DOI: 10.1007/s11099-018-0792-x PHOTOSYNTHETICA 56 (1): 11-43, 2018

REVIEW

Living off the Sun: chlorophylls, bacteriochlorophylls and rhodopsins

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Abstract

Pigments absorbing 350–1,050 nm radiation have had an important role on the Earth for at least 3.5 billion years. The ion pumping rhodopsins absorb blue and green photons using retinal and pump ions across cell membranes. Bacteriochlorophylls (BChl), absorbing in the violet/blue and near infra red (NIR), power anoxygenic photosynthesis, with one photoreaction centre; and chlorophylls (Chl), absorbing in the violet/blue and red (occasionally NIR) power oxygenic photosynthesis, with two photoreaction centres. The accessory (bacterio)chlorophylls add to the spectral range (bandwidth) of photon absorption, *e.g.*, in algae living at depth in clear oceanic water and in algae and photosynthetic (PS) bacteria in microbial mats. Organism size, *via* the package effect, determines the photon absorption benefit of the costs of synthesis of the pigment–protein complexes. There are unresolved issues as to the evolution of Chls *vs.* BChls and the role of violet/blue and NIR radiation in PS bacteria.

Introduction

The Sun's energy has been potentially available to power energy transduction on the Earth since its formation, although early physical conditions would have made this unlikely. The Earth orbits a G-type star (Figs. 3–7) with biologically significant characteristics of the spectrum <400 nm and various H_2O and CO_2 absorption bands >700 nm. Even allowing for the faint young sun (*see* "Implications of a Faint Sun") the Sun's spectrum would not have changed enough to influence the development of pigments involved in energy transduction. Likewise one can be fairly confident in predicting what systems would develop on extra-terrestrial planets (Wolstencroft and Raven 2002, Kiang *et al.* 2007a,b; Ritchie *et al.* 2017).

Today on the Earth energy-transducing pigment–protein complexes are widespread. Ion-pumping rhodopsins (bacteriorhodopsin, halorhodopsin, proteorhodopsin, and xanthorhodopsin) occur in Archaea, Bacteria, and Eukarya. BChls and Chls occur in Bacteria, while Chls occur in all photosynthetic Eukarya. Photochemistry by (bacterio)chlorophylls yields an oxidant and a reductant with a large redox potential difference between them; the energy-transducing rhodopsins do not generate reduced and oxidised products but do generate an electrochemical potential for protons or other ions.

Interestingly, and not fully resolved at the present time, is the divergence between BChl in the photosynthetic (PS) anoxygenic bacteria and Chl in the oxygenic cyanobacteria, eukaryotic algae, and embryophytes. If one takes the view that the PS bacteria employ earlier forms of photosynthesis, albeit anoxygenic, *i.e.* not extracting electrons from water (and not forming oxygen as a by-product) and that cyanobacteria and eukaryotic PS organisms are derived from these, then an explanation is at hand (Mauzerall 1973, Bjorn 1976, 2009; Hohmann-Marriott *et al.* 2011). However, this leaves the puzzle

Received 8 September 2017, *accepted* 20 December 2017, *published as online-first* 8 February 2018.
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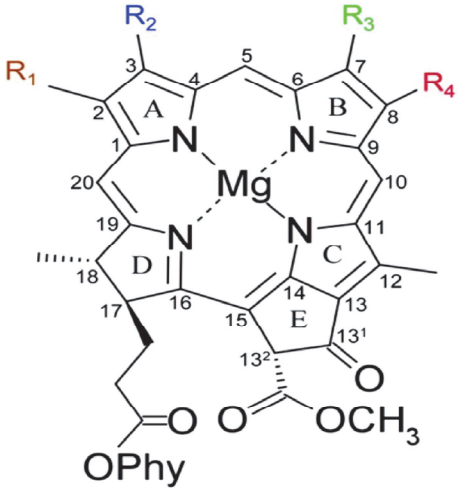
Abbreviations: AAPB – aerobic anoxygenic aerobic photosynthesis; BChl – bacteriochlorophyll; Chl – chlorophyll; ETR – electron transport rate; GOE – Great Oxidation Event; HPLC – high performance liquid chromatography; LED – light-emitting diode; LGT – lateral gene transfer; MgDVP – magnesium-2,4-divinyl phaeoporphyrin monomethyl ester A5; PBP – phycobiliprotein; RC – reaction center; TLC – thin layer chromatography; UV – ultraviolet.
Acknowledgements: The University of Dundee is a registered Scottish charity, No. 015096. RJR wishes to thank Prince of Songkla University - Phuket campus for providing the facilities for the project. AWDL thanks the Global Climate Cluster, University of Technology Sydney for ongoing support.

that BChl in contemporary organisms is formed on a biosynthetic pathway that first forms Chl and its molecular relatives (Fig. 1) (Granick 1965, Larkum 2006, 2008). An alternative view, much less popular, is that PS evolved in primitive procyanoabacterial organisms (Mulkidjanian *et al.* 2006, Cardona 2016, Cardona *et al.* in review) which subsequently gave rise on the one hand to the cyanobacteria with photosystem I and II (Govindjee *et al.* 2017), and on the other to anoxygenic PS bacteria, with either PSI-like or PSII-like reaction centres. According to this view, the first anoxygenic PS organisms produced Chl rather than BChl. Absorptance curves, however, show that the Soret (Q_X – *see* Reimers *et al.* 2013) window, available for blue light-absorbing BChl and Chl pigments, absorb about as many photons per absorption band as the Q_Y band windows for both Chl *a* and BChl *a/b* (Ritchie *et al.* 2017, and this paper, *see* Figs. 3–7). Perhaps this common use of similar blue bands subsequently drove more cryptic anoxygenic PS bacteria to adopt BChl which can harvest visible light but just as importantly can harvest far-red radiation, depending on the organism, up to 1050 nm (Larkum 1991, 2003, 2006, 2008; Kiang *et al.* 2007a,b; Stomp 2007, Ritchie *et al.* 2017). However, the use in photochemistry of these lower-energy far-red photons means that the energy stored in photochemistry is limited and less than half of the excitation energy of absorbed photons at 450 nm is usable in photochemistry at 950 nm, as compared to two-thirds for photochemistry at 680 nm (using Chl *a*). Unfortunately, we are dealing here with a time more than 3.5 billion years ago (BYA) when few identifiable fossils exist (but *see* Rosing *et al.* 2004, Nutman *et al.* 2016) and molecular phylogenetic analysis becomes unreliable because so many of the various photosynthetic lines seem to be about the same very ancient age (Harel *et al.* 2015).

Much has been written on the reasons why BChls are used in photoredox reactions of anoxygenic photosynthesis, and Chl *a* (very occasionally Chl *d*) in the photoredox reactions of oxygenic photosynthesis (Mauzerall 1973, Nishio 2000, Wolstencroft and Raven 2002, Kiang *et al.* 2007a,b; Stomp *et al.* 2007, Björn *et al.* 2009, Milo 2009, Raven 2009, Marosvölgyi and van Gorkum 2010, van Hohman-Mariott and Blankenship 2011, Raven and Ralph 2015, Kume *et al.* 2016, Kume 2017). Provisional conclusions are that the main consideration is energy per photon relative to the energy stored in the products of photochemistry, with subsidiary effects of spectral attenuation by the medium.

There are four other Chls besides Chl *a* (Fig. 1). These are Chls *b, c* (various subtypes), *d*, and *f*. The absence of a Chl *e* is because reports of its occurrence in *Tribonema bombycium* and *Vaucheria hamata* (Allen 1996, *see* Meeks 1974) proved unfounded; the original reports of Chl *e* did not provide a chemical structure and no further investigations have been published. Chl *b* and *c* [(c_1, c_2, and c_3 and magnesium 2.4-divinyl phaeoporphyrin monomethyl ester A5 (MgDVP)] have been labelled accessory Chls because they act purely in a light-harvesting role, are not present in reaction centres, and do not carry out (productive) photochemistry; and the same may be true for Chl *f*. Chl *d* and Chl *f*, absorb near-infra-red (NIR) radiation using their far-red Q_Y bands. Both occur in cyanobacteria and not in any *known* eukaryotic algae (for Chl *d*, Larkum and Kühl 2005, for Chl *f*, Chen *et al.* 2010). These Chls allow those cyanobacteria which possess them, to live in environments enriched in NIR, *e.g. Acaryochloris* (Miyashita *et al.* 2006) and *Halomicronema* (Chen *et al.* 2012), and also have a contribution, with carotenoids, and have the additional, rarely noted, effect of widening the blue absorption band (Fig. 4–5). Whether other Chls,



Chlorophylls	R1	R2	R3	R4	Q_Y [nm]
Chl *a*	CH_3	$CH{=}CH_2$	CH_3	$CH_2{-}CH_3$	665
Chl *b*	CH_3	$CH{=}CH_2$	CHO	$CH_2{-}CH_3$	652
Chl *d*	CH_3	CHO	CH_3	$CH_2{-}CH_3$	696
Chl *f*	CHO	$CH{=}CH_2$	CH_3	$CH_2{-}CH_3$	707
8-vinyl Chl *a*	CH_3	$CH{=}CH_2$	CH_3	$CH{=}CH_2$	666
8-vinyl Chl *b*	CH_3	$CH{=}CH_2$	CHO	$CH{=}CH_2$	658

Fig. 1. Structure of chlorophylls *a, b, d*, and *f*. The R groups (1 to 4) of various chlorophylls are shown in the Table as well as their Q_Y peaks in acetone solvent. Chls *a, b, d*, and *f* all have 10 double bonds in the tetrapyrrole ring (20 π electrons), *i.e.* they are chlorins. Chlorophylls c_1 and c_2 do not have a phytol tail and ring D is oxidised to yield 22 π electrons in what is a porphyrin ring. Chlorophyll c_3 is phytylated (Zapata and Garrido 1997) but also has 22 π electrons. BChl *a, b*, and *g* are bacteriochlorins with reduced B and D pyrrole rings (18 π e^-) and BChls *c, d, e*, and *f* are chlorins with a reduced ring D (20 π e^-) (refer to Scheer 2006). Phy – phytol tail.

potentially with NIR absorption, will be found it has been discussed (Chen and Blankenship 2011, Schliep *et al.* 2013) but none so far have been discovered or bio-engineered. Interestingly, there are special Chl *a*–protein complexes that allow absorption of radiation up to 760 nm, such as the special form in *Ostreobium* spp. (*see* below); the reason is the conjugation of the Chl *a* to a special protein (Trissl 2003, *see* also Chen *et al.* 2005). In all these far-red and NIR-absorbing systems it is necessary for the absorption of long-wavelength photons to pass on their energy to pigments whose absorption maxima are at shorter wavelengths. In the case of Chls *a* it is migration of energy from ~760 nm to the absorption maximum of P680, the major reaction centre pigment of PSII. This is called "uphill" energy transfer. It is quite feasible to explain by quantum physics; for *Ostreobium* (Trissl 2003, Wilhelm and Jacob 2006), and for *Acaryochloris see* Nieuwenburg *et al.* (2003), but it comes with an energy cost. Also in the case of *Acaryochloris* Chl *d* is used in both reaction centres, and the PSII RC has a P705 so the uphill energy migration is not so steep. In the case of Chl *f* organisms, the nature of the Chl in reaction centres (RCs) is not known but provisionally it is assumed that it is Chl *a* in P680 and P700 (Chen *et al.* 2012, Chen 2014).

What the existence of Chl and BChl tells us in terms of the evolution of photosynthesis is, as mentioned above, a matter of debate (*see* for example Chen 2014). Just as interesting is what the existence of Chl *d* and Chl *f* tell us about the evolution of the Chls. These Chls are formed from Chl *a* or chlorophyllide *a* by modification of one of the hydroxyls on the porphyrin ring A to a formyl group (Fig. 1). At the most simple level of interpretation, this says that Chl *a* was the first pigment in the cyanobacteria. But in reality this does not necessarily mean that Chl *a* preceded Chl *d* or Chl *f* in the early cyanobacterial or procyanobacterial organisms. In the case of Chl *f* it is now known that the final enzymatic step is the addition of an oxygen to a methyl group on the first porphyrin ring (A) and is brought about by a protein with affinities to a very early form of D1 protein, which does not have the $Mn_4Ca_1O_5$ centre (Ho *et al.* 2016). This is not incompatible with the hypothesis that at this early stage Chl *f* was the major chlorophyll of procyanobacteria. However, a corollary would be that Chl *f* once functioned as the redox Chl in the PSII RC, as does Chl *d* in *Acaryochloris*.

It would be a hope that the phylogeny of cyanobacteria would tell us which group gave rise to the plastids of eukaryotic algae and whether or not there was a monophyletic plastid origin. A polyphyletic origin could easily give rise to obscure results. The results so far are not conclusive (*e.g*. Harel *et al.* 2015) but molecular phylogenies together with fossil evidence are improving the time estimates and yield indications of the nearest living ancestor (Cardona 2016, Shih *et al.* 2017, Sánchez-Baracaldo *et al.* 2017, and references therein). What is clear is that there are three types of primary plastid in eukaryotic algae, *i.e*. plastids having a single set of outer (envelope) membranes; these occur in the three phyla: Chlorophyta and allies [with Chl (*a*+*b*)], Rhodophyta (with Chl *a* and PBP including rhodophytan phycoerythrin), and Glaucocystophyta (with cyanelles possessing Chl *a* and either cyanobacterial PC or PE) (Larkum 2003, 2006, 2008; Larkum *et al.* 2007, Price *et al.* 2012; algal taxonomy here and subsequently follows Graham *et al.* 2016 and http://www.algaebase.org). It is usually assumed that these primary plastids arose by a single endosymbiosis. All other algae have plastids that show indications of two or more serial endosymbioses (Larkum 2006).

The discussion that follows addresses the relationship between the energy content of a photon at the wavelength of photochemistry, migration of the absorbed photonic energy to the site of photochemistry and the energy stored in the photoproduct, and the incident photon spectrum, both where the organisms occur today, and where and when they evolved.

Relation of the energy per photon used in photochemistry to the energy stored in a stable form

Ion-pumping rhodopsins

The ion-pumping rhodopsins have a retinal chromophore (Fig. 2) and an apoprotein that uses the photon energy absorbed by the retinal pigment to pump the ions. H^+ is the most commonly transported ion (although Na^+ and Cl^- can also be pumped, *see* below), and the H^+-pumping bacteriorhodopsin from the Archaean *Halobacterium halobium* was the first ion-pumping rhodopsin to be identified (Osterhelt and Stoeckenius 1971, Kandori 2015). Most rhodopsins are barrel-shaped membrane spanning porins with the retinal head wrapped in its hydrocarbon tail in a pocket on the outer part of the protein (Baumann *et al.* 2014). The direction of H^+ transport is almost always from the cytosol to the external medium in Archaea and Bacteria, including the oxygenic photosynthetic cyanobacterium *Gloeobacter violaceous* that lacks thylakoids (Rexroth *et al.* 2011). In Gloeobacter, H^+ efflux across the plasma membrane can be driven by the respiratory electron transport chain in the dark, with the addition of both photosynthetic and rhodopsin-based H^+ efflux in the light (Rexroth *et al.* 2011, Choi *et al.* 2014).

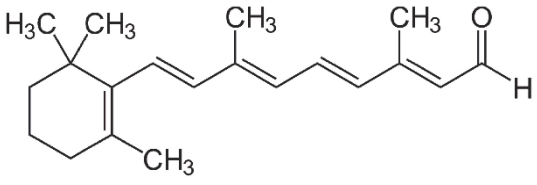


Fig. 2. The structure of retinal showing its head group and phytol-like tail. Most rhodopsins are barrel-shaped membrane spanning porins with the retinal head wrapped in its hydrocarbon tail in a pocket on the outer part of the protein (Baumann *et al.* 2014).

The roles of the two mechanisms could be tested in cells by illumination in the presence of DCMU, when linear electron flow between PSII and PSI is prevented. The remaining light-dependent H^+ efflux would be driven by the H^+-pumping rhodopsin or by cyclic electron flow around PSI: theoretically distinguishable by their action spectra; however, thus far, experimentally measured action spectra have not fully distinguished between these two means of H^+ energization (Choi *et al.* 2014).

