

Anoxygenic Photosynthesizers: Signs of Early Earth's First Microbial Proletariat

A Description and History of Anoxygenic Photosynthesis and Implications for the Remote Detection of Life on Extrasolar Planets

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ABSTRACT

Oxygenic photosynthesis dominates the primary productivity of Earth's biosphere by many orders of magnitude due to the wide availability of photon energy to drive redox gradients by splitting water. However, it is likely that an interval of time existed during the Archean when anoxygenic photosynthesizers dominated the primary productivity of the biosphere, though the length of this interval is in question. Studies of astronomically detectable biosignatures often focus on absorption by free oxygen (O_2), its photochemical product ozone (O_3), or surface signatures of land plants (e.g., the red edge). However, the Earth lacked these signatures during the Archean, before atmospheric oxygenation and long before the development of green vascular plants. In this review I briefly describe the biochemistry of photosynthesis, the geological evidence for the prevalence of anoxygenic photosynthesis in the Archean, and the timeline for the transition to oxygenic photosynthesis as the biosphere's primary source of productivity. I argue that anoxygenic photosynthesis may have played an important role on the early Earth, and is relevant to the search for biosignatures on yet to be discovered Earth-

like planets. I explore some of the potentially detectable spectral signatures of an anoxic biosphere.

INTRODUCTION

Photosynthetic organisms create the overwhelming majority of biomass and bioavailable energy on Earth (Blankenship, 2010; Hohmann-marriott & Blankenship, 2012). They are the source of fixed carbon, used to create living material, and the source of oxidized species that can be respired by themselves or other organisms. The advent of oxygenic photosynthesis drastically changed the composition and redox chemistry of our atmosphere (Catling, Zahnle, & McKay, 2001). Aerobic heterotrophs (i.e., animals) are dependent on both organic matter and free oxygen as a source of energy, as aerobic respiration is simply the reverse reaction of oxygenic photosynthesis. Human civilization is powered by fossil fuels derived from the time-integrated largess of a productive photosynthetic biosphere. It also stands to reason that the most productive organisms on any planet would produce the most detectable biosignatures (Kiang, Segura, et al., 2007a; Tinetti et al., 2006). Understanding photosynthesis is therefore crucial for understanding the evolution of a global biosphere, whether the goal is to better understand the history of our own planet or current states of habitable extraterrestrial worlds.

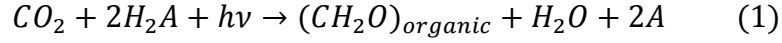
1. Overview of Photosynthesis

The term photosynthesis is derived from the Greek *phos* (“light”) and *synithenai* (“put together”) to describe the complex chemical process that transforms light energy and suitable reactants to stable chemical energy (Gest, 2002). This chemical energy can be used catabolically for maintenance and activity or anabolically for biomass synthesis.

Photosynthesis is fundamentally a redox “reduction-oxidation” process wherein electromagnetic energy from the Sun is converted into biologically available chemical energy by exciting electrons from pigment-protein complexes. These electrons are then transferred to acceptor molecules along the electron transport chain and are replaced by reductants found in the environment. The entire light harvesting process, from photon absorption to export of stable products, is accomplished by protein complexes called photosystems. There are two known photosystems (photosystem I, or PSI, and photosystem II, or PSII). PSI involves a Fe-S reaction center while PSII contains a pheophytin-quinone reaction center. Even a passable cursory review of all the biochemistry involved in photosynthesis is beyond the scope of this paper, so I refer the reader to an extensive treatment by Blankenship (2002). I will instead describe the basic stoichiometry of photosynthesis and the details that are required to explore the history of photosynthesis on Earth and its remotely detectable signatures.

1.1 Photosynthetic Chemistry

The schematic empirical equation for photosynthesis is:



where H_2A is a reducing agent (e.g., H_2 , H_2S , H_2O_2 or H_2O), $h\nu$ is the energy per photon, and CH_2O represents biomass. Other reductants, such as elemental sulfur and ferrous iron, don't quite fit into the above equation, but are still useful electron donors (Olson, 2006). Table 1 shows the net chemistry in terms of the reduced reactant and the oxidized product (i.e., the light harvesting and electron generation portion of the above equation, following Seager, Schrenk, & Bains, 2012):

Table 1: Photosynthetic Net Reactions

Input Reductant	Photons	Output Oxidant
H_2	$h\nu \rightarrow$	H_2O
H_2S	$h\nu \rightarrow$	S
H_2O	$h\nu \rightarrow$	O_2
S	$h\nu \rightarrow$	H_2SO_4
$S_2O_3^{2-}$	$h\nu \rightarrow$	H_2SO_4
Fe^{2+}	$h\nu \rightarrow$	Fe^{3+}
NO_2^-	$h\nu \rightarrow$	NO_3^-
As^{2+}	$h\nu \rightarrow$	As^{4+}

