CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

1 Environmental Changes Impacting on, and Caused by, the Evolution of Photosynthetic Organisms

John A. Raven

1.1 Overview

The weak young Sun requires a larger greenhouse effect to explain evidence of liquid water from the late Hadean. The early Earth was anoxic. The origin of life at least 4 Ga ago could have involved chemolithotrophy. Carbon isotope evidence is consistent with the occurrence of Rubisco (ribulose-1,5-bisphosphate carboxylase-oxygenase) and the Benson–Calvin–Bassham cycle from ~4 Ga but is also consistent with some other autotrophic CO_2 fixation pathways. Molecular genetic evidence is consistent with an early origin of the photochemical reaction centre, with the possibility of the occurrence of two photosystems (PSII and PSI) in series and the possibility of oxygenic photosynthesis before the origin of cyanobacteria, explaining 'whiffs of O_2', before the Great Oxidation Event (GOE) 2.4–2.3 Ga ago. Oxygenic photosynthesis may have preceded the occurrence of the multiple clades of anoxygenic photosynthetic bacteria with either RCI (type I reaction centre; homologue of PSI) or RCII (type II reaction centre; homologue of PSII). The occurrence of oxygenic photolithotrophy is a necessary, but not sufficient, condition for the occurrence of the GOE and the Neoproterozoic Oxidation Event (NOE). What other factors are involved in initiating these two oxidation events is a matter of debate.

1.2 Introduction

The Universe came into existence ~13.8 billion years ago (Ga), and the solar system at ~4.6 Ga. The Sun is a G2V star whose radiant energy output has increased ~20–30%, accompanied by an increase in its surface temperature and a decrease in the wavelength of maximum photon output and the rather shorter wavelength of maximum energy output, over the last 4.6 Ga. Other things being equal, the 'faint young Sun' would require a large greenhouse for liquid water to occur on Earth early in its existence (Molnar and Gutowski 1995; Tyrell 2013; Knoll 2015; Catling and Zahnle

Discussions with John Beardall, Dianne Edwards, Paul Falkowski, Mario Giordano†, Andrew Knoll and Stephen Maberly have been very helpful. †Deceased 28 December 2019. The University of Dundee is a registered Scottish charity, No. SC015096.

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

2020). However, other things were not equal. The Moon-forming impact, involving the collision of a Mars-size object with a Venus-size object, occurred about 4.42–4.47 Ga and caused very significant heating of the Earth (Bottke et al. 2015; Connelly and Bizzaro 2016). The early Earth could not have allowed liquid water to condense for 10 million years after the heating by the Moon-forming impact and the runaway greenhouse effect of CO_2 and gaseous H_2O, exacerbated by the Late Heavy Bombardment of asteroids (Sleep 2010; Sleep et al. 2014). After this a decreased greenhouse effect allowed the Earth's surface to cool sufficiently to allow liquid H_2O, essential for life as we know it, to form, with the possibility of an ocean on the Earth's surface as long ago as 4.3 Ga (Harrison 2009).

As well as the partial pressure of greenhouse gases (e.g., H_2O vapour, CO_2, CH_4 and N_2O), the greenhouse effect depends on the total atmospheric pressure. One method for measuring atmospheric pressure in the past was used by Som et al. (2012) who followed a suggestion of Lyell (1851) on the use of impressions of fossil raindrops to constrain past atmospheric pressure. Som et al. (2012) showed that atmospheric pressure at 2.7 Ga was less than twice the present value and was probably 0.5–1.05 times that found today; other methods resulting in similar values are discussed by Catling and Zahnle (2020). Payne et al. (2020) used the extent of oxidation of micrometeorites to suggest either a low partial pressure of N_2 or a high partial pressure of CO_2 at 2.7 Ga contributing to an atmospheric pressure of 0.6 the present value, consistent with a glaciation at about that time. Plate tectonics and the first continental crust exposed to the atmosphere occurred >4.03 Ga years ago (Bauer et al. 2017; but see also Carwood et al. 2018), allowing liquid H_2O to occur on land. Land surface area between 4 Ga and 2.4 Ga was only about 0.1 of the present value (Krissansen-Totton et al. 2018).