The aerobic anoxygenic photosynthetic bacterium, *Fulvimarina pelagi*, contains bacteriorhodopsin- and xanthodopsin-based H^+ pumps (Kang *et al.* 2010) (Table 1). The archaean *Halobacterium halobium* with halorhodopsin (Matsuno-Yagi and Mukohata 1977, Schobert and Lanyi 1982) normally pumps Cl^- from the medium to the cytosol powered by green light, but halorhodopsin can also catalyse the downhill entry of H^+ using blue light (Hegemann *et al.* 1985, Oesterhelt *et al.* 1985, Bamberg *et al.* 1993). The flavobacterium *Nonlabens marinus* has a proteorhodopsin Cl^- pump, proteorhodopsin NM3, which evolved independently of the archaean Cl^- pump (Yoshizawa *et al.* 2014, Tsukamoto *et al.* 2017). Gaudana *et al.* (2014) suggested that cyanobacterial proteorhodopsin could be genetically engineered to catalyse active transport of HCO_3^- into cells, but this has not yet been achieved.

Table 1. Ion-pumping rhodopsins: phylogenetic distribution, nature of the ion pumped, wavelength of maximum absorption, and occurrence in organisms with chlorophyll-based photochemistry. Sources: Fuhrman *et al.* (2008), Raven (2009), Slamowitz *et al.* (2011), Inoue *et al.* (2013), Kirchman and Hanson (2013), Yoshikawa *et al.* (2014), Bogachev *et al.* (2016), Kato *et al.* (2016), Tsukamoto *et al.* (2017). [1]H^+-pumping proteorhodopsins occur in some oxygenic photosynthetic cyanobacteria (Gaudana *et al.* 2014); the *Gloeobacter* H^+-pumping rhodopsin is relatively distantly related to other proteorhodopsins and has been termed GR to distinguish it from PR (the core proteorhodopsins): Ganapathy *et al.* (2017). An H^+-pumping xanthorhodopsin is also found in an aerobic anoxygenic photoheterotrophic bacterium (Kang *et al.* 2010). [2]H^+-pumping proteorhodopsins occur in the oxygenic photosynthetic ulvophycean marine green alga *Acetabularia* (Raven 2009, Tsunuda *et al.* 2006), in some marine oxygenic photosynthetic diatoms (Slamowitz *et al.* 2011, Marchetti *et al.* 2012), and in some marine oxygenic photosynthetic dinoflagellates (Slamowitz *et al.* 2011, Marchetti *et al.* 2012) as well as some non-photosynthetic dinoflagellates (Slamowitz *et al.* 2011, Marchetti *et al.* 2012, Jahnke *et al.* 2013, Guo *et al.* 2014).

Category of ion-pumping rhodopsin	Wavelength of maximum absorption	Archaea	Bacteria	Eukarya
Bacteriorhodopsin	568 nm	+ (H^+)	-	-
Halorhodopsin	578 nm	+ (Cl^-)	-	-
Proteorhodopsin	490 nm or 525 nm	+ (H^+)	+ (H^+)[1] +(Na^+) + (Cl^-)	+ (H^+)[2]
Xanthorhodopsin	560 nm	-	+ (H^+)[1]	-

More recently, rhodopsins that pump Na^+ out of bacterial cells have been found to pump H^+ in the same direction in the absence of Na^+ (Inoue *et al.* 2013, Bogachev *et al.* 2016, Kato *et al.* 2016, Suomovuori *et al.* 2017). *Nonlabens marinus* also has a proteorhodopsin H^+ efflux pump (NM1) and a proteorhodopsin Na^+ efflux pump (NM2), as well as the Cl^- pump NM3 mentioned above (Yoshizawa *et al.* 2014), as well as the Cl^-. There are two possible exceptions in eukaryotes to the paradigm that ion-pumping rhodopsins catalyse H^+ or Na^+ efflux, or Cl^- influx, at the plasmalemma. One is the work of Tsunuda *et al.* (2006), who examined the proteorhodopsin of the marine ulvophycean *Acetabularia acetabulum* (formerly *A. mediterreana*). When the proteorhodopsin was heterologously expressed (in *Xenopus oocytes*) it pumped H^+ from the cytosol to the medium, although this proteorhodopsin expressed in *Acetabularia acetabulum* catalyses an inwardly-directed, downhill, current carried by H^+. The other example is proteorhodopsin of the phagotrophic, non-photosynthetic dinoflagellate *Oxyrrhis marina* (Jahnke *et al.* 2013), which is apparently expressed in the endomembrane system where it operates in the topologically identical manner to efflux across the plasmalemma, *i.e.* from a compartment of high protein diversity to a compartment of low protein diversity. This would acidify the endomembrane lumen and possibly aid digestion in food vacuoles if proteases with acid pH optima exist (Slamovitz *et al.* 2011). Such food vacuole acidification could help to explain the increased survival of starving *Oxyrrhis marina* in the light relative to that in the dark (Guo *et al.* 2014) (Table 1).

Longer light survival than dark survival of cells expressing ion-pumping rhodopsins has been more widely documented for Archaea and Bacteria (Fuhrman *et al.* 2008, Kirchman and Hanson 2013), as is the case for aerobic anoxygenic photosynthetic bacteria (AAPB) with BChl-based photochemistry (Kirchman and Hanson 2013). More direct estimates of the role of light than simple survival tests are needed: for example, nobody appears to have attempted to measure photosynthetic electron transport rates (pETR) in cultured AAPBs using PAM fluorometry, which is known to work in a variety of RC-2 type photosynthetic bacteria (Ritchie 2013, Ritchie and Runcie 2013, Ritchie and Mekjinda 2015). This might be technically difficult because AAPB bacteria have very low amounts of BChls per cell. Nevertheless, it seems feasible because it has been shown that there is a correlation of 800-nm fluorescence at the ocean surface with the BChl content (Kolber *et al.* 2000, 2001). In the cases of both the ion-pumping rhodopsin-based and BChl-based systems there are rather fewer cases of light-stimulation of growth (Kirchman and Hanson 2013, Pinhassi *et al.* 2016). The analysis of Kirchman and Hanson (2013) shows that the net energy gain (energy harvested, corrected for the cost of production of the light energy transduction apparatus) is greater for BChl-based than rhodopsin-based systems. This difference between

the BChl-based and rhodopsin-based energy transduction systems is reflected in both contributions to maintenance costs, and to growth rates (Gómez-Consarnau *et al.* 2007, 2010; Fuhrman *et al.* 2008, Kirchman and Hanson 2013, Courties *et al.* 2015). Ferrera *et al.* (2017) showed, for the first time, that light enhances growth of aerobic anoxygenic phototrophic (AAPB) in natural populations. An important point is that organisms with rhodopsin-based energy transduction lack the machinery specific to autotrophic CO_2 assimilation (Palovaara *et al.* 2014), unless the organism also has oxygenic photosynthesis. Aerobic anoxygenic photosynthetic bacteria also lack the machinery specific to autotrophic CO_2 assimilation (Fuchs *et al.* 2007, Li *et al.* 2013, Zeng *et al.* 2013, Mathusamy *et al.* 2014, Zheng *et al.* 2015) and so live photoheterotrophically.

The absorption maxima are 490 nm for the blue-absorbing proteorhodopsins, 525 nm for the green-absorbing proteorhodopsins, 560 nm for xanthorhodopsin, 568 nm for bacteriorhodopsin, and 578 nm for halorhodopsin (Fuhrman *et al.* 2008). The energy of 490-nm photons is 244 kJ mol^{-1}(photon), and for 578-nm photons it is 207 kJ mol^{-1}(photon). The largest H^+ electrochemical potential difference generated across a membrane by a H^+-pumping rhodopsin is 27 kJ mol^{-1} in the archaean *Halobacterium halobium* in the presence of N,N'-dicyclohexylcarbodiimide (DCCD), which limits the re-entry of the H^+ pumped out of the cells (Michel and Oesterhelt 1980). In comparing the energy per photon with the maximum energy stored in the ion gradient it is important to consider the photon efficiency of the light-driven pumps. For BChl the quantum efficiency of H^+ transport was determined by Govindjee *et al.* (1990) as 0.64 ± 0.04, with previously published values in the range of 0.3–0.79 (Hagemann *et al.* 1985, Oesterhelt *et al.* 1985).

As indicated above, organisms with ion-pumping rhodopsins lack photoautotrophic CO_2-assimilating machinery unless the rhodopsins occur in organisms with Chl-based photosynthetic autotrophy (*e.g.* oxygenic photosynthesis as in *Gloeobacter violaceous*). However, it is worth exploring the "what if" question of the energy, as photons, cost of autotrophic CO_2 fixation with ion-pumping rhodopsins as the light energy transducers. For comparison with a (bacterio)chlorophyll-based photosynthetic system, the purple proteobacterial anoxygenic photosynthetic system is used because here light energy transduction is also solely through H^+-pumping in cyclic electron flow, around its PSII-like photosystem (Klamt *et al.* 2008, Feniouk and Junge 2009, Nicholls and Ferguson 2013). In both cases an electron donor capable of reducing ubiquinone is used, as is autotrophic CO_2 fixation using the Benson-Calvin cycle in the absence of O_2 with a ratio of 3 ATP:2 NADH:1 CO_2. The absence of O_2 is essential for the synthesis of BChl in anoxygenic photosynthetic bacteria and is consistent with the presence of S^{2-} or other reductants of similar or lower redox potential as an electron donor able to reduce ubiquinone. Many photosynthetic bacteria will grow quite well in an unstirred conical flask open to the atmosphere because such a culture has redox gradients near the surface of the culture: thus lower levels of the culture are suitable for BChl synthesis and most photosynthetic bacteria are highly motile. If such cultures are aerated over several hours they turn white. Photosynthetic electron transport can be demonstrated in anaerobic anoxygenic photosynthetic bacteria filtered onto filter disks under atmospheric oxygen concentrations (Ritchie 2013, Ritchie and Runcie 2013, Ritchie and Mekjinda 2015) even though they require anoxic conditions to actually make BChl. Streaks on aerobically incubated agar plates typically appear white on the edges with a pink interior. This explains why anoxygenic photosynthetic bacterial blooms often occur on the surfaces of mudflats, on lake surfaces and particularly in sewage and wastewater ponds (Ritchie *et al.* 2017). The metropolitan sewage pond in Phuket in Thailand has a floating photosynthetic bacterium: just about the least likely organism one would expect to encounter in today's modern atmosphere (Ritchie, unpublished). Aerobic anoxygenic photosynthetic bacteria are obligately aerobic for growth (Yurkov and Beatty 1998). They only synthesise BChl in the dark (*e.g.* the dark phase of the light–dark cycle). While BChl is obviously only used in photochemistry in the light (*e.g.* the light phase of the light–dark cycle), BChl is also lost in the light as a result of dilution in growth, rather than breakdown in the absence of synthesis (Yurkov and Beatty 1998).

For the proteobacterial anoxygenic PS bacteria it is assumed that one photon absorbed by the photosynthetic pigments moves one electron from reduced cytochrome *c* to ubiquinone. Cyclic electron flow returns the electron from ubiquinol to oxidised cytochrome *c* and pumps 2 H^+ from the cytosol to the thylakoid lumen or the external medium. Each electron moved from ubiquinol (produced by reduction of ubiquinone by S^{2-}) to NAD^+ by a NADH-ubiquinone oxidoreductase involves 2 H^+ moving from the thylakoid lumen or the external medium to the cytosol (Klamt *et al.* 2008, Nichols and Ferguson 2013). The reduction of 2 NAD^+ to 2 NADH therefore needs 4 photons. With an H^+:ATP ratio of 3.3 for the F_oF_1 ATP synthase (Klamt *et al.* 2008, Feniouk and Junge 2009, Nicholls and Ferguson 2013) the production of 3 ATP needs 10 H^+ moving from the thylakoid lumen or the external medium to the cytosol, involving 5 photons. The photon costs of the production of the 2 NADH and 3 ATP used to reduce 1 CO_2 to the redox level of carbohydrate means that the autotrophic assimilation of 1 CO_2 requires 9 absorbed photons. This is a lower limit of the photon cost, since the photon cost of moving an electron from reduced cytochrome *c* to ubiquinone in purple photosynthetic proteobacteria using their PSII-like photosystem is 0.3–0.6 electrons moved per mol(photon absorbed) as estimated from fluorescence studies (Kolber *et al.* 2000). This is consistent with maximum photosynthetic efficiencies found in photosynthetic bacteria by PAM fluorometry (Ritchie 2013, Ritchie and Runcie 2013,

Ritchie and Mekjinda 2015). However, a direct estimate of the photon cost of photochemistry of *Rhodopseudomonas spheroides* gives a value not statistically distinguishable from 1.0 (*see* above), contrasting with the directly comparable fluorescence-derived value of 0.7 (Wraight and Clayton 1974).

Turning to the hypothetical case of autotrophic CO_2 assimilation with energization using a H^+-pumping rhodopsin, we assume one H^+ pumped per photon absorbed (a low photon cost relative to the measured values discussed above) and make all the assumptions on the use of the H^+ gradient in generating 2 NADH and 3 ATP as were made above for the anoxygenic BChl-based system in proteobacteria. The outcome is that the conversion of 1 CO_2 to the redox level of carbohydrate means that the autotrophic assimilation of 1 CO_2 would require 18 absorbed photons. In such a system NADH would have to be made by processes unrelated to the photochemical reactions. In the case of RC-2 photosynthetic organisms, the photosynthetic electron transport chain makes ATP and not NADH, so NADH has to be otherwise manufactured: estimates of the number of photons required to fix CO_2 using RC-1 photosynthesis are about 11 but this rises to about 16 to 18 in the case of RC-2 organisms (Ritchie *et al.* 2017).

For comparison, Raven *et al.* (2014) calculated a minimum absorbed photon cost of 9.9–11.0 photons per CO_2 conversion to fixed carbon (CH_2O) for oxygenic photosynthetic organisms, depending on the inorganic acquisition pathway. Raven *et al.* (2014) made the following assumptions:

(*1*) One electron moved through PSI per photon absorbed by that photosystem, and 0.8 electron moved through PSII per photon absorbed by that photosystem.

(*2*) 3 H^+ moved from the stroma (eukaryotes) or cytosol (cyanobacteria) to the thylakoid lumen per electron moving from H_2O to a neutral (CO_2 or O_2) in linear electron flow.

(*3*) 4 H^+ moved from the stroma (eukaryotes) or cytosol (cyanobacteria) to the thylakoid lumen per electron cycling in cyclic electron flow passing from reduced ferredoxin to oxidised cytochrome c_6 or oxidised plastocyanin.

(*4*) 4 H^+ moved from the thylakoid lumen to the stroma (eukaryote) or cytosol (cyanobacteria) per ATP produced from ADP plus phosphate.

(*5*) Where a CO_2 concentrating mechanism is used, half of the CO_2 accumulated round Rubisco leaks back to the medium.

The assumptions all minimize the photon cost of CO_2 conversion to fixed carbon (CH_2O), apart from assumption (*5*) where there are values of CO_2 leakage below 0.5, decreasing energy costs, as well as values above 0.5.

To summarise, the predicted minimum absorbed photon cost of 1 CO_2 conversion to 1 (CH_2O) with H_2S as electron donor and proteorhodopsin photochemistry is ≈18, much greater than the minimum value of ≈11 for Type 1 (RC-1, PSI-like) BChl photochemistry and is about the same as estimates of about 16 to 18 for Type 2 (RC-2, PSII-like) photochemistry (*see* Ritchie *et al.* 2017 for a discussion), and the minimum values of 9.9–11.0 for the Chl *a* photochemistry of oxygenic photolithotrophy with H_2O as the electron donor. Thus, the ability to make NADH as part of the photochemistry of PSII/PSI oxygenic photosynthesis and RC-1 photosynthesis cuts the photon requirement for carbon fixation by about half compared to RC-2 organisms.

