The Archean atmosphere

David C. Catling1* and Kevin J. Zahnle2

The atmosphere of the Archean eon—one-third of Earth’s history—is important for understanding the evolution of our planet and Earth-like exoplanets. New geological proxies combined with models constrain atmospheric composition. They imply surface O2 levels <10⁻⁶ times present, N2 levels that were similar to today or possibly a few times lower, and CO2 and CH4 levels ranging ~10 to 2500 and 10² to 10⁴ times modern amounts, respectively. The greenhouse gas concentrations were sufficient to offset a fainter Sun. Climate moderation by the carbon cycle suggests average surface temperatures between 0° and 40°C, consistent with occasional glaciations. Isotopic mass fractionation of atmospheric xenon through the Archean until atmospheric oxygenation is best explained by drag of xenon ions by hydrogen escaping rapidly into space. These data imply that substantial loss of hydrogen oxidized the Earth. Despite these advances, detailed understanding of the coevolving solid Earth, biosphere, and atmosphere remains elusive, however.

INTRODUCTION: BACKGROUND TO ARCHEAN EARTH

The environment of the Archean eon from 4 to 2.5 billion years (Ga) ago has to be understood to appreciate biological, geological, and atmospheric evolution on our planet and Earth-like exoplanets (Fig. 1) [e.g., (1, 2)]. Its most distinguishing characteristic was negligible O2, unlike today’s air, which contains, by dry volume, 21% O2, 78% N2, 0.9% Ar, and 0.1% other gases. With its radically different atmosphere and lack of macroscopic, multicellular life, the Archean world was alien. However, at that time, the beginnings of modern Earth emerged. For example, cyanobacteria probably evolved [e.g., (3)] during this period, and these oxygenic photoautotrophs eventually oxygenated the air, setting the stage for later, complex life, including us (4).

The earliest well-preserved sedimentary and volcanic rocks are Archean and provide insights into atmospheric composition, climate, and life. These perspectives are unavailable for the Hadean eon from ~4.6 to 4 Ga ago, which generally lacks these rocks. For context, the Archean precedes the Proterozoic eon of 2.5 Ga to 541 ± 1 million years (Ma) ago, and Archean eras provide a timeline for our discussion: the Eoarchean (4 to 3.6 Ga ago), Paleoarchean (3.6 to 3.2 Ga ago), Mesoarchean (3.2 to 2.8 Ga ago), and Neoarchean (2.8 to 2.5 Ga ago).

The Archean was originally conceived to span the time from after the origin of life to the advent of free O2 (5). While the origin of life dates back to before 3.5 to 3.8 Ga ago or earlier [e.g., (6)], newer information puts atmospheric oxygenation after ~2.4 Ga ago, inside the Proterozoic. Here, considering the Archean in the older sense, the origin of life falls outside this Review, while the story of oxygen’s rise falls within.

Data about the Archean atmosphere come from how individual gases, or the air as a whole, affected chemical and physical phenomena (e.g., the composition of aerosols, chemical reactions in soils, raindrop terminal velocity, isotopic fractionations, etc.) that were recorded in rocks. So, after a brief discussion of the Hadean, we review what the Archean atmosphere was made of. However, because of limited proxy data, major uncertainties remain about the exact levels of atmospheric gases over time.

Our discussion also considers evidence for early life and its possible global influence. We assume that metabolically useful gases would have been consumed, while waste gases would have been excreted, as they are today.

Oxygenic photosynthesis produced the most impactful waste gas. The O2 from cyanobacterial ancestors flooded the atmosphere rapidly at a time between 2.4 and 2.3 Ga, with the transition marked in the rocks by the sudden disappearance of mass-independent fractionation (MIF) of sulfur isotopes (discussed in detail later) (7, 8). The Great Oxidation Event (GOE) thus began, which ended ~2.1 to 2.0 Ga ago (9, 10). Although this switch to an oxygeanted atmosphere and shallow ocean occurred in the Paleoproterozoic era (2.5 to 1.6 Ga ago), the weakly reducing atmosphere that was eliminated typified the Archean [e.g., (11)]. Here, “weakly reducing” means minor levels of reducing gases, such as CO, H2, and CH4, in an anoxic atmosphere of bulk oxidized gases, CO2 and N2. A major outstanding question concerns how trends of biological and geological evolution relate to the GOE.

Atmospheric composition, in turn, affected Archean climate. At 4 Ga ago, solar luminosity was 25 to 30% lower than today (12, 13), but Archean Earth was not persistently frozen because abundant evidence shows an active hydrological cycle. Liquid water under a fainter Sun likely implies more abundant greenhouse gases than today (14, 15). We review what the gases were and their levels.

In addition to a gradual increase in solar luminosity, slow changes in the solid Earth over time provided boundary conditions for atmospheric evolution. On geological time scales, volcanic and metamorphic gases replenish atmospheric volatiles that escape to space or are chemically sequestered into solid materials.

We will not attempt to resolve controversies over how much solid Earth evolution drove atmospheric evolution. Consequently, we omit the large topic of how Earth’s outgassing history depended on debated tectonic and geological evolution models.

A BRIEF OVERVIEW OF THE ENVIRONMENT BEFORE THE ARCHEAN

The composition of the Hadean atmosphere is obscured by a lack of well-preserved rocks, but analysis of zircons—crystals of zirconium silicate (ZrSiO4)—suggests that continents, oceans, and perhaps life all originated in the Hadean (16). Zircons are tiny (<0.5 mm) durable pieces of continental crust. Elevated 18O/16O in 4.3-Ga-old zircons was possibly inherited from 18O-enriched, weathered surface rocks that were later buried and melted, which implies the presence of surficial liquid water and even land (17, 18). In addition, graphite inside a 4.1-Ga-old zircon...
HSEs to those in enstatite chondrite and achondrite meteorites suggest removed HSEs. Similarities of isotopes and relative proportions of these relative to concentrations expected after Earth

meteorite shocks (~4.2 to 4.0 Ga ago, based on the ages of lunar rocks and bombardment superposed on the general decline, which occurred between 4.2 and 4.0 Ga ago, based on the ages of lunar rocks and meteorite shocks (24), although many dispute that the LHB was a discrete event (25). Regardless, an LHB would likely not sterilize Earth (26); any microbial life would have rebounded (27).

The mantle contains excess highly siderophile elements (HSEs) relative to concentrations expected after Earth’s iron core formed, which removed HSEs. Similarities of isotopes and relative proportions of these HSEs to those in enstatite chondrite and achondrite meteorites suggest that this highly reducing meteoritic material was delivered late in Earth’s accretion (28). Thus, carbon and nitrogen were supplied in graphite and nitrides. Therefore, the Hadean atmosphere and mantle were probably initially highly reducing, before subsequent oxidation either by hydrogen escape (29) or disproportionation of mantle FeO accompanied by Fe loss to the core (30, 31). In any case, iron-cored impactors would reduce seawater to hydrogen and create transient, highly reducing atmospheres that may have been important for the origin of life (32, 33).

