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Reviews and syntheses: Photosynthetic oxygen evolution in plants-A potential inheritance from early abiotic oxygen production on Earth

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Abstract. The phenomenon of photosynthetic oxygen evolution by plants, as the basis of life on our planet, has long attracted scientists from various disciplines. This process converts natural energy and inorganic carbon into organic matter and oxygen, which are not only crucial for maintaining terrestrial ecosystems but also reveal the early evolution of the Earth's biosphere. In this review, we present evidence from various disciplines, such as paleontology, biochemistry, stratigraphy, geochemistry, and molecular evolutionary biology, to support the proposition that abiotic processes generated the earliest detected oxygen on Earth. The bicarbonate photolytic oxygen release mechanism in photosynthetic organisms is, in our opinion, an inheritance of the abiotic oxygen release mechanism. In contrast, the water photolytic oxygen release mechanism evolved in response to insufficient availability of inorganic carbon. This review provides insights into the evolution of oxygen production mechanisms and their implications for the design of artificial photosynthetic reactors.

1 Background and Challenge

Oxygenic photosynthesis, originating in cyanobacteria and spreading to green algae and plants, is a key event in Earth's geological and biological history (Hohmann - Marriott and Blankenship, 2011). This process significantly changed the planet's atmosphere, introducing free oxygen and triggering the Great Oxidation Event (GOE), which enabled the rise and diversification of complex, oxygen-dependent life (Schirrmeister et al., 2013). Current consensus suggests that photosynthetic oxygen originates from water. However, recent evidence, including the bicarbonate effect, pH-dependent thylakoid carbonic anhydrase activity, photosystem II (PSII) crystalline structure insights, and re-evaluated heavy oxygen isotope labeling experiments, indicates that both water and bicarbonate photolysis contribute to photosynthetic oxygen generation. Examining bicarbonate photolysis thermodynamic efficiency, photosynthetic stoichiometry, the global water-carbon cycle, and the Dole effect reveals bicarbonate photolysis as a fundamental process, equally significant to water photolysis in photosynthetic oxygen evolution (Wu, 2021; 2023; Guo et al., 2024).

The evolution of photosynthetic organisms is inherently tied to atmospheric oxygen escalation. Earth has experienced two GOEs: the first, 2.4-2 billion years ago, marked by cyanobacteria's emergence, saw atmospheric oxygen levels gradually rise to 1-2% of modern levels. Following this initial GOE, oxygen concentrations likely plateaued until about 850 million years ago, after which they ascended to approximately 20% of present atmospheric levels, with potential spikes to 30–35% during the Carboniferous era. The second GOE is closely associated with the proliferation of photosynthetic eukaryotes, which substantially enhanced photosynthesis and witnessed a notable increase in algal and lichen productivity, especially in terrestrial environments (Holland, 2006). Elevated atmospheric O_2 levels during the Carboniferous (~360–300 Ma) coincided with vascular plant evolution and enhanced carbon sequestration (Berner, 1999). Currently, the rise in atmospheric O_2 levels is correlated with cyanobacteria's emergence, leading scientists to conclude that aerobic photosynthesis independently originated within these taxa (Fischer et al., 2016; Hohmann - Marriott and Blankenship, 2011).

However, above conclusion hinges on the premise that significant abiotic oxygen sources were absent in early Earth's atmosphere (Fischer et al., 2016). Recently, researchers studying the Clarion-Clipperton Zone's seafloor ecosystem have discovered that polymetallic nodules in ancient sediment layers 4000 meters deep emit considerable oxygen (Sweetman et al., 2024). This challenges the idea that early Earth lacked significant abiotic oxygen sources. Moreover, photosynthesis is a derived trait in extant taxa, including cyanobacteria, phylogenetically (Fischer et al., 2016). Challenging the view that aerobic photosynthesis originated exclusively in cyanobacteria, we hypothesize that it may have evolved from early abiotic oxygen-generating processes, with bicarbonate photolysis being an inherited trait from primitive Earth's abiotic oxygen production mechanisms. This review critically examines the hypothesis across three key domains: early abiotic oxygen production, the potential ancestry of PSII, and the two-substrate photosynthetic oxygen evolution (Fig. 1).

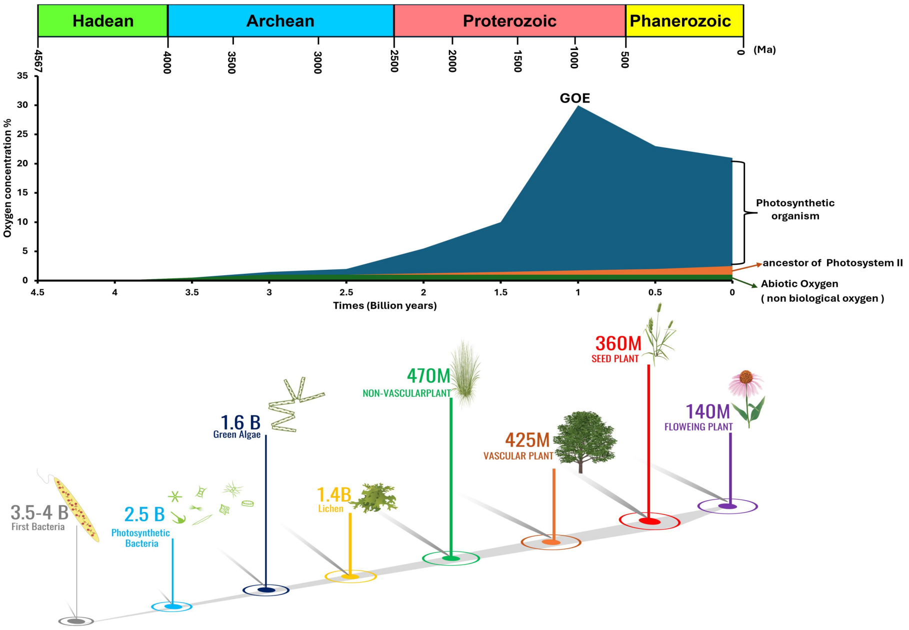

Figure 1. The connection between oxygen levels in Earth's atmosphere, the evolutionary milestones in plant life, and the early processes that contributed to oxygen generation. It highlights the role of abiotic oxygen-generating processes before the emergence of biological oxygen production. The enzyme carbonic anhydrase is suggested as a potential precursor to PS II, a key component of the photosynthetic process responsible for oxygen production. It also depicts the evolution of the two-substrate photosynthetic oxygen-evolving process, which is critical for the significant rise in oxygen levels, particularly during the Great Oxygenation Event (GOE), which leads to the diversification of complex plant life.