(Bacterio)chlorophylls

For all BChls energy loss occurs, since photons absorbed at the shorter wavelength (Soret absorption, Q_X band, second excited state) can only pass on energy *via* the first excited state (Q_Y) in the (infra)red in photochemistry (Scheer 2006). There are also absorption losses (Ritchie and Runcie 2014) that need to be measured either with a reflectance-absorptance-transmission (RAT) apparatus or using integrating sphere spectroscopy (Ritchie 2013, Ritchie and Runcie 2013, Ritchie and Mekjinda 2015). Williams and Laurens (2010) calculated a 20% loss of absorbed energy in this conversion for 400→700 nm. In lamentable ignorance of this paper, Raven and Donnelly (2013) did the calculation for 350→700 nm and found 21% loss. Zhu *et al.* (2008) just used the difference in energy between the first and second excited states of Chl *a*, rather than integrating the absorption over the 400–700 nm, or 350–700 nm, to calculate a minimum loss of 6.6% of the incident solar radiation. The energy loss as a fraction of the total absorbed photons must be greater for BChl-based photochemistry with longer wavelengths for photochemistry. For organisms with RC-1 reaction centres the wavelengths are 798 nm (Heliobacteria) and 840 nm (Chlorobi), while for RC-2 reaction centres, the wavelengths are 865 nm (Chloroflexi) and 850 or 880 nm (Proteobacteria) (Blankenship *et al.* 1995, Ritchie *et al.* 2017). Figs. 6 and 7 show absorptance curves for four different anoxygenic photosynthetic bacteria. All are very good at harvesting blue light, using the Soret (Q_X) band, and perform at least as well as oxygenic organisms (Figs. 4, 5). Q_Y band absorption, although useful as a selection mechanism in the microbiology laboratory (using NIR diodes or incandescent light bulbs) may give a misleading picture of what light these organisms are actually using in nature (Ritchie *et al.* 2017). Action spectra based on simple growth experiments under different irradiances can be highly informative (Hellingwerf *et al.* 1982) because action spectra using PAM methods would be very difficult for technical reasons.

Relation of the wavelength at which photochemistry occurs to the incident photon spectrum, both where the organisms occur today, and where and when they evolved

Ion-pumping rhodopsins

As indicated above, the range for absorption maxima for naturally occurring energy-transducing rhodopsins is from 490 to 578 nm (Fuhrman *et al.* 2008). The red-sensitive cone photoreceptor rhodopsins of vertebrate retinas have absorption maxima in the range of 552–620 nm (Havosi 1976, Bowmaker *et al.* 1980, Merbs and Nathans 1992). No known naturally occurring ion-pumping rhodopsins have absorption maxima red-shifted to 620 nm or greater wavelengths. However, constructs involving genetic modification of opsins from proteorhodopsins and retinal analogues, such as 3-methylamino-16-nor-1,2,3,4-dihydro-retinal (MMAR) (compare to Fig. 2), have red shifts of the absorption maxima of up to 200 nm (Ganapathy *et al.* 2017). However, the present constructs have relatively low H^+- pumping specific reaction rates at light saturation (Ganapathy *et al.* 2017), and there appear to be no published measurements of the photon yield of H^+ pumping by the constructs.

The organisms with energy-transducing rhodopsins are found on the surfaces of leaves of terrestrial plants (Atamna-Ismaeel *et al.* 2012) and in/on soils (Finkel *et al.* 2013) as well as in freshwater and brackish habitats (Atamno-Ismaeel *et al.* 2008). They also occur in marine environments (Béjà *et al.* 2001, Man *et al.* 2003, Tsunuda *et al.* 2006, Gómez-Consarnau *et al.* 2007, Sabehi *et al.* 2007, Slamowitz *et al.* 2011, Inouye *et al.* 2013, Janke *et al.* 2013, Kirchman and Hanson 2013, Guo *et al.* 2014, Palovaara *et al.* 2014, Bogachev *et al.* 2016), hypersaline habitats (Michel and Oesterhelt 1980, Oesterhelt *et al.* 1980, Hegemann *et al.* 1985, Bamberg *et al.* 1993), and within marine stromatolites (Albarracin *et al.* 2016). Some of the data on the occurrence of energy-transducing rhodopsins depend solely on genomic data, but transcriptomics data are available for some, and ion-pumping has been shown experimentally for only a few of the rhodopsins thought to be energy-transducing based on genomics data (references in previous sentence).

Bacteria with ion-pumping rhodopsins that occur on the adaxial surface of leaves at the top of the canopy, and on the soil surface, are exposed to the solar spectrum as modified by the atmosphere (Figs. 4, 5) (Jones 2013). Ion-pumping rhodopsins below terrestrial plant canopies, and those in water bodies, are subjected to a solar spectrum significantly modified by absorption by organisms, water, and chemical substances (Falkowski and Raven 2007, Kirk 2011). There are some correlations of spectral absorption and habitat, with green-absorbing ion-pumping rhodopsins nearer the surface of the ocean, and blue-absorbing forms deeper in the ocean (Man *et al.* 2003, Sabehi *et al.* 2007). For the data from the extremely oligotrophic Eastern Mediterranean *see* Pinhassi *et al.* (2016). Furthermore, green-absorbing ion-pumping rhodopsins are more common in coastal marine waters and blue-absorbing forms predominate in the open ocean (Brindefalk *et al.* 2016, Pinhassi *et al.* 2016). However, in the Sargasso Sea, blue-absorbing forms occur at all depths (data of Sabehi *et al.* 2007, Pinassi *et al.* 2016), and both green- and blue-absorbing forms occur in the brine channels of sea ice at the surface of the Antarctic Ocean (Kohl *et al.* 2010); the green form predominates, while the blue form occurs in the mid-section of the ice. The green form of proteorhodopsin occurs in marine stromatolites (Albracin *et al.* 2016).

Light stimulation of growth of the proteorhopsin-expressing psychrophilic *Psychroflexus torquis* increases with increasing salinity (Feng *et al.* 2013), consistent with additional involvement of ion-pumping rhodopsins when the bacteria are incorporated into brine channels of sea ice. Proteorhodopsin transcripts in marine diatoms from Fe-limited habitats are increased when Fe is limiting the growth rate in cultures (Marchetti *et al.* 2012). This increased expression could relate to the much lower Fe cost of energy transduction than that of alternatives, such as photosynthetic and oxidative phosphorylation, both processes have heavy Fe requirements for synthesis of cytochromes (Raven 2009, Marchetti *et al.* 2012).

There is evidence of (positive) selection of proteorhodopsin in response to different irradiances (Bieliwski *et al.* 2004), and directed evolution has been shown for spectral properties of the proteorhodopsin of the oxygenic photosynthetic cyanobacterium *Gloeobacter violaceous* (Engquist *et al.* 2015). Redistribution of pre-existing genetic variants of proteorhodopsins by horizontal gene transfer has clearly taken place, *e.g.* from a marine planktonic bacterium to an Archaean (Friggard *et al.* 2006). One mechanism of horizontal transmission is *via* viruses, since proteorhodopsin sequences are found in giant viruses of eukaryotic microorganisms (Yutin and Koonin 2012, Brindefalk *et al.* 2016). The prediction by Yutin and Koonin (2012) of the function of the viral proteorhodopsins is that they are primarily for sensory signalling (as electrical potential) rather than bulk ion-pumping, but *see* Brindefalk *et al.* (2016).

Although it has been suggested that ion-pumping rhodopsins evolved before (bacterio)chlorophyll-based photosynthesis (*e.g.* Raven and Smith 1981, Sparks *et al.* 2007), there seem to be no estimates of when the ion-pumping rhodopsins evolved. The question might never be satisfactorily resolved because both rhodopsins and Chls evolved very early in evolutionary history where it is not possible to accurately calibrate molecular clocks.

(Bacterio)chlorophylls
Chlorophyll *a*
General features

Much has been written on the "greenness" of Chl *a*, and the "red edge" effect, *i.e.* a large decrease in absorption of vegetation above about 700 nm (Figs. 4, 5) and the associated wavelengths of photochemistry of PSI (700 nm) and PSII (680 nm) (Mauzerall 1973, Björn 1976, Nishio 2000, Raven and Wolstencroft 2002, Wolstencroft and Raven 2002, Kiang *et al.* 2007a,b; Stomp *et al.* 2007, Björn *et al.* 2009, Milo 2009, Raven 2009, Marosvölgyi and van Gorkum 2010, van Hohman-Mariott and Blankenship 2011, Kume *et al.* 2016, Kume 2017, Ritchie *et al.* 2017). The red drop is often suggested as a diagnostic test for the presence of land-based vegetation on an extrasolar planet but Ritchie *et al.* (2017) pointed out that its application is not as straightforward as it might appear. Björn *et al.* (2009) cite Sir Walter Rayleigh as asking ''Man cannot give a true reason for the green under our feet. Why it should be green, rather than red or some other colour". The ability to distinguish green has been demonstrated in pre-verbal infants with normal colour vision (Skelton *et al.* 2017), so distinguishing 'green' in the visible spectrum is not just by lexical convention.

The blue and red absorption maxima, of *in vivo* Chl *a*, with a green minimum (Figs. 6, 7), has been criticized in natural selection terms since the maximum solar radiant energy output is in the green part of the spectrum although the solar spectrum is very flat in the region from 450 to 761 nm (Fig. 3). But it can be assumed that BChl (or Chl) photosynthesis evolved as a more efficient mechanism available in early organisms to power photon capture rather than by total radiant energy, and therefore the relevant aspect of solar radiation is the maximum of photon emission in the orange–red (*e.g.* Wolstencroft and Raven 2002, Kiang *et al.* 2007a,b) (Figs. 3–7). These considerations apply most clearly to Chl *a* (but also to BChl) at infinite dilution; for higher Chl contents in the light path the package effect (Duysens 1956) becomes more important. The absorption minimum in green light does not imply that green light cannot drive photo-synthesis; it simply means that green photons are absorbed inefficiently. Deepwater algae typically have very high contents of Chls such that they have an absorptance >90% in the blue (400 nm) under the spectrum of light in very deep water (>100 m, Fig. 3) (Runcie *et al.* 2008). At an individual cell level, there is increased absorption of PAR with increased cell size at a given pigment concentration, and with an increased pigment concentration in a given cell size (Duysens 1956, Kirk 2011). This increased package effect is most significant at absorption peaks, and means that Chl *a* has a lower ratio of blue to green, or red to green, absorption (Duysens 1956, Kirk 2011). The greater absorptance of Chls in the blue and red than in the green

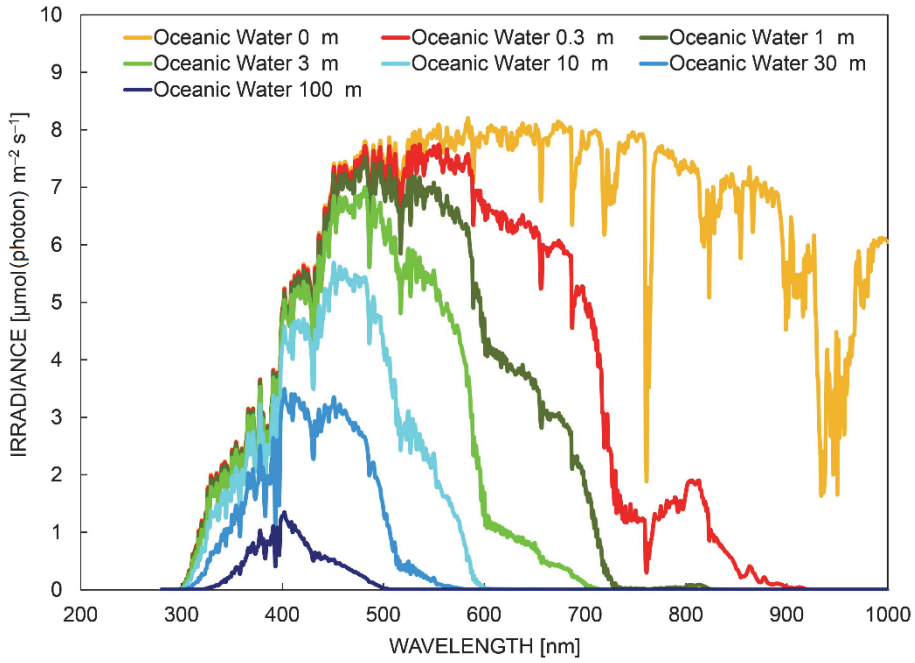


Fig. 3. The total emission spectra of the Sun [µmol(photon) m^{-2} s^{-1} nm^{-1}] at the top of the atmosphere (TOA) of the Earth based on the *SMARTS* (2011) software for the Equator at noon equinox decrease in irradiance *vs*. depth in deep water for Earth. Near infrared (750–799 nm) and infrared (I) (800–949 nm) and infrared II (950–1,100 nm) is largely eliminated in less than 0.3 m of water and completely eliminated in 1 m of water. Most far red light and then red light is absorbed in very shallow water and so the irradiance spectrum changes rapidly with depth. As depth increases longer wavelengths are progressively eliminated: infrared (II) → infrared (I) → near infrared → far red → red → orange → green. Violet light is also progressively eliminated in deep water leaving blue light centred on a wavelength of 400 nm. (From Ritchie *et al.* 2017 with permission Cambridge Press©).

spectral region means that, with increasing Chl per unit area exposed to the radiation, the photon absorption increases with photon flux density more rapidly in the blue and red than in the green (Duysens 1956, Kirk 1975a,b; 1976; Morel and Bricaud 1981, 1986; Kirk 2011). The dependence of the package effect on the size of single cells (taking into account the spectral distribution of incident photosynthetically active radiation), and of colonies and organisms, has important physiological and ecological consequences (Kirk 1975a,b; 1976, 2011; Morel and Bricaud 1981, 1986; Falkowski and Raven 2007).

Ecological considerations of mats and single cells

The size of the smallest free-living cells is determined by a variety of non-scalable components, including the number of genes, required for a given trophic mode (Pirie 1964, 1973; Raven 1986a, 1986b, 1998, 1999; Raven *et al.* 2009, 2013a). The smallest picoplanktonic cyanobacterial cells (*Prochlorococcus* spp.) and oxygenic eukaryotic cells (*Ostreococcus* spp., Prasinophyceae *sensu lato*) have minimum equivalent spherical diameters of about 0.5 μm and 0.9 μm, respectively, or similar to that of photosynthetically useful light (Raven *et al.* 2013). These organisms have minimal package effects, so, for a vector radiation field, there is a minimal difference in PAR between the side of the cell nearest, and furthest from, the light source. This has relevance to the enhancement of photosynthesis, under certain circumstances, by temporally fluctuating PAR. Thus, while the frequency of rotation of the cells resulting from small-scale thermally-driven water movements is in the range that might cause stimulation of photosynthesis, the limited PAR gradient across small cells means that these natural rotations cannot stimulate photosynthesis as a result of fluctuating PAR (Raven 1998, 1999; Raven and Ralph 2015). Fluctuating light is perceived to be disadvantageous for photosynthesis because it takes time for reaction centres to open and close and during the adjustment phase the potential photosynthetic activity mismatches the light available (Greene and Gerard 1990, Kübler *et al.* 1996, Litchman *et al.* 2000, Raven and Ralph 2015). One consequence is that sunflecks cannot easily be optimally utilised if the frequency of change of irradiance is too high (Kübler *et al.* 1996).

As cell size increases with a constant pigment per cell volume and constant cell geometry, the package effect increases with cell size (Duysens 1956, Kirk 1975a,b; 1976, Morel and Bricaud 1981, 1986; Raven 1984, 1986a,b; 1998, 1999). However, the photosynthetic pigment per unit volume decreases with cell size in eukaryotic microalgal cells (Raven 1984, Agusti and Phlips 1992, Beardall *et al.* 2009, Finkel *et al.* 2010). The small range of cyanobacterial unicell sizes available show no size dependence upon pigment per unit volume (Agusti and Phlips 1992). Cyanobacterial colonies, like eukaryotic algal unicells, show a decrease in pigment per unit volume with increasing size (Agusti and Phlips 1992, Gao and Ai 2004).