Because a liquid ocean likely existed by ~4.4 Ga ago, feedbacks in the geologic carbon cycle (discussed later) probably stabilized the long-term climate (34). However, consumption of CO2 in the weathering of impact ejecta by carbonic acid suggests a cool early Hadean surface near 0°C under the faint Sun (35, 36).

Estimates of nitrogen bound in today’s solid Earth range a few to ~40 bar equivalent (37, 38), which allows for considerable N2 in the Hadean atmosphere unless N was incorporated into a reducing, deep layer of magma—a magma ocean—formed after the Moon-forming impact ~4.5 Ga ago [(39) and references therein]. So, although N2 was one of the bulk atmospheric gases, its Hadean level—higher than today or lower—remains unclear.

In summary, at the end of the Hadean, Earth had oceans, continents (16), an anoxic atmosphere likely rich in CO2 and N2, and probably life (Fig. 1).

WHAT WAS THE ARCHEAN ATMOSPHERE MADE OF?

Proxies constrain Archean atmospheric composition. Gases reacted with the seafloor or land, leaving chemical traces in seafloor minerals (40, 41) or in soils that became paleosols (42, 43). In addition, atmospheric particles carried isotopic signatures into sediments that were diagnostic of atmospheric composition (44–47). Occasionally, fluid inclusions in rocks trapped seawater with dissolved air (48–50) or even microbial gases (51).

Sometimes the physical environment affected rocks and minerals. Their preservation allows estimates of environmental temperature (52–55) and barometric pressure (56, 57).

Table 1 summarizes inferences about the composition of the Archean atmosphere and ocean. Here, gas concentrations are generally for the base of the troposphere. Although the Archean lacked a stratospheric ozone layer, it remains valid to refer to a troposphere and stratosphere as vertical regions where, respectively, convection and radiation dominated the energy transfer.

Negligible Archean O2 but oxygen oases after oxygenic photosynthesis evolved

The strongest constraint on Archean atmospheric composition is that the ground-level mixing ratio of O2 was <10−6 PAL (present atmospheric level) or <0.2–parts per million by volume (ppmv) O2 for air of 1 bar, indicated by the presence of sulfur isotope MIF (S-MIF) in Archean sedimentary minerals (Fig. 2A) (44, 47). An oft-quoted limit of 10−5 PAL O2 derives from an earlier photochemical model that could not address O2 levels in the range of 10−5 to 10−15 PAL (45). Usually, isotope fractionation is proportional to the mass difference between isotopes; e.g., in diffusive separation of sulfur-containing gases, 34S becomes about half as abundant, relative to 32S, as 33S. However, some particular photochemical reactions produce MIF that, by definition, deviates from proportionality to mass.

Archean S-MIF is tied to the production of elemental sulfur, S0, from photochemistry in anoxic air; in contrast, in an oxic atmosphere, S-MIF
## Table 1. Archean environmental constraints

Constraints on atmospheric gases at ground level (unless stated otherwise) and some bulk marine species. Gas level constraints are given in the same units as in the cited papers: partial pressure in bar or atm, where 1 bar = 0.9869 atm, or as mixing ratios (ppmv = parts per million by volume; S-MIF = sulfur isotope mass-independent fractionation).

### Archean atmospheric gases

| Parameter or species | Published constraint | Age (years before present) | Basis of constraint |
|----------------------|----------------------|---------------------------|---------------------|
| **O₂**               | <10⁻⁶ × present O₂   | >2.4 Ga                   | Modeled S₈ flux needed to create and carry S-MIF (44) |
|                      | <3.2 × 10⁻⁵ atm      | 2.415 Ga                  | Detrital uraninite (66), if the river length feeding the Koegas subgroup is accurately estimated |
| **O₃ column**        | <10¹⁵ molecules m⁻²  | >2.4 Ga                   | Modeled for ground-level O₂ < 0.2 ppmv (44, 270) |
| **Surface barometric pressure** | <0.52–1.1 bar | 2.7 Ga                  | Maximum fossil raindrop imprint size (57) |
| **N₂**               | <1.1 bar (2σ)        | 3.5–3.0 Ga                | N₂/³⁶Ar in fluid inclusions (48) |
|                      | <1 bar (2σ)          | 3.3 Ga                    | Derived from Fig. 4A and Table 2 of Avice et al. (49). |
| **HCN**              | Up to ~100 ppmv      | >2.4 Ga                   | Photochemistry if CH₄ was ~10³ ppmv (166, 167) |
| **N₂O**              | ~Few ppbv            | >2.4 Ga                   | Lightning production of NO and HNO in a reducing atmosphere, dissolution of HNO, and evaporation |
| **CO₂**              | >0.0004 bar (0°C), >0.0025 bar (25°C), >0.26 bar (100°C) | 3.2 Ga | Siderite weathering rinds on river gravel (257) |
|                      | 0.03–0.15 bar        | 2.77 Ga                   | Mt. Roe paleosol, Australia (43) |
|                      | 0.02–0.75 bar        | 2.75 Ga                   | Bird paleosol, South Africa (43) |
|                      | 0.003–0.015 bar      | 2.69 Ga                   | Alpine Lake paleosol, MN, United States (168) |
|                      | 0.05–0.15 bar        | 2.46 Ga                   | Pronto/NAN paleosol, Canada (43) |
|                      | ~<0.8 bar            | 2.4 Ga                    | The survival of detrital magnetite in rivers, if Fe³⁺-reducing microbes are assumed (200) |
| **CH₄**              | >20 ppmv             | >2.4 Ga                   | Lower limit for sufficient reductant for S-MIF (44) |
|                      | >~5000 ppmv          | >3.5 Ga                   | Enough methane to induce sufficiently rapid hydrogen escape to drag Xe²⁺ and fractionate Xe isotopes (187) |
| **CO**               | Less than a few ppmv | After the origin of CO consumers | Thermodynamic limit if microbes used available free energy of CO [appendix A of Krissansen-Totton et al. (250)] and limit if transfer of gas through the atmosphere-ocean interface restricts CO consumption (183) |
|                      | <300 ppmv            | >2.4 Ga                   | Assuming that methanogens used available free energy from consuming H₂ (197, 271) and the transfer of gas through the atmosphere-ocean interface restricts H₂ consumption (183). |
|                     | 10 s–100 ppmv        | After the origin of methanogens | The survival of detrital magnetite in rivers, if Fe³⁺-reducing microbes are assumed (200) |
| **H₂**               | <0.01 bar            | 3.0–2.7 Ga                | The survival of detrital magnetite in rivers, if Fe³⁺-reducing microbes are assumed (200) |