2 Early abiotic oxygen production

Earth originated ~4.5Ga ago, cooling ~100Ma post-formation, leading to rock genesis (Wilde et al., 2001). Despite a significant rise in atmospheric O_2 levels during the first GOE, ~2.5-2.3Ga ago, studies of redox-sensitive trace elements and isotopes in Archean sedimentary (metamorphic) rocks suggest the presence of O_2 several hundred million years, or possibly over a billion years, before the emergence of photosynthetic cyanobacteria(Fischer et al., 2016; Hohmann-Marriott and Blankenship, 2011; Xiong and Bauer, 2002).

Investigations into interstratified Fe and Ca-carbonate minerals within thick carbonate platforms (~2.9-2.8 Ga) of Canada's western Superior Province suggest that dynamic chemoclines, driven by oxygenic processes at platform edges, were common in the Archean. Dissolved iron oxidation likely significantly influenced marine Ca-carbonate precipitation during that era (Ridinget al., 2022). Isotopic analysis of Mo in rocks from the ~2.95 Ga Sinqeni Formation, Pongola Supergroup, South Africa, indicates that O_2 accumulation in shallow marine environments commenced >500 Ma before the first GOE (Planavsky et al., 2014). Additionally, high-resolution chem-stratigraphic analyses of redox-sensitive metals (Mo, Re) in the late Archean Mount McRae Shale, Western Australia, suggest their introduction to Archean oceans via oxidative weathering of crustal sulfides. This implies the existence of minimal oxygen levels >50 Ma prior to the first GOE (Anbar et al., 2007). Moreover, chromium isotope and redox-sensitive metal studies in the ~3-Ga-old Nsuze palaeosol and Ijzermyn iron formation (Pongola Supergroup) indicate significant atmospheric oxygen presence at that epoch (Crowe et al., 2013). In-depth analysis of the Manzimnyama Banded Iron Formation (BIF) from South Africa's Fig Tree Group indicates substantial oxygen levels in shallow marine environments ~3.2Ga ago (Satkoski et al., 2015). Lastly, iron isotope analysis from the Isua Supracrustal Belt (ca. 3.77 Ga), West Greenland, suggests that iron oxidation was pivotal in BIF deposition at that time (Czaja. et al.,2013).

Despite the presence of oxygen since 3.8Ga ago in the Archean, there remains considerable debate among scientists on whether the oxygen from that era to the rise of cyanobacteria 2.35Ga ago was biologically generated over a span of 1.4 Ga. The argument for oxygen generation by biological processes during this period is mainly supported by carbon isotope evidence and fossil records. For example, researchers have found metamorphosed pelagic shale in West Greenland, dating to 3.7Ga ago, with reduced carbon exhibiting $\delta^{13}C$ values as low as −25.6‰ PeeDee Belemnite (PDB) (Rosing and Frei, 2004). Additionally, negative $\delta^{13}C$ values have been traced in organic matter from sedimentary rocks as old as 3.8 Ga (Schidlowski, 1988). Investigations of 2.724-Ga-old Tumbiana Formation stromatolites from Australia's Fortescue Group have shown that their thin layers' clusters of organic globules strikingly resemble organic-mineral structures in modern stromatolites (Lepot et al., 2008). Additionally, research on the 3.465-Ga-old Apex chert from the Warrawoona Group, Western Australia, has revealed 11 filamentous structures resembling cyanobacterial microfossils (Brasier et al., 2005; Schopf, 1993; Schopf and Packer, 1987). Furthermore, investigations of sedimentary rocks from the Barberton Supergroup in the Barberton Mountains of South Africa have identified numerous filamentous structures resembling cyanobacteria-like microorganisms at two distinct stratigraphic levels within the 3.5-Ga-old Onverwacht Group (Walsh and Lowe, 1985).

Increasing research has raised questions about the reliability of interpreting Archean carbon isotopes and microfossil evidence as indicators of oxygen emergence (Fischer et al., 2016; Hohmann-Marriott and Blankenship, 2011) Negative $\delta^{13}C$ values are also present in organic compounds generated in numerous geological environments (McCollom and Seewald, 2006); moreover, the genetic machinery for carbon fixation is not exclusive to photosynthetic organisms (Lindell et al., 2005). Extensive analysis of microfossil-like structures found in 3.465-Ga-old Apex chert from the Warrawoona Group in Western Australia employed advanced techniques, including optical and electron microscopy, micro-Raman spectroscopy, etc. These formations, previously identified as "microfossils" in metalliferous hydrothermal vein chert and volcanic glass, are now recognized as pseudo-fossils. They form from carbonaceous material reorganization during amorphous silica's recrystallization into spheroidal structures. It's plausible that carbon isotopes in Apex chert's carbonaceous material experienced fractionation within hydrothermal systems (Brasier et al., 2002; 2005). Furthermore, given hydrothermal and groundwater alterations in Apex chert, it's unlikely it preserved early life forms (Pinti et al., 2009). Microscopic and Raman spectroscopic analyses of microfossils in Apex chert reveal filaments as mere quartz- and hematite-filled cracks, with carbonaceous matter dispersed in the surrounding quartz matrix, not associated with these fissures (Marshall et al., 2011). Thus, oxygen presence before the first GOE likely resulted from abiotic geological processes of the Archean era, not from oxygenic photosynthesis.