1.3 Origin of Life

Thus far, no site, and associated mechanism, yet explains life's origin (Kitadai and Maruyama 2018). Life on Earth could have originated elsewhere in the Universe and been transferred to Earth on (for example) a meteorite, that is, 'Panspermia', or at least have been dependent on essential components of life from outside Earth (Kitadai and Maruyama 2018). Panspermia moves the mystery of the origin of life on Earth to some other planet or moon and will not be considered further here. Assuming the origin of life on Earth, there are still several, partially mutually exclusive, suggestions as to the site and requirements of the origin of life (Kitadai and Maruyama 2018). Evidence of life goes back to 3.95 Ga (Schidlowski 1998, 2001; Noffke et al. 2013; Tashiro et al. 2017; Flannery et al. 2018; Garcia et al. 2021).

Suggestions of the origin of life on Earth involving aquatic habitats on the land surface, as opposed to the Ocean, can be found in Follman and Brownson (2009), Damer and Deamer (2020) and Toner and Catling (2020). However, many hypotheses of the origin of life involve the Ocean; some of these involve marine alkaline

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

hydrothermal vents, with the possibility of chemiosmotic adenosine triphosphate (ATP) synthesis using the proton-motive force (PMF) across the membrane separating the vent fluid from seawater (Russell and Hall 2002; Russell and Martin 2004; Martin et al. 2008, 2018; Weiss et al. 2018). Chemolithotrophic growth is possible using the PMF and oxidation–reduction reactions depending on reductants in the vent water and oxidants in seawater and CO_2 fixation using, for example, the Wood–Ljungdahl pathway (Martin et al. 2008; Wang et al. 2009; Shih et al. 2016; Martin et al. 2018; Weiss et al. 2018; Hudson et al. 2020). The reductants in the vent water are at a low enough redox potential to, with ATP generated by F-ATP synthase using the PMF, convert carbon dioxide to organic carbon (Martin et al. 2018; Weiss et al. 2018). Mulkidjanian and Galperin (2010) suggest that the F-V family of ATPases-ATP synthases occurred in the Last Universal Common Ancestor of all extant organisms.

The $\delta^{13}C$ of organic C relative to that of coeval carbonate C has, in the words of Garcia et al. (2021), been 'curiously constant over billions of years of Earth-life co-evolution' (Schidlowski 1998, 2001; Garcia et al. 2021). A very early C isotope fractionation value is that of Tashiro et al. (2017); see also Knoll and Nowack (2017), who found that the $\delta^{13}C$ of organic C was 25‰ more negative than the $\delta^{13}C$ of inorganic C (carbonate) in 3.95 Ga rocks from the Saglek Block in Labrador. A slightly younger value is that of Flannery et al. (2018), who found that the $\delta^{13}C$ of organic C was 29–45‰ more negative than the $\delta^{13}C$ of inorganic C (carbonate) in 3.43 Ga stromatolites from the Strelley Pool formation. These differences between ^{13}C:^{12}C of organic C and that of carbonate C are widely considered to indicate autotrophic C assimilation by Rubisco, consistent with the occurrence of autotrophic CO_2 assimilation using Rubisco or, much less likely, phosphoenolpyruvate carboxykinase (Fry 1996; Raven 2009). Large values of the difference between the ^{13}C:^{12}C of organic C and that of carbonate C in the Archean could have been produced by methanogenesis–methanotrophy cycles (Hayes 1994; Flannery et al. 2018; Garcia et al. 2021), or by the Wood–Ljungdahl pathway (Knoll and Canfield 1998; Fischer et al. 2009; Flannery et al. 2018; Garcia et al. 2021). Smaller differences between the ^{13}C:^{12}C of organic C and that of carbonate C could also be produced by the Wood–Ljungdahl pathway or, less likely, the reverse tricarboxylic acid cycle or the 3-hydroxypropionate bi-cycle (Garcia et al. 2021). Methanogenesis, the Wood–Ljungdahl pathway and the reverse tricarboxylic acid cycle cannot operate in the presence of O_2 (Hayes 1994; Garcia et al. 2021). However, after the (GOE), these pathways could occur in anoxic habitats and make a minor contribution to the difference between the ^{13}C:^{12}C of organic C and that of carbonate C in the rock record (Table 1 in Garcia et al. 2021).