1.2 Oxygenic vs. Anoxygenic Photosynthesis

Oxygenic photosynthesis refers solely to the pathway that evolves O_2 from H_2O and light energy. All other phototrophic pathways are anoxygenic. Oxygen-producing organisms are, by far, the most productive organisms across the planet due in large part to the wide availability of water as a reductant (Leslie, 2009). Both photosystems are utilized by oxygenic photosynthesis: PSI is used to strip electrons from chlorophyll to synthesize ATP while PSII (the strongest oxidant found in nature) replaces lost electrons by stripping them from water (Hohmann-marriott & Blankenship, 2012). Anoxygenic photosynthesizers use one photosystem or another but never both. The available evidence suggests that oxygenic photosynthesis evolved only once, perhaps as the result of a lateral gene transfer of the genetic machinery of one photosystem to an organism containing the other, or the wholesale fusion of two organisms (Blankenship, 2010; Hohmann-marriott & Blankenship, 2012). The large oxidizing potential required to split water explains the preference of some oxygenic cyanobacteria to substitute H_2S as a reductant when available and most likely elucidates the evolutionary sequence of anoxygenic to oxygenic (Allen & Williams, 2011).

1.3 Photosynthetic Organisms

Chlorophyll-based photosynthesis has been identified only in the Bacterial and Eukaryotic domains (Blankenship, 2010). No photosynthetic Archaeal lineage is known. The presence of photosynthesis in Eukaryotes such as algae and green land

plants is almost universally believed to be the result of endosymbiosis of a cyanobacteria-like organism and a eukaryotic cell (Margulis, 1992). Therefore, it is more accurate to view primary phototrophy as a purely bacterial trait. The phyla in which phototrophy is found are spread widely through the bacterial domain, suggesting past lateral gene transfer of relevant genes (Raymond, Zhaxybayeva, Gogarten, Gerdes, & Blankenship, 2002). These phyla include the oxygenic cyanobacteria and the anoxygenic purple bacteria, green sulfur bacteria, heliobacteria, filamentous anoxygenic phototrophs (once mistakenly called green non-sulfur bacteria), and acidobacteria (Blankenship, 2010). The purple bacteria and filamentous anoxygenic phototrophs use PSI-like light harvesting complexes (LHC) while the green sulfur bacteria, the acidobacteria, and the heliobacteria contain PSII-like LHCs (Hohmann-marriott & Blankenship, 2012).

The primary absorbing pigments found in each lineage vary. Purple bacteria have bacteriochlorophylls (Bchls) a and b, while the green bacteria have Bchls a, c, d, and e. Bchls tend to have absorption peaks at longer wavelengths (in the VIS/NIR), possibly as an adaptation by anaerobic phototrophs living deep in microbial mats where radiation in the so-called photosynthetically active region (PAR; ~400-700 nm) has been attenuated by overlying oxygenic phototrophs (B. K. Pierson, Sands, Frederick, & Frederickt, 1990; B. Pierson, Oesterle, & Murphy, 1987). Additionally, there are a wide variety of accessory pigments, such as carotenoids, which also facilitate photoprotection and can be found in non-phototrophs. (Sandmann, 2009)

It is interesting to draw a distinction between anaerobic and aerobic anoxygenic phototrophs and further between facultative and obligate anaerobic phototrophs. Aerobic anoxygenic photosynthesizers do not generate oxygen but require it for respiration (Yurkov & Beatty, 1998). Large amounts of free oxygen are not necessary to support these phototrophs; however, while locally produced oxygen would be sufficient to maintain them, they would be tied to the productivity of oxygen-producing phototrophs. Anaerobic phototrophs are guaranteed to have existed at a time prior to large concentrations of oxygen. Facultative anaerobes such as *chloroflexus* maintain an active role in the oxic world of the Phanerozoic by possessing a flexible metabolism and resistance to oxidative damage (B. K. Pierson & Castenholz, 1974).

2. History and Evolution of Photosynthesis

The origin and early evolutionary history of photosynthesis remains largely shrouded in mystery (Blankenship, 2010). We do know that photosynthesis is ancient and that early photosynthesizers thrived in an anoxic atmosphere for up to two billion years (Olson, 2006), but whether the primary production in the late Archean was dominated by anoxygenic phototrophs or cyanobacteria whose oxygen production was immediately consumed by chemical or biological sinks is a point of great contention (Buick, 2008). It is also possible that anoxygenic photosynthesis played a substantial role in the Proterozoic after the Great Oxidation Event (GEO), but while oceans were euxinic and limited by the availability of trace metals and fixed

nitrogen, i.e. the “Canfield Ocean” era (Johnston, Wolfe-Simon, Pearson, & Knoll, 2009).