Land's geological light capture systems and "dark" oxygen on the deep ocean floor provide stronger evidence for abiotic oxygen release (Lu et al., 2019; Sweetman et al., 2024). Scientists employed electron microscopy, X-ray absorption spectroscopy, and micro-Raman spectroscopy to investigate semiconducting iron and manganese (oxyhydroxy) oxide mineral coatings on rock and soil surfaces. They discovered that these oxyhydroxy coatings function as "photoelectric devices," capable of absorbing light and converting it into electricity (Lu et al., 2019). In-situ benthic chamber experiments at 4,000m depth in the Pacific revealed that polymetallic nodules can markedly enhance oxygen levels, tripling ambient concentrations within 48hrs. Furthermore, these nodules displayed high voltage potentials, reaching up to 0.95V(Sweetman et al., 2024) (**Fig.2**) .

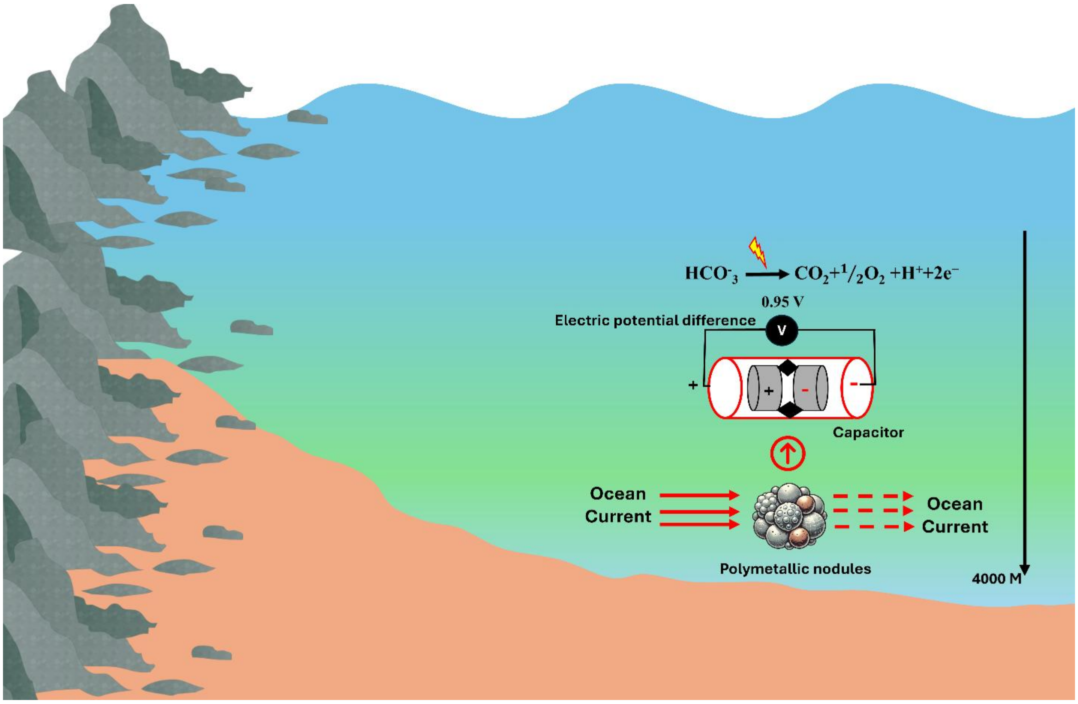

Figure 2. A schematic model showing the role of deep-sea polymetallic nodules, which act as energy storage systems, akin to capacitors, in the presence of ocean currents and hydrodynamic forces. The ocean currents flowing over the surface of these nodules generate an electric potential difference (shown as 0.95 V). Although this voltage is insufficient to drive water molecule decomposition (which requires about 1.5 V), it is enough to facilitate the decomposition of HCO_3^-. This reaction leads to the release of O_2 and CO_2. The process highlights an abiotic pathway for oxygen generation, suggesting that non-biological sources of oxygen could have existed during the Archean. This discovery broadens our understanding of early Earth's oxygen generation mechanisms, indicating that these nodules may have contributed to oxygen production before the rise of biological photosynthesis.

Sunlight interaction with iron-manganese oxide "mineral coatings" on rocks facilitates a non-biological oxygen generation pathway. These semiconducting mineral layers absorb solar radiation, producing photoelectrons that catalyze redox reactions, transforming light into chemical energy. This enables the photo-catalytic breakdown of water or bicarbonate ions, yielding oxygen (Lu et al., 2019)(**Fig. 3**) . Furthermore, polymetallic nodules on the abyssal seafloor serve as unique electrochemical reactors. Exposed to ocean currents and hydrodynamic forces, they harness various energy inputs on their surfaces, effectively functioning as capacitor (Wang et al., 2021). The generated surface voltage, inadequate for direct water molecule decomposition (~1.5 V needed) (Sweetman et al., 2024), but suffices for bicarbonate ion dissociation, resulting in oxygen release (Dismukes et al., 2001)(**Fig.2**) . This implies that non-biological O_2 sources were likely prevalent on Earth during the Archean. Absence of definitive carbon isotope and microfossil evidence from this era suggests that significant non-biological O_2 sources lend robust support to the hypothesis that O_2 existed pre-GOE. Furthermore, non-biological O_2 production mechanisms are akin to those of photosynthetic organisms. Moreover, organic carbon from non-biological processes shows isotopic traits similar to photosynthetic assimilation (McCollom and Seewald, 2006).