In macroalgae there are many published *in vivo* spectra of photon absorptance [Abt_λ = incident PAR set to 100, minus reflectance (%) minus transmittance (%)] (Haxo and Blinks 1950, Fork and Amesz 1969, Lűning and Dring 1985, Gómez and Huovinen 2011, Lichtenberg *et al.* 2015, Vásquez-Elizondo *et al.* 2017), showing a flattening of the spectra relative to that of dilute solutions of the extracted pigments. The flattening is greater for spatially and optically thicker tissues. The spectrally averaged absorptance is, as predicted, greater for thicker thalli with absorptance values up to 0.95 in the thicker thalli (Frost-Christensen and Sand-Jensen 1992, Markager and Sand-Jensen 1992, Markager 1993, Enríquez *et al.* 1994, Gómez and Huovinen 2011, Vásquez-Elizondo *et al.* 2017). Very high absorptance values (> 0.90) are found for the Phaeophyceae (Lűning and Dring 1985, Gómez and Huovinen 2011), Rhodophyta (Gómez and Huovinen 2011), and Ulvophyceae (Lűning and Dring 1985, Vásquez-Elizondo *et al.* 2017). The much higher absorptances of thicker thalli of macroalgae means that the some thalli of all three clades with their different photosynthetic 'accessory' pigments have very low reflectance and minimal spectral variation in reflectance and appear almost black, hence the suggestion (references and discussion in Raven and Hurd 2012) that the younger stages of algae (with smaller spatial and optical thickness) are more useful than older stages in assigning an alga to its pigment category, *i.e.* clade. The absorptances of macroalgal thalli has implications for their photon yield on an absorbed photon basis (*e.g.* Lűning and Dring 1985) and hence on the distribution of benthic macroalgae with depth and the interactions among algae (Dring and Lűning 1985, Binzer and Sand-Jensen 2002, Tait *et al.* 2014, 2017). The old paradigm of chromatic adaptation amongst green, brown, and red benthic algae was shown to be wrong long ago (Crossett *et al.* 1963); but nevertheless red algae do predominate at the greater depths in the sea because crustose coralline algae have evolved to live in low light with low metabolic rates (Larkum and Barrett 1983). Microalgae and photosynthetic bacteria filtered onto glass fibre discs to act as artificial algal mats for PAM studies can be used to simulate similar optical properties (Ritchie 2013, 2014; Ritchie and Runcie 2013, 2014; Ritchie and Mekjinda 2014).

Terrestrial embryophytes with leaves

For terrestrial tracheophytes, Jones (2013) cites a mean PAR leaf absorptance of 0.85. Some higher values are known, *e.g*. 0.896–0.925 for four species of tropical rain forest species at different vertical positions in the canopy (Poorter *et al.* 1995), and 0.875–0.917 for sun leaves, and 0.869–0.939 for shade leaves of 13 species of cloud forest trees (Poorter *et al.* 2000). Among aquatic tracheophytes, Durako (2007) found lower absorptance values (0.45–0.68) for eight species of Australian seagrass. Absorptances at the red and blue peaks of Chl in leaves of terrestrial tracheophyte can be considerably higher and approach 1.0 (Ritchie and Runcie 2014) even though red-green-blue (RGB) averages for "white" light are usually about 0.85: white light absorptance can hence be misleading, particularly for understory plants which experience irradiance depleted in blue and red light [similar to the effect on lower cell layers in a microbial mat composed of green Chl (*a*+*b*) cells; Kühl and Fenchel 2000, Hubas *et al.* 2011, Ohkubo *et al.* 2017)].

There are resource cost-benefit reasons that put an upper limit on the tissue absorptance and these are related to the package effect. It is relatively easy to make a small cell (< 10 μm) optically black using high pigment concentrations but not large vacuolated cells. The energy cost of synthesis and maintenance of photochemical and light-harvesting pigment–protein complexes must not exceed the energy usable from the photons absorbed by the complexes over their lifetime (Raven 1984, Raven and Hurd 2012). There are also considerations of the other resource costs, *e.g*. carbon, nitrogen (as a component of amino acids but also through the RNA needed for protein synthesis), and phosphorus. Overloading with pigment would hence be selected against except in habitats where very slow growth is not a disadvantage (cryptic habitats, low light environments in caves and in very deep water) (Raven 1984, Raven and Cockell 2006, Runcie *et al.* 2008, Cockell *et al.* 2009).

In summary, the solar spectral irradiance incident on the top of vegetation canopies on land, or at the ocean surface becomes modified: on land the spectrum is modified by layering of plants whether the vegetation is terrestrial plants in a forest or layering in a microbial mat; in aquatic environments water depth modifies the spectrum considerably, depending on chemical sustances in the water and the density and type of phytoplankton in the water column (Fig. 3). Differential absorption of blue and red photons by Chl *a*-dominated organisms (lacking phycobilins) enriches radiation deeper in the canopy or water body in the green region of the spectrum; in water bodies longer PAR wavelengths are absorbed by water itself and by organic solutes (yellow substance) in coastal marine and fresh waters (Falkowski and Raven 2007, Kiang *et al.* 2007a,b; Stomp *et al.* 2007, Kirk 2011). At the algal or aquatic plant community level (Krause-Jensen and Sand-Jensen 1998), the overall package effect is greater than for the individual organisms since there are more moles of photosynthetic pigments per habitat area than for each organism. There is the possibility of complementarity of spectral absorptance between strata in the community, *e.g*. phycoerythrin-containing red algae with high absorptance in the green under brown algae or seagrasses with lower absorptances in the green than in the blue and red, thus limiting the influence of the package effect. However, the available evidence shows that this is not a significant effect (Dring 1981, Lüning 1990, Kirk 2011).

As is discussed below, these arguments need to be augmented when organisms with photochemistry catalysed by Chl *a* co-occur with those photosynthetic organisms absorbing beyond 700 nm, *e.g*. those with long-wavelength forms of Chl *a*, or with Chls *d* or *f*, as well as anoxygenic photosynthetic bacteria with BChl as commonly occurs in microbial mats, stromatolites and in wastewater ponds.

Photosynthesis in mats (including stromatolites)

Sparks *et al.* (2007) suggested that an early biological photochemistry using a green-absorbing ion-pumping rhodopsin could have been an evolutionary driver of BChls in photoredox biochemistry with absorption at shorter and longer wavelengths than the rhodopsin, thus limiting competition for light with the incumbent rhodopsin. However, the time of origin of ion-pumping rhodopsins is not clear (*see* above), and this hypothesis has not moved from a conference abstract (Sparks *et al.* 2007) to a peer-reviewed journal.

The relatively flat peak of photon emission in the present solar spectrum could be a consideration (Figs. 3–7), since the wavelengths at which RCs operate are just on the long wavelength side of the maximum photon emission peak at 669 nm on the ground on Earth (Wolstencroft and Raven 2002). The young Sun (a G-star) would have been cooler and dimmer than today and its spectrum would have been shifted to longer wavelengths, *i.e*. toward the spectrum of a K-star (*see* "Implications of a Faint Sun"). However, the total emission spectra of K-stars are not greatly different from G-stars except for a displacement of about 100 nm in the emission peak to the red end of the spectrum. Red Dwarfs, however, have a very different spectrum to the sun and differ considerably from that of a Planck black body because of absorption by compounds in the stellar atmospheres of Red Dwarfs (Ritchie *et al.* 2017).

Is the epi- or endolithic modern habit of *Gloeobacter* on land indicative of the Archaean habitat of the proto-

cyanobacteria, the first organisms to carry out photochemistry using Chl *a*. Blank and Sanchez-Baracaldo (2010) showed that *Gloeobacter* is basal among extant cyanobacteria, and Mareš *et al.* (2013) demonstrated that *Gloeobacter* is a widely distributed rock (*e.g*. limestone and dolomite) organisms. In addition to the type species *Gloeobacter violaceous,* another species, *Gloeobacter kilaueensis*, was described by Saw *et al.* (2013) growing on igneous rocks in lava caves at Kilaua in Hawai. The limited points available make calibration of molecular clock estimates of the timing of the origination of proto-/cyanobacteria (Mulkidjanian *et al.* 2006, Blank and Sanchez-Baracaldo 2010, Sanchez-Baracaldo *et al.* 2014, Butterfield 2015, Sanchez-Baracaldo 2015, Cardona 2016, Schirrmeister *et al.* 2016). Butterfield (2015) argues that extant cyanobacteria represent the crown group, while estimating the time of cyanobacterial origin from molecular clock requires that some extant cyanobacteria represent the stem group (Blank and Sanchez-Baracaldo 2010, Sanchez-Baracaldo *et al.* 2014, Schirrmeister *et al.* 2016).

More widely, cyanobacteria are also represented in the Terrabacteria, a large group of prokaryotes with ancestral adaptations to life on land (Battistuzzi *et al.* 2004, Battistuzzi and Hedges 2009). The terrabacterial adaptations to life on land include tolerance to desiccation, high PAR, high UV, and high salinity, and the clades involved are the Actinobacteria, Chloroflexi (anoxygenic photosynthetic organisms), the phylum Deinococcus-Thermus and Firmicutes as well as Cyanobacteria (Battistuzzi *et al.* 2004, Battistuzzi and Hedges 2009). More recently, it was found that the sister clade to the oxygenic Cyanobacteria is the newly characterised Melainabacteria (Soo *et al.* 2014, 2017). Soo *et al.* (2017) suggest that the ancestor to the Melainabacteria and what they term the Oxyphotobacteria (Cyanobacteria as understood elsewhere) was non-photosynthetic, *i.e*. the Melainabacteria did not lose photosynthesis so that photosynthesis in Cyanobacteria arose by horizontal gene transfer (Soo *et al.* 2014, 2017). Cardona (2016) and Cardona *et al.* (in review) dispute this, and argue for a much earlier occurrence of RCI and RCII in the same organism and for the evolution of oxygenic photosynthesis in the Archaean. It is probable that oxygenic photosynthesis arose early (before 3.0 Ga) even though there was no significant accumulation of O_2 in the atmosphere (>1% of present value) until the Great Oxidation Event (GOE) (*see* Ritchie *et al.* 2017).

Is a terrestrial (or shallow freshwater) origin of Chl *a*-based photochemistry possible, followed by early oxygenic photosynthesis? BChl-based photolithotrophic growth needs at least 0.01 μmol(photon) m^{-2} s^{-1} of photosynthetically active radiation (Raven *et al.* 2000), and hence the possibility of exposure to damaging solar UV. Beraldi-Campesi (2013), Raven *et al.* (2017), and Ritchie *et al.* (2017) point out that there is good evidence for life on terrestrial and very shallow water habitats more than 3 Ga ago and so the UV environment on the Earth's surface might have been more benign than usually envisaged. Indeed, Mulkidjaninan *et al.* (1997) argued that photosynthesis evolved out of early attempts to screen organisms from UV radiation. Alternatively, as Cockell and Raven (2008) and Raven *et al.* (2017) point out, endolithic or hypolithic components of terrestrial and very shallow fresh waters could have provided screening sufficient for the UV flux commonly associated with the low O_2 and O_3 atmosphere before the GOE.

The atmosphere before the GOE about 2.3 Ga ago had very low O_2, and probably also a low total atmospheric gas content and hence barometric pressure (Lyell 1851, Som *et al.* 2012, Som *et al.* 2016). While these mean that there would be, low O_3 and thus a minimal UV screen, there is evidence suggestive of O_2 >1% of the present value in the upper atmosphere in the Archaean (Tomkins *et al.* 2016) that could have generated O_3 under the influence of a weak young Sun's solar UV (Krauss *et al.* 2012, *see* "Implications of a Faint Sun"), thus producing a UV-absorbing screen. This O_2 might have been entirely of abiotic origin from the photolysis of water. Even without this, or UV-screening by atmospheric organic compounds, Cockell and Raven (2008) and Raven (2017) suggested that terrestrial photolithotrophic growth could have been possible for endolithic or hypolithic organisms, granted optical properties of the rocks such that attenuation of UV was much greater than that of photosynthetically active radiation. The basal extant cyanobacterium *Gloeobacter violaceous* grows endolithically as well as epilithically (Horath and Bachofen 2009).

There is evidence for the presence of trace concentrations of oxygen (Wellman and Strother 2015, Lenton and Daines 2017) from oxidative weathering and palaeosols of terrestrial biota from just over 3 Ga ago Meso-Archaean, and of terrestrial photosynthesis from organic carbon content and the natural abundance of stable carbon isotopes from 2.6 Ga, *i.e*. some 0.3 Ga before the GOE. This gives at least 300 Ma of terrestrial and potentially oxygenic photosynthesis before the large atmospheric, and oceanic surface, oxygen increase of the GOE; and many other workers in the field suggest a much longer timeline for the existence of oxygen-producing (proto-)cyanobacteria (*e.g*. Rosing *et al.* 2004, Cardona 2016).

Implications of a faint young Sun

What of the faint young Sun with lower effective temperatures, and hence longer wavelengths of maximum photon emission, than the present Sun (Claire *et al.* 2012)? There is only a small influence (power of –0.25) of effective surface temperature on the wavelength of maximum photon emission, so the rather flat photonic irradiance peak of the modern Sun (Fig. 3) would have been extended to only slightly longer wavelengths just

before the GOE than is the case today. The young Sun (G spectral type) would have had a spectrum slightly closer to that of a cooler star of K spectral type. The faint young Sun wavelength of maximum photon emission would have been on the short wavelength side of the 680 nm and 700 nm absorption maxima of the pigments doing the photochemistry of PSII and PSI for the great majority of oxygenic photosynthetic organisms with Chl *a* in the reaction centres of both photosystems. As discussed above, one major constraint on the wavelength of photons used in photochemistry is the energy content of the photons relative to the energetics of the reactions catalysed and as will be seen below slightly longer wavelengths for photochemistry occur in Chl *d*- and *f*-containing cyanobacteria, lower energy input to the reactions driven by the photochemistry has been shown to have little effect on the rate and efficiency of the reactions examined (Loughlin *et al.* 2013, Allakhverdiev *et al.* 2016).

The higher fraction of photons on the land and sea surface >700 nm under the weak young Sun might have favoured organisms with Chl *d* and *f* (*see* below) because reaction centres and LHCs equipped with Chl *d* or Chl *f* would have with red absorption maxima at longer wavelengths (Ritchie *et al.* 2017) but would have made attenuation of longer wavelength irradiance by water more severe than found today (Fig. 3). While the lower colour temperature of the young Sun means a lower steady UV flux at the top of the atmosphere, it is possible that greater periodic UV flare activity of the young Sun would mean an overall higher UV flux over long (millions of years) periods (Krauss *et al.* 2012). Flare activity is a major limitation for the habitability of planets of Red Dwarfs (Ritchie *et al.* 2017).

Cyanobacteria *vs.* eukaryotic algae

The capacity to make significant use of photons at >700 nm in photosynthetic O_2 production is not limited to cyanobacteria. Öquist (1969) cultivated the freshwater trebouxiophycean green alga *Chlorella pyrenoidosa* autotrophically under incandescent irradiation with a 0.1-m water filter. Growth was slower in the far-red cultures, and acclimation to the two radiation regimes was complete in six weeks (Öquist 1969). Exposure to infrared radiation increased the absorbance and the capacity for light-limited photosynthesis in the wavelength range 700–740 nm by about two-fold. However, the capacity for light-saturated photosynthesis (P_{max}) was lower for the infrared-grown cells. An Emerson enhancement effect has been shown for *Chlorella* acclimated (less likely to be genetically acclimated) to growth in far-red radiation (Öquist 1969). The increased rate of light-limited photosynthesis, when radiation was below 700 nm and above 700 nm are supplied simultaneously relative to the sum of the photosynthetic rates, when the two radiation regimes are supplied independently, occurred in both the far-red acclimated (adapted?) *Chlorella* cells and the control grown cells (Öquist 1969).

In some other eukaryotic algae there are genetic adaptations that enable increased photosynthesis in radiation regimes above 700 nm than is the case in the majority of eukaryotic algae. A long wavelength Chl *a*–apoprotein combination can energize PSII in the marine ulvophycean green alga *Ostreobium* sp. (Fork and Larkum 1989, Koehne *et al.* 1999, Wilhem and Jakob 2006), and the chromerophycean (Alveolata) marine *Chromera velia* (Bína *et al.* 2014, Katabova *et al.* 2014). Two species of the Eustigmatophyeae (Ochrista or Heterokontophyta) can also use photons >700 nm for photosynthesis; one is the freshwater planktonic *Trachydiscus minutus* (Prĭbyl *et al.* 2012, Pazderninik 2015). The one as yet un-named freshwater eustigmatophycean Forest Park Isolate 5 (FP5) has Chl *a* as the sole Chl but is able to grow when illuminated solely by 740 nm LEDs (Wolf *et al.* 2017). This ability means that one or more of the Chl *a*–protein complexes with significant absorbance >700 nm isolated from FP5 is associated with PSII (Wolf *et al.* 2017). Low rates of photosynthetic O_2 production occur out to 780 nm in the flowering plant *Helianthus annuus* and *Phaseolus vulgaris* (Pettai *et al.* 2005a,b) and PSII activity occurs out to 780 nm in the flowering plant *Spinacia oleracea* (Hughes *et al.* 2006, Thapper *et al.* 2009). Shlodder *et al.* (2014) showed that PSI activity can be excited by photons out to 808 nm; for wavelengths longer that 750 nm direct excitation of a charge transfer complex is proposed. There seem to have been no published attempts to demonstrate Emerson-type enhancement by far-red light in *Acaryochloris* even though it would yield important information about PSI/PSII in the organism.

