

# Abiotic oxidants promoted cyanobacteria's evolution and Earth's oxidation

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Oxygenic photosynthesis by cyanobacteria, green algae and plants effectively converts solar energy and provides free oxygen, which is vital to life. In Earth's history, the innovation of oxygenic photosynthesis absolutely is a pivotal event because the released O<sub>2</sub> initiated the redox revolution of the Earth surface system, ultimately leading to the rise of atmospheric oxygen level around 2.4 Ga at the Archean-Proterozoic transition (the Great Oxidation Event, GOE). As we know, cyanobacteria originated from its ancestors, anoxygenic phototrophs, and a basic requirement for the evolution of oxygen-producing photosynthesis is that the early oxygen-producing organisms should not be killed by their metabolic products (e.g., intracellular O<sub>2</sub>). That means, prior to the innovation of oxygenic photosynthesis, ancestral cyanobacteria should have gained the ability to cope with the toxicity of O<sub>2</sub> and reactive oxygen species (ROS, e.g., hydroxyl radical (•OH), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)). However, there emerges a chicken-and-egg dilemma that oxygenic photosynthesis and free oxygen, which came first?

Recent phylogenetic analyses<sup>1</sup> indicate that antioxidant enzymes deeply encoded in genome of Archaea and Bacteria, even in the Last Universal Common Ancestor (LUCA). This suggests that early life including ancestral cyanobacteria were accessible to abiotic oxidants, so that they acquired a

defensive ability against oxidants even utilized these oxidants. Accordingly, the source of abiotic oxidants on the early Earth is the key to decipher the evolution of oxygenic photosynthesis.

Here, we introduce the advance in the discovery of Archean abiotic oxygen-producing pathway that involves the generation of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> at mineral-water interfaces (Figure 1). In the Archean, mineral abrasion in turbulent subaqueous environments could have served as a persistent source of abiotic oxidants, creating an evolutionary impetus for the origin of oxygenic photosynthesis<sup>2</sup>.

## TWO POSSIBLE EVOLUTION SCENARIOS OF OXYGENIC PHOTOSYNTHESIS

From the perspective of molecular biology, it would have been difficult for the ancestor of modern cyanobacteria to extract four electrons from water, a very stable compound, before the development of chlorophyll-*a* and the water-oxidizing complex<sup>3</sup>. One corollary is that during the transition from anoxygenic to oxygenic photosynthesis, the electron donor for ancestral photosystem II must have been a small molecule oxidized directly by the reaction center with a modest midpoint reduction potential, which is higher than previ-

