How did life survive Earth's great oxygenation?

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Life on Earth originated and evolved in anoxic environments. Around 2.4 billion-years-ago, ancestors of *Cyanobacteria* invented oxygenic photosynthesis, producing substantial amounts of O_2 as a byproduct of phototrophic water oxidation. The sudden appearance of O_2 would have led to significant oxidative stress due to incompatibilities with core cellular biochemical processes. Here we examine this problem through the lens of *Cyanobacteria* — the first taxa to observe significant fluxes of intracellular dioxygen. These early oxygenic organisms likely adapted to the oxidative stress by co-opting preexisting systems (exaptation) with fortuitous antioxidant properties. Over time more advanced antioxidant systems evolved, allowing *Cyanobacteria* to adapt to an aerobic lifestyle and become the most important environmental engineers in Earth history.

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Introduction

Data from the geological record indicate that life was present on Earth very early in its history. Intriguing observations of graphitic carbon in some of the oldest rocks and minerals have been proposed to be traces of Earth's early biosphere [1,2]. By ∼3.4–3.2 billion years ago (giga annum or Ga), a range of observations indicate the presence of microbial cells [3,4] with diverse anaerobic metabolisms [5–8]. Even using the most conservative estimate of 3.2 Ga for the origin of life, it was clearly present long before O_2 appeared in significant amounts in Earth's atmosphere.

The first organisms to encounter significant and sustained oxidative stress due to O_2 were ancestral *Oxyphotobacteria* — members of the bacterial phylum *Cyanobacteria*,

capable of oxygenic photosynthesis. These organisms likely supported themselves largely by means of anoxygenic photosynthesis at first, perhaps with only intermittent production of O_2 in relatively small amounts. At this stage in Earth history, life did not have the defenses necessary to deal with an oxidant as powerful as O_2 [9••]. How did early *Oxyphotobacteria* survive the intracellular production of O_2 and make the transition from a strictly anaerobic to aerobic metabolism? Here we integrate data from bioinorganic chemistry and comparative biology to infer the evolution of oxygen tolerance in *Oxyphotobacteria*. Notably, ancestral *Oxyphotobacteria* could have coped with small amounts of O_2 during the transition to oxygenic phototrophy by co-opting preexisting systems with fortuitous antioxidant properties. This would have allowed time for more modern antioxidant systems to evolve. We discuss non-enzymatic, small-molecule solutions to mitigate O_2 stress that were present in early cells, followed by some specific adaptations that the *Oxyphotobacteria* developed to enable the transition to an oxygenated world.

Geological record of O_2

Today O_2 comprises nearly 21% of the atmosphere, however a wide array of observations made over the past sixty years from the geological record illustrates that it was extremely scarce prior to the evolution of oxygenic photosynthesis [10•]. How scarce? An exact paleobarometer for O_2 remains out of reach, but there are several types of geological and geochemical data that can be converted into O_2 concentrations that are thought to be accurate within an order of magnitude or two (Figure 1). Sedimentary rocks older than 2.4 Ga, composed of pebbles and sand eroded from the crust and deposited by rivers, are distinct from those seen in younger strata because they contain abundant physically rounded redox-sensitive minerals, such as pyrite (FeS_2), uraninite (UO_2), and siderite ($FeCO_3$) [11]. These minerals are quickly oxidized and destroyed in the presence of even trace O_2, so their presence constrains O_2 levels to less than ∼10^{-5} atm before 2.4 Ga [11]. Additional independent geochemical proxies support this view. For example, multiple sulfur isotopes in marine sedimentary rocks older than 2.4 Ga display a widespread and unusual type of mass independent fractionation (MIF) caused by the photochemistry of SO_2 in an atmosphere largely devoid of O_2 ($\ll 10^{-5}$ atm and likely closer to 10^{-10} atm). This corresponds to astonishingly low environmental levels of O_2 — sufficiently low that the anaerobic microorganisms that existed at the time may not have ever encountered biologically meaningful amounts of oxygen related stress.