The role of these long wavelengths in light harvesting involve uphill excitation energy transfer from wavelengths longer than that of the reaction centres, with a decreasing fraction of the absorbed energy from longer wavelength excitation reaching the reaction centre as the wavelength difference between incident radiation and the reaction centre increases (Nieuwenburg *et al.* 2003, Pettai *et al.* 2005b, Wilhelm and Jakob 2006, Mimuro *et al.* 2007, Toms *et al.* 2014, Behrend *et al.* 2015, Raven and Ralph 2015). As pointed out above, such mechanisms are thermodynamically possible but come at considerable thermodynamic cost.

Finally, it is necessary to relate the discussion above to that of other Chls, especially the redox active Chl *d*. The first excited states of Chl *a*, as moderated by apoproteins reaction centres of PII and PSII clearly energize $NADP^+$ reduction, H_2O oxidation, and associated H^+ pumping using 2 photons per electron, moderated by the maximal efficiency of ≈0.8 for PSII electron transfer per photon. The kinetics and efficiency of redox reactions are not markedly different in organisms with Chl *d* as opposed to

Chl *a*, in the sense of photochemical and maximal light-harvesting efficiency of the harvesting pigment (Allakhverdiev *et al.* 2016). This means that there is not an absolute energetic requirement to use Chl *a* in oxygenic photochemistry, as demonstrated by Chl *d* (*see* below) and there is a real possibility that Chl *f* could prove to be a third redox active chlorophyll.

Chlorophyll *b*

Chl *b* differs from Chl *a* in molecular structure in having a hydroxyl (OH) at position C7 on porphyrin ring B (Fig. 1) [instead of a methyl (CH_3) group]. This brings about a shift to the red in the Soret (Q_x) peak from 436 nm (in acetone solvent) to 465 nm and a similar shift *in vivo,* apparent in Fig. 4. In the Q_Y peak the shift is to the blue (batho-chromic) from 665 nm to 645 nm with a similar shift *in vivo* (Fig. 4). The overall effect is to narrow the gap in absorption of light between the Soret and Q_Y peaks of Chl *a*. Both shifts are significant and hence improve the light-harvesting ability of organisms that possess both pigments conjugated to a joint protein, since the peak wavelengths of Chl *b* augment those of Chl *a* and the energy is passed on efficiently to the RCs. Considering that MgDVP (and by inference the various types of Chl *c*), with only a small red-shift to ~452 nm (and only a small peak in the red region at about 630 nm), have been successful light-harvesting pigments (Raven 1996; and *see* below), Chl *b* must have been even more successful and this is borne out in terms of its widespread occurrence in nature, especially in embryophytes: however, in the oceans MgDVP and Chls *c* (*see* below) predominate, not only in numbers of species using them. However, in terms of biomass abundance: *Prochlorococcus,* with 'Chls (*a*+*b*)' has been one of the most successful organisms there; it has divinyl forms of Chls *a* and Chl *b*, and it also possesses MgDVP (Goericke and Repeta 1992, 1993; Ritchie *et al.* 2017) and therefore has the best of both worlds. It is true that a number of carotenoids harvest light efficiently in the blue region but the widespread occurrence of Chl *b* in these same organisms must mean that this pigment makes a strong contribution to gross productivity. In fact most light-harvesting Chl (LHC) proteins bind both Chl *a* and Chl *b*, as well as carotenoids, but, depending on the LHC and the organism, in different amounts (Larkum 2006). The overall effect, on land and in shallow aquatic

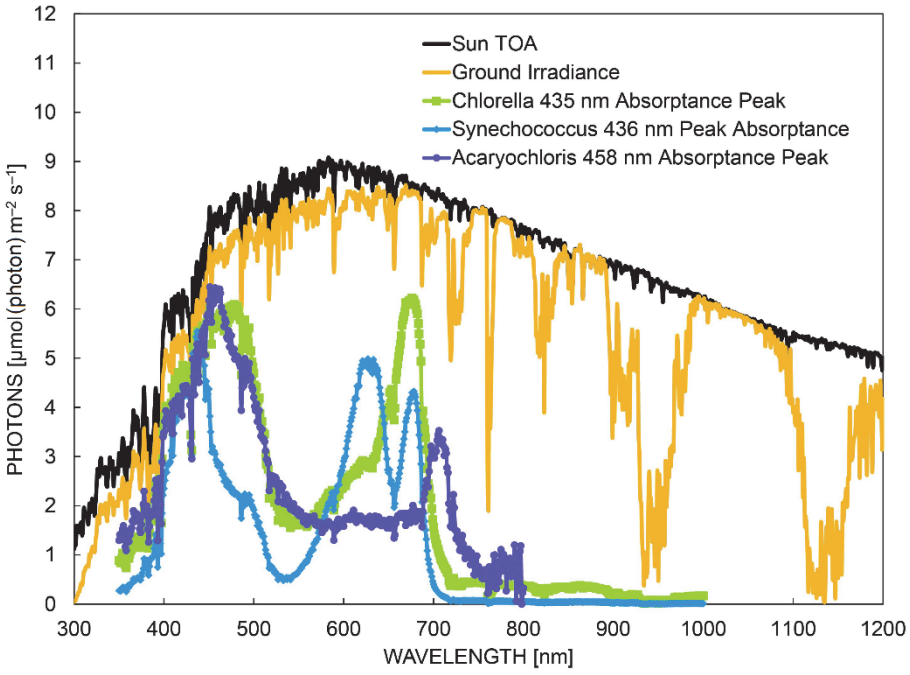


Fig. 4. The solar spectrum at ground level is from Fig. 3. *In vivo* absorptances (Abt) are based on integrating (Taylor) sphere measurements of the transmission (T, %) and reflectance (R, %) of cell suspensions. Measurements were made on two UV-VIS spectrophotometers fitted with a Taylor Sphere: *Model A&E-S90-2D* (*A&E Lab Co. Ltd*, London N14 5BP, U.K.) for *Chlorella* and *Synechococcus* and a *Shimadzu UV-2550* fitted with a *ISR-240A* Taylor Sphere (*Shimadzu Corp*., Kyoto, Japan) for *Acaryochloris*. Absorptance (Abt, %) was calculated as Abt% = 100 - T% - R%. Absorptances were standardised to 90% absorptance [Abt = Log_{10} (100/Abt%) = 1] at the pigment absorptance peak. *Synechococcus* has an absorptance peak at the blue peak for Chl *a* but it is very narrow compared to the blue absorptance peaks of *Chlorella* [Chl (*a*+*b*)] and *Acaryochloris* [Chl (*a*+*d*)] which extend from 350 to about 550 nm. *Synechococcus* has a strong absorptance band at 627 nm (very close to the ground-level maximum emission of the Sun) due to the non-chlorophyll blue pigment, phycocyanin, and a Q_Y band Chl *a* peak at 678 nm.

environments, of the presence of Chl *b in vivo,* is to help close the gap in light harvesting between the blue and red peaks of Chl *a* (Fig. 4), but while this results in only a "knee" on the shorter wavelength (bathochromic) side of the Chl *a* red peak it has a substantial effect in widening blue light absorption (in conjunction with carotenoids) towards longer wavelengths (Fig. 4) compared to cyanobacteria such as *Synechococcus*. Thus, the red-shift in the Soret band of Chl *b* is highly significant in increasing harvesting of light.

Interestingly, the cyanobacteria *Prochlorococcus*, *Prochloron*, and *Prochlorothrix* are the only cyanobacteria to have incorporated Chl *b* into their photosynthetic systems alongside Chl *a*. How Chl *b* evolved is not clear, but presumably it did so as a bioenergenically "cheaper" and perhaps space-saving light-harvesting adaptation that dispensed with phycobiliproteins (PBPs) in favour of Chl *b* in LHCs (Larkum 2003, 2006). Since PBPs are nitrogen expensive, because they are proteins, this strategy presumably evolved as a nitrogen conservation adaptation: and an important hint in support of this hypothesis is that none of the organisms mentioned have nitrogen fixation genes. Furthermore, *Prochlorococcus* and *Prochloron* live in environments where N is scarce (the first, most successfully, in deep layers of the ocean and the second in nitrogen poor coral reef waters, albeit in the cloacal cavity of didemnid ascidians). The special Chl *a*/*b*-binding proteins of *Prochlorococcus* and *Prochloron*, which are similar, have been identified (La Roche *et al.* 1996); and they are distinct from the family of proteins that conjugate Chl *a/b* and Chl *a/c* in eukaryotic algae and Chl *a/b* in terrestrial plants (La Roche *et al.* 1996). A similar protein complex exists in *Prochlorothrix* (Herbstova *et al.* 2010), although there it has also been shown that Chl *b* binds to a ring around PSI (Bumba *et al.* 2005, Boichenko *et al.* 2007).

In this discussion it is also relevant to discuss the presence of divinyl forms of Chls *a* and *b* (Fig. 1) in *Prochlorococcus* (Chisholm *et al.* 1992, Goericke and Repeta 1992, 1993). This chemical change modifies the absorption peaks. For the Soret peaks the shift is from 436 nm to 446 nm for divinyl Chl *a* and from 465 nm to 475 for divinyl Chl *b*. This means that for a deep-water phytoplankton organism the absorption spectrum in the blue band is widened and more closely matches the blue light spectrum of the ocean at depth for these organisms (Figs. 3, 8) (Goericke and Repeta 1993, Ritchie *et al.* 2017).

Chl *b* was somehow inherited by a group of eukaryotic algae collectively known as the green algae, *i.e.* Chlorophyta comprising the Palmophyllophyceae, Prasinophyceae, Chlorophyceae, Trebouxiophyceae, and Ulvophyceae, and the algal members (Charophyceae) of the Streptophyta (Kantz *et al.* 1990, Leliaert *et al.* 2016), with MgDVP in some Prasinophyceae. Thus, in eukaryotic algae Chl *b* is restricted to the Chlorophyta and Streptophyta, and secondary endosymbioses involving endosymbiosis of a chlorophyte alga: in the Chlorarachniophyta, in the Rhizaria, in Euglenophyta, and in the Excavata (Graham *et al.* 2016). The restriction of Chl *b* to these photosynthetic eukaryotes can be rationalised in terms of a single endosymbiotic primary plastid, *i.e.* a monophyletic Archaeplastida (Price *et al.* 2012, Sanchez-Báracaldo *et al.* 2017) with no lateral gene transfer (LGT). This requires the presence of both Chl *b* and phycobilins in the cyanobacterium ancestral to primary plastids (Tomitani *et al.* 1999), with loss of Chl *b* in the Glaucocystophyta and the Rhodophyta, and hence the algae that gained plastids by secondary endosymbiosis of red algae. Furthermore, it would require loss of MgDVP in the cyanobacterial ancestor of eukaryotic plastids; and its reappearance (by LGT?) in some prasinophytes (Larkum 2006) and the Palmophyllophyceae (Leliaert *et al.* 2016). The absence of PBP in the Chlorophyta and Streptophyta would require loss of PBPs at the origin of these clades. Another explanation is a polyphyletic origin of plastids, with multiple endosymbiosis, but also with much LGT (Larkum *et al.* 2007). Monophyly does not preclude the involvement of LGT.

It could be coincidental (Gould and Lewontin 1979) that the group of algae which gave rise to land plants (embryophytes) came from one group of Chlorophyta, the streptophytes with Chl (*a*+*b*) (Waters 2003, Raven 2017). Thus, the embryophytes inherited only the light-harvesting strategies of the streptophytes and more broadly of Chlorophyta. Clearly this light-harvesting strategy has been very successful; however, had the line that conquered the land also possessed PBP the light-harvesting strategies might have been just as successful (compare Figs. 4 and 5) (Ritchie *et al.* 2017). The spectral width gain in the blue part of the spectrum in cells with Chls (*a*+*b*) is substantial and appears to be advantageous compared to a phycocyanin-type *Synechococcus* cyanobacterium with no phycoerythrin (Fig. 4); but this needs further experimental examination at an ecological/physiological level. However, Chl (*a*+*b*) organisms are much better at using terrestrial irradiance than is sometimes thought (Fig. 4).

Chlorophyll *c* and MgDVP

The various types of Chl *c* as mentioned above have a Soret (blue) band not far different from Chl *a* with peaks at 447 nm (solvent acetone) for Chl c_1, 450 nm for Chl c_2, and 452 nm for Chl c_3 (Zapata and Garrido 1997). These wavelengths are very close to the Soret peak for Chl *a*. So what is to gain from their synthesis? Furthermore, considering the fact that the *in vivo* Q_Y band peak (≈630 nm) is very small (Fig. 5), brings into question the role of these Chl *c* accessory pigments. However, Fig. 5 shows that the blue absorptance peak of Chl *c*-containing organisms (*Isochrysis* and *Chaetoceros*) is conspicuously wider than in *Synechococcus* which only has Chl *a* and

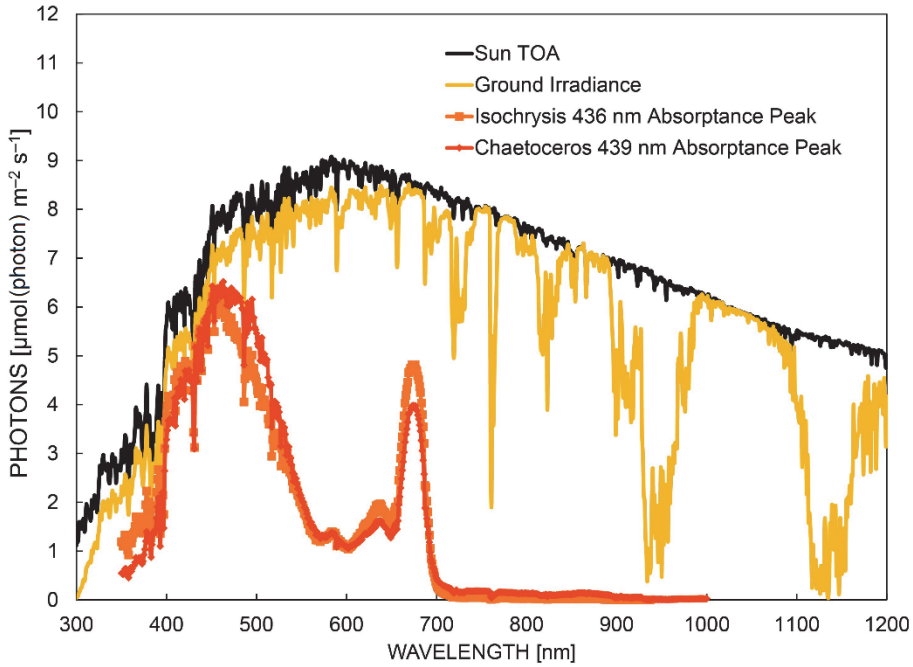


Fig. 5. The solar spectrum at ground level is from Fig. 3. *In vivo* absorptances (Abt) are based on integrating (Taylor) sphere measurements of the transmission (T, %) and reflectance (R, %) of *Isochrysis* (Cryptophyceae) and the diatom *Chaetoceros* (Bacillariophyceae) cell suspensions measured using the *A&E* spectrophotometer fitted with a Taylor Sphere. Absorptances were standardised to 90% absorptance [Abt = Log_{10} (100/Abt %) = 1] at the pigment absorptance peak. The absorptance spectra of *Isochrysis* [Chl (*a*+c_2)] and *Chaetoceros* [Chl (*a* + c_1 + c_2)] are very similar. Both have a very wide blue absorptance peak (350 to about 550 nm) with peaks at 436 and 439 nm, respectively. *Isochrysis* and *Chaetoceros* have a Q_Y band red peak at about 676 nm but note how narrow it is compared to the blue band. The red Chl *c* absorptance peak is at about 639 nm but absorption by Chl *c* at its Q-band peak is only a very minor component of the total absorptance of these chromophytes.

phycocyanin (Fig. 4). *Chlorella* which is a classic chlorophyte with Chl (*a*+*b*), also has a much wider blue absorptance band than *Synechococcus* (Fig. 4). Is this enhanced harvesting of blue light the main reason for the use of Chl *c* as an accessory pigment or does it perform a role in some other way in light harvesting? The mere fact that there are three major Chls *c*, other less well Chl *c* variants and magnesium 2,4-divinyl-pheoporphyrin monomethyl ester A5 (MgDVP) may suggest that they perform some other function or act in association with some special carotenoids (such as fucoxanthin in Phaeophyta and peridinin in dinoflagellates). The situation is further complicated by the existence of MgDVP as a physiologically functional pigment of Chl–protein complexes (Larkum, 2003, 2006, 2008): it is very close to Chl *c* biosynthetically and in molecular structure, is on the biosynthetic pathway to all BChls and Chl *c* (Hunter and Coomber 1988, Burke *et al.* 1993), and has a Soret peak very close to that of the Chls *c*. It is found in a few chlorophytan planktonic algae in the Prasinophyceae (Rowan 1989, Kantz *et al.* 1990, Zingone *et al.* 2002, Latasa *et al.* 2004) and the Palmophyllophyceae (Leliaert *et al.* 2016). Raven (1984, 1996) surmised that MgDVP and by implication Chls *c* do contribute to a significant degree to light harvesting in the light-harvesting complexes (LHC) where MgDVP and Chls *c* occur. Other authors, *e.g.* Larkum (2008), have speculated that these pigments play a role in energy migration from the pigment perhaps *via* specific carotenoids (*see* above) to the reaction centres. The latter possibility would go some way to explain why there are a variety of Chl *c* compounds.