2.1 Photosynthesis in the Archaean (3.9-2.5 Gya)

While some propose photoautotrophy as a primordial metabolism (Hartman, 1998), photosynthesis is almost universally believed to have originated some time after life arose (Olson, 2006). It is almost as universally believed that anoxygenic preceded oxygenic photosynthesis (Blankenship, 2010), and genomic analysis suggests this is true (Mulkidjanian et al., 2006). A big question is by how much – e.g., *for how long was the global productivity dominated by anoxygenic photosynthesis?* It is possible that this timescale was relatively short (Buick, 2008). Both the origin of photosynthesis itself and the development of oxygenic photosynthesis must be considered to achieve an estimate for the interval of anoxygenic dominance.

The large rise of oxygen from $\sim 10^{-14}$ PAL to $> 10^{-3}$ PAL ~ 2.4 Gya, just before the Makganyene Glaciation, sets a stringent lower limit for the age of the first oxygenic photosynthesizers (Kopp, Kirschvink, Hilburn, & Nash, 2005). Oxygen levels before this time are known to be limited by the presence of non-mass dependent fractionation in sulfur isotopes (Farquhar, 2000), although there might have been a temporary “whiff” of oxygen ~ 100 My before this (Anbar et al., 2007). (Note: We shouldn’t expect that oxygen would build up in Earth’s atmosphere just because oxygen-producing microbes had evolved. The reaction that produces oxygen is reversible and back reaction with organic carbon, whether through respiration or

abiotically, would consume it. Some level of carbon burial, or atmospheric escape of hydrogen (Catling et al., 2001), is necessary to create a net increase in oxygen levels).

Rosing & Frei (2004) attribute large organic carbon accumulation and suggestive carbon isotope fractionations in graphite particles in the 3.7 Gya Isua Supercrustal Belt of Greenland to early oxygenic cyanobacteria. This has also been interpreted as evidence of H₂-driven photosynthesis (Olson, 2006) under the assumption that the Early Earth atmosphere contained substantial amounts of H₂ (~0.1 bar), originally invoked to explain the Faint Young Sun Paradox (Wordsworth & Pierrehumbert, 2013). Since the redox potential required to oxidize H₂ is lower than all other possible reductants, wide availability of H₂ would preclude evolutionary pressure to use other reductants, including water. Rosing & Frei (2004) argue that U-Th-Pb isotopes found in Greenland are indicative of photic zone oxygenation and provide the earliest evidence of oxygenic photosynthesis; however, this signature has not been found in other Archean sediments. The elemental and isotopic evidence from Isua is in such dispute it cannot be held as a reliable indicator of any particular metabolism (Buick, 2008).

There is evidence for anoxygenic CO₂ fixation in the 3.42-Gya Buck Reef Chert in South Africa. Tice & Lowe (2004) report structures reminiscent of filamentous bacteria in photosynthetic mats present in carbonaceous laminations. These laminations were confined to shallow water areas and contained carbon isotope

compositions (-35 to -20 ‰ $\delta^{13}\text{C}$) suggestive of CO_2 fixation with known anoxygenic or oxygenic pathways. The lack of ferric oxides indicates that neither oxygen production or iron oxidation was occurring.

Old Archean stromatolites provide evidence of phototrophic behavior with laminations that increase in thickness over flexure crests (Buick, Dunlop, & Groves, 1981), although the biogenicity of stromatolites older than 3.2 Gya has been questioned (Lowe, 1994). Buick, Groves, Dunlop, & Lowe (1995) maintained that stromatolites found at North Pole are probably of biological origin. Though extant stromatolites and microbialites have their primary productivity dominated by cyanobacteria, this doesn't imply that Archean stromatolites are diagnostic of cyanobacteria. Experiments have shown that anoxygenic microbes, specifically *Rhodopseudomonas palustris*, can stimulate the precipitation of calcite in solution and can enhance the growth of proto-lamina; a role distant evolutionary cousins may have played in the Archean (Bosak, Greene, & Newman, 2007).