### Archean seawater species

| Parameter or species | Published constraint | Age (years before present) | Basis of constraint |
|----------------------|----------------------|---------------------------|---------------------|
| **pH**               | 6.4–7.4              | At 4 Ga                   | 95% confidence ranges from a carbon cycle model with 10⁴-ppmv Archean CH₄ (34). |
|                      | 6.75–7.8             | At 2.5 Ga                 |                     |
| **SO₄²⁻(aq) (bulk sea)** | <2.5 μM      | >2.4 Ga                   | Lack of mass-dependent sulfur isotope fractionation (75) |
| **NO₃⁻(aq) (bulk sea)** | ~0            | >2.4 Ga                   | By analogy to the deep, anoxic Black Sea (272) |
| **NH₄⁺(aq) (probably porewater rather than seawater)** | 0.03–10.3 mM | >3.8 Ga | From the N content of biotites (originally clays), derived from adsorption of dissolved NH₄⁺(aq) (148) |
|                       | (probably porewater rather than seawater) | 3.8–2.4 Ga |                     |
| **Fe²⁺(aq) (deep sea)** | 40–120 μM (2–7 ppm by weight) | >2.4 Ga | Based on solubility constraints of Fe²⁺ (139) |
| **Salinity (g/kg)**   | ~20–50 at 40°–0°C versus modern of 35 | 3.5–3.0 Ga | From seawater fluid inclusions in quartz (50) |
| **Potassium**         | CI/K ~50 versus modern 29 | 3.5–3.0 Ga | From seawater fluid inclusions in quartz (50) |
that dominantly imparted S-MIF are debated: They include polysulfur formation (61), SO2 photolysis, and other reactions (46, 59). In any case, when S8 particles fell to Earth’s surface, their S-MIF isotopic composition complemented that of sulfate particles, allowing preservation of different S-MIF signs in these phases as sedimentary pyrite (FeS2) and barite (BaSO4) (62). Sulfate, of course, could later be microbiologically transformed to pyrite.

Numerous redox-sensitive tracers corroborate negligible Archean O2 [reviewed, e.g., in (10, 63, 64)]. Anoxia proxies that have long been recognized include the lack of pre-GOE continental sediments stained by red ferric oxides (redbeds), detrital grains from well-aerated rivers of siderite (FeCO3), uraninite (UO2), or pyrite that would oxidize and dissolve or rust at high pO2 (65, 66), and paleosols with iron washed out by anoxic rainwater [e.g., (67)]. Furthermore, Archean marine sediments have low concentrations of elements that enter rivers during oxidative continental weathering (68–70). Conversely, glacial sediments contain continental materials lacking oxidative weathering loss of molybdenum (71).

Iron formations (IFs), which are marine chemical sedimentary rocks rich in iron and silica [15 to 40 weight % (wt %) Fe and 40 to 60 wt % SiO2], indicate that the deep Archean ocean contained Fe3+(aq) and so was anoxic [e.g., (72)]. In “Superior-type IFs” that formed near-shore, rare earth elements show that dissolved iron was partly sourced from seafloor hydrothermal vents and upwelled onto continental shelves where the iron precipitated. In today’s deeply oxygenated oceans, oxidized iron instead precipitates locally around vents. Archean shallow-water IFs constrain atmospheric O2 to <2.4 x 10−4 bar (73).

The absence or presence of mass-dependent fractionation of various isotopes can also indicate anoxic versus oxic conditions. In the case of sulfur, today’s oxidative weathering of continental sulfides produces soluble sulfate, which rivers carry to the ocean. When bacteria reduce sulfate to pyrite in seafloor sediments, they impart mass-dependent S isotope fractionation if sulfate is present at sufficient concentrations as in the modern oceans, but usually not in Archean seawater (74, 75). The absence of this isotope fractionation indicates little Archean seawater sulfate and implies anoxic air. Using similar arguments of O2-sensitive weathering, transport, and fractionation, isotopes of Cu (76), Cr (77), Fe (78), U (79), Mo [e.g., (80, 81)], and Se (82) indicates an anoxic Archean atmosphere.

Atmospheric oxidation of 2.7-Ga-old iron-nickel micrometeorites has been used to argue for O2 near-modern levels above ~75-km altitude (83, 84). However, given copious evidence for an anoxic Archean atmosphere, an alternative explanation is that high CO2 levels (perhaps >70%) oxidized the micrometeorites (85).

Nonetheless, even under a globally anoxic atmosphere, lakes and shallow seawater inhabited by oxygenic photosynthesizers could have become “oxygen oases”—local or regional areas with elevated O2. Modern surface seawater dissolves 0.25 mM O2 at 15°C, while estimates for Archean oxygen oases range from 0.001 to 0.017 mM (0.4 to 7% of present) (86, 87).

When exactly oxygenic photosynthesis began and dominated over anoxicogenic photosynthesis is debated, but signs of biological carbon fixation appear early. Graphite in a ~3.7-Ga-old outcrop of sedimentary rock is 13C-enriched in amounts typical of photosynthetic microbes (88, 89). Then, at 3.52 Ga ago, 813C in kerogen of ~24‰ and associated marine carbonate of ~2‰ found in Australia is similar to biological isotope fractionation in modern oceans (90).

Fossil evidence for Archean cyanobacteria is reported. Light organic carbon isotopes and structures like those made by filamentous
cyanobacteria found within stromatolites or other microbi ally induced sedimentary structures are consistent with cyanobacteria by 3.2 to 2.7 Ga ago (91–94). Cyanobacteria could be corroborated by biomarkers, which are remnant organic molecules from particular organisms. However, putative Archean biomarkers have been plagued by younger contamination [e.g., (95)].

Instead, cyanobacterial interpretations are strengthened by geochemical data suggesting O2 oases by 3.2 to 3.0 Ga ago. Fractionated iron and molybdenum isotope s and levels of redox-sensitive metals suggest marine photic zone O2 (96–99). [Chromium isotope data have been used to argue for the existence of ~3 Ga-old terrestrial oxygen (100), but they were probably caused by modern oxidative weathering (101).]

Then, by 2.8 to 2.6 Ga ago, increasing concentrations and isotopic fractionation of Mo and S in marine shales suggest that O2 proximal to cyanobacterial mats and stromatolites on land oxidized sulfides and boosted sulfate and Mo riverine fluxes to the oceans (70, 80, 102–104). These trends are consistent with isotopic evidence for Neoarchean methanotrophy and oxidative nitrogen cycling (105–109).