All forms of Rubisco that are active in carboxylation also have an oxygenase activity; in an O_2-containing environment the occurrence of the oxygenase activity involves metabolic reactions (photorespiration) that process the product (2-phosphoglycolate) of Rubisco oxygenase (Raven et al. 2017). Figure 4 in Iniguez et al. (2020) is a dated phylogeny, showing Form III Rubisco at 3.6 Ga and Form II Rubisco at 3.5 Ga. In organisms contributing at least half of present-day global

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

primary productivity (Raven et al. 2017), there are CO_2 concentrating mechanisms that increase the CO_2:O_2 ratio at the active site of Rubisco (Raven et al. 2017).

1.4 Origin of Photosynthesis

Photoautotrophy involves the conversion of CO_2 and an inorganic reductant, energised by light, into organic carbon and an inorganic oxidant. Light energy is always involved in generating a PMF that, with F-ATP synthase, phosphorylates adenosine diphosphate (ADP) to ATP, and, almost invariably, light energy is involved in energising electrons from a high redox potential donor to produce a reductant at a low enough redox potential to be involved in reducing CO_2 to organic carbon. A possible exception is when the external reductant is H_2, with a low enough redox potential to be involved in CO_2 conversion to organic carbon without further energisation. However, Larsen et al. (1952) found that the energy cost in terms of mole absorbed photons required to convert one mole CO_2 to organic C in the anoxygenic photoautotroph *Chlorobium* was independent of whether H_2 (low potential) or $S_2O_3^{2-}$ or $S_4O_6^{2-}$ (higher potential) was the reductant. Despite the large quantity of information on redox, including H^+-pumping, components used in photosynthesis in anoxygenic photoautotrophs, there is still lack of clarity on the relative roles of non-cyclic and cyclic electron transport in supplying the reductant and ATP used in photosynthesis (Larkum et al. 2018). Cyclic electron transport, involving electron transport from the reducing end of the photosystem (RCI in Chlorobi; RCII in Chromatiales (γ-Proteobacteria)), has only a PMF (and hence ADP phosphorylation) as the energetic outcome. Non-cyclic electron transport, by contrast, involves net electron transport from a (high potential) reductant to a low-potential oxidant. In the case of the Chromatiales, non-cyclic electron transport is by uphill electron transport driven by part of the PMF generated by cyclic electron transport generating a PMF, the rest being used in ADP phosphorylation (Larkum et al. 2018). The situation in the Chlorobi (green sulfur bacteria) is not clear for cyclic electron transport; non-cyclic electron transport in Chlorobi is a direct result of photochemistry by RCI (Larkum et al. 2018). It is clear that the cytochrome $bcFe_{nh}$ complex (or its evolutionary derivative cytochrome b_6fFe_{nh}) is invariably present in photoautotrophic organisms and is involved in cyclic electron transport in anoxygenic and oxygenic photoautotrophs (Larkum et al. 2018). Dibrova et al. (2017) argue, although it is not a mainstream opinion, that the cytochrome $bcFe_{nh}$ complex evolved in phototrophs, since only photochemistry could generate the high-potential oxidants needed for functioning of the complex in the anoxic (apart from 'whiffs of oxygen') world before the GOE.