After H_2 , the next most energetically favorable reductant present in the Archean would have been H_2S . Sulfates present in evaporates found in the Warrawoona Megasequence (WM) could have originated from either sulfur-oxidizing bacteria or oxygen-producing cyanobacteria (Olson, 2006). Putative filamentous bacteria fossils found in the Early Apex Basalt of the WM are consistent with cyanobacteria or anoxygenic phototrophs, since their morphologies and size overlap (Schopf, 1993). The designation of these structures as fossils is in dispute (Brasier et al., 2002).

As volcanic activity on the slowed, H₂S's status as the dominant reductant could have been usurped by ferrous iron (Olson, 2006), assuming oxygenic photosynthesis hadn't been invented yet. There are plausible avenues to creating Banded Iron Formation by photoautotrophic oxidation of ferrous iron or reactions of ferrous iron with free oxygen (Olson, 2006).

The most compelling fossil and geochemical evidence for the emergence of oxygenic photosynthesis pre-GOE comes from the late Archean biomarkers (Buick, 2008). Sterols produce mostly by eukaryotes require O₂ at many steps (Summons, Bradley, Jahnke, & Waldbauer, 2006) and thus their presence is thought to be diagnostic of the existence of oxygenic photosynthesis. Some hopanols are almost exclusively found in cyanobacteria. These biomarkers have been found in shales and stromatolites from 2.7-2.45 Gya with increasing certainty of oxygenic providence for younger samples (Buick, 2008).

To summarize this section, while the onset of oxygenic photosynthesis assuredly occurred by ~2.4 Gya, there is substantial uncertainty with regard to how long it predated the GOE. The interval of time in which anoxygenic photosynthesis dominated is therefore unknown, but could have been more than 1 Gyr or less than 100 Myr. Olson (2006) provides a plausible timeline for the dominant reductant on Earth and suggests the advent of oxygenic photosynthesis by 2.7 Gya. His Figure 1 is reproduced as Table 2 here:

Table 2 -Timeline for Archean photosynthesis with proposed reductants (Olson, 2006)

Reductant	Ga	Marker
H ₂ O	2.3	Oxygen levels increase
	2.4	
H ₂ O	2.5	Hamersley Biff
H ₂ O	2.6	Nauga cyanobacteria
H ₂ O	2.7	Pilbara methylhopane / Tumbia Stromatolites
	2.8	
	2.9	
Fe(OH)+	3.0	Protocyanobacteria and proteobacteria emerge?
	3.1	
H ₂ S	3.2	Swaziland barites
	3.3	
?	3.4	Buck Reef microbial mats
H ₂ S	3.5	Warrawoona evaporates, stromatolites, possible fossils
	3.6	
	3.7	
H ₂	3.8	Isua carbon isotope fractionation

3. Spectral Signatures of Photosynthesis

Remotely detectable biosignatures can be split into two main categories: 1) atmospheric signatures from biogenic gases and 2) surface reflectance signatures from pigments, carotenoids, etc (Kiang, Segura, et al., 2007b; Marais & Harwit, 2002; Sagan, Thompson, Carlson, Gurnett, & Hord, 1993; Sara Seager et al., 2012; Tinetti et al., 2006) . I will discuss each of these categories in this section.

3.1 Spectral signatures from biogenic gases

Molecular oxygen and its photochemical product ozone have received the most attention as possible biosignatures. This is due to oxygen's short atmospheric lifetime and the need for a large flux to maintain its concentration at present atmospheric levels. The simultaneous presence of oxygen and methane in Earth's atmosphere is seen as even a stronger indicator for life, as it shows strong chemical disequilibrium, a "gold standard" for the presence of life (Marais & Harwit, 2002; Sagan et al., 1993). Alone, methane, while produced by chemoautotrophic bacteria, is not a biosignature due to abundant abiotic sources, such as serpentinization.

The only known source for this free oxygen is photosynthesis. However, for about half of Earth's history, the planet did not possess oxygen in great quantities. From Table 1, we can see that all redox products of anoxygenic photosynthesizers have abiotic sources. This seems to rule out using biogenic gases as tracers of anoxygenic photosynthesizers, at least from direct photoautotrophic products. It is true, however, that nitrous oxide is a plausible biosignature gas (Seager et al., 2012), produced as a result of an incomplete denitrification cycle and having no large abiotic source (Buick, 2007). While N_2O is not a direct sign of photosynthesis, its presence in large quantities would indicate a productive biosphere and should be searched for on anoxic worlds. A disadvantage of N_2O is that it is most absorptive in the 4.4-4.6 micron range, overlapping with the 4.3 micron CO_2 feature and in a region of the spectrum widely regarded as problematic due to low total flux and degeneracies between reflected and thermal radiation. Nitrous oxide also has an

absorption feature in the MIR from 7.5-8.0 microns, in the Earth's window region where spectral flux is higher, but presently has a small spectral signature due low concentrations on the present Earth. It has been proposed that N_2O could have existed in larger concentrations during the Canfield Ocean era (Buick, 2007) to the extent that greenhouse warming due to the molecule would have been nonnegligible (Roberson, Roadt, Halevy, & Kasting, 2011), implying a large spectral signature.