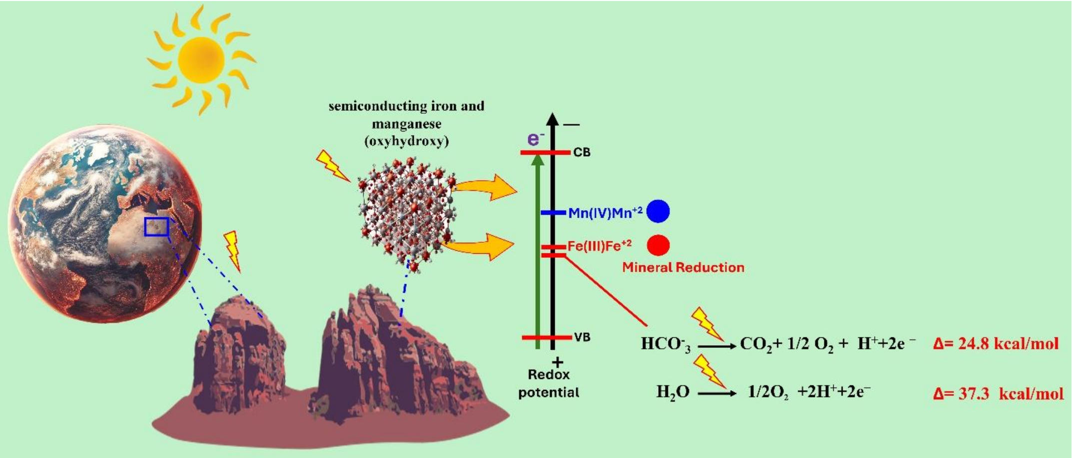

Figure 3. A schematic model illustrates the uppermost layer of Earth's semiconducting mineral coating, composed of iron and manganese oxyhydroxides. These semiconducting minerals, located at the Earth's surface, play a vital role in capturing and transforming solar energy. The energy absorbed by these minerals drives the photolysis (light-driven breakdown) of bicarbonate and water, leading to the release of O_2 and the production of CO_2. This mineral-driven process

introduces abiotic pathway for harnessing solar energy, expanding the scope of solar energy utilization from the organic biosphere to include inorganic semiconducting materials in the geosphere. Through mineral reduction, the redox reactions involving Fe(III)/Fe^{2+} and Mn(IV)/Mn^{2+} serve to mediate electron transfer.

3 Potential ancestor of Photosystem II

Photosynthetic O_2 evolution is catalyzed by the Mn_4CaO_5 cluster in PSII of cyanobacteria and photosynthetic eukaryotes, facilitated by a suite of enzymes and proteins (Cardona et al., 2019). The Mn_4CaO_5 cluster in PSII represents an extraordinarily efficient oxygen-evolving complex, which has been pivotal in elevating atmospheric oxygen concentrations by six orders of magnitude (Catling and Zahnle, 2020). This raises an intriguing question: How did the process of oxygen production evolve from inefficient geological mechanisms to the highly efficient photosynthetic oxygen evolution system? Focusing solely on the Mn_4CaO_5 oxygen-evolving cluster in PSII and setting aside the evolution of other associated enzymes and proteins, we propose that the precursor to this cluster could be carbonic anhydrase.

CAs (Carbonic Anhydrases, EC 4.2.1.1) constitute a vast enzyme family with over 2,000 identified members in diverse organisms, including bacteria, archaea, fungi, plants, and animals (Badger and Price, 1994; Moroney et al., 2001; Wu and Rao, 2023). These enzymes within a diverse superfamily of metalloenzymes facilitate the reversible CO_2 hydration to bicarbonate. Without CA, this typically takes around a minute, but with CA, the reaction time is drastically reduced to 10^{-6} seconds (Prince and Woolley, 1973). CAs, versatile biocatalysts, are crucial in various chemical and biochemical processes. Notably, transition metal-incorporating CAs not only supply protons and electrons but also exhibit redox functionalities (Mesbahuddin et al., 2021). This is why they are deemed precursors to PSII's Mn_4CaO_5 oxygen-evolving complex.

Thylakoid CA (tCA) and PSII exhibit significant functional parallels across various dimensions (Wu, 2021). Specific anions and cations critical for photosynthetic processes, such as Cl^-, Ca^{2+}, and Mn^{2+}, influence both tCA and PS II activities in a comparable manner (Lu and Stemler, 2007; Stemler, 1986; 1997) . High-intensity light inhibits the activity of both tCA and PS II, causing photoinhibition due to electron transport disruption (Kyleet al., 1984; Stemler, 1986). Moreover, far-red light enhances the activity of both tCA and the Hill reaction (Govindjee et al. 1960; Stemler, 1997) . Crucially, tCA's sensitivity to alterations in ambient redox potential mirrors

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PS II's behavior (Bearden and Malkin, 1073; Moubarak-Milad and Stemler, 1994). PSII not only displays traits of photosynthetic O_2 evolution but also exhibits CA activity (Dai et al., 2001; Khristin et al., 2004; Ignatov et al., 2011; Koroidov et al., 2014; Stemler, 1986). PSII encompasses both extrinsic and intrinsic CAs, which are inseparable from it (Enami et al., 2008; Hillier et al., 2006; Ignatov et al., 2011; Lu and Stemler, 2002; Moskvin et al., 2004; Shitov et al., 2009; Villarejo et al., 2002). PS II's oxygen-evolving activity, linked to intrinsic CA, is clearly associated with the Mn cluster, while its CA activity is independent of the Mn cluster's presence (Shitov et al., 2009). Moreover, CA(Mn), where manganese replaces zinc at the catalytic site, has demonstrated the capacity to produce O_2 in the presence of H_2O_2 and HCO_3^- (Okrasa and Kazlauskas, 2006). Hence, it's reasonable to posit that manganese integration into PSII's intrinsic CA is pivotal for photosynthetic O_2 evolution, with the CA at the manganese-substituted active site metal possibly being the precursor to PSII's Mn_4CaO_5 O_2-evolving complex.