Concentration spikes at 2.5 to 2.66 Ga ago in Mo, Se, and Re and isotopic excursions of Mo, Se, U, and N have been interpreted as arising from O2 transients or “whiffs” of O2 (110–113). Critics argue that the data derive from post-GOE alteration (114, 115) [but see (116)]. Alternatively, oxygen oases of cyanobacteria within soils or lakebeds may have mobilized these elements into rivers and then the sea (117).

Phylogenetic analyses mostly suggest that cyanobacteria originated by 2.8 Ga. Molecular clocks must be calibrated by physical evidence, and phylogenetic methods are themselves debated. While some argue that oxygenic photosynthesis evolved only 50 to 100 Ma before the GOE (115), most studies suggest an earlier Palearchean or Mesoarchean age [e.g., (3, 118, 119)].

A major unresolved issue is how the GOE was related to underlying geological or biological trends (Fig. 2A). Life on its own cannot change the net redox state of the global environment because each biological oxidant is complemented by a reductant. In oxygenic photosynthesis, a mole of organic carbon accompanies every mole of O2.

\[
\text{CO}_2 + \text{H}_2\text{O} \xleftrightarrow{\text{photosynthesis}} \text{CH}_2\text{O} + \text{O}_2 \tag{1}
\]

Today, with ~4.4 × 10^5–Tmol surface organic matter and ~9000 Tmol/year of oxidative decay or respiration (120), reaction 1 reverses in ~50 years. Consequently, for long-term O2 accumulation, some organic carbon must be segregated from the O2 and buried. Alternatively, O2 molecules are liberated if microbes use the organic carbon from reaction 1 to make other reductants, such as sulfides from sulfates, that are buried. However, Archean seawater sulfate concentrations were small (Table 1), so organic carbon burial is the O2 flux that matters for the GOE. Atmospheric oxidation also occurs when hydrogen escapes to space after the photochemical breakdown of gases such as H2 and CH4, which ultimately derive from water and are relatively abundant in anoxic air.

Atmospheric O2 is determined by net redox fluxes into and out of the atmosphere. This simple truth is deceptive because these redox fluxes are themselves controlled by less easily constrained oxidative weathering (both seafloor and continental) and volcanic and metamorphic degassing, as well as hydrogen escape to space. Permanent atmospheric oxygenation requires ~3 × 10^{-3} PAL O2 or more to prevent a destabilizing positive feedback of photochemical destruction of tropospheric O2 that otherwise occurs when an incipient ozone column is still transparent to far UV (44, 121, 122).

These O2 levels would have only been attained when the O2 flux from the burial of organic carbon exceeded the kinetically efficient sink from O2-consuming gases (CO, H2, H2S, and SO2) from volcanism and metamorphism plus fluxes of reducing cations such as Fe2+ from sea-level vents (9, 120, 121, 123, 124). A minority argue that such a flux imbalance applied as soon as oxygenic photosynthesis evolved, mandating a rapid rise of O2 (125). In the consensus assessment that oxygenic photosynthesis evolved long before the GOE, efficient consumption of O2 initially suppressed O2 levels.

Hypotheses about the GOE tipping point are reviewed elsewhere [(64), chap. 10]. Briefly, ideas favoring increased O2 fluxes from organic burial appeal to more continental shelf area available for burial (126), more phosphorus to stimulate photosynthesis (127, 128), or subduction of organic carbon relative to ferric iron (129). Because organic carbon burial extracts 12C and leaves inorganic carbonates 12C depleted, it is difficult to reconcile these hypotheses with the remarkable constancy of the carbon isotope record, which indicates little change in average organic burial rates between the Archean and Proterozoic (130). However, an increase in organic burial might have occurred if negligible oxidative weathering of 12C-rich organics on land or a sink of seafloor carbonate meant that the operation of the carbon cycle or the isotopic composition of carbon input into the surface environment differed from today (130–132).

Hypotheses for a slowly decreasing O2 sink to the GOE tipping point rely on a decline in the ratio of reduced-to-oxidized species from volcanic, metamorphic, and hydrothermal sources (9, 123, 124, 133, 134). Some emphasize the role of hydrogen escape to space in oxidizing solid Earth, lowering Earth’s capacity to release O2-consuming reductants (121, 135, 136). New evidence from xenon isotopes supports rapid Archean hydrogen escape, as discussed below.

Nitrogen gases in the Archean

Molecular nitrogen dominates today’s atmosphere, and three lines of evidence have begun to constrain Archean N2 levels (Fig. 2B). First, the largest size of 2.7-Ga-old fossil raindrop imprints provides a conservative limit of paleopressure of <2.1 bar and a probable limit of <0.52 to 1.2 bar (57). [Criticism of the raindrop paleopressure constraint (137) is refuted in (138).] Second, the N2/36Ar ratio in fluid inclusions indicates pN2 <1.0 bar [2σ] at 3.3 Ga ago and <1.1 bar at 3.5 to 3.0 Ga ago (48, 49). Third, vesicle volumes in 2.7-Ga-old basaltic lava flows erupted at sea level imply a 0.23 ± 0.23–bar [2σ] paleopressure (56).

The inferred history of pN2 depends on how the geologic nitrogen cycle has changed over time. Nitrogen can only greatly accumulate as atmospheric N2 or in rocks as ammonium, amide, or nitride, or organic nitrogen. Under typical mantle temperatures and redox conditions, volcanic gases contain N2, not ammonia [e.g., (139), p. 49], and because N2 is unreactive, it enters the air. Today, N2 is also produced when oxidative weathering of organic matter on the continents makes nitrate (NO3-) that undergoes rapid biological denitrification into N2 (140). Within large uncertainties, volcanic and oxidative weathering inputs of N2 are comparable [(64), p. 204]. Using sedimentary C/N data, Berner (140) argues that the sum of these N2 sources was balanced over the Phanerozoic primarily by N burial in organic matter, so that the Phanerozoic partial pressure of nitrogen, pN2, varied little.

Som et al. (56) proposed that low Archean paleopressure arose because today’s long-term N2 atmospheric input from oxidative weathering and denitrification was absent. If so, pN2 would have risen at the
Ammonia (NH₃) levels of 10 to 100 ppmv would provide a greenhouse effect to counteract the faint young Sun (FYS) (14), but these levels of NH₃ cannot be sustained against UV photolysis (161). Possibly, a stratospheric organic haze, such as that on Saturn’s moon, Titan, shielded tropospheric NH₃ from UV (162). However, whether this shielding actually occurred depends on whether hazes actually existed and on the size and radiative properties of haze particles, which remain uncertain (1, 163).