Hydrothermal vents emit infrared radiation with a very low photon flux density at short wavelength tail (<1,000 nm) of black body radiation of superheated water that nevertheless seems to be capable of supporting growth of an obligately photolithotrophic anoxygenic photosynthetic of the Chlorobi (Beatty et al. 2005; Martin et al. 2018). These bacteria use the reverse tricarboxylic acid cycle for CO_2 assimilation

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

producing reduced C (Beatty et al. 2005), the pathway formerly favoured as occurring in the earliest-evolving autotrophs, which were thought to be chemolithotrophs rather than photolithotrophs (Hartman 1975). However, the currently favoured earliest autotrophic CO_2 fixation pathway in hydrothermal vents is the Wood–Ljungdahl pathway producing acetyl CoA (Martin and Russell 2007; Martin et al. 2018). Martin et al. (2018) point out that, despite the very much lower photon influx density of <1,000 nm radiation at hydrothermal vents relative to the solar radiation incident on the water or land surface, they do have the advantage of lacking the damaging short wavelength UVB and, especially, the shorter wavelength UVC, of solar radiation.

The hypothesis of the origin of photosynthesis at deep ocean hydrothermal vents is attractive in that the overlying liquid H_2O would absorb the damaging UVB and, especially, UVC solar radiation that would reach the land and sea surface in the absence of a stratospheric O_3 shield (Perez et al. 2013; Raven and Donnelly 2013). Stratospheric O_3 only formed with the GOE at ~2.3–2.4 Ga (Gumsley et al. 2017; Knoll and Russell 2017). However, Martin et al. (2018) suggest that the ancestral reaction centres of photosynthesis (RC1 and RC2) evolved in the ancestors of the last common ancestor of cyanobacteria, with PSI and PSII becoming the energisers of linear electron transport from H_2O, using the Mn_4CaO_5 oxygen evolving complex, PSII, plastoquinone, cytochrome b_6fFe_{nh}, cytochrome c_6/plastocyanin, PSI, ferredoxin/flavodoxin and NADPH to CO_2 in cyanobacteria and thence to plastids. Horizontal gene transfer then accounted for RCII in Chloroflexi, Proteobacteria and *Gemmatimonas*, and RCI in Chlorobi, Heliobacteria and Acidobacteria (Martin et al. 2018). This evolutionary sequence is consistent with the early origin of O_2-producing PSII (Cardona et al. 2015, 2019). Coupling of this ancient PSII to the oxygen evolving complex could explain the occurrence of 'whiffs of O_2' before the GOE (Cardona et al. 2015; Knoll et al. 2016; Martin et al. 2018; Cardona et al. 2019). This scheme does not necessarily imply the use of H_2O as the earliest electron donor for photosynthesis; H_2O is a thermodynamically and kinetically difficult electron donor in photosynthesis, and it has been argued that H_2, S^{2-} then Fe^{2+} (Olson 2006; Thompson et al. 2019) would have been used as thermodynamically and kinetically simpler electron donors while they were present in the anoxic Archean environment. However, Martin et al. (2018) and Hamilton (2019) point out that some cyanobacteria can oxidise S^{2-} to S^0 using PSI, and to more oxidised S species (SO_3^{2-}, $S_2O_3^{2-}$) using PSII. This is not the case for Fe^{2+} oxidation in cyanobacterial photosynthesis; external Fe^{2+} oxidation by photosynthesising cyanobacteria is a result of Fe^{2+} oxidation by photoproduced O_2 rather than by photo-oxidation of Fe^{2+} by PSI or PSII (Swanner et al. 2015, 2017). Furthermore, the occurrence of chlorophyll *a* in the reaction centre of cyanobacteria (other than *Acaryochloris* with chlorophyll *d*) rather than bacteriochlorophyll in anoxygenic photosynthetic bacteria agrees with ancestors of cyanobacteria occurring before ancestors of extant anoxygenic photosynthetic; chlorophyll *a* is earlier in the chlorophyll – bacteriochlorophyll synthetic pathways than bacteriochlorophylls, that is, anoxygenic photosynthetic bacteria produce chlorophyll *a* as an intermediate in bacteriochlorophyll synthesis (Granick 1965; Martin et al. 2018; Hamilton 2019).