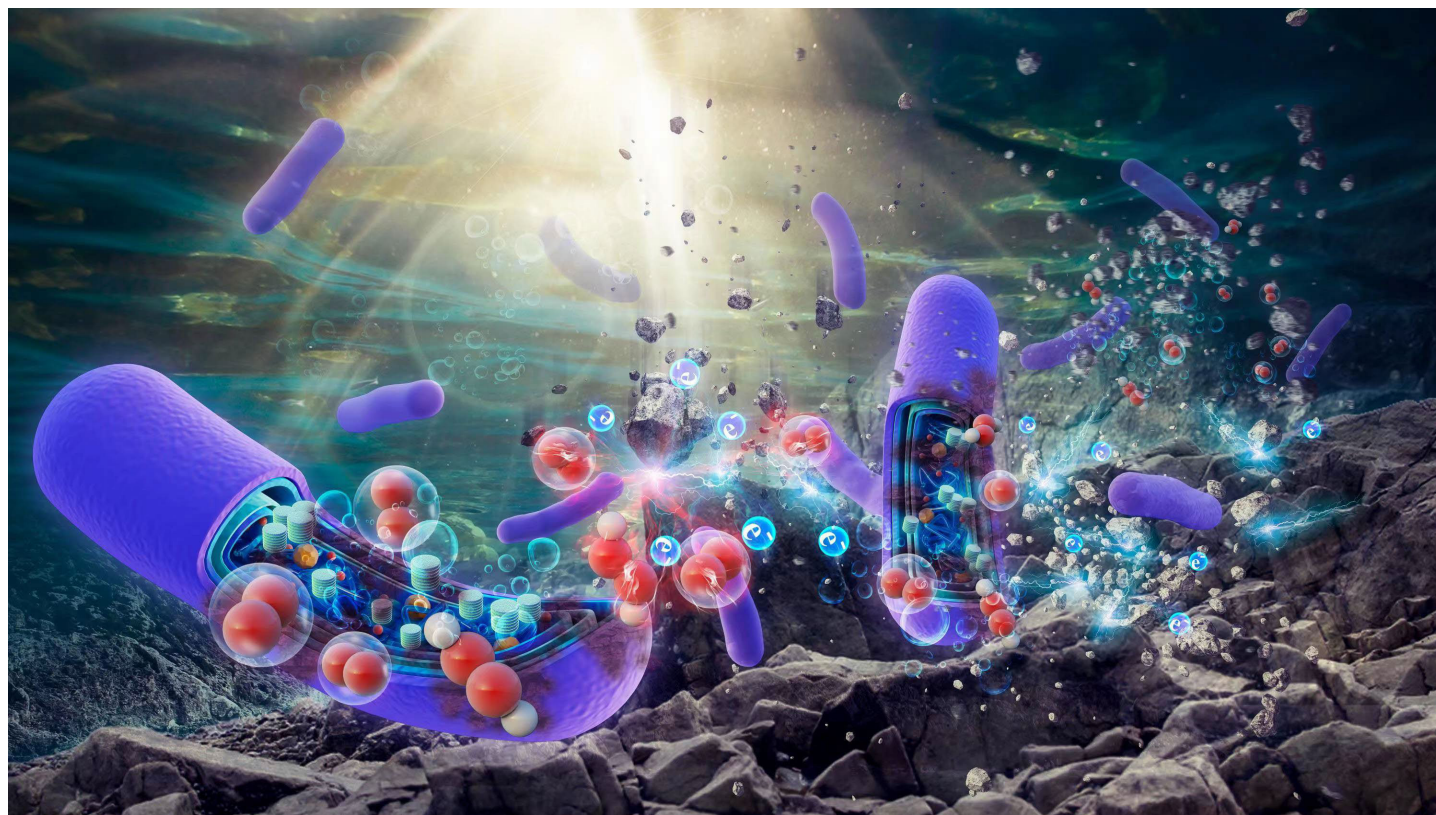


Figure 1. The abiotic H<sub>2</sub>O<sub>2</sub>-induced evolutionary impetus on the organisms that conduct anoxygenic photosynthesis in turbulent subaqueous environments. The red ball, blue ball and the purple cylinder are oxygen, electron, and anoxygenic phototrophic bacteria, respectively.

ous substrates ( $\text{Fe}^{2+}$ ,  $\text{H}_2$ ,  $\text{S}_0$ , etc.) but lower than  $\text{H}_2\text{O}$  (+0.82 V). Some plausible intermediates were proposed, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , +0.27 V) and divalent manganese ( $\text{Mn}^{2+}$ , +0.6~0.92 V) are discussed extensively<sup>2,3</sup>.

The hypothesized  $\text{Mn}^{2+}$ -oxidizing phototrophy could have been sensitive to high-potential oxidants (e.g.,  $\text{O}_2$  and its derivatives), because the environmental  $\text{Mn}^{2+}$  could be consumed by the oxidants, suggesting that it may live in reduced conditions. However, as mentioned above, the ancestral cyanobacteria would have inhabited weakly oxic primordial microenvironments and adapted to oxidative stress before they invented oxygenic photosynthesis<sup>1,3</sup>. And the ancestors of cyanobacteria used catalase and superoxide dismutase enzymes to remove  $\text{H}_2\text{O}_2$  and its derivatives, superoxide radical ( $\cdot\text{O}_2^-$ ), respectively, at least 3.3–3.6 billion years (Gyr) ago<sup>1</sup>. Given that the oxidant sequestration requirements for the hypothesized  $\text{Mn}^{2+}$ -oxidizing phototrophy are contradictory to the weakly oxic environments where ancestral cyanobacteria inhabited,  $\text{H}_2\text{O}_2$  was more likely to serve as the transitional electron donor.

For the hypothesis of  $\text{H}_2\text{O}_2$ -oxidizing phototrophy, since it has been proposed by Blankenship and Hartman<sup>3</sup>, two disputes aroused on this: (1) Whether a sequence homology existed between the manganese catalases and the manganese binding domain of reaction center subunits in the photosystem II; (2) Whether an exogenous source of  $\text{H}_2\text{O}_2$  existed on the early Earth. For the distant homology, an alternative possibility is the incorporation of an inorganic Mn cluster (e.g.,  $\text{MnO}_2$  minerals) into the primitive reaction center, rather than using manganese catalases. However, for the source of abiotic oxidants, although atmospheric photochemistry was conventionally regarded as the source of abiotic oxidants, recent calculations indicated that the ground level of photochemically produced  $\text{H}_2\text{O}_2$  is insufficient to fuel aerobic respiration and photosynthesis<sup>2</sup>. Accordingly, the key problem for the hypothesis is whether a persistent source of bioavailable  $\text{H}_2\text{O}_2$  existed on the terrestrial surface of Archean Earth.