Another nitrogen-bearing gas, hydrogen cyanide (HCN) is more stable photochemically than NH₃ and made in reducing atmospheres by lightning, impacts (164, 165), or UV-driven photochemistry. In particular, N atoms from N₂ photolysis in the upper atmosphere can mix to lower levels and react with CH₄ photolysis products to make HCN (166, 167). At Archean biogenic methane levels of ~10⁻³ ppmv, HCN concentrations reach ~10⁻³ ppmv.

**Carbon gases in the Archean: CO₂, CH₄, and CO**

Let us now consider carbon gases, starting with carbon dioxide. Since the early Hadean, CO₂ has probably always been Earth’s most important noncondensable greenhouse gas. CO₂ also affects seawater pH and influences the carbon cycle through the formation of carbonates and organic matter. However, direct evidence for Archean CO₂ levels remains scanty.

Paleosols provide some estimates. Acid leaching in Archean soils arose from CO₂ dissolved in rainwater. Mass-balance calculations give 10 to 50 PAL of CO₂ at 2.7 Ga ago and 23 ± 3 PAL of CO₂ at 2.2 Ga ago (42, 168). However, these analyses assume that all the CO₂ that entered the soils caused dissolution, so pCO₂ could have been higher if only a fraction of CO₂ had been used. Another study used an analysis with an estimate of the composition of temperature-dependent aqueous solutions during weathering and, because of a weaker dependence of weathering on pCO₂, obtained higher pCO₂ of 85 to 510 PAL at 2.77 Ga ago, 78 to 2500 PAL at 2.75 Ga ago, and 160 to 490 PAL at 2.46 Ga ago (Fig. 3A) (43).

High Archean pCO₂ does not have to induce acidic seawater and dissolve marine carbonates. Instead, an increase in Ca²⁺ concentrations could maintain an ocean saturated in calcium carbonate at alkaline pH; alternatively, seawater pH could be slightly lower than today, but calcium carbonate would remain saturated. In fact, sedimentary marine carbonates appear from 3.52 Ga ago onward [98 and references therein].

Calcium isotopes might provide insight into coupled Archean seawater pH and pCO₂. These two variables and carbonate alkalinity (Alk = [HCO₃⁻] + 2[CO₃²⁻]) define a system where any two variables imply the third. In evaporating seawater, Ca isotopes could undergo Rayleigh distillation if [Ca²⁺] << Alk, but limestones from 2.6-Ga-old Campbellrand marine evaporites show no spread in δ⁴⁴/⁴₀Ca, which might imply [Ca²⁺] >> Alk and pH of 6.4 to 7.4 for a likely range of Neoarchean pCO₂ (Table 1) (169).

Siderite (FeCO₃) in Archean IFs has been proposed as a pCO₂ proxy if it precipitated in equilibrium with the atmosphere (170, 171). However, data suggest that this siderite was diageneric (172, 173), so we omit this proxy from Fig. 3A and Table 1.

Potentially, two negative feedbacks control long-term pCO₂. First, the net consumption of CO₂ in acid weathering of continents or the seafloor ends up making carbonates (174)

$$X\text{SiO}_3^− + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{XCO}_3^− + \text{SiO}_2 + \text{H}_2\text{O}$$

where X is a cation. Seafloor weathering occurs when water in the permeable abyssal plains dissolves basaltic minerals, releasing calcium ions...
consistent with possible biological CH4 fluxes into atmospheres of rising O2 levels.

Fig. 3. History of CO2 and a CH4 schematic since the Archean. (A) The black line is median CO2 from a carbonate-silicate climate model, and yellow shading indicates its 95% confidence interval (34); this curve merges with a fit to CO2 proxy estimates for 0.42 Ga ago to present from (256). Various Precambrian pCO2 proxy estimates are shown (42, 43, 168, 257–259). (B) A very schematic history of CH4. Constraints include a lower limit (blue) required for Archean S-metasomatism such as iron sulfide that were probably widespread (~3.5 Ga ago, i.e., >5000 ppmv (34)). Evidence points to high levels of Archean CH4 (Fig. 3B). First, signs of methanogens and methanotrophs from light carbon isotopes in Archean organics imply methane’s presence [e.g., (109)]. Second, Archean S-MIF requires >20-ppmv CH4 to generate particulate sulfur, S8 (Table 1). Third, the deuterium-to-hydrogen (D/H) ratio of 3.7 Ga-old seawater estimated from serpentine minerals is 2.5% lighter than today, which could be explained by rapid Archean escape of hydrogen and isotopic fractionation (185, 186). This hydrogen was likely derived from UV photolysis of CH4 in the upper atmosphere (135). Later, we discuss how fractionation of xenon isotopes in the Archean suggests that, ~3.5-Ga ago, CH4 levels were >0.5%, i.e., >5000 ppmv CH4 also contributed to the greenhouse effect.

Anoxic Archean air could hold 1000 s of parts per million by volume of CH4 if a microbial flux of CH4 was comparable to today’s (135, 183, 184). Phylogenetically, methanogens date back to >3.5 Ga ago (23). In contrast, the modern oxygenated atmosphere destroys reducing gases rapidly, limiting tropospheric CH4 and H2 abundances to 1.8 and 0.55 ppmv, respectively.

Evidence points to high levels of Archean CH4 (Fig. 3B). First, signs of methanogens and methanotrophs from light carbon isotopes in Archean organics imply methane’s presence [e.g., (109)]. Second, Archean S-MIF requires >20-ppmv CH4 to generate particulate sulfur, S8 (Table 1). Third, the deuterium-to-hydrogen (D/H) ratio of 3.7 Ga-old seawater estimated from serpentine minerals is 2.5% lighter than today, which could be explained by rapid Archean escape of hydro- gen and isotopic fractionation (185, 186). This hydrogen was likely derived from UV photolysis of CH4 in the upper atmosphere (135). Later, we discuss how fractionation of xenon isotopes in the Archean suggests that, ~3.5-Ga ago, CH4 levels were >0.5%, i.e., >5000 ppmv CH4 (187).

Fourth, globally extensive glaciations during the GOE [e.g., (188)] provide circumstantial evidence for high Archean CH4. At the tipping point, air flaps from anoxic to oxic in only ~105 years, causing a ~10°C temperature drop by oxidizing CH4. This chemical transition is far faster than the ~106- to 107-year response of the carbonate-silicate thermostat.

Another carbon-containing gas, carbon monoxide (CO), was probably not abundant in the presence of an Archean microbial biosphere. The Last Universal Common Ancestor was likely capable of anaerobic CO consumption (189), which involves water as a substrate and catalysts such as iron sulfide that were probably widespread

\[ H_2O + CO \rightarrow CO_2 + H_2 \] (4)

With this reaction, microbes would draw CO down to 10^6 to 10^7 ppmv (183). However, episodic CO levels at percent levels may have occurred when large impacts delivered cometary CO ice or organic matter that was oxidized (190).