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

1.5 Photosynthesis Pigments and Energetics in Relation to the Solar Spectrum as Modified by the Atmosphere and the Water Bodies

The wavelength of light, and the corresponding energy per photon, at which the photochemical reactions of photosynthesis occur is related to the energetics of the primary redox products of photochemistry and to the spectral distribution of radiation incident on the organism (Wolstencroft and Raven 2002; Falkowski and Raven 2007; Kiang et al. 2007a, 2007b; Stomp et al. 2007; Larkum et al. 2018; Holtrop et al. 2021). For oxygenic photosynthesis photochemistry occurs at 680 nm (PSII) and 700 nm (PSI). These wavelengths are slightly longer, that is, have lower energy per photon, than the present peak wavelength of solar photons incident at the top of the atmosphere (Wolstencroft and Raven 2002). Since the peak wavelength of photon output of the Sun has decreased during the time for which oxygenic photosynthesis has occurred, the match between the peak solar photon output and the wavelength of photochemistry of PSII and PSI could have been closer when oxygenic photosynthesis originated (Wolstencroft and Raven 2002; Larkum et al. 2018). Too much should not be made of this relationship since the solar spectrum is modified by absorption by the atmosphere, which has varied over time, and, for aquatic organisms, absorption by liquid water (Wolstencroft and Raven 2002; Kiang et al. 2007a, 2007b; Stomp et al. 2007; Larkum et al. 2018). Water absorbs longer wavelengths more than shorter wavelengths of photosynthetically active radiation for oxygenic photosynthetic organisms, so blue wavelengths are relatively enriched at greater depths (Wolstencroft and Raven 2002; Kiang et al. 2007a, 2007b; Stomp et al. 2007; Larkum et al. 2018). This outcome is modified in waters that contain blue light-absorbing organic compounds (gilvin or gelbstoff) (Kirk 2011).

For anoxygenic photosynthetic bacteria, the wavelength at which photochemistry occurs is at longer wavelengths, that is, 800–960 nm (Kiang et al. 2007a), and this has been related both to the energetics of the primary products of photochemistry and to absorption of radiation by overlying water (Kiang et al. 2007a, 2007b; Stomp et al. 2007; Larkum et al. 2018). The argument from water absorption implies that anoxygenic photosynthesis evolved under water, possibly related to avoiding damaging UV. Not immediately related to solar radiation, an origin of anoxygenic photosynthesis at hydrothermal vents using the short wavelength tail of black body radiation from superheated water could be related to a compromise between the energetics of the photochemical reaction setting an upper wavelength limit and the decreasing photon flux with decreasing wavelength setting a lower wavelength limit (Beatty et al. 2005).

1.6 Photosynthesis and Oxygen

Granted that photosynthesis originated in very low O_2 habitats, there are implications for the involvement of metals in early photosynthesis in relation to their

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

availability in anoxic environments (Raven et al. 1999; Saito et al. 2003). Redox chemistry of both Fe^{2+}-dominated and S^{2-}-dominated Archaean oceans had the following sequence of metal availability Fe > Mn, Ni, Co > Cd, Zn, Cu (Saito et al. 2003; Hamilton 2019; Wade et al. 2021). Photosystem I has 12 Fe per complex, cytochrome b_6f Fe_{nh} has 5 Fe per complex and PSII has 2 Fe per complex (Falkowski and Raven 2007). Cyanobacteria (as do Glaucophyta and Rhodophyta) have higher PSI:PSII ratios, than other oxygenic photosynthetic organisms, and thus higher Fe requirement per linear electron transport pathway, than other oxygenic photosynthetic organisms, corresponding to the high Fe availability in the Archaean (Raven et al. 1999; Saito et al. 2003). The synthesis of the Mn_4CaO_5 oxygen evolving complex would have been favoured by Mn availability in the Archaean (Raven et al. 1999; Saito et al. 2003). Although Co was also available in the Archaean (Raven et al. 1999; Saito et al. 2003), there are no known cases for Co substituting for Mn in the Mn_4CaO_5 complex in vivo, this substitution has been produced in vitro (Gates et al. 2022). The in vitro Co_4CaO_5 complex is active in O_2 production, though the rate of O_2 production per Co complex is only 25% of that of the Mn complex; this may explain why no in vivo case of a Co_4CaO_5 oxygen evolving complex is known. Electron transport from cytochrome b_6f Fe_{nh} to PSI could have involved cytochrome c_6 rather than plastocyanin in the Archaean since Fe (cytochrome c_6) was much more available than Cu (plastocyanin) (Raven et al. 1999; Saito et al. 2003). Likewise, electron transport from PSI to $NADP^+$ could have involved the Fe-containing ferredoxin rather than the metal-free flavodoxin (Raven et al. 1999; Saito et al. 2003). For the CO_2 acquisition reactions of photosynthesis, the high CO_2 availability in the Archaean would have meant a lower requirement for the metal-containing carbonic anhydrases (Raven et al. 2017). Any carbonic anhydrase in the Archaean could have used the more available Co (a potential alternative metal cofactor in some present-day carbonic anhydrases) or Mn (the metal cofactor of the recently discovered ι-carbonic anhydrase from a diatom and a bacterium: Jensen et al. 2019; De Prete et al. 2020), rather than the much less available Zn (the commonest metal cofactor in extant carbonic anhydrases) or Cd (obligately used in some diatom carbonic anhydrases today) (Raven et al. 1999; Saito et al. 2003). Interestingly in this context, a metal-free carbonic anhydrase has recently been reported from the cyanobacterium *Anabaena* and the chlorarachniophyte *Bigelowia* (Hirakawa et al. 2021; Nocentini et al. 2021).