Figure 1
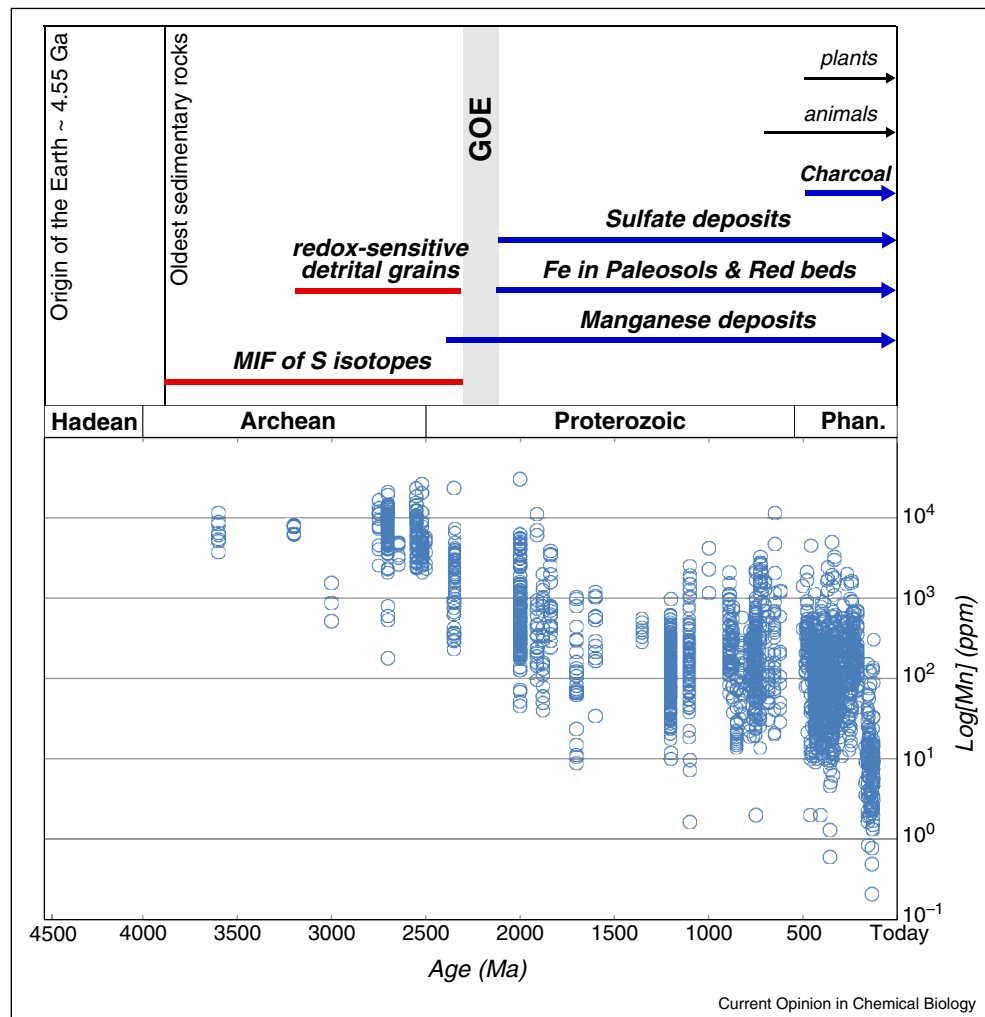
Geological and geochemical data reveal a large first-order, irreversible change in the redox state of Earth surface environments marked by the rise of O_2 2.4–2.35 billion years ago. *Upper panel*: The widespread presence of redox-sensitive detrital grains, like pyrite and uraninite, in Archean and early Paleoproterozoic sandstones and conglomerates illustrates that O_2 levels were lower than 10^{-5} atm in the atmosphere and Earth surface waters to explain their survival through the rock formation processes of weathering, transport, deposition and lithification. A similar pattern is provided by the mass-independent fractionation (MIF) of multiple S isotopes in Archean and early Proterozoic strata [89,90]. The MIF signal results from photochemistry involving SO_2 in the early atmosphere and models constructed to evaluate the O_2 concentrations consistent with these observations suggest that O_2 levels were exceedingly low, much less than 10^{-5} atm, and perhaps closer to 10^{-10} atm [10•]. These observations are juxtaposed by a number of observations that show a rise of O_2 between 2.4 and 2.35 Ga. MIF and redox-sensitive detrital grains disappear from sedimentary rocks [11,12]. Iron becomes oxidized and retained in preserved soils (paleosols) during weathering of bedrock [13], and it forms abundant hematite (Fe_2O_3) grains and cements in sedimentary rocks (red beds). And sulfate salts become conspicuous sulfur cycle-sinks of sulfate derived from weathering of sulfide-bearing minerals [15]. Though young by comparison, the charcoal record [91] provides an important constraint on atmospheric oxygen because it illustrates that as long as there was plant biomass around on the land surface that could burn, it did. Mn deposits (Mn-rich sedimentary rocks >1 wt.% Mn) do not occur until just prior to the rise of O_2, an observation that motivates the hypothesis that Mn(II) was a substrate for phototrophy prior to the evolution of the water-oxidizing complex of PSII, and photosynthetic O_2 fluxes [29••]. The rise of O_2 marks the oldest certain age for the evolution of biological water splitting by *Oxyphotobacteria* [10•]. The origins of animals and plants are shown for context. *Lower panel*: Mn(II) content of calcite-bearing ($CaCO_3$) and dolomite-bearing ($CaMg(CO_3)_2$) sedimentary rocks provides a coarse measure of the amount of Mn^{2+} present in seawater (data from Shields and Veizer [18]). Before the GOE, carbonates precipitated from seawater are highly enriched in Mn(II), implying high concentrations in seawater. After the rise of oxygen, Mn-oxide minerals form an important sink of Mn, and the Mn content of seawater subsequently decreased [14]. These measurements exhibit substantial variation due to post-depositional recrystallization and interaction with later fluids, which tend to enrich carbonates in Mn(II).

The geological record indicates that a rapid and irreversible rise of O_2 occurred between 2.4 and 2.35 Ga — a transition known as the Great Oxygenation Event (GOE) (Figure 1) [10•,12]. Many of these observations record changes in the biogeochemical cycles of major redox-active elements, such as Fe, Mn, and S. At this time MIF [10•] and redox sensitive detrital grains disappeared [11]. Ferrous iron in igneous minerals became oxidized and