Dimethyl sulfide (DMS) is emitted by marine algae as part of a secondary metabolism, but is present in such small concentrations as to preclude remote detection in a disk-average spectrum (Seager et al., 2012). Its existence suggests the importance of considering secondary metabolic products in the search for biosignatures. Domagal-Goldman et al. (2011) explore the possibility of organic sulfur gases as plausible biosignatures on anoxic planets and find that DMS or dimethyl disulfide (DMDS) can rise to detectable levels in cases of extremely low UV fluxes. They also find that the strongest indication of biogenic organic sulfur gases is the ratio of the ethane (C_2H_6) to methane concentration; in other words, a disparity between the concentration ethane on biologically active worlds with the amount that the concentration of methane would predict to occur abiogenically.

3.2 Reflectance signatures

The other plausible class of biosignatures originates in the reflectance spectrum of a planet. The propensity of green vascular land plants to become highly reflective in the NIR, dubbed the "red edge", is a classic example (Sagan et al., 1993; Seager,

Turner, Schafer, & Ford, 2005). Other chlorophyll-containing organisms exhibit such signatures, although the wavelengths at which they become highly reflective vary and the effect on the present Earth's disk-integrated spectrum are much smaller (Kiang, Siefert, Govindjee, & Blankenship, 2007). The "green bump" due to the color peak of land plants is a potentially detectable signature, although it is less pronounced than the red edge. The green bump is not due to a lack of absorption in the green part of the spectrum, but simply less efficient absorption. Kiang et al. (2007a) construct a set of rules to predict where photosynthetic pigments will peak in absorbance. They suggest that the wavelengths where peak absorption will occur are "(1) the wavelength of peak incident photon flux; (2) the longest available wavelength for core antenna or reaction center pigments; and (3) the shortest wavelengths within an atmospheric window for accessory pigments." These rules are used in Kiang et al. (2007b) to predict the peak absorbances of photosynthetic pigments on planets around main sequence stars with a range of spectral types, with a "blue edge" predicted for hot, F2V stars. Table 3 lists the wavelengths of absorption maxima of major chlorophylls (Chls) and Bchls, but note that photosynthetic organisms employ a wide variety of accessory pigments including over 600 different carotenoids, some of which are utilized by non photosynthetic life (Sandmann, 2009). It is also unknown how prescriptive features from pigments evolved on the Earth would be in considering signatures from biospheres with a different evolutionary history; however, there are likely physical and biochemical reasons why the pigments preferentially absorb at these wavelengths beyond evolutionary happenstance (Hohmann-marriott & Blankenship, 2012).

Table 3 - Peak Absorbances of Selected Pigments

Pigment	Bacterial phyla	Absorption Maxima (nm)
Chl a	Cyanobacteria	430, 662
Chl b	Cyanobacteria	453, 642
Carotenoids*	All photosynthesizers, many non photosynthesizers	460-550
Bchl a	Green Sulfur Bacteria, FAP (e.g. Chloroflexus), Purple Bacteria, Heliobacteria	805, 830-890
Bchl b	Purple Bacteria	835-850, 1020-1040
Bchl c	Green Sulfur Bacteria, FAP	745-755
Bchl d	Green Sulfur Bacteria	705-740
Bchl e	Green Sulfur Bacteria	719-726
Bchl g	Heliobacteria	670, 788

The green bump and red edge are relatively recent developments and extend only as far back as the origin of land plants, which both produce oxygen and require it for respiration. (All land-based organisms of course benefit from the UV shielding effect of ozone.) However, Kiang et al. (2007a) find that some anoxygenic bacteria, such as purple bacteria, have NIR edges as well. One could therefore imagine detectable signatures on an anoxic world with a productive biosphere derived from widely available H_2 or H_2S . Kiang et al 2007b explore the productivity of photon-limited biospheres orbiting stars with varied spectral energy distributions. They find anoxic M star planets could be a substantial fraction of (or even exceed) Earth's productivity if a contribution by anoxygenic photosynthesizers utilizing wavelengths beyond 1.1 microns is allowed. The relation of pigment absorption with atmospheric composition is also explored, with stronger absorption by

pigments predicted at wavelengths coinciding with atmospheric windows.