Increasing O_2 availability with the GOE and the Neoproterozoic O_2 increase has decreased the availability of Fe and increased that of Cu, Zn and Cd, with implications for plastocyanin vs. cytochrome c_6, flavodoxin vs. ferredoxin and Zn and Cd vs. Co in carbonic anhydrase. These increases in O_2 have allowed the oxygenase activity of Rubisco to be expressed and contribute to the selective advantage of a CO_2 concentrating mechanism, especially as CO_2 availability declines (Raven et al. 2017); this is considered further under ‘Photosynthesis and Carbon Dioxide’.

A further product of increased O_2 over time is the possibility of linear electron flow from H_2O oxidised by the oxygen evolving complex of PSII to electron acceptors resulting in O_2 uptake, that is, water–water cycles. The water–water cycles are

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

the plastid terminal oxidase (PTOX) involving only PSII, and the Mehler peroxidase Asada–Halliwell–Foyer reaction and the flavodi-iron reaction involving PSII and PSI (Raven et al. 2020a). These reactions are coupled to H^+ accumulation in the thylakoid lumen (or the periplasm in the thylakoid-less cyanobacterium *Gloeobacter*), so, in the absence of an uncoupling protein (H^+ channel) in the photosynthetic membrane of oxygenic photosynthetic organisms, the extent of these water–water cycles are limited by the extent of H^+ flux through the CF_oCF_1 ATP synthase and hence on the demand for ATP. There is insufficient evidence on the O_2 affinities of the various water–water cycles (Raven et al. 2020b) to suggest the significance of particular water–water cycles at different stages of oxygen increase.

A possible effect of increased O_2 is inhibition of O_2 production by PSII and the oxygen evolving complex, either thermodynamically through reactions close to equilibrium or kinetically based on in vitro studies (Clausen and Junge 2004, 2005; Clausen et al. 2005). However, analysis of in situ responses to high O_2 (Raven and Larkum 2007) and further studies on more resolved preparations of the PSII-oxygen evolving complex (Kolling et al. 2009; Shevela et al. 2011) show no evidence of O_2 inhibition of O_2 production at up to four times the present air-equilibrium O_2 concentration.

1.7 Photosynthesis and Carbon Dioxide

All oxygenic photosynthetic organisms have Rubisco and the Benson–Calvin–Bassham cycle at the core of autotrophic CO_2 acquisition. Both of the Rubisco forms (Forms I and II) involved in autotrophic CO_2 fixation have both carboxylase and oxygenase activities (Poudel et al. 2020) and have significant phylogenetic variations in their catalytic kinetics with a generally negative correlation of the CO_2-saturated rate of carboxylation and the affinity for CO_2 and also selectivity of CO_2 relative to O_2 (Tcherkez et al. 2006; Iniguez et al. 2020). The Form I Rubiscos are found in all oxygenic photosynthetic organisms, except basal dinoflagellates and chromerids that have Form II Rubiscos obtained by horizontal gene transfer from autotrophic proteobacteria (Raven et al. 2020b).