To date, nine genetically distinct CA families have been identified, each characterized by unique amino acid sequences. These families are classified as α-, β-, γ-, δ-, ε-, ζ-, η-, θ-, and ι-CAs. Despite functional similarities, they lack significant sequence identity and have evolved independently (Wu and Rao, 2023). The γ-CA, originating 3-4 Ga ago, epitomizes Earth's earliest CA form (Hewett-Emmett and Tashian,1996; Tripp et al., 2004). The enzyme's active center metal ion is Fe(II), aligning its existence closely with the genesis of life itself (Knoll and Nowak, 2017). Non-biological oxygen production preceded the advent of primitive photosynthetic cyanobacteria by roughly 1 Ga, albeit in minuscule quantities (Des Marais, 2000; Fischer et al., 2016).

Approximately 3.8 Ga, oceans were largely anoxic, with Fe(II) levels 10,000-100,000 times higher than Mn(II) (Anbar, 2008). Despite Fe(II) and Mn(II)'s similar ionic radii, Mn rarely substitutes Fe in γ-CA, leading to the scarcity of γ-CA[Mn] in the early Archean. This precluded the use of Mn-based redox reactions for phototrophy, allowing only photoferrotrophic organisms to emerge (Czaja et al.. 2013). As γ-CA[Mn] levels progressively increased, oxygen-evolving photosynthetic efficiency gradually enhanced. However, the inefficient oxygen evolution by γ-CA[Mn] led to the evolution of solely phototrophic organisms during the mid-Archaean era (Tice and Lowe, 2004).

In the early Archean, seawater pH was between 6.5 and 7.0 (Halevy and Bachan, 2017). Without CA, CO_2 hydrolysis in seawater to bicarbonate is severely constrained. Analogous to the Mn_4CaO_5 cluster's photosynthetic O_2 evolution, a γ-CA with trace γ-CA[Mn] complex fulfills multiple key roles. Primarily, it functions as a CA, catalyzing CO_2 hydrolysis to produce substantial bicarbonate. Moreover, with ample bicarbonate, a minor Mn fraction in γ-CA[Mn] reacts to form Mn(II)-bicarbonate complexes (Baranov et al., 2000; 2004; Khorobrykh et al., 2008). This interaction reduces the system's redox potential from 1.19 V to 0.52-0.68 V, thereby initiating manganese oxidation over iron, as the redox potential for trivalent iron is 0.77 V (Lovyagina and Semin, 2022). Ultimately, within the Mn(III, IV)-bicarbonate complex, enzymatic release of bicarbonate ions leads to their subsequent oxidation, liberating O_2 and CO_2 (Stemler, 1986). Upon comparing the redox potentials, the thermodynamic favorability of bicarbonate decomposition versus Mn(II) oxidation to Mn(III,IV) is evident (Dasgupta et al., 2006; Kozlov et al., 2004; 2010; Yun et al., 1997). Notably, similar processes occur in PS II (Dai et al., 2001; Klimov et al., 1995; Shevela et al., 2008).

Rock weathering significantly contributes Mn^{2+} to Earth's aquatic systems; elevated Mn^{2+} levels are observed in both surface and deep waters of Archaean basins (Fischer et al., 2015). Mn(II) oxidation necessitates robust oxidants, e.g., O_2 or its derivatives, for redox cycling. This process occurs at a notably slow pace, even under oxygen-rich conditions, especially without biocatalysts (Morgan 2005). Mn-rich Fe formations were found in the Koegas Subgroup, Griqualand West structural sub-basin, Kaapvaal Craton, South Africa, dating back ~2.415 Ga (Johnson et al., 2013). A Mn-enriched thin horizon was also identified in the Turee Creek strata, Western Australia, dating to the same period (Williford et al., 2011). Elevated Mn levels, relative to other Archaean successions, were detected in early Witswatersrand and Mozaan Basin sediments, South Africa, dating to ~2.9 Ga (Planavsky et al., 2014; Smith and Beukes, 2023) . Evidently, biocatalysts akin to γ-CA[Mn] likely facilitated the manganese oxidation cycle during the Archaean era. With γ-CA[Mn]'s enhanced bicarbonate decomposition capacity, increased manganese oxidation ensues, resulting in elevated manganese levels in sediments. This, in turn, may explain that the Griqualand West sub-basin's sediments (~2.415 Ga) exhibit higher manganese levels than those of the older Witswatersrand and Mozaan Basins (~2.9 Ga).

CA is crucial for calcium carbonate deposition (Kim et al., 2012; Rodriguez et al., 2019). Similarly, the γ-CA[Mn]-like enzyme, facilitating bicarbonate decomposition and oxygen release, also fosters carbonate precipitation. Organic carbon signatures in 3.8-Ga-old meta-carbonate rocks from West Greenland's Archaean Isua supracrustal belt have been identified (Schidlowski, 1988), along with clusters of organic microspheres in thin stromatolite layers from the 2.724-Ga-

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old Tumbiana Formation of Australia's Fortescue Group (Lepot et al., 2008). Considering the γ-CA[Mn]-like enzyme's capacity to break down bicarbonate and liberate O_2, it's reasonable to deduce that these organic carbons weren't generated by cyanobacteria-like photosynthetic organisms. Instead, organic carbon in meta-carbonates likely derived from geological processes, whereas that in stromatolites may have been produced by macromolecules akin to γ-CA[Mn]. Thus, despite the presence of organic carbon in 2.5 Ga-old stromatolite carbonates, no cyanobacteria-like microfossils have been identified within these structures (Fischer et al., 2016). Fig. 4 depicts the hypothesis that γ-CA[Mn] enzyme may serve as a precursor to primitive PSII offering a logical rationale for these observations. Nonetheless, further chemical, geological, and biological evidence is required to conclusively validate this hypothesis.

