoic is characterized by a burial fraction

~20% organic carbon and ~80% carbonate carbon [86], basically the same as Phanerozoic [87] and Archean averages [50,88]. In this case, a decrease in the O_2 sink would have been the key factor for the Paleoproterozoic rise of O_2 [13,89–91]. The simplest suggestion is that as Earth’s interior cooled [92], the flux of volcanic reducing gases dwindled, lessening the sink for O_2 . However, increased past volcanic outgassing would have also injected proportionately more CO_2 . Since ~20% of the CO_2 was buried as organic carbon, increased past outgassing, on its own, cannot explain the oxic transition because going back in time, O_2 production due to organic burial would have paralleled O_2 losses.

The problem with the previous idea can be overcome if the proportion of reducing gases in volcanic and metamorphic fluxes has decreased. A decrease in the H_2 to CO_2 ratio in outgassing would flip the atmosphere to an O_2 -rich state (Section 6.1). Recent papers have therefore proposed that volcanic gases became less reducing with time [13,89,90]. However, studies of redox-sensitive chromium and vanadium abundance in igneous rocks [93,94] show that the mantle’s oxidation state, which controls the redox state of volcanic gases, only permits an increase in H_2 relative to CO_2 by a factor ≤ 1.8 . Catling et al. [91] emphasized the potential importance of a decrease in the reducing sink from metamorphic gases, which is independent of mantle redox state. Holland [13] presents another argument concerning sulfur. Today, pyrite burial contributes ~40% of net O_2 production (via Eq. (2)). But if sufficient H_2 were outgassed, all accompanying SO_2 would be reduced and pyrite burial would no longer generate O_2 :



Currently, ~1/6 of the flux of O_2 associated with reductant burial is consumed by reducing gases (Fig. 3), which suggests a factor of ~6 increase in the H_2 proportion of outgassing fluxes is needed to get $K_{oxy}=1$ in Eq. (11). But by accounting for sulfur, the factor needed is possibly only ~2–3 [13]. Given sulfate-poor Archean oceans, subduction zone outgassing may have been sulfur-poor compared to today, producing gases rich in H_2 relative to sulfur. With sufficient H_2 to accomplish reaction Eq. (12) and

consume O_2 from organic burial fluxes, the atmosphere would be anoxic (Fig. 9).

Abundant atmospheric H_2 is unlikely to persist because it is microbial “food” that gets transformed into methane — a lower energy molecule that is less easily microbially consumed in the sulfate-poor, anoxic Archean (Section 4.1). Oxygenic photosynthesis would have also increased the amount of organic matter available for fermentation and methane production (Eq. (9)). With $\sim 10^2\text{--}10^3$ ppmv CH_4 predicted for the Archean [95], net methane production (i.e., the excess CH_4 flux that does not react with O_2) is balanced by ultraviolet decomposition in the upper atmosphere. Such methane photolysis promotes rapid escape of hydrogen to space, oxidizing the Earth. Indeed, without hydrogen escape, the number of moles of equivalent O_2 in the Earth’s crust would be balanced by equimolar reduced carbon (Eq. (1)), but instead there is excess oxygen (Fig. 10). The excess can be quantitatively reconciled with time-integrated hydrogen escape and oxidation

expected from a methane-rich Archean atmosphere [91].

In summary, a plausible explanation for why the late Archean atmosphere was anoxic is that excess reductants scavenged O_2 , making $K_{oxy} < 1$ (Eq. (11)). Hydrogen escape may have oxidized the Earth, lowering the sink flux for O_2 by Le Chatelier’s principle, until an oxic transition occurred. Fig. 11 summarizes this self-consistent conceptual history of redox fluxes, atmospheric gases, and oceanic sulfate.

7. The Neoproterozoic second rise of oxygen

O_2 is inferred to have increased from about 1–3% to greater than 5–18% of present levels in the Neoproterozoic [3,4,96] based on sedimentary sulfides with ^{32}S -enrichment exceeding the isotope discrimination of sulfate-reducing bacteria. The ^{32}S -enrichment can be explained if sulfide was re-oxidized at the sediment–water interface to SO_4^{2-} and cyclically