Sanromá, Pallé, & García-Muñoz (2013) attempt to reconstruct plausible disk-integrated spectra of the Earth 500 Mya and transition between desert, microbial mat, and vegetated surface with realistic cloud cover. They test cases with 50-100% of the land with microbial mats and find strong signatures on a time variable basis as the continents come in and out of view. The strength of contrast in the NIR bands are as viable a surface signature of life as the red edge. The signatures of their microbial mats are relevant since there could have been cyanobacteria-containing mats on the Earth before the rise of oxygen in the atmosphere. However, 50-100% coverage of land by microbial mats seems incredibly unrealistic.

4. Summary and Discussion

I have reviewed the basic biochemistry of photosynthesis, the categories of photosynthetic organisms, and some of the geological evidence for the appearance of anoxygenic and oxygenic photosynthesis. While we are certain that oxygenic photosynthesis had arisen by the GOE, it could have evolved much earlier. Stromatolite, microfossil, and isotope evidence suggests that photosynthesis existed by 3.4 Gya and perhaps by 3.8 Gya. The period during which anoxygenic photosynthesis was the largest contributor could have been anywhere from less than 100 My to more than 1 Gy. We might expect a world to remain free of oxygenic photosynthesizers if there is a wide availability of reductants such as H_2 or H_2S , stalling evolutionary pressure to use water as a reductant, which requires a much

larger redox potential. The presence of substantial H_2 or H_2S in a planetary atmosphere could be a counter indicator to oxygenic photosynthesis and a reason to look for the spectral reflectance signature of anoxygenic phototrophy. This assumes it was availability of reductants that limited (or limits, as the case may be) anoxygenic photosynthesizers and not scarcity of nutrients (elements such as nitrogen and phosphorus) as it is on the modern Earth.

It is interesting to contemplate how Archean stromatolites or microbial mats would have differed from extant ones and, more generally, how microbial mats on planets with only anoxygenic photosynthesizers would be structured. Modern microbial mats consist of several layers, with the top layers containing cyanobacteria and deeper layers containing anoxygenic photosynthesizers like green and purple sulfur bacteria. The deepest layers may contain anaerobic phototrophs like *chloroflexus*. There is interplay between decreasing oxygen levels and PAR penetration, with the anaerobic phototrophs settling for the lower quality photons that remain unabsorbed by the organisms in the upper layers. Bchl pigments are adapted for absorbing what they can from this attenuated radiation; however, before the advent of cyanobacteria, other photosynthesizers in mats would have had unrestricted access to the entire PAR spectrum; thus pigments of phototrophic anaerobes may have been more similar to cyanobacteria's in the past.

The spectral energy distribution of the host star and the composition of the host planet's atmosphere may drive the evolution and development of photosynthetic

pigments and thus our search for surface signatures of life. Since the Earth was anoxic for roughly half its history, we must consider the likelihood of life-bearing anoxic exoplanets and possible surface signatures other than those afforded by land plants and biosignature gases other than O₂, such as organic sulfur gases and N₂O.

REFERENCES

- Allen, J. P., & Williams, J. C. (2011). The evolutionary pathway from anoxygenic to oxygenic photosynthesis examined by comparison of the properties of photosystem II and bacterial reaction centers. *Photosynthesis research*, 107(1), 59–69. doi:10.1007/s11120-010-9552-x
- Anbar, A. D., Duan, Y., Lyons, T. W., Arnold, G. L., Kendall, B., Creaser, R. A., Kaufman, A. J., et al. (2007). A whiff of oxygen before the great oxidation event? *Science (New York, N.Y.)*, 317(5846), 1903–6. doi:10.1126/science.1140325
- Blankenship, R. E. (2002). *Molecular Mechanisms of Photosynthesis*. (R. E. Blankenship, Ed.). Oxford, UK: Blackwell Science Ltd. doi:10.1002/9780470758472
- Blankenship, R. E. (2010). Early evolution of photosynthesis. *Plant physiology*, 154(2), 434–8. doi:10.1104/pp.110.161687
- Bosak, T., Greene, S. E., & Newman, D. K. (2007). A likely role for anoxygenic photosynthetic microbes in the formation of ancient stromatolites. *Geobiology*, 5(2), 119–126. doi:10.1111/j.1472-4669.2007.00104.x
- Brasier, M. D., Green, O. R., Jephcoat, A. P., Kleppe, A. K., Van Kranendonk, M. J., Lindsay, J. F., Steele, A., et al. (2002). Questioning the evidence for Earth's oldest fossils. *Nature*, 416(6876), 76–81. doi:10.1038/416076a
- BUICK, R. (2007). Did the Proterozoic ?Canfield Ocean? cause a laughing gas greenhouse? *Geobiology*, 5(2), 97–100. doi:10.1111/j.1472-4669.2007.00110.x
- Buick, R. (2008). When did oxygenic photosynthesis evolve? *Philosophical transactions of the Royal Society of London. Series B, Biological sciences*, 363(1504), 2731–43. doi:10.1098/rstb.2008.0041
- Buick, R., Dunlop, J. S. R., & Groves, D. I. (1981). Stromatolite recognition in ancient rocks: an appraisal of irregularly laminated structures in an Early Archaean chert-barite unit from North Pole, Western Australia. *Alcheringa: An*