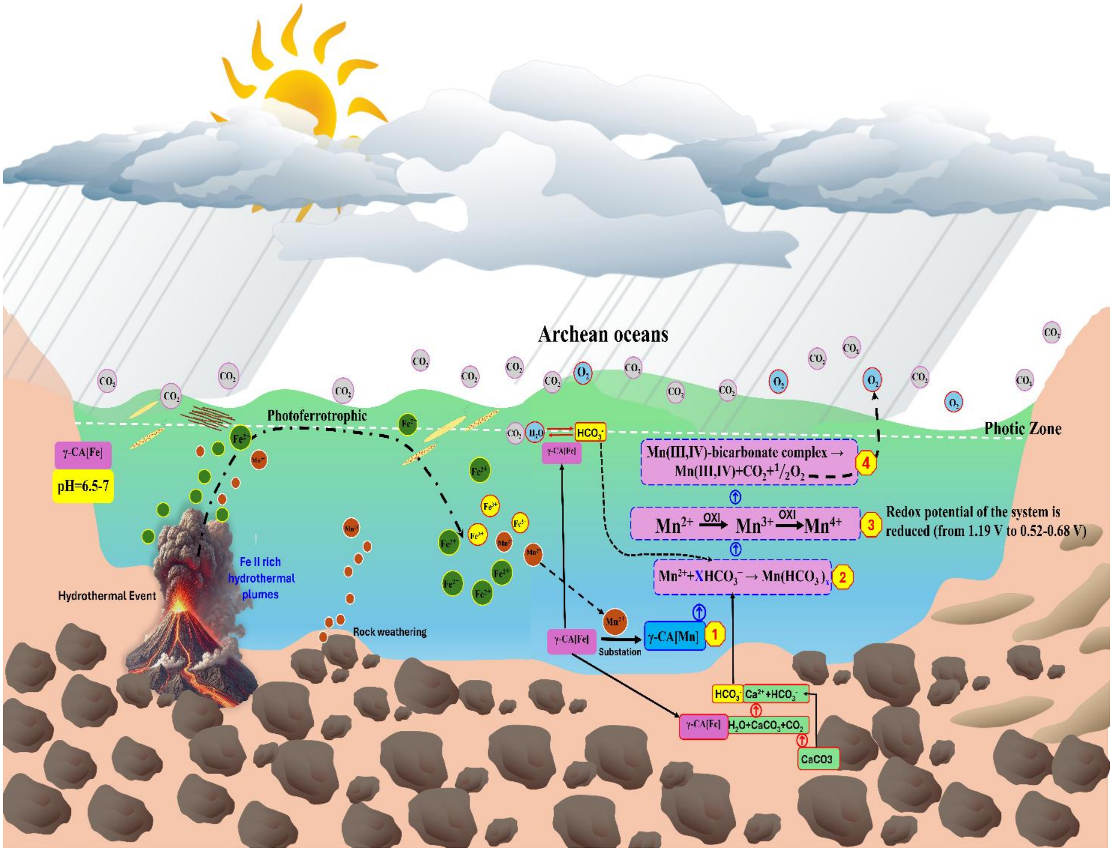

Figure 4. Illustration of an early Archean ocean ecosystem where hydrothermal vents release large amounts of Fe^{2+} (ferrous iron), which is oxidized to Fe^{3+} (ferric iron) through

photoferrotrophy by early microorganisms using sunlight. This oxidation process, along with Mn^{2+} cycling, leads to the substitution of Fe by Mn in enzyme complexes like γ-CA[Mn], potentially ancestral to Photosystem II. These processes contribute to carbonate rock dissolution, CO_2 cycling, and oxygen release, gradually reducing the system's redox potential. Overall, this ecosystem reflects the interplay between iron, manganese, and carbon cycles, laying the groundwork for oxygenic photosynthesis and early atmospheric oxygenation.

4 Two-substrate photosynthetic oxygen evolution

Both geological O_2 evolution and γ-CA[Mn]-analogous O_2 production likely involve thermodynamically favorable bicarbonate decomposition to release O_2. However, despite rapid bicarbonate-water isotopic exchange during photosynthesis, early experiments with ^{18}O-labeled bicarbonate merely indicate that photosynthetic O_2 evolution is a dual-substrate process5. In essence, bicarbonate is integrated into the Kok-Joliot cycle's $S_4 \rightarrow S_0$ transition state, and water is integrated into the $S_2 \rightarrow S_3$ transition state. Since the photolysis of bicarbonate demands only two-thirds of the free energy needed for water photolysis, thus occurring at a significantly faster rate (Dismukes et al., 2001). Consequently, the $S_3 \rightarrow S_4 \rightarrow S_0$ transition features a low energy barrier and an ultra-short-lived S_4 state, posing challenges for detection with current instruments (Guo et al.,2024; Wu and Guo, 2024).

Although photosynthetic O_2 evolution can be replicated *in vitro*, it markedly differs from that *in vivo*. Photosynthetic O_2 evolution in chloroplast thylakoid membranes is regulated by physiological factors including pH and redox potential. Hydroxylamine disruption and PSII crystallography studies conducted *in vitro* necessitate analysis considering normal physiological parameters.