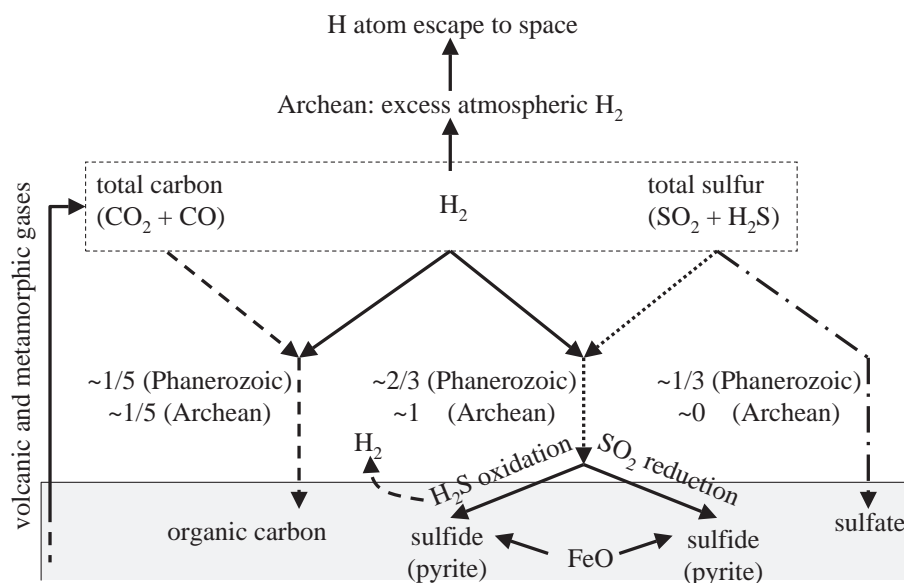


Fig. 9. A schematic diagram showing the dependence of the atmospheric redox state on changes in the reduction of sulfur, following Holland [13]. The dashed box indicates an average batch of volcanic and metamorphic gas. Hydrogen is ultimately used to reduce carbon gases to organic carbon and to reduce SO_2 to sedimentary sulfide. Geochemical data suggests that over the course of Earth history the fraction of carbon gas converted to organic matter has been about $\sim 1/5$ (dashed arrows). The fraction of sulfur gas reduced to pyrite has been $\sim 2/3$ in the Phanerozoic (dotted arrows). If enough H_2 had been present in Archean volatiles to convert all of the SO_2 to sulfide, excess H_2 would have accumulated in the Archean atmosphere making it anoxic. The consequence would be loss of hydrogen to space and oxidation of the lithosphere. As a result, volcanic and metamorphic H_2 fluxes would gradually dwindle. Eventually, not enough H_2 would be present to convert all the SO_2 to sulfide and instead SO_2 would be oxidized to create sulfate minerals (dash-dot arrows).

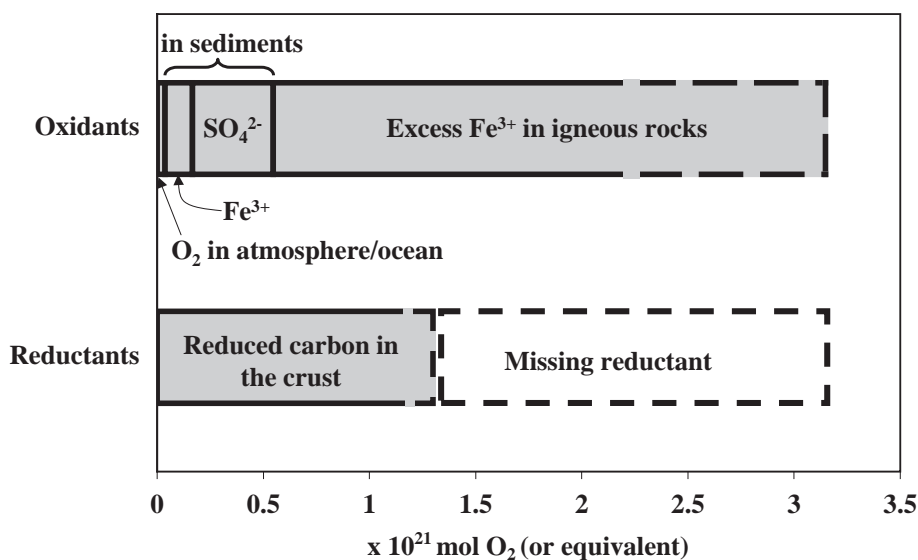


Fig. 10. The inventory of oxygen in the Earth's crust shows that there is excess oxygen. Data is from a tabulated compilation in [91].

reduced, increasing the isotope fractionation. Possibly, O_2 increased to the point where it penetrated marine sediments, ending a deeply sulfidic ocean [3]. A second increase in O_2 is important for understanding the evolution of animals [1,16]. Recent molybdenum [97] and sulfur isotope studies [98,99], as well the geochemistry of the final stages of BIF deposition [100], provide some support for a deeply sulfidic Proterozoic ocean. In the Neoproterozoic, like the Paleoproterozoic, low-latitude glacial deposits occur along with extraordinary $\delta^{13}C$ excursions in carbo-

nates perhaps associated with a second rise of O_2 [84,101,102]. Possibly, Mesoproterozoic CH_4 persisted at $\sim 10^1$ – 10^2 ppmv until the Neoproterozoic if the global biogenic CH_4 flux were larger than today [101]. Today, a vast flux of seafloor CH_4 is consumed by microbial SO_4^{2-} reduction at the CH_4 – SO_4^{2-} transition zone in sediments [103]. But in a deeply sulfidic ocean, considerable methane perhaps fluxed to the atmosphere [101]. Thus, a possible explanation for the Neoproterozoic “Snowball Earth” is a second rise of O_2 and collapse in methane.