The various types of Chl *c* are found in a wide range of eukaryote chromist algae (Larkum 2006), *i.e.* those algae that do not possess Chl *b* and, apart from the Cryptophyta, do not possess PBP: the chromists are the Cryptophyta, Haptophyta, and Ochrista (= Ochrophyta) (*e.g.* brown alga and diatoms), as well as the basal, peridinin-containing, Dinoflagellata (Pyrrophyta), also including dinoflagellates with diatom tertiary endosymbiotic plastids. Two exceptions here are the cryptophytes which possess Chl c_2 and PBP (Larkum 2006) and *Prochloron* (one of the Chl *b*-containing cyanobacteria) that also possesses MgDVP (Larkum *et al.* 1994) as well as a number of species of the Chl *b*-containing Prasinophyceae (formerly Micromonadophyceae; Fawley2004, Rowan 1989, Zingone *et al.* 2002, Latasa *et al.* 2004) and Palmophyllophyceae (a new group of early chlorophytes allied to the Prasinococcales and separate from the Prasinophyceae; Leliaert *et al.* 2016). MgDVP also occurs in Chl *d*-containing organisms (Miyashita *et al.* 1997, Schliep *et al.* 2007), so it is now apparent that it is a rather widespread pigment in Chl *b*- and Chl *c*-containing algae. The PBP of Cryptophytes,

however, is not in the form of a phycobilisome that is "plugged into" PSII as is found in Glaucocystophytes, Rhodophytes, and cyanobacteria (Kana *et al.* 2009, Graham *et al.* 2016).

As mentioned above, for Chl *b*, the possession of Chl *c* in only one of the three groups, which possess primary plastids poses a problem for the proposition of a monophyletic origin of plastids. One possible explanation is that Chl *c* arose, alongside the special carotenoids that such algae possess *de novo* to satisfy special absorption criteria; but beware of the Panglossian argument that every part of the phenology of an organism must necessarily have a purpose rather than being incidental (Gould and Lewontin 1979). However, no such special advantageous criterion has been satisfactorily put forward; but it has been carefully pointed out here that it would more likely involve blue light absorption (Soret band) rather than of 630 nm light (Figs. 4, 5). Nevertheless, Chl *c* could have arisen independently and the fact that two groups of algae, the dinoflagellates, and cryptophytes have only Chl c_2 whereas the other groups have Chl c_1 and c_2 (as well as, in some instances, Chl c_3) suggests that Chl c_2 evolved first: and this fits with the biosynthetic pathway in which Chl c_2 is a precursor to Chl c_1 (Larkum 2003, 2006). Most forms of Chl *c* do not have a phytol tail but the existence of phytylated forms in some eukaryotic algae, but as yet in *no known* prokaryote, suggests independent evolution (Zapata and Garrido 1997).

It is interesting, furthermore, that certain lines of chromophytic algae with Chl *c*-containing relatives have either Chl *a* alone or no Chl at all (but loss of all Chl is not restricted to chromophytes, *e.g*. *Prototheca*, *Polytoma*, and *Polytomella*). As is the case in many organisms of obvious Chl (*a*+*b*) affinities, there are examples of chromophytes lacking any variety of Chl *c* such as the Eustigmatophyceae (*e.g. Nannochloropsis*) and chromerids such as *Chromera* and *Vitrella* (Pan *et al.* 2012).

Chlorophyll *d*

The unique Chl, Chl *d* (Fig. 1) serves a similar function to Chl *a* in that it functions as both a redox active special pair substituting for Chl *a* in the equivalent position of P680 (possibly at 713 nm) and P700 (P740) of cyanobacteria that possess it and additionally as a light-harvesting pigment (Larkum 2006, Telfer *et al.* 2007, Ohashi *et al.* 2008, Mohr *et al.* 2010, Loughlin *et al.* 2013, 2014). The only exception here, for the substitution of Chl *d* for Chl *a* in the reaction centres, is the need for phaeophytin *a* as the primary (acceptor of the special pair, P697) of PSII, which is synthesised from Chl *a*, and therefore requires the formation of a small amount of Chl *a*. Apart from that and a small metabolic pool of Chl *a*, *Acaryochloris marina* seems to be able to function with mostly Chl *d* (up to ~97%); with Chl *d* also acting as a light-harvesting Chl with its own Chl–protein (Chen *et al.* 2005). The relative abundance of Chl *d* (the Chl *d/a* ratio) varies depending on the light regime under which it is grown (Miyashita *et al.* 1996, Chen *et al.* 2005, Gloag *et al.* 2007, Chen 2014), varying from a minority to majority Chl under favourable conditions. For the *in vivo* absorptance of *Acaryochloris* compared to *Synechococcus* (Chl *a*) and *Chlorella* [Chl (*a*+*b*)] *see* Fig. 4.

Chl *d* is synthesised from Chl *a* by substituting a methyl group on position C5 of ring A with a hydroxyl group with the oxygen derived from O_2 (*see* Fig. 1) (Schliep *et al.* 2010). How this oxygen is added is not known, but *see* Loughlin *et al.* (2014).

Chlorophyll *f*

Chl *f* (Fig. 1) was discovered in a filamentous cyanobacterium from living stromatolite material collected from intertidal columnar stromatolites from Hamelin Pool, Shark Bay, Western Australia (Chen *et al.* 2010, Niedzwiedzki *et al.* 2014, Tomo *et al.* 2014). It has since been found in a number of other cyanobacteria, both filamentous and globular (Chen 2014, Itoh *et al.* 2015). It is found in hot spring cyanobacteria and a number of the latter organisms have been well researched by Bryant and his group (Ho *et al.* 2016, Ho *et al.* 2017), who have shown that Chl *f* is induced under far-red light (Ho *et al.* 2016a). As previously pointed out, the final synthetic step, the addition of oxygen to C3 methyl to form a formyl group (Fig. 1) is brought about by a primitive form of D1 protein (Ho *et al.* 2016). In all these organisms Chl *f* constitutes only a small proportion of the total Chl (<10%), the rest being Chl *a*; and the formation of Chl *f* is NIR-dependent, *i.e*. the amount of Chl *f* in white light is very small (Ho *et al.* 2016a).

As far as is known, Chl *f* functions only in a light-harvesting role (Chen 2014). The energy transfer mechanisms have been studied by Li *et al.* (2012) and Akimoto *et al.* (2015) and the structure of Chl *f* has been presented by Willows *et al.* (2013). Details on the evolution of this pigment are not known. It has a red-shifted Q_Y peak at 707 *vs.* 696 nm for Chl *d* (in organic solvents) (Chen *et al.* 2010, 2015), which means that it is able to function further into the NIR than Chl *d*, but this depends on the conjugation to specific proteins.

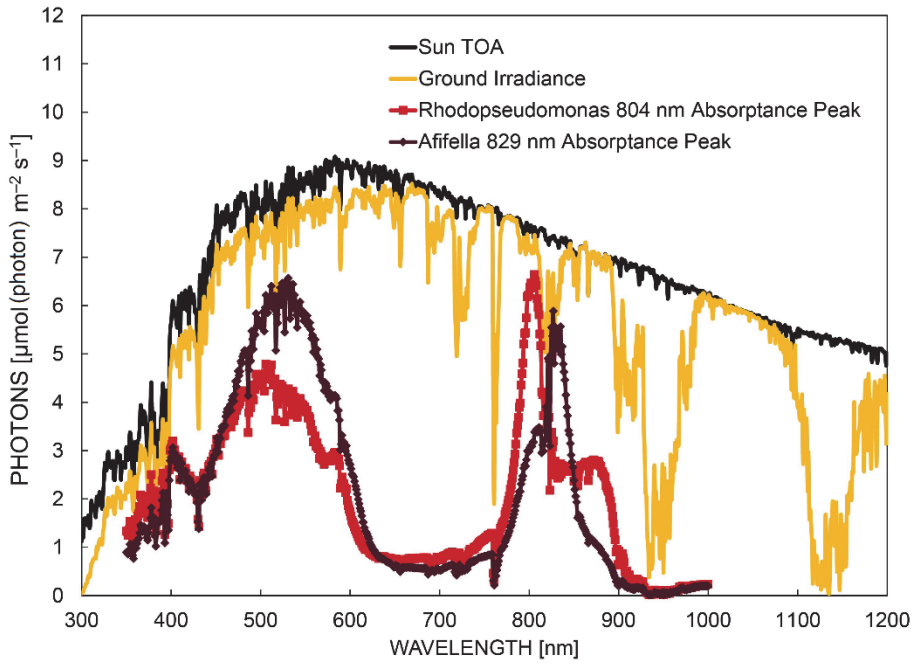


Fig. 6. Comparison of the absorptance properties of two non-sulphur RC-2 type photosynthetic bacteria: *Rhodopseudomonas palustris* and *Afifella marina*. The solar spectrum at ground level is from Fig. 3. *In vivo* absorptances (Abt) are based on integrating (Taylor) sphere measurements. Absorptances were standardised to 90% absorptance pigment absorptance peaks, in these cases the Q_Y-band absorptance peaks were slightly higher than the blue absorptance peaks (*Rhodopseudomonas*, 804 nm; *Afifella*, 839 nm) but this makes little difference in the absorptance curves because peak absorptance in the blue part of the spectrum is close to the Q_X band absorptance maximum. Both only have BChl *a*, however, *Rhodopseudomonas* has an NIR double absorptance peak as found in most *Rhodopseudomonas* and in the purple sulphur bacterium, *Thermochromatium* (Fig. 5) (Ritchie and Mekjinda 2015, Ritchie *et al.* 2017). *Afifella* has a conspicuous peak at 839 nm and minor peak "knees" on both sides. Both have very wide blue absorptance peaks (350 to about 600 nm) with two peaks at about 402 nm and 510 to 530 nm, respectively. The 402-nm peak can be attributed to BChl *a,* but the 510–530 nm peaks are due to carotenoids and xanthophylls. These photosynthetic bacteria can use blue and green light just as effectively or more effectively than oxygenic Chl (*a*+*b*), Chl (*a*+*d*), and Chl (*a*+*c*) organisms.

Bacteriochlorophylls

BChls (*a*–*g*), like Chls *a, b, d,* and *f*, have a tetrapyrrole ring and usually have a phytol tail but some have a geranylgeraniol (farnesol) tail: they differ from Chls in the higher degree of reduction of their tetrapyrrole ring (Fig. 1) (Scheer 1991, Blankenship *et al.*1995, Frigaard *et al.* 1996, 2006; Larkum 2006). There are two primary groups of BChl organisms: BChl *a, b*, and *g* are found in the reaction centres in BChl–protein complexes (reactions centres of type RC-1 or RC-2 and LHC) and so all photosynthetic bacteria have either BChl *a, b* or *g* as part of their RC-1 or RC-2 reaction centre although in some organisms the abundance of the primary photosynthetic pigment BChls may be very low compared to the total BChl of the organism [*e.g. Chlorobaculum tepidum* (Chlorobiceae) shown in Fig. 7] (Aronoff 1966, Bryant and Frigaard 2006), the second group of BChls *c, d, e*, and *f* are all accessory pigments (in chlorosomes of Chlorobiaceae and related organisms, Scheer 1991, 2006) (*see* also Harada *et al.* 2012). All BChls have an *in solvent* Soret band absorption peak in the violet to blue parts of the spectrum (350–500 nm): BChl *a, b*, and *g* ≈350 nm; *c, d*, and *f* ≈430 nm; and BChl *e* at ≈470 nm (Brockmann and Lipinski 1983, Beer-Romero and Gest 1987, Frigaard *et al.* 1996, Vogl *et al.* 2012). In common with Chls, *in vivo* Soret peaks of BChls are close to those measured *in solvent* (Figs. 6,7) but *in solvent* and *in vivo* Q_Y absorption bands can be considerably different with the *in vivo* peaks being moved far into the infrared as a result of interaction with the BChl-binding proteins. BChl *a, b*, and *g* have Q_Y absorption bands *in solvent* at 750–800 nm, considerably further into the red end of the spectrum than Chl *a* but *in vivo* the BChl complexes are in the range 800–900 nm for BChl *a* (Figs. 6,7) and *g* (Beer-Romero and Gest 1987) but in the case of BChl *b* it is even further into the NIR at 1012 nm (Fig. 7; Hoogewerf *et al.* 2003, Kiang *et al.* 2007a,b). The accessory BChls *c, d, e*, and *f* have Q_Y band absorbance peaks very similar to Chl *a*, at about 650 nm *in solvent* but their *in vivo* peaks are in the far-red at about 750 nm (*see Chlorobaculum* in Fig. 7). BChl *c* of *Chlorobium*-type green sulphur bacteria by far dominates their pigmentation (Bryant and Frigaard 2006). The *in solvent* spectrum of BChl *c* so closely resembles Chl *a* that it is easily mistaken for Chl *a*, and was for a long time thought to be Chl *a* and was called *Chlorobium*-chlorophyll (Aronoff 1966, Senge and Smith 1995, Bryant and Frigaard 2006). An interesting common feature of BChls is that they have a Q_X–Q_Y absorption band (Reimers

et al. 2013) at about 600 nm both *in solvent* (Frigaard *et al.* 1996) and *in vivo* (Figs. 6 and 7, and for BChl *g see* Beer-Romero and Gest 1987). These Q_X–Q_Y bands are very conspicuous for BChl *a, b*, and *g* but in general less conspicuous for the accessory BChls. Q_X–Q_Y absorption is very conspicuous in *Thermochromatium* (RC-2, Fig. 7) but less so in *Rhodopseudomonas* (RC-2, Fig. 6). Action spectra experiments based on growth criteria on *Rhodobacter* (BChl *a*) have shown that the Q_X–Q_Y absorption band is useable for photosynthesis (Hellingwerf *et al.* 1982). In light harvesting it is important not to forget that, like oxygenic photosynthetic organisms, most photosynthetic bacteria have significant absorption by carotenoids (carotenes and xanthophylls) (compare Figs. 4 and 5 with Figs. 6 and 7).

The importance of blue light for photosynthesis is particularly the case in marine photosynthesis (Raven 2007, Falkowski and Raven 2007) and this applies also to photosynthetic anoxygenic bacteria. Fig. 3 shows that red/far-red radiation is quickly eliminated exponentially with depth in sea water. Five m of sea water is enough to eliminate all far-red radiation and NIR as far as net photosynthesis is concerned and nearly all visible light >600 nm and 10 m of water eliminates available light >600 nm. This means that no Q_Y band light or even Q_X–Q_Y band light is available for either oxygenic or anoxygenic photosynthetic organisms even though the photosynthesis maximum normally found in oceanic waters is at around 10 m depth (Falkowski and Raven 2007). The depth of 10 m can be used as a representative depth for photosynthesis in clear oceanic water (Figs. 8, 9); at 10-m depth irradiance is zero beyond about 600 nm eliminating absorption of orange, red, and far-red light by *Synechococcus*, *Chlorella*, and *Acaryochloris* (Fig. 4): 400–600 nm light is about 686 µmol(photon) m^{-2} s^{-1} or about 31% of ground level but this is sufficient to saturate photosynthesis of most aquatic organisms and most terrestrial plants.