A high-altitude Archean organic haze?

Because of relatively abundant CH4, a high-altitude Archean organic haze might have formed, as mentioned earlier. The idea was first
suggested in the 1980s (191). Empirically, if the CH₄:CO₂ ratio exceeds ~0.1 in a UV-irradiated CO₂-N₂-CH₄ mixture, radicals from methane photolysis polymerize into organic particles (192).

When and whether an organic haze formed are uncertain. A haze could have affected tropospheric sulfur gases by blocking UV photons. Consequently, the structure of S-MIF variations in Archean sedimentary minerals and their correlation with light, organic δⁱ³C have been attributed to episodic hazes driven by variable atmospheric CH₄:CO₂ ratios (60, 193–196). However, given—dare we say—only a hazy understanding of which species and reactions are important for S-MIF (see earlier), interpretations of episodic hazes are permissive rather than definitive.

**Hydrogen abundance**
The Archean lower atmosphere is unlikely to have been H₂-rich given the antiquity of methanogens (23, 51, 197), some of which convert H₂ into methane through a net reaction

\[ 4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (5) \]

Anoxicogenic photosynthesis also consumes H₂ [e.g., (198)]. In models with methanogens and H₂-based photosynthesizers, atmospheric H₂ mixing ratios depend on assumed H₂ outgassing and biological productivity but generally are ≤10⁻⁴ (183, 184). These levels preclude H₂ as an important Archean greenhouse gas. Detrital magnetite carried in rivers 3.0- to 2.7-Ga ago would have dissolved at high pH₂ via microbial reduction of Fe³⁺ to soluble Fe²⁺ using H₂ (199), providing an upper limit of pH₂ ≤ 10⁻² bar (200).

**Xenon isotopic constraints on oxygen, hydrogen, and methane levels, plus Earth’s oxidation**
Changes in atmospheric Xe isotopes through the Archean stop after the GOE (analogous to S-MIF) (49) and potentially tell us about O₂, CH₄, and H₂ levels (187), including in the otherwise hidden Hadean, as discussed below. The trend also relates to how much hydrogen escaped from Earth and hence Earth’s total oxidation over time.

Xenon in fluid inclusions in Archean rocks becomes isotopically heavier through the Archean relative to an initial solar composition until the fractionation reaches that of modern air around 2.1 to 2.0 Ga ago (Fig. 4) (49). Xenon dragged out into space by escaping hydrogen during the Archean and Hadean best explains the progressive mass fractionation (49, 187). An alternative explanation from trapping of Xe⁺ in organic hazes (201) has the problem that weathering or microbial processing of buried organics would release xenon and modulate the Xe isotopes in post-Archean air, which is not observed (202).

Today, the nine atmospheric Xe isotopes [124 to 136 atomic mass units (amu)], have a huge fractionation of 4.2% per amu relative to solar or chondritic sources, whereas the six, lighter krypton isotopes (76 to 86 amu) are barely fractionated. Earth’s Xe/Kr ratio is also 4 to 20 times less than meteorites, implying selective Xe loss.

Unlike lighter krypton, xenon is easily ionized by solar UV or charge exchange with H⁺ ions, so Xe⁺ can be dragged out to space by escaping H⁺ ions (187). Whereas Xe⁺ is unreactive with H₂, H₂O, or CO₂ (203), any Kr⁺ ions are neutralized via Kr⁺ + H₂ → KrH⁺ + H and KrH⁺ + e⁻ → Kr + H, explaining the lack of Kr isotope fractionation. Ions are tethered to Earth’s magnetic field lines, but a “polar wind” of hydrogen ions escapes along open field lines at the poles, accounting for ~15% of all hydrogen escapes today. Xe⁺ ions could be dragged by a vigorous ancient polar wind. That requires copious hydrogen to be derived from relatively abundant CH₄ and/or H₂ in the lower atmosphere. UV decomposes CH₄ in an anoxic upper atmosphere, releasing hydrogen [e.g., (166)].

The hypothesized xenon escape works only in anoxic air, so, like S-MIF, Xe isotopes record the GOE (Fig. 4). Oxidic air destroys H₂ and CH₄, making their abundances too low to supply enough hydrogen to drag along xenon. In addition, O₂ would remove Xe ions in a resonant charge exchange reaction (203)

\[ \text{Xe}^+ + \text{O}_2 \rightarrow \text{Xe} + \text{O}_2^+ \quad (6) \]

Our preliminary model finds that Xe can escape when the total hydrogen mixing ratio exceeds ~1% for the solar extreme UV flux expected around ~3.5 Ga ago (187). The total hydrogen mixing ratio, f₁(H₂), in equivalent H₂ molecules, is

\[ f_1(\text{H}_2) = 0.5 f_\text{H}_2 + f_\text{H}_2\text{O} + 2 f_{\text{CH}_4} + \ldots \quad (7) \]

Thus, if nearly all Archean hydrogen was biologically converted into CH₄ (Eq. 5), we interpret the xenon escape constraint of >1% f₁(H₂) to be >0.5% CH₄, which is a rare empirical constraint on Archean CH₄ (Fig. 3B).

The inferred escape of a strong reductant, hydrogen, would oxidize entire Earth. The total oxidation during the Archean is equivalent to oxygen from a tenth of more of an ocean (187).

**Sulfur gases**
S-MIF proves that Archean S-containing gases existed but tells us little about their concentrations. All sulfur gases apart from S₈, which condenses, are susceptible to UV photolysis and are short lived and inter-converting. Consequently, atmospheric sulfur is sequestered into stable sulfuric acid aerosols by oxidation or S₈ aerosols by reduction. For a wide range of Archean atmospheric redox conditions, both types of aerosol should form and precipitate (44).

Although sulfur gases absorb UV, they probably did not shield Earth’s surface. Surface temperatures greater than ~50°C would be required to produce enough atmospheric S₈ vapor to shield surface life from UV (204).

**THE ARCHEAN CLIMATE**
**The Faint Young Sun problem**
Related to atmospheric composition, discussed above, is another basic problem: How the Archean climate remained clement under a fainter Sun. In the Sun’s core, nuclear reactions fuse four protons into helium nuclei, increasing the mean molecular mass and decreasing the number of particles per unit volume. In response, the weight of the overlying column presses inward, and the core temperature rises. A greater radial temperature gradient drives more outward radiation flux, so the Sun brightens. Solar evolution models show that the Sun was 25 to 30% fainter at 4 Ga ago (12, 13, 15).