Based on the kinetics of Rubisco in extant representatives of the various clades and the variations in CO_2 and O_2, Raven et al. (2017) calculated the external dissolved CO_2 concentrations at which CO_2-concentrating mechanisms (CCMs) that catalyse energised accumulation of CO_2 at the site of Rubisco activity could be selectively favoured relative to diffusive CO_2 entry in aquatic phototrophs. These calculations suggested that CO_2 concentration below 10 times the present atmospheric value favoured CCMs in cyanobacteria (and, probably, basal dinoflagellates and chromerids) and twice the present value for eukaryotes with Form I Rubiscos (Raven et al. 2017, 2020b). The calculations depend, among other things, on the absence of evolutionary change in the kinetics of Rubisco clades since their origination; however, such changes have occurred (Young et al. 2012, 2016; Heureux et al. 2017; Rickaby and Hubbard 2019; Goudet et al. 2020; Iniguez et al. 2020). Furthermore, the basal cyanobacterium *Gloeobacter* occurs naturally in mats and forms aggregates in suspension

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

culture (Saw et al. 2013), imposing diffusive limitation on inorganic C availability to the cells. The evolution of CCMs and the mechanisms involved are considered further in Chapter 3, this volume.

1.8 The Role of Oxygenic Photosynthetic Aquatic Organisms in Changing Atmospheric CO_2 and O_2

CO_2 has decreased, and O_2 increased, over the last 4 Ga (Raven et al. 2017).

The atmospheric CO_2 partial pressure 4 Ga ago was in excess of 10 kPa, compared to 41 Pa today (Krissansen-Totton et al. 2018). CO_2 decrease has not been monotonic, for example, with an increase after the low level in the Carboniferous and then a decrease to the Pleistocene ice ages (Raven et al. 2017). This decreasing atmospheric CO_2 has helped, via the greenhouse effect, in maintaining a habitable planet as the energy output of the Sun increased since the Hadean faint young sun, but a direct feedback link has no mechanistic basis (Tyrell 2013). Atmospheric CO_2 is a significant correlate of ocean pH, which was pH 6.6 at 4 Ga, increasing to pH 8.2 today (Krissansen-Totton et al. 2018).

O_2 increase has also not been monotonic, with three major periods of increase: the Palaeoproterozoic GOE 2.4–2.2 Ga, the NOE 800–540 Ma, and the Paleozoic oxidation event (POE) 400–250 Ma (Tyrell 2013; Canfield 2014; Gumsley et al. 2017; Alcott et al. 2019). The model of Alcott et al. (2019) suggests that this stepwise oxygenation is an inherent property of global biogeochemical (C, O and P, as well as S and Fe) cycles. However, there have also been suggestions of a role of interactions of variations in the increase of daylength over time with photosynthesis (Klatt et al. 2021), and of evolutionary changes in cell structure increasing the potential for photosynthesis (Guégin and Maréchal 2022), in the GOE and NOE.

Klatt et al. (2021) relate the relative constancy of the Earth's rotation (and hence change of the length of the day) in the 'boring billion' between the GOE and NOE, preceded and followed by decreasing rates of the Earth's rotation and increasing daylengths, to the biology and physics of cyanobacterial mats that increase net O_2 production (and organic C burial) per unit gross primary productivity. Klatt et al. (2021) argue that a constant time is needed after dawn for the nocturnal metabolism effects to be overcome and net O_2 production to begin. The argument depends crucially on the occurrence of sufficient variations in the rate of decrease of the Earth's rotation (Figure 4 of Klatt et al. 2021).