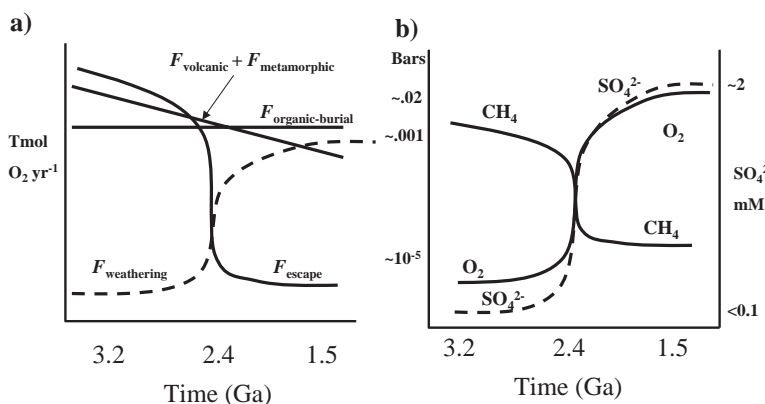


Fig. 11. (a) A schematic diagram showing a plausible evolution of redox fluxes due to oxidative weathering, hydrogen escape, volcanic and metamorphic gases, and the burial of organic carbon (a net source of O_2). (b) A schematic diagram showing the evolution of atmospheric gases (CH_4 , O_2) and oceanic SO_4^{2-} from the late Archean to Proterozoic.

What could have caused a second rise of O_2 ? One hypothesis involves a larger biological ballast flux that dragged a greater amount of organic carbon into seafloor sediments. Logan et al. [104] suggested that the evolution of fecal pellets played this role. However, fecal pellets are found near the Cambrian boundary [105], after the increase in oxidation indicated by sulfur isotopes [3,96]. Also, aerobic organisms large enough to produce significant ballast are likely to have evolved in response to higher O_2 . Furthermore, greater organic carbon burial should shift carbon isotope compositions through time, but there is no obvious secular trend [50]. Perhaps the answer lies within the sulfur cycle. If the Proterozoic ocean were deeply sulfidic, seafloor sulfide would be subducted, given its refractory nature [106]. Such burial of sulfides is a net source of O_2 (Eq. (2)). The loss of isotopically light biogenic sulfur would make oceanic sulfate more ^{34}S -enriched over the Proterozoic (e.g., $\sim 10\%$ for $0.2 \text{ Tmol year}^{-1} \text{ S loss}$) but the paucity of sulfur isotope data for Mesoproterozoic marine sulfates does not permit a statistically meaningful analysis of trends. Finally, another possible cause of a second rise of O_2 is hydrogen escape to space. If atmospheric methane persisted from ~ 2.2 to ~ 0.8 Ga at ~ 100 ppmv, as suggested by [101], time-integrated hydrogen escape over 1.4 b.y. would produce the equivalent of ~ 25 times of all the O_2 in the modern atmosphere and ocean, following the theory of [91].

8. Conclusions and future directions

The atmosphere evolved from an anoxic to oxygenated state. Good theoretical reasons imply that the prebiotic atmosphere had negligible O_2 and was weakly reducing with $\sim 0.1\%$ H_2 . The evolution of methanogens and anoxygenic photosynthesis would have increased atmospheric CH_4 at the expense of H_2 . Geochemical evidence for a rise of O_2 at 2.4–2.3 Ga is strong. However, oxygenic photosynthesis appears to have existed at least 0.3 billion years beforehand. A self-consistent explanation for the delay between the origin of oxygenic photosynthesis and oxygenation of the atmosphere is that excess volatile reductants efficiently scavenged O_2 (Sections 2.3 and 6.1) Hydrogen escape through a CH_4 intermediary is a possible mechanism that oxidized the Earth, lowering the

sink on O_2 until the oxic transition occurred. Following oxygenation, increased sulfate and associated pyrite burial would elevate the O_2 source. The ocean is hypothesized to have been deeply anoxic and sulfidic until the Neoproterozoic when a second rise of O_2 occurred and the ocean became fully oxygenated [107].

Considerable further research is needed to understand the history of O_2 . Additional study of mass independent fractionation across the Paleoproterozoic is warranted, complemented by paleosol studies. Biogeochemical cycles of carbon, sulfur and nitrogen also need further constraint. Accurate dating and geological context is particularly important for correlating the large oscillations in carbon isotopes in the Paleoproterozoic and Neoproterozoic [6]. The Proterozoic sulfur cycle will be better understood with more isotopic determinations from sulfates, including substituent sulfates in carbonates [108]. Whether there was a deeply-sulfidic Proterozoic ocean [4] can be established by studying redox-sensitive metals [109], molybdenum isotopes [97], and the terminal phases of BIF deposition [100]. Currently, our understanding of the ancient nitrogen cycle is extremely poor. Precambrian nitrogen isotope data is sparse [26,110,111] and a reliable proxy for marine nitrogen isotopes is lacking. Biomarkers could also reveal the organisms in the Precambrian biosphere [39], including methanogens and methanotrophs [112,113]. Perhaps Archean biomarkers could settle whether anoxygenic photosynthesis predominated over oxygenic photosynthesis or vice-versa. Also, while biogeochemical models have illuminated the evolution of Phanerozoic O_2 and CO_2 [12], such models are largely lacking for the Precambrian. Finally, radiative-photochemical models, and time-dependent photochemical models coupled to biogeochemical box models are needed to decipher Precambrian atmospheric chemistry.

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