One solution to the FYS is that the young Sun was not faint but more massive and therefore as bright as today (205, 206). The Sun would then need to lose enough mass over time so that a declining weight of the column above the core matched the pressure loss from particles fused in the core. However, observations are unsupportive: Fast mass loss only happens in the first ~200 Ma after Sun-like stars form (207, 208).
As well as solar luminosity, Earth’s mean global temperature depends on the Bond albedo (the reflectivity over all wavelengths) and greenhouse effect [e.g., (64), pp. 34 to 36]. Some FYS hypotheses invoke clouds: that the Archean Bond albedo was low because of substantially different cloud cover (170, 209) or that abundant high-altitude cirrus clouds warmed early Earth (210). However, no plausible combination of few low clouds (which tend to reflect sunlight) and many high, icy clouds (which tend to warm the surface with downwelling infrared) solves the FYS problem (211). Three-dimensional climate models with a lower solar flux produce weaker evaporation and fewer low clouds, but a strong greenhouse effect is still required because the albedo decrease is small (212, 213).

The most plausible solution to the FYS is a big greenhouse effect (14, 214, 215). Water vapor is an important greenhouse gas but, on its own, cannot solve the FYS problem. Water vapor condenses into rain and snow, so its abundance is limited by the saturation vapor pressure that depends only on temperature, which is set by noncondensable greenhouse gases, such as CO₂ and CH₄.

Consequently, substantial CO₂ is the most obvious driver of an enhanced Archean greenhouse effect. We would expect Archean pCO₂ to have been high because of Earth’s carbonate-silicate cycle thermostat (Eq. 2) (174). If global temperatures and CO₂ are low, CO₂ removal via rainfall is slow, as are rates of continental and seafloor silicate weathering. Then, geological emissions of CO₂ raise atmospheric CO₂ levels, increasing global temperatures. Conversely, if the climate warms too much, greater rainfall and silicate weathering consume CO₂ and cool Earth.

These negative feedbacks would have moderated the Archean climate to a mean global temperature of 0° to 40°C (or 0° to 50°C without land and only seafloor weathering) (34). CO₂ alone could have solved the FYS problem with 0.004- to 0.03-bar CO₂ at 2.5 Ga ago and 0.024- to 1-bar CO₂ at 4 Ga ago, where the spread comes from uncertain carbonate-silicate model parameters.

However, without O₂ in the atmosphere, a CH₄ greenhouse bears consideration. Methane levels of 10⁴ to 10⁶ ppmv produce ~10 to 15 K of Archean greenhouse warming, which lowers the pCO₂ needed to warm the Archean Earth (Table 1). Some of this warming comes from a few parts per million by volume of ethane, C₂H₆, which is derived from CH₄ (215).

Both substantial CH₄ and CO₂ may be necessary if lower bounds on pN₂ discussed earlier are valid. Although N₂ itself is not an effective greenhouse gas, it pressure broadens line and continuum infrared absorption, enhancing the greenhouse effect. If Archean pN₂ was about half of today, a few kelvin would be lost from the greenhouse effect (143).

However, too much CH₄ relative to CO₂ would create the high-altitude organic haze mentioned earlier, which may cool Earth by up to ~20 K (1, 215) by absorbing incoming solar radiation and radiating energy back to space in a so-called “anti-greenhouse effect” (216). A cooling limit exists because as a haze becomes more UV absorbing, it shields CH₃ molecules from the photolysis needed for further haze formation. Thus, attenuation of sunlight saturates (1, 163).

Earlier, we noted that an organic haze might protect tropospheric ammonia from UV (162), but whether NH₃ was a viable greenhouse gas is unclear. The composition of organic aerosols in the Archean where sulfur was present and the C/O ratio was <1 was different from particles on Titan where sulfur is absent and C/O > 1. Consequently, the UV attenuation properties of early Earth haze particles remain uncertain.
Another proposed early greenhouse gas is H₂, if it attained percentage abundances (14, 217, 218). Molecular collisions produce temporary charge separation, allowing H₂ to undergo collision-induced absorption of infrared photons. For reasons given previously, Archean H₂ is unlikely to have been abundant. Instead, H₂ may be relevant for the Hadean greenhouse if percentage H₂ levels arose from H₂ outgassing or impacts.

Sulfur gases were likely unimportant for warming. SO₂ is a strong greenhouse gas, but tropospheric SO₂ dissolves in rainwater, and Archean stratospheric SO₂ photochemically disproportionates into UV-stable polysulfur and sulfuric acid aerosols, as noted previously. The latter raises the albedo and more than offsets any SO₂ greenhouse warming. H₂S is a weak greenhouse gas that overlaps in the absorption with CH₄ and is UV fragile. Carbonyl sulfide (OCS) has been suggested as an Archean greenhouse gas because UV photolysis of OCS was postulated to explain observed relationships in S-MIF (219). OCS persists today because it is not oxidized by OH radicals that cleanse the troposphere of other pollutants. However, in the absence of an ozone shield, OCS is susceptible to photolysis and cannot build up significantly (46).

Last, an alternative to the carbonate-silicate cycle stabilization of Earth’s climate is the “Gaia hypothesis,” which proposes that life interacts with inorganic Earth as a self-stabilizing system that maintains habitable conditions [e.g., (220)]. The Archean biosphere was surely important for atmospheric composition, which intertwines Earth’s in-habitation and habitability. However, debate continues about if and how adaptive evolution of the biosphere can produce a more stable climate than an abiotic Earth (221, 222).

**Physical and geochemical evidence of a moderate Archean climate**

Let us now consider proxy data for the Archean climate. Glacial rocks are one line of evidence. These include dropstones in sediments from melted icebergs, unsorted clasts mixed with silt and clay deposited at the base of glaciers that are preserved as diamictites, and striations made by rocks embedded in moving glaciers that scoured underlying surfaces. In the Archean, any indication of polar environments from glacial rocks would suggest a relatively cool world given that since ~34 Ma, a climate with poles covered in ice has required average global temperatures below ~20°C (223).

Glacial rocks are reported from 3.5, 2.9, and 2.7 Ga ago. The oldest, from the Barberton of South Africa, includes clasts in finely laminated sediments, interpreted as dropstones, found below diamictites (55). Later, in the ~2.9-Ga-old Pongola in South Africa, which was 43° to 48° paleolatitude (224), diamictites contain striated clasts, while associated silty laminates have dropstones with splash-up of substrata (54). Then, at 2.7 Ga ago, diamictites with dropstones occur in India (225) and Montana (226).

Another line of evidence about paleotemperature are ratios of ¹⁸O/¹⁶O in marine cherts and carbonates. These ratios decline with increasing age, which, at face value, suggests Archean ocean temperatures of 50° to 85°C (227). Cherts and carbonates precipitated from seawater acquire less ¹⁸O relative to the seawater as temperature increases because, at equilibrium, warmth allows stronger ¹⁸O bonds to be broken and replaced with ¹⁶O. Not all Archean isotopic studies infer hot temperatures, however. Combined O and H isotope ratios have suggested surface temperatures ~40°C (52), while O isotopes in Archean phosphates have produced 26° to 35°C upper limits (53).