At pH 6.0, hydroxylamine-induced disruption of PSII's oxygen-evolving center didn't result in CO_2 release (Shevela et al., 2008; Ulas et al., 2008), but this doesn't conclusively refute bicarbonate binding sites in PSII. This is because prior to hydroxylamine's interaction with the oxygen-evolving center, bicarbonate dissociation was already triggered by weak acid treatment. In fact, both tCA and PSII can actively regulate the pH and redox potential of their surrounding environment *in vivo* (Brinkert et al., 2016; Moubarak-Milad and Stemler, 1994). Under normal physiological conditions, bicarbonate binding to the oxygen-evolving complex of PSII is facilitated. This binding is influenced by both crystal formation conditions and the plant's physiological state. Bicarbonate binding to the oxygen-evolving complex is absent in PSII crystals cultivated at pH < 7 (Bhowmick et al. 2023; Lol et al., 2005; Umena et al., 2011). However, bicarbonate binding to the oxygen-evolving center was noted in PSII crystals cultivated *in vitro* at pH 7.5 (Ferreira et al., 2004). This phenomenon can be explained as follows: at pH< 7.0, the bicarbonate binding force to the oxygen-evolving complex of PSII is significantly reduced. Despite potential binding events, their detection is challenging due to the ultra-short lifespan of the S_4 transition state within the Kok-Joliot cycle. In contrast, at pH 7.5, the likelihood of bicarbonate binding to the oxygen-evolving complex increases substantially, making it more readily observable.

The long-standing belief that bicarbonate does not serve as a substrate for oxygen evolution in photosynthesis, backed by experiments with ^{18}O-labeled bicarbonate and PSII crystallography, is increasingly contested. However, recent studies suggest bicarbonate is crucial for photosynthetic O_2 evolution (Fig.5). Besides bicarbonate effect and the thermodynamic advantages of bicarbonate photolysis, photosynthetic oxygen evolution in chloroplasts appears to be reliant on CO_2 (Walker et al., 1971). Bicarbonate acts as a crucial ligand in forming the manganese cluster on PSII's electron donor side (Klimov et al., 1995), functioning as both an electron donor and proton acceptor within the photosynthetic oxygen evolution center (Allakhverdievet al., 1997; Dai et al., 2001). Moreover, bicarbonate drives O_2 and CO_2 generation under illumination (Dai et al., 2001), with CO_2 formation from bicarbonate documented on both the electron donor and acceptor sides of PSII (Shevela et al., 2020). Significantly, bicarbonate binding sites have been identified both on the electron acceptor side of PSII and on the electron donor side at the core of oxygen evolution (Stemler and Castelfranco, 2023). Conclusively, above evidence supports that PSII's electron donor side facilitates a photosynthetic oxygen evolution reaction, employing bicarbonate as the substrate: $HCO_3^- \rightarrow 1/2\ O_2 + 2e^- + H^+ + CO_2$.

Water, another substrate in the photosynthetic O_2 evolution, likely evolved in plants due to reduced inorganic carbon (bicarbonate/CO_2) availability. During the Archean era (~2.5 Ga ago), atmospheric CO_2 levels ranged from 0.9 to 900 kPa, contrasting sharply with the period from 75 Ma ago to the pre-industrial Holocene, where CO_2 concentrations hovered around 0.03 kPa. Similarly, the bicarbonate levels in Archean seawater varied between 15 and 15,000 mM, whereas from 75 Ma ago to the Holocene, bicarbonate levels in seawater were reduced to just 2 mM (Dismukes et al., 2001).

The dissolution of silicate and carbonate rocks is Earth's primary geological process for CO_2 sequestration. Silicate rock dissolution occurs through the reaction: [$CO_2+Ca(Mg)SiO_3 \rightarrow Ca(Mg)CO_3+SiO_2$]. Carbonate rock dissolution, or karstification, follows the equation:[$Ca(Mg)CO_3+H_2O+CO_2 \leftrightarrows Ca(Mg)^{2+}+2HCO_3^-$]. The interplay between karstification and photosynthesis is crucial for maintaining equilibrium of inorganic carbon in the atmosphere and oceans(Wu and Rao, 2023). Throughout geological history, elevated atmospheric CO_2 levels have coincided with reduced photosynthetic activity. E.g., early Paleozoic's high CO_2 was linked to terrestrial plants' absence, whereas Permian-Carboniferous's lower CO_2 levels corresponded with vascular plants' emergence, development, and proliferation (Berner, 1990; Knoll et al., 2017; Moulton and Berner, 1998). The rise of efficient eukaryotic photosynthetic organisms 75 Ma ago necessitated coping with scarce inorganic carbon (bicarbonate/CO_2). Consequently, these organisms evolved the capability to leverage abundant water to evolve oxygen and enhancing inorganic carbon assimilation. These photosynthetic organisms have undergone evolutionary milestones, encompassing the development of PS I and PS II, the evolution of the photosynthetic oxygen-evolving center and associated proteins, and the emergence of electron transport and photosynthetic phosphorylation mechanisms (Badger and Price, 1994; Fischer et al., 2016; Hohmann-Marriott and Blankenship, 2011; Xiong and Bauer, 2002). These evolutionary adaptations, which facilitate oxygen release from water, likely enhanced photosynthesis efficiency by significantly boosting oxygen production.

Optimal energy use and photosynthetic efficiency are achieved through equivalent photolysis of HCO_3^- and H_2O, exemplifying the coupling between karstification and photosynthesis (Fig.5). Since photolysis of bicarbonate requires less energy than water photolysis, it results in CO_2 being the sole carbon source for photosynthetic inorganic carbon assimilation. This CO_2 is then fully incorporated into the Calvin-Benson cycle by Rubisco, driving the biogeochemical cycle and maintaining elemental equilibrium on Earth (Wu and Rao, 2023).

Investigating PSII's dual-substrate nature is pivotal for advancing artificial photosynthetic reactors, which could bolster carbon sequestration and oxygen production to mitigate climate change. Insights from this research may also guide agricultural innovations, enhancing plant photosynthesis and resilience to high CO_2 levels, emulating ancient photosynthetic adaptations.