#### DISCOVERY OF A PERSISTENT SOURCE OF ABIOTIC OXIDANTS

Searching for an alternative source of abiotic oxidants, geologists revisit the oxygen-producing physical chemistry in general geologic processes. Recent progress on the mechanism of mineral-water reactions provides opportunities to the discovery of abiotic oxidants<sup>2</sup>. Special chemical behaviors of radicals on fresh surface of minerals have drawn the researchers' attention because these reactive sites could be readily produced in mechanic processes and react with water to generate  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  (Figure 1). In the simulated Archean atmosphere conditions, high yields of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  were found in quartz-water reactions<sup>2</sup>. Importantly, quartz abrasion can cause continuous ROS generation in hydrodynamic environments, e.g., rivers, estuaries and deltas. By extrapolating the experimental results to depositional scale<sup>2</sup>, the  $\text{H}_2\text{O}_2$  producing rate at the Archean delta/shore could reach  $4.87 \times 10^{11}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , which is 5 magnitudes higher than that of atmospheric photochemistry ( $\sim 10^6$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ). Thus, the mineralogical mechanochemical oxidants is a previously unrecognized but geologically significant oxygen-producing pathway.

A key geological constraint on the evolution of ancestral cyanobacteria is the formation of oxidized environments. The calculations suggest that locally oxidized environments could be formed at the Archean delta/shore, and the continuing source of ROS and  $\text{O}_2$  can produce an oxidized front moving outward from the delta to the open ocean that was characterized by ferruginous seawater<sup>2</sup>. Certainly, Archean oxic microsites were vulnerable to environmental changes, e.g., storms carrying ferrous ions. Even if locally oxidized environments were disrupted, the  $\text{H}_2\text{O}_2$  concentration could regain to micro-molar levels within several days. Thus, the in-situ  $\text{H}_2\text{O}_2$ -producing process at Archean delta/shore could have maintained local weak oxic conditions for ancestral cyanobacteria, which has been supported by increasing geochemical evidence<sup>4</sup>.

#### EVOLUTIONARY INNOVATION DRIVEN BY ARCHEAN ENVIRONMENTAL OXIDATION

Given that biological innovation is tightly related to environmental change, the evolution of ROS-detoxifying system and oxygenic photosynthesis in ancestral cyanobacteria should not be a fortuitous impulse, but the adaption to the gradually oxidized geological landscape in the Meso- and Neoproterozoic.

A more recent work reported that ROS production not only occurs at quartz-water interface, but also in various silicate-water interfaces, and its magnitude increases from mafic- to felsic-silicates<sup>4</sup>. In the context of early continent formation, e.g., the Kaapvaal and Pilbara basins between 3.5 to 3.2 Gyr, the emplacement of feldspar and quartz rich granitoids and their subsequent exposure to physical weathering might have provided at least  $1.73 \times 10^8$  mol  $\text{O}_2$  per year, even before the evolution of biological  $\text{O}_2$  production<sup>4</sup>. Notably, once substantial granitoids formed in the crust and plate tectonics initiated globally in the Archean, aggressive tectonics and physical weathering of the felsic rocks could have led to a higher ROS-producing flux. Thus, more oxic microsites appeared on terrestrial surface in the Meso- and Neoproterozoic<sup>5</sup>, which could have provided the special ecological niche for ancestral cyanobacteria. Ultimately, oxygenic photosynthesis successfully evolved in cyanobacteria.

Besides, the discovery of the abiotic oxygen-producing pathway brings insights into the evolution of the Archean marine biosphere. Such oxidants may have oxidatively mobilized redox-sensitive elements (e.g., Mo) to seawater prior to the GOE, enhancing the availability of bioessential nutrient elements. These metals were assimilated into early microbes and synthesized enzymes, such as nitrogenase and nitrate reductase enzymes, which would effectively increase the size and activity of the Archean marine biosphere.

#### CONCLUDING REMARKS

The discovery of this novel abiotic source of Archean  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  advances our understanding in the oxidation adaption of early life and the origin of oxygenic synthesis. These works also verified a new geochemistry view that some existing Archean proxies of  $\text{O}_2$  are not necessarily tied to early oxygenic photosynthesis. Geochemical records of the 3.22 Gyr Moodies Group (South Africa) suggest the coeval shallow seawater was mildly oxidized<sup>2</sup>. This may provide support for the intermediate stage of cyanobacteria that inhabited the high-energy hydrodynamic intertidal zone with substantial  $\text{H}_2\text{O}_2$  produced in quartz abrasion. Importantly, the temporal and historical changes of this abiotic ROS flux implies that the transformation of mafic crust to felsic crust is critical for the promotion of Earth's habitability<sup>4</sup>, and mineral evolution may be the intrinsic links in coevolution of the lithosphere, hydrosphere, atmosphere, and biosphere.

In future, more studies are needed to build a direct link between geological records and the abiotic oxidants generated at mineral-water reactions. Because oxygen on mineral surface could transfer into  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  in mineral-water reactions<sup>5</sup>, the analysis of oxygen isotope composition of sedimentary rocks may be a key breakthrough.

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#### DECLARATION OF INTERESTS

The authors declare no competing interests.