- Australasian Journal of Palaeontology*, 5(3), 161–181.
doi:10.1080/03115518108566999
- Buick, R., Groves, D. I., Dunlop, J. S. R., & Lowe, D. R. (1995). Geology Reply, 2–4.
doi:10.1130/0091-7613(1995)023<0191
- Catling, D. C., Zahnle, K. J., & McKay, C. (2001). Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Science (New York, N.Y.)*, 293(5531), 839–43. doi:10.1126/science.1061976
- Domagal-Goldman, S. D., Meadows, V. S., Claire, M. W., & Kasting, J. F. (2011). Using biogenic sulfur gases as remotely detectable biosignatures on anoxic planets. *Astrobiology*, 11(5), 419–41. doi:10.1089/ast.2010.0509
- Farquhar, J. (2000). Atmospheric Influence of Earth's Earliest Sulfur Cycle. *Science*, 289(5480), 756–758. doi:10.1126/science.289.5480.756
- Gest, H. (2002). History of the word photosynthesis and evolution of its definition. *Photosynthesis research*, 73(1-3), 7–10. doi:10.1023/A:1020419417954
- Hartman, H. (1998). Photosynthesis and the origin of life. *Origins of life and evolution of the biosphere : the journal of the International Society for the Study of the Origin of Life*, 28(4-6), 515–21.
- Hohmann-marriott, M. F., & Blankenship, R. E. (2012). Photosynthesis. (J. J. Eaton-Rye, B. C. Tripathy, & T. D. Sharkey, Eds.), 34, 3–32. doi:10.1007/978-94-007-1579-0
- Johnston, D. T., Wolfe-Simon, F., Pearson, a, & Knoll, a H. (2009). Anoxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth's middle age. *Proceedings of the National Academy of Sciences of the United States of America*, 106(40), 16925–9. doi:10.1073/pnas.0909248106
- Kiang, N. Y., Segura, A., Tinetti, G., Govindjee, Blankenship, R. E., Cohen, M., Siefert, J., et al. (2007a). Spectral signatures of photosynthesis. II. Coevolution with other stars and the atmosphere on extrasolar worlds. *Astrobiology*, 7(1), 252–74. doi:10.1089/ast.2006.0108
- Kiang, N. Y., Segura, A., Tinetti, G., Govindjee, Blankenship, R. E., Cohen, M., Siefert, J., et al. (2007b). Spectral signatures of photosynthesis. II. Coevolution with other stars and the atmosphere on extrasolar worlds. *Astrobiology*, 7(1), 252–74. doi:10.1089/ast.2006.0108
- Kiang, N. Y., Siefert, J., Govindjee, & Blankenship, R. E. (2007). Spectral signatures of photosynthesis. I. Review of Earth organisms. *Astrobiology*, 7(1), 222–51. doi:10.1089/ast.2006.0105