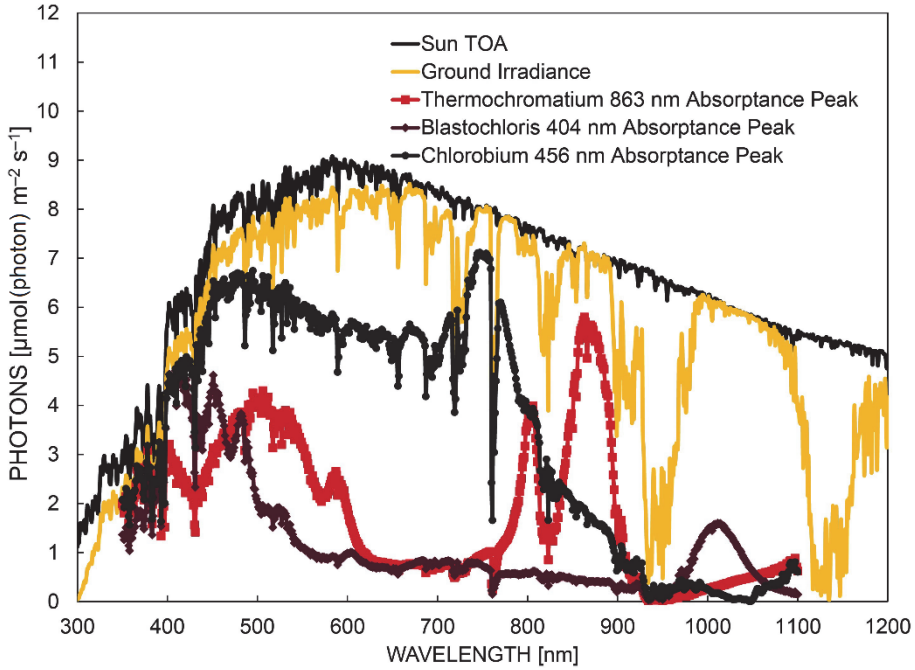


Fig. 7. Comparison of the absorptance properties of three more photosynthetic bacteria: *Thermochromatium* (a purple sulphur BChl *a* RC-2), *Blastochloris* (BChl *b* RC-2), and *Chlorobaculum* (Chlorobium) [BChl (*a*+*c*) RC-1]. Absorptances were standardised to 90% absorptance pigment NIR absorptance peak for *Thermochromatium* (863 nm), in the case of *Chlorobaculum* and *Blastochloris* the absorptance peaks were Soret bands (456 and 404 nm, respectively). The absorptance spectrum of *Thermochromatium* is essentially similar to *Rhodopseudomonas* (a broad blue peak and twin NIR absorptance bands at 806 and 863 nm) (Ritchie and Mekjinda 2015, Ritchie *et al.* 2017) but the Q_X–Q_Y band at about 600 nm is more conspicuous. *Blastochloris* has the most NIR shifted BChl Q_Y band peak of any known organism (1,012 nm) (Kiang *et al.* 2007a,b) but nevertheless. its peak absorptance is a Soret band (404 nm). *Blastochloris* has good absorptance characteristics for a broad range of blue light: absorptance by the Q_Y bands is of less significance. *Chlorobaculum* has a very conspicuous Q_Y band absorption peak at 745 nm due to BChl *c*, which acts as an accessory pigment, the amount of the primary pigment (BChl *a*) present is very low and its peak at about 830 nm is not conspicuous. Nevertheless, the absorptance maximum is the BChl *c* Soret band at 465 nm. Comparison of Figs. 4, 5, 6, and 7 shows that *Chlorobaculum* has the most efficient absorptance of visible and NIR light of any of the organisms in this study. The reason is that it has so much BChl *c* that it is essentially optically black in photosynthetically useful light.

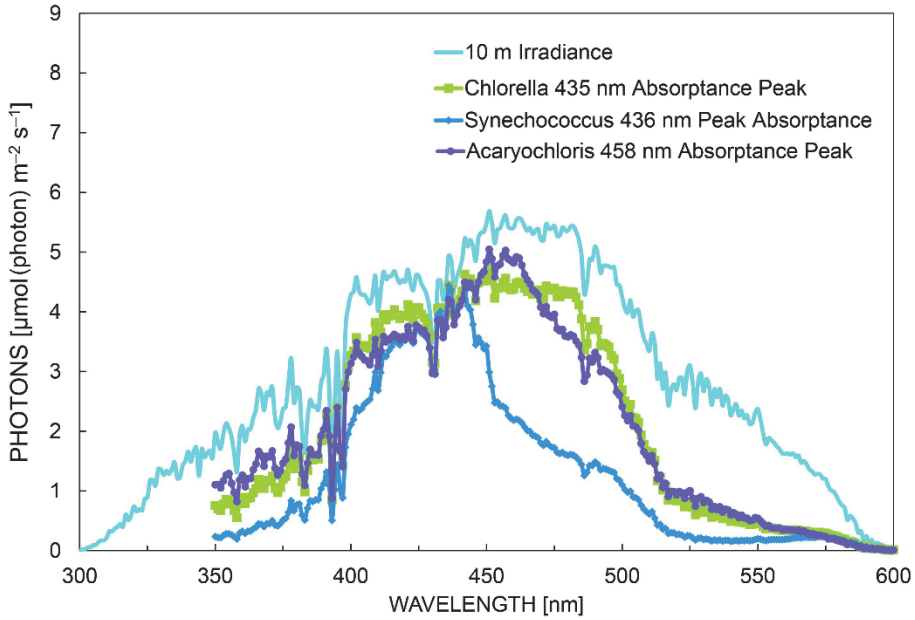


Fig. 8. The solar spectrum at 10 m in sea water from Fig. 4 can be used as a representative optimum depth for photosynthesis in clear oceanic water. At 10 m, irradiance is zero beyond about 600 nm eliminating absorption of orange, red, and far-red light by *Synechococcus*, *Chlorella*, and *Acaryochloris* (Fig. 4): 400–700 nm light is about 686 µmol(photon) m^{-2} s^{-1} or about 31% of ground level but this is sufficient to saturate photosynthesis of most aquatic organisms and most terrestrial plants. Taking the absorptance (Abt %) data used in Fig. 4 it is possible to calculate absorptance of irradiance under 10 m of water for *Synechococcus*, *Chlorella*, and *Acaryochloris*. A flat mat of *Synechococcus* with an absorptance maximum of 90% would absorb 270 mol(photon) m^{-2} s^{-1} (39%) of the available irradiance; *Chlorella* would absorb 448 mol(photon) m^{-2} s^{-1} (65%), and *Acaryochloris* 411 mol(photon) m^{-2} s^{-1} (60%).

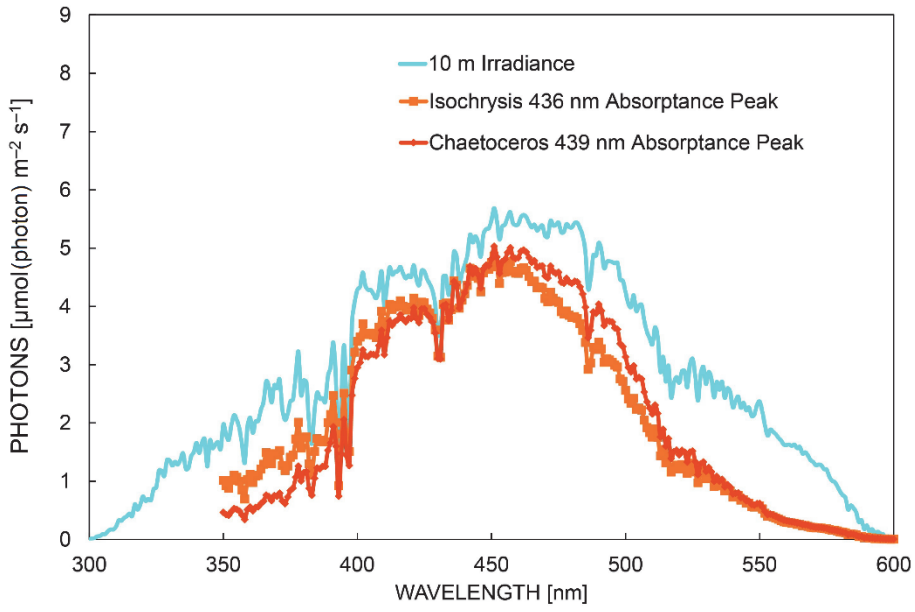


Fig. 9. Absorptance of light at 10-m depth by the chromophytes, *Isochrysis* and *Chaetoceros*, where light in the region of the Q_Y bands of Chl *a* and Chl c_1 and c_2 has been eliminated (Fig. 3). A flat mat of *Isochrysis* with an absorptance maxima of 90% would absorb 418 µmol(photon) m^{-2} s^{-1} (61%) of the available irradiance and *Chaetoceros* would absorb 440 µmol(photon) m^{-2} s^{-1} (64%).

As a class BChls have some interesting similarities and differences to Chls. All photosynthetically active known BChls have a phytol or geranylgeraniol tail: there are no known "Manx" tail-less photosynthetically active forms in wild-type populations although greenish mutants with accumulations of presumably protoporphyrin IX, MgDVP, and other similar compounds are common in the laboratory. It is likely that they have not been looked for

specifically in BChl–protein complexes, hence the emphasis on known above. Tail-less forms are easily prepared in the laboratory (Brockmann and Lipinski 1983), so why do they not seem to be functionally involved in anoxygenic photosynthesis? The Chl *c*-like MgDVP was mentioned earlier in connection with the Prasinophyceae and Palmophyllophyceae; it also occurs in a number of PS bacteria (as in all Chl and BChl *a* organisms as a biosynthetic intermediate) but not apparently in BChl–protein complexes. In *Prochloron* [one of the three cyanobacteria with Chl (*a*+*b*), *see* "Chlorophyll *b*"] it was discovered essentially by accident when an HPLC apparatus was taken to One Tree Island on the Great Barrier Reef and *Prochloron* was initially used as a test organism not supposed to have Chl *c* (Larkum *et al.* 1994). It was observed visually as a very immobile spot on a TLC plate and subsequently identified as MgDVP. A tail-less BChl would be very difficult to identify by eye on a TLC plate because its Q_Y bands would be in the infrared and like the various unphytylated forms of Chl *c* and MgDVP are likely to be very immobile either on TLC or in an HPLC column and would also be missed on HPLC. Solvent extracts from BChl *a* and *b* organisms vary from a light brown, light olive green or are transparent to the human eye. Nothing or almost nothing except carotenoids are visible to the naked eye on a TLC plate. No photosynthetically active Zn-Chl has ever been identified but one anoxygenic photosynthetic bacterial organism, *Acidophilium rubrum,* has a photosynthetically functional Zn-BChl *a* (Wakao *et al.* 1996). As Bryant and Frigaard (2006) point out, our knowledge of the pigmentation of PS bacteria is based on a very small number of culturable types and the light regime (infrared radiation) is often used as a selection agent and so we may be inadvertently selecting only for types with known light preferences. Photosynthetic bacteria grow well under fluorescent lighting used for growing oxygenic photosynthetic organisms and do not need infrared light (Ritchie 2013, Ritchie and Runcie 2013, Ritchie and Mekjinda 2015). More experiments along the lines of Hellingwerf *et al.* (1982) are needed. Growth experiments do not give very precise action spectra but growth is definitive evidence that an organism is using its light environment for production of new cellular material either phototrophically or photoheterotrophically.

Figs. 6 and 7 show *in vivo* absorptance curves for *Rhodopseudomonas* (BChl *a*), *Afifella marina* (BChl *a*), *Thermochromatium* (BChl *a*), *Chlorobaculum* [BChl (*a*+*c*)], *Blastochloris* (BChl *b*) all standardised for a 90% absorptance at their absorptance peak. Absorptances were measured using spectrophotometers fitted with integrating spheres. All 5 organisms have predominant absorption of blue light by Soret band absorption by a combination of BChl absorptance and carotenoids of various types. Q_X–Q_Y band absorption at about 600 nm is conspicuous in *Rhodopseudomonas*, *Afifella*, and *Thermochromatium* but is not conspicuous in *Blastochloris*

(BChl *b*) or *Chlorobaculum*. Most, but not all, photosynthetic bacteria with RC-2 and BChl *a* have a characteristic double absorptance (and absorbance) band (Q_Y) at about 800 and 860 nm, respectively (Fig. 6). The relative heights of these bands varies between species and physiological conditions, such as light regime, organic carbon source, microaerobic/anaerobic conditions (redox environment), *etc*. For example, in the *Rhodopseudomonas palustris*, used in the present study, the ≈800-nm band is greater than the ≈860-nm band but if grown under microaerobic conditions the relative magnitude of the bands is reversed. *Afifella marina* (BChl *a*) actually has 3 *in vivo* Q_Y bands but the central one at ≈830 nm is much larger than the bands with maxima at ≈800 and 860 nm (Ritchie and Runcie 2013). The Chlorobiaceae RC-1 bacterium, *Chlorobaculum*, has so much BChl *c*, in chlorosomes, that it is essentially optically black at visible and far-red wavelengths (Fig. 7): its BChl *a in vivo* Q_Y band is barely discernable on absorbance scans and it can just be recognised on Fig. 7 at about 850 nm. *Blastochloris* can absorb 350–550 nm light but absorptance is very low at all wavelengths from 550 to about 1000 nm where the *in vivo* BChl *b* Q_Y maxima occurs at 1012 nm. Overall *Blastochloris* and its relatives are reputed to be not very effective in using solar radiation, particularly in the visible 400–700 nm range, and thrive in only a few habitats such as microbial mats underneath algae and microbes (Figs. 4–7) (Hoogewerf *et al.* 2003).

Chlorobium is a popular organism for biotechnology and one major reason for this is its proficiency in using visible and far-red light; so will thrive on almost any light source (Frigaard *et al.* 2003, Muyzer and Stams 2008) (Fig. 7). Its very favourable optical properties are not often appreciated: it is very small, hence optimal for minimal package effect in cell suspensions and its pigment content is very high per cell volume making it essentially optically black over its very wide photosynthetically useful absorption range.

Photosynthetic performance at the depth of maximum photosynthesis in oceanic water

Taking the absorptance (Abt, %) data used in Fig. 4 it is possible to calculate absorptance of irradiance under 10 m of water for *Synechococcus*, *Chlorella*, living under saline conditions, and *Acaryochloris* (Fig. 6) and the marine Haptophyte *Isochrysis* and marine Ochristan (diatom) *Chaetoceros* (Fig. 7). This is a somewhat unrealistic model because one would ideally like to compute light penetrating a uniform suspension of cells down the water column. However, as these computations are problematic due to varying cell size and the package effect (*see* the discussion below), together with varying spectral effects, it is instructive to consider what a mat of cells would do at

10 m in oceanic water. A flat mat of *Synechococcus* with an absorptance maximum of 90% would absorb 270 mol(photon) m^{-2} s^{-1} (39%) of the available irradiance, *Chlorella* would absorb 448 mol(photon) m^{-2} s^{-1} (65%), and *Acaryochloris* 411 mol(photon) m^{-2} s^{-1} (60%), which shows, in the last example, the value of possessing PBPs. Long wavelength-absorbing green algae such as *Ostreobium* would also be able to perform well under 10 m of water using Soret-band absorption in a similar way to *Acaryochloris* even though far-red light would be absent (Koehne *et al.* 1999). A flat mat of *Isochrysis* with an absorptance maximum of 90% would absorb 418 µmol (photon) m^{-2} s^{-1} (61%) of the available irradiance and *Chaetoceros* would absorb 440 µmol(photon) m^{-2} s^{-1} (64%).