Most researchers have doubted the isotopic inferences of persistently high Archean surface temperatures because the climate was sometimes cold enough for the aforementioned glaciations, and chemical weathering of quartz from hot climates is lacking (228). Two alternative interpretations are as follows: (i) Archean surface temperatures were similar to today’s because the oxygen isotope composition of seawater, δ¹⁸Oseawater, increased by ~15% since 3.5 Ga ago (229, 230). (ii) Older cherts and carbonates have nonprimary δ¹⁸O from high alteration temperatures or hydrothermal fluids (55, 231).

The first explanation relies on changes in the relative rates of high and low temperature water-rock interactions. Hydrothermal seafloor interactions increase δ¹⁸Oseawater, whereas low-temperature seafloor and continental weathering decrease δ¹⁸Oseawater. Archean oceans with shallow seafloor hydrothermal circulation and an increase in Phanerozoic pelagic sediments that lowers seafloor weathering might cause secular increase in δ¹⁸Oseawater [e.g., (229)]. However, measurements find ancient δ¹⁸Oseawater ~ 0‰ (Vienna standard mean ocean water) in 2-Ga-old ophiolites (232), 3.8-Ga-old serpentine minerals (185), Archean pillow basalts (233), and kerogens in Archean cherts (234). In addition, clumped isotopes show little change in Phanerozoic δ¹⁸Oseawater [e.g., (235)]. Alternatively, ²⁹O isotopes in iron oxides since 2 Ga ago suggest a secular increase in δ¹⁸Oseawater (236).

The second possibility is that δ¹⁸O of cherts and carbonates is more altered with age. Microanalysis shows how chert replaced sedimentary carbonates and did not precipitate from seawater (231). In addition, stringent geochemical and petrographic selection criteria for paleothermometry eliminate Archean cherts (237). The same issue applies for silicon isotopes in Archean cherts, which have been used to infer hot surface temperatures (238). Last, the triple O isotope composition of Archean cherts cannot be reconciled with equilibrium precipitation from seawater and requires alteration (239).

Phylogenetic inferences of early thermophilic microbes have also been used to argue for hot Archean oceans (240, 241). However, other more convincing reconstructions and biochemical considerations suggest a mesophilic (~50°C) common ancestor (242, 243).

Temperature limits on mineral formation may also favor a temperate Paleoarchean. Pseudomorphs of barite after gypsum are reported in 3.5-Ga-old evaporites that are now partially silicified (244). In halite-saturated brines, gypsum (CaSO₄·2H₂O) forms at <18°C; otherwise, anhydrite (CaSO₄) precipitates (245). It has been claimed from x-ray tomography that hydrothermal barite, not gypsum, was actually primary (246). However, three-dimensional universal stage petrography found interfacial angles diagnostic of gypsum at the original crystal faces (244), which are partially replaced by quartz and draped by quartz, so cannot show up in x-ray density contrasts.

**Additional external parameters and their effect on Archean climate**

Additional factors may have affected the Archean climate. One external parameter was a faster rotation of early Earth. Today, the Moon recedes ~4 cm year⁻¹ from Earth due to tides, so Earth is despinning over time to conserve angular momentum in the Earth-Moon system. Going back in time, depositional cycles in the 2.45-Ga-old banded iron Weeli Wolli Formation, Australia indicate a ~17-hour day (247).

In general, a faster Archean rotation rate reduces heat transport from equator to pole (212, 213), particularly if the atmosphere had less mass (248). Thus, warm tropics and glaciated poles would arise if the Archean had a thin atmosphere.

External parameters that modulate the carbonate-silicate cycle would also affect the long-term climate. These include land fraction, CO₂ outgassing, and biological modification of weathering. In general, how CO₂ outgassing changed with time dominates the uncertainty (34).
CONCLUSIONS AND OUTLOOK

The general view that emerges is an Archean atmosphere devoid of O₂ and enriched in CO₂ and CH₄ greenhouse gases that countered the FYS. N₂ was a bulk gas, but proxy data, although debated, suggest that N₂ levels were similar to today or possibly a factor of a few lower, which, if correct, requires understanding of how the nitrogen cycle operated differently in an anoxic world. With the present information, a schematic overview of atmospheric evolution is shown in Fig. 5A.

The Archean climate was probably mostly moderate (Fig. 5B). Although some argue for a hot Archean climate, glacial rocks at 2.7, 2.9, and 3.5 Ga ago and recent isotopic analyses call that idea into question; indeed, our current understanding of feedbacks in the geologic carbon cycle suggests surface temperatures within 0° to 40°C.

Reconstructing the history of O₂ is informed by proxies, but they are often indirect. Once cyanobacteria evolved, local or regional oxygen oases in lakes or shallow seawater are possible, and various redox-sensitive proxies suggest that these oases actually existed by 3.2 to 2.8 Ga ago under globally anoxic air. The newest relevant data are mass fractions of xenon isotopes, which gradually increase through the Archean relative to initial solar values. These data are best explained by xenon escaping to space as an ion dragged out by hydrogen originating photolytically from an anoxic atmosphere enriched in methane until the GOE.

Despite improved knowledge of the Archean, a relative dearth of uncontested data that constrain basic environmental variables, such as Archean seawater pH, climatic temperature, barometric pressure, and changing levels of the greenhouse gases CO₂ and CH₄ through time, means that more proxy development and measurements are critical. It is also implausible that the Archean—one-third of the history of Earth—had a constant climate. However, our knowledge of Archean climatic variability is meager.

The biosphere was surely a major influence on Archean atmospheric composition, as it is today. Consequently, resolving when key biological innovations evolved—such as nitrogen fixation, methanogenesis, anoxygenic photosynthesis, and oxygenic photosynthesis—and understanding their influence are essential for improving models of atmospheric evolution.

This understanding may help us interpret future exoplanet data because atmospheres on other rocky Earth-sized worlds would initially be anoxic. On Earth, oxygenic photosynthesis evolved only once, perhaps because of its biochemical complexity (249). Consequently, if life exists elsewhere, inhabited planets with Archean-like atmospheres may be the most common type. So, determining what the Archean atmosphere was made of, and if the influence of life, could help us distinguish biogenic gases in exoplanet atmospheres and so find life elsewhere (2, 250).

Last, the connection between atmospheric evolution and debated trends in solid Earth evolution was outside the scope of this review. However, quantifying temporal changes in land area, surface rock composition, weathering, the size of volcanic and metamorphic fluxes of gases, and the redox evolution of outgassing all need further development to understand their implications for Earth’s atmospheric evolution or to extrapolate to exoplanets.

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