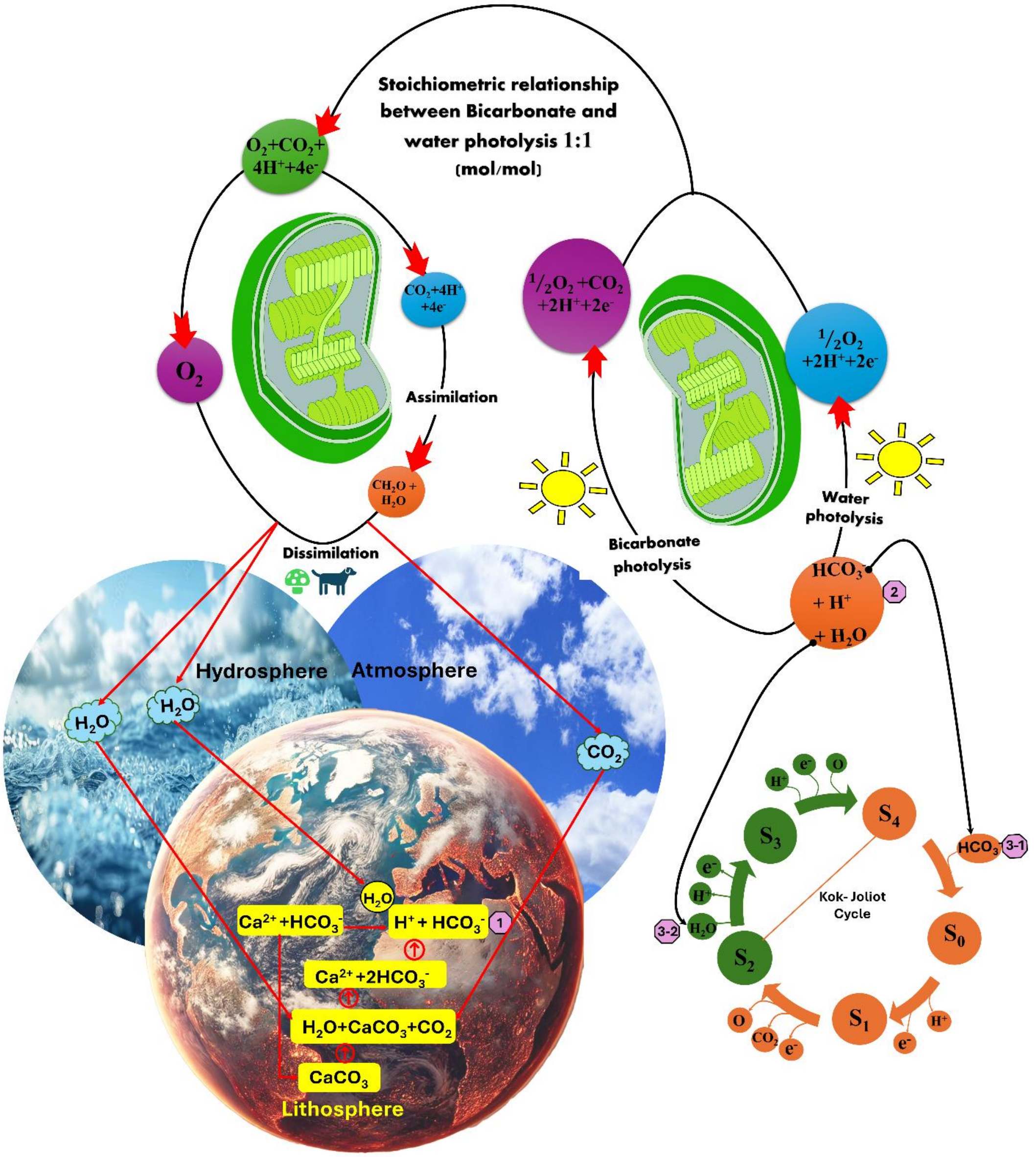

Fig. 5 The dual-substrate nature of photosynthetic oxygen evolution, involving both HCO_3^- and H_2O, with bicarbonate playing a key role in the $S_4 \rightarrow S_0$ transition and water in the $S_2 \rightarrow S_3$ transition of the Kok-Joliot cycle. Bicarbonate photolysis is more energy-efficient than water, enabling faster oxygen release. The process operates in a 1:1 molar ratio between bicarbonate and water photolysis, driving oxygen and CO_2 production. The image also connects this mechanism to

Earth's geological carbon cycles, highlighting how the dissolution of carbonate and silicate rocks, coupled with photosynthesis, regulates atmospheric carbon levels. This model reflects the evolutionary adaptation of early photosynthetic organisms to utilize water and bicarbonate for oxygen generation, which plays a critical role in maintaining Earth's elemental balance.

Conclusion

The complex biochemical intricacies of modern photosynthesis may trace back to Earth's primordial geological processes, providing a transformative perspective on the continuum between inorganic and organic evolution. Building upon this profound insight, we propose that the biochemical mechanism responsible for photosynthetic oxygen evolution in plants evolved gradually from simpler, abiotic geological oxygen production processes. Origins of bicarbonate photolysis in photosynthetic O_2 evolution may trace back to early abiotic O_2-generating systems. This hypothesis is a potentially groundbreaking perspective on the evolution of life, suggesting that key aspects of photosynthesis, once believed to be exclusive to biological systems, may have originated in pre-biological processes. This concept underscores the seamless transition from inorganic to organic processes in nature. Validating this hypothesis would profoundly impact our comprehension of life's origins and the evolution of intricate biochemical processes. It would also imply that the mechanisms underlying photosynthesis are deeply rooted in ancient abiotic processes. Further research is essential to substantiate this claim, but pursuing this line of inquiry could open new avenues for understanding the origins of photosynthesis and the intricate interplay between inorganic and organic chemistry in shaping Earth's biosphere.

Data availability: Data will be made available on request.

Authors' Contributions

Y.W. Conceptualization, writing raw manuscript, and validation, M.A. writing and review and visualization, C.L. validation and revision. All authors have read and agreed to the published version of the manuscript.

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