Absorption efficiencies in the 60% range for all the algae with accessory Chls is impressive when compared to the relatively poor performance of *Synechococcus* R-2 used in the present study which only has phycocyanin (orange/red absorption peak ≈630 nm, which is outside the irradiance range available under 10 m of water). *Synechococcus* has an absorption efficiency of only 39% because phycocyanin has the wrong spectrum for absorption of light under 10 m of water. Cyanobacteria and Cryptophytes with phycoerythrin, *e.g. Rhodomonas*, would be expected to do as well or better under 10 m of water as do *Chlorella*, *Isochrysis*, and *Chaetoceros*.

Unfortunately, only absorbance data was available for *Rhodomonas* (a phycoerthryin-containing cryptophyte, Ritchie *et al.* 2017) but not absorptance data, which would be needed if it was to be included in the present study. Qualitatively Fig. 1 in Ritchie *et al.* (2017) shows that *Rhodomonas* would be expected to be able to use light at 10 m with very high efficiency. Considering that green algae and terrestrial plants [those with Chl (*a*+*b*)] are often perceived as being poor utilisers of light (Chen and Blankenship 2011, Chen and Scheer 2013, Ort *et al.* 2015) it is ironic that a *Chlorella* mat with a 90% absorptance maximum at 435 nm (Fig. 4) turns out to be the best absorber of light at the optimum photosynthetic depth in the open ocean of all four oxygenic photosynthetic organisms, which have accessory Chls and that are included in the present study. Just why are plants green indeed (Mauzerall 1973, Bjorn 1976, Nishio 2000, Larkum 2006, 2008; Björn *et al.* 2009, Raven 2009, Kume *et al.* 2016, Kume 2017)? It turns out that green plants [Chl (*a*+*b*)] have much better photosynthetic light absorption performance than they are often taken for at both ground level and even underwater (Figs. 4, 8). Perhaps why are plants green is not such an accident after all; perhaps emphasis on the blue-band absorption is the key to appreciating why land plants are green [Chl (*a*+*b*)].

Absorptance curves for photosynthetic bacteria using data shown in Figs. 6 and 7 can also be used to calculate absorptance curves in microbial mats under 10 m of water. The absorptance curves are essentially similar to those calculated for the oxygenic organisms (Figs. 8, 9) because at this depth the blue light absorption curves of the photosynthetic bacteria closely resemble those of oxygenic organisms. The *Rhodopseudomonas* used here (Ritchie 2013) was a freshwater species but marine *Rhodopseudomonads* are common. *Afifella* is a marine purple non-sulphur photosynthetic bacterium (Ritchie and Runcie 2013). BChl *a in vivo* is able to absorb 350-nm light and so the total irradiance from 350 to 600 nm was calculated [805 µmol(photon) m^{-2} s^{-1}). At 10-m depth both the Q_X–Q_Y and Q_Y *in vivo* absorption bands of BChl *a* (Fig. 6) are ineffective because of the negligible irradiance at 600 nm and above, and hence the strong Q_X–Q_Y band at ≈600 nm would be ineffective. The Soret band *in vivo* of BChl *a* is at about 380–400 nm (Figs. 6, 7). Flat mats of *Rhodopseudomonas* and *Afifella* with absorptance maxima of 90% would absorb 280 µmol(photon) m^{-2} s^{-1} (35%) of the available irradiance and 356 µmol(photon) m^{-2} s^{-1} (44%), respectively. Absorptance by *Rhodopseudomonas* and *Afifella* in the blue part of the spectrum is not as high as found in the case of *Chlorella*, *Acaryochloris*, *Isochrysis*, and *Chaetoceros*, but nevertheless both are higher than found in *Synechococcus* [270 mol(photon) m^{-2} s^{-1}, 39%].

Rhodopseudomonas and *Afifella* are both RC-2 purple nonsulphur photosynthetic bacteria. The effective irradiance for these organisms was 350–600 nm because the blue peak of BChl *a* is below 400 nm. As in the case of *Rhodopseudomonas* and *Afifella* at 10-m depth, the Q_X–Q_Y *in vivo* absorption bands of BChl *a*, *b*, and *c* (at about 600 nm *see* Figs. 6 and 7) are ineffective because of the negligible irradiance at 600 nm and above. Flat mats of *Thermochromatium* with absorptance maxima of 90% absorbed ≈275 µmol(photon) m^{-2} s^{-1} (34% of the available irradiance) and the spectrum is little different to that found for *Rhodopseudomonas* although the Q_X–Q_Y band at 600 nm is more conspicuous (Fig. 7). *Blastochloris* (BChl *b*) absorbed 233 µmol(photon) m^{-2} s^{-1} or only 29% of the available light and so *Blastochloris* has the poorest performance at 10 m of any of the photosynthetic organisms included in the present study. On the other hand, *Chlorobaculum* BChl (*a*+*c*) absorbed 465 µmol(photon) m^{-2} s^{-1} or 58% of 350–700 nm light at 10-m depth. This is the highest absorption capacity of any photosynthetic organism included in the present study and is a result of its extremely high absorptance in the 350–600 nm range (Fig. 7). Comparison of Figs. 4 and 5 with Figs. 6 and 7 suggest that photosynthetic organisms with only a single BChl are at a conspicuous disadvantage in using blue light and the role of accessory BChls is to broaden blue-band absorption by themselves and to enhance the efficiency of utilisation of light absorbed by carotenoids.

While the absorptance data give a good indication of the capacity for photon absorption, it is also important to have action spectrum data and to calculate absorptance for suspensions of small cells with large package effects over a wide range of dilutions. While several action spectra are available for oxygenic photosynthetic organisms, this is not the case for the anoxygenic photosynthetic bacteria. For the purple non-sulphur bacteria there are only two

published action spectra. The early study with few wavebands (French 1937) suggests a lower quantum yield in the blue region than at longer wavelengths, but a later more detailed action spectrum study suggested an essentially constant quantum yield at all wavelengths and showed that Soret (Q_X), Q_X–Q_Y, and Q_Y bands were all used photosynthetically (Hellingwerf *et al.* 1982). For the oxygenic photosynthetic organisms the action spectrum also generally follows the absorption spectrum relatively closely (*e.g.* Lűning and Dring 1985). Researchers in the field have long been impressed by the fact that most oxygenic organisms are able to use blue and red light but are poor absorbers of green and orange light (550–625 nm) light and suggestions to improve the performance of photosynthesis are frequently made (Chen and Blankenship 2011, Chen and Scheer 2013, Ort *et al.* 2015). This deficiency is often overestimated and is contrary to our conclusions drawn at several points in the present paper (Figs. 4, 5). Blankenship *et al.* (2011) has suggested that PSI in oxygenic organisms could be replaced by RC-1 from photosynthetic bacteria using recombinant DNA technology. Scrutiny of Figs. 4–7 for terrestrial and Figs. 8 and 9 for marine conditions strongly suggest that any gains from such a genetic recombination would be marginal because the number of photons absorbed by a Chl *a* based LHC/PSI/PSII would be of a similar magnitude as could be collected by an RC-1 organism with its associated LHCs. A recombinant organism with functional PSII/PSI and RC-1 (a Chl/BChl-hybrid version of a three photosystem model) (Wolstencroft and Raven 2002) for oxygenic photosynthesis (PSII/PSI/PSIII) might offer gains in total spectral light utilisation. Govindjee *et al.* (2017) give a historical overview of two and three photosystem models of oxygenic photosynthesis; Wolstencroft and Raven's (2002) paper considers these two models in an astrobiological context.

The absorptance results shown in Figs. 4, 5, 8, and 9 tend to downplay the significance of the red, far-red absorption bands of Chls. However, the relatively larger blue absorption bands include contributions from carotenoids (some of which could be involved in photoprotection rather than light harvesting) as well as Chls. Ideally, action spectra of photosynthesis should also be used more extensively. It is notable that all the photosynthetic organisms considered in the present study in sunlight and even more so at 10-m depth in clear oceanic water are using predominantly blue light [Soret (Q_X) band] for photosynthesis. In the case of photosynthetic bacteria the routine use of far-red and NIR as a selection agent (incandescent light bulbs and NIR diodes) and neglect of blue-light absorption has probably resulted in an excessive focus on photosynthesis under red light/far red irradiance to give the impression that they must be using far red and NIR as their primary light sources in nature. Certainly under oceanic conditions, all photosynthetic organisms are using only blue light for photosynthesis in water deeper than about 5 m (Fig. 3) and so the red/far red absorption properties of the photosynthetic pigments are not relevant to photosynthetic electron transport in anything but very shallow water or terrestrially. Even the trophically problematic aerobic anoxygenic photosynthetic bacteria (AAPB) (Jiao *et al.* 2007, Garcia-Chaves *et al.* 2016, Stoecker *et al.* 2017) would be using mainly blue light. For example, the very small Q_Y absorptance maximum of Chl c_1 and c_2 *in vivo* (≈630 nm) make it very implausible that the significance of chromophytes having Chl c_1 and c_2 has much to do with absorptance at 630 nm: having Chl *c* as an accessory pigment is much more likely to have important consequences in the absorptance of blue light (Figs. 5, 9).

The conclusion for photosynthetic bacteria with BChls is that they do best using blue light; their famed ability to use far red irradiation only applies when they exist in light environments where only far red irradiation is available or in very low light environments where the use of any light available from 350 to 1,050 nm is an advantage. In this regard, the predominance of PS bacteria in modern stromatolites (Burns *et al.* 2004) may be informative in terms of early evolution (*see* "Microbial mats", below). This again reinforces the conclusion that modern photosynthetic bacteria evolved after the evolution of Chl organisms in cryptic environments, where the ability to absorb far red radiation was a significant advantage in terrestrial environments but far red was only useable in very shallow water environments (Figs. 3, 6, 7) (Larkum 2006, 2008).

Further progress in comparing the spectral properties of organisms with different Chls and BChls requires basing the absorptance values on the quantity of the main BChls, with units of $m^2\ mol^{-1}$(pigment) (Morel and Bricaud 1981), $m^2\ g^{-1}$(cell organic C) (Falkowski *et al.* 1985) or spacial volume of the reaction centres (nm^2 per reaction centre) (*e.g.* Key *et al.* 2009). Consideration is also needed of the influence of the package effect on the values obtained, with increasing influence of the package effect in larger cells or colonies or clumps of cells and with higher concentrations of pigment per unit cell volume or colony volume (Kirk 2012, Klughammer and Schreiber 2015).

Microbial mats

Microbial mats (including stromatolites) have aroused great interest in photosynthetic research and have been found to be the habitats of very interesting organisms (Wakao *et al.* 1996, Burns *et al.* 2004, Vopel and Hawes 2006, Mohr *et al.* 2010, Hohmann-Marriott and Blankenship 2011, Ohkubo *et al.* 2017). Microbial mats are not necessarily aquatic, for example desert crusts (Lange *et al.* 1992). Much research has focused on the layering of organisms in microbial mats and the attenuation of light inside the mat matrix and redox

gradients (Kühl and Fenchel 2000, Raven *et al.* 2000, Stomp *et al.* 2007, Marosvölgyi and van Gorkum 2010, Hubas *et al.* 2011, Chen *et al.* 2012, Ohkubo *et al.* 2017). They are the earliest known manifestations of photosynthetic life on the Earth (Tice and Lowe 2004, Butterfield 2015, Wellman *et al.* 2015, Nutman *et al.* 2016). Chromatic gradients in microbial mats most likely date to the very beginnings of photosynthesis on the Earth.

Layered microbial mats are hence of great interest to those interested in photoadaptation of photosynthetic organisms. Serial absorption by different microbial layers is understood in qualitative terms but quantitative or semi-quantitative considerations are rare. Here we will consider a microbial mat with a green alga [Chl (*a*+*b*)] (Fig. 4) on the surface and cyanobacteria and *Acaryochloris* living underneath (consider the light environment under oxygenic organisms, Figs. 4, 5). *Chlorella* can be used as a model Chl (*a*+*b*) organism and has characteristic absorption and transmission properties although it is not usually found in microbial mats, but is used here as a model organism. Transmission [%] of cell suspensions was measured using an integrating sphere as part of the calculation of absorptance (Abt, %) of *Chlorella* (Fig. 4). Because Abt (%) is calculated from both transmission (T, %) and reflectance (R, %) data, T (%) is not simply proportional to Abt (%). To estimate the effect of a *Chlorella* overlayer in a microbial mat, the transmission was scaled to the absorptance maximum at 435 nm to set the minimum transmission to 10% at 435 nm. The layer of *Chlorella* cells shown in Fig. 4 would transmit about 1,020 μmol(quanta) m^{-2} s^{-1} (≈46%) of incident sunlight (350–750 nm). Under a layer of *Chlorella,* the cyanobacterium *Synechococcus* (Chl *a*) and *Acaryochloris* (Chl *d*) would be able to survive quite well on light that passed through the layer of *Chlorella* cells [$Abt_{350\text{-}750\ nm}$ S*ynechococcus* ≈231 μmol(quanta) m^{-2} s^{-1}; $Abt_{350\text{-}750\ nm}$ *Acaryochloris* ≈309 μmol(quanta) m^{-2} s^{-1}]. *Ostreobium*, the green alga with Chl (*a*+*b*) pigmentation but with Chl–protein complexes that allow it to use far-red light would also be able to grow well under a *Chlorella* shade mat (Fork and Larkum 1989, Koehne *et al.* 1999). Similar findings were made for the scenario of a *Chaetoceros* diatom mat with a 10% transmission minimum at 439 nm (Fig. 5) overlaying *Synechococcus* or *Acaryochloris*. The light regime under a layer of diatoms would easily support photosynthesis by other photosynthetic organisms with different light preferences.

Similar calculations can be made for the scenario where a layer of *Chlorella* cells overlays a layer of photosynthetic bacteria (Fig. 4, compared to Figs. 6 and 7). Here, *Thermochromatium* (BChl *a*), *Chlorobaculum* [BChl (*a*+*c*)], and *Blastochloris* (BChl *b*) will be used as examples. The layer of *Chlorella* cells would transmit about 2,553 μmol(quanta) m^{-2} s^{-1} (≈51%) of incident sunlight (350–1,100 nm). Under a layer of *Chlorella* acting as a green sunshade the RC-2 *Thermochromatium* would absorb ≈652 μmol(quanta) m^{-2} s^{-1} ($Abt_{350\text{-}1100\ nm}$), *Chlorobaculum* would absorb ≈1,175 μmol(quanta) m^{-2} s^{-1} ($Abt_{350\text{-}1100\ nm}$), and *Blastochloris* would absorb ≈331 μmol(quanta) m^{-2} s^{-1} ($Abt_{350\text{-}1100\ nm}$). Growth under a layer of *Chlorella* provides a very favourable light environment for all three photosynthetic bacteria, in particular *Chlorobaculum*. As above for the case of an overlaying layer of the diatom *Chaetoceros* (Fig. 5), it can be shown that all three photosynthetic bacteria would have more than adequate light available under a layer of *Chaetoceros* with a 10% transmission minimum at 439 nm.

Cultures mentioned in the present study

Chlorella sp. (freshwater and euryhaline marine) was grown in freshwater BG-11 medium although it grows equally well in enriched seawater (Seatae *et al.* 2014), *Synechococcus* PCC-7942 was also grown in BG-11 medium, *Acaryochloris marina* (Miyashita *et al.* 2003), *Isochrysis* sp., and *Chaetoceros* sp. were grown in f-2 enriched seawater as described previously (Ritchie 2008, Ritchie *et al.* 2017). The photosynthetic bacteria were grown in PM media as previously described (Ritchie 2013, Ritchie and Runcie 2013, Ritchie and Mekjinda 2015). All were grown under fluorescent lights (cool-daylight) with no supplemental far-red or NIR light [≈150 μmol(photon) m^{-2} s^{-1}, PAR 400–700 nm].

Global estimates of annual photosynthetic net primary production and organic carbon assimilation by organisms with photochemical energy transduction

It is appropriate here to consider attempts to quantify global photolithotrophy by oxygenic and anoxygenic organisms, as well as the uses of photosynthetically produced organic carbon by organisms with photochemical energy transduction. Global oxygenic photolithotrophy has been much investigated, with significant variation in estimates. Some estimates for photosynthetic organisms suggest that anoxygenic photolithotrophy contributes less than 0.1% of the total of anoxygenic plus oxygenic photolithotrophy. Johnston *et al.* (2009) and Raven (2009) have estimated that anoxygenic photolithotrophy in marine