- Kopp, R. E., Kirschvink, J. L., Hilburn, I. A., & Nash, C. Z. (2005). The Paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proceedings of the National Academy of Sciences of the United States of America*, 102(32), 11131–6. doi:10.1073/pnas.0504878102
- Leslie, M. (2009). On the origin of photosynthesis. *Science*, 323(March), 1286–1287.
- Lowe, D. (1994). Abiological origin of described stromatolites older than 3.2 Ga. *Geology*. doi:10.1130/0091-7613(1994)022<0387
- Marais, D. Des, & Harwit, M. (2002). Remote sensing of planetary properties and biosignatures on extrasolar terrestrial planets. ..., 2(2).
- Margulis, L. (1992). The Inheritance of Acquired Microbes. In W.H. Freeman (Ed.), *Symbiosis in Cell Evolution* (2nd ed., Vol. 9, p. 452).
- Mulkidjanian, A. Y., Koonin, E. V., Makarova, K. S., Mekhedov, S. L., Sorokin, A., Wolf, Y. I., Dufresne, A., et al. (2006). The cyanobacterial genome core and the origin of photosynthesis. *Proceedings of the National Academy of Sciences of the United States of America*, 103(35), 13126–31. doi:10.1073/pnas.0605709103
- Olson, J. M. (2006). Photosynthesis in the Archean era. *Photosynthesis research*, 88(2), 109–17. doi:10.1007/s11120-006-9040-5
- Pierson, B. K., & Castenholz, R. W. (1974). A phototrophic gliding filamentous bacterium of hot springs, *Chloroflexus aurantiacus*, gen. and sp. nov. *Archives of Microbiology*, 100(1), 5–24. doi:10.1007/BF00446302
- Pierson, B. K., Sands, V. M., Frederick, J. L., & Frederickt, J. L. (1990). Spectral Irradiance and Distribution of Pigments in a Highly Layered Marine Microbial Mat Spectral Irradiance and Distribution of Pigments in a Highly Layered Marine Microbial Mat, 56(8).
- Pierson, B., Oesterle, A., & Murphy, G. L. (1987). Pigments, light penetration, and photosynthetic activity in the multi-layered microbial mats of Great Sippewissett Salt Marsh, Massachusetts. *FEMS Microbiology Letters*, 45(6), 365–376. doi:10.1111/j.1574-6968.1987.tb02412.x
- Raymond, J., Zhaxybayeva, O., Gogarten, J. P., Gerdes, S. Y., & Blankenship, R. E. (2002). Whole-genome analysis of photosynthetic prokaryotes. *Science (New York, N.Y.)*, 298(5598), 1616–20. doi:10.1126/science.1075558
- Roberson, A. L., Roadt, J., Halevy, I., & Kasting, J. F. (2011). Greenhouse warming by nitrous oxide and methane in the Proterozoic Eon. *Geobiology*, 9(4), 313–20. doi:10.1111/j.1472-4669.2011.00286.x

- Rosing, M. T., & Frei, R. (2004). U-rich Archean sea-floor sediments from Greenland – indications of >3700 Ma oxygenic photosynthesis. *Earth and Planetary Science Letters*, 217(3-4), 237–244. doi:10.1016/S0012-821X(03)00609-5
- Sagan, C., Thompson, W. R., Carlson, R., Gurnett, D., & Hord, C. (1993). A search for life on Earth from the Galileo spacecraft. *Nature*, 365(6448), 715–21. doi:10.1038/365715a0
- Sandmann, G. (2009). Evolution of carotene desaturation: the complication of a simple pathway. *Archives of biochemistry and biophysics*, 483(2), 169–74. doi:10.1016/j.abb.2008.10.004
- Sanromá, E., Pallé, E., & García-Muñoz, A. (2013). On the effects of the evolution of microbial mats and land plants on the Earth as a planet. Photometric and spectroscopic light curves of paleo-Earths. *arXiv preprint arXiv:1302.4232*.
- Schopf, J. W. (1993). Microfossils of the Early Archean Apex Chert: New Evidence of the Antiquity of Life. *Science*, 260(5108), 640–646. doi:10.1126/science.260.5108.640
- Seager, S, Turner, E. L., Schafer, J., & Ford, E. B. (2005). Vegetation's Red Edge : A Possible Spectroscopic, 5(3), 372–393.
- Seager, Sara, Schrenk, M., & Bains, W. (2012). An astrophysical view of Earth-based metabolic biosignature gases. *Astrobiology*, 12(1), 61–82. doi:10.1089/ast.2010.0489
- Summons, R. E., Bradley, A. S., Jahnke, L. L., & Waldbauer, J. R. (2006). Steroids, triterpenoids and molecular oxygen. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences*, 361(1470), 951–68. doi:10.1098/rstb.2006.1837
- Tice, M. M., & Lowe, D. R. (2004). Photosynthetic microbial mats in the 3,416-Myr-old ocean. *Nature*, 431(7008), 549–52. doi:10.1038/nature02888
- Tinetti, G., Meadows, V. S., Crisp, D., Kiang, N. Y., Kahn, B. H., Bosc, E., Fishbein, E., et al. (2006). Detectability of planetary characteristics in disk-averaged spectra II: synthetic spectra and light-curves of earth. *Astrobiology*, 6(6), 881–900. doi:10.1089/ast.2006.6.881
- Wordsworth, R., & Pierrehumbert, R. (2013). Hydrogen-nitrogen greenhouse warming in Earth's early atmosphere. *Science (New York, N.Y.)*, 339(6115), 64–7. doi:10.1126/science.1225759
- Yurkov, V. V., & Beatty, J. T. (1998). Aerobic anoxygenic phototrophic bacteria. *Microbiology and molecular biology reviews : MMBR*, 62(3), 695–724.