Guégin and Maréchal (2021) suggested that the GOE might be related to the origin of thylakoids in cyanobacteria. The membrane-associated photosynthetic reactions of the basal extant cyanobacterium *Gloeobacter* and other species of Gloeobacterales (Grettenberger 2021; Rahmatpour et al. 2021) all occur in the plasma membrane, where there are also membrane-associated respiratory reactions, ion-pumping rhodopsin, and nutrient transporters (Guégin and Maréchal 2022; Raven and Sánchez-Baracaldo 2021). In other cyanobacteria, the membrane-associated photosynthetic processes occur in intracellular thylakoids, providing a larger area per cell volume for

© in this web service Cambridge University Press & Assessment www.cambridge.org

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-82298-5 — Evolutionary Physiology of Algae and Aquatic Plants
Mario Giordano , John Beardall , John A. Raven , Stephen C. Maberly
Excerpt
More Information

the light-harvesting chromophores and their covalently bound proteins (phycobilins) or associated apoproteins (chlorophylls and carotenoids), the photochemical reaction centres of PSI and PSII, and downstream reactions leading to O_2 production, ADP phosphorylation and $NADP^+$ reduction (Guégin and Maréchal 2022). Guégin and Maréchal (2022) suggest that, if the origin of thylakoids occurred at the start of the GOE, this change in the location of membrane-associated photosynthesis might mean more O_2 production per unit cyanobacterial volume. Guégin and Maréchal (2022) suggest further that the origin of eukaryotic photosynthetic organisms by endosymbiosis in the Mesoproterozoic could further increase the potential for O_2 production and might be related to the subsequent (Neoproterozoic) NOE. However, there are very limited data on the area of thylakoids per non-vacuolar volume for cyanobacteria and eukaryotic microalgae. Furthermore, for unicellular organisms of the same size, the range of maximum photoautotrophic specific growth rates in the Chlorophyta is the same as that of cyanobacteria (Nielsen 2006). Further work is needed to test the validity of the suggestions of Guégin and Maréchal (2022).

The equation of oxygenic photosynthesis converting one mole CO_2 to carbohydrate involves production of one mole O_2. There is no net change in CO_2 or O_2 in the environment if all the carbohydrate is converted back to CO_2 in respiration. Net O_2 accumulation and CO_2 drawdown need sequestration of the reduced product of photosynthesis away from the respiratory conversion to CO_2; in water bodies, this is the biological carbon pump, followed by sedimentation in fine-grained material; some of the organic C is biologically oxidised using O_2, NO_3^- and SO_4^{2-} that diffuse in from overlying water, but further sedimentation puts that organic C out of diffusive range of O_2, NO_3^- and SO_4^{2-} from overlying water (Raven 2017). This particulate organic C can, if not physically disturbed, remain for long periods and, if subducted, many Ma before oxidation and release to the atmosphere or ocean in volcanoes or submerged vents (Raven 2017). The onset of oxygenic photosynthesis and the biological pump involved a delay in O_2 accumulation as a result of O_2 consumption in the oxidation of H_2, Fe^{2+} and S^{2-} that had not been consumed in anoxygenic photosynthesis, and that was resupplied to the biosphere from volcanoes and vents.

The occurrence of oxygenic photosynthesis was thus a necessary, but not sufficient, requirement for the GOE: cyanobacteria, and before that, their oxygenic photosynthetic predecessors, predate the GOE. Thus, oxygenic photosynthesis is an ultimate cause of the GOE, but not the proximate cause. Papineau (2010) suggests increased phosphate weathering and supply to the ocean with increased productivity and also deposition of phosphorites, possibly related to the Huronian glaciation. Eguchi et al. (2019) suggest a tectonic transition that increased volcanic CO_2 output, thereby stimulating global photosynthesis, while increased subduction removes organic C sedimented by the biological pump, which is thus removed from reconversion to CO_2 in the biosphere.

The Lomagundi–Jatuli Event or Lomagundi–Jatuli Excursion (LJE) at 2.2–2.1 Ga is recognised by an increase of ≤10‰ in the $\delta^{13}C$ of marine carbonate deposits. This is interpreted in terms of increased photosynthetic primary productivity and/or increased organic C sequestration in the surface ocean, preferentially removing

© in this web service Cambridge University Press & Assessment www.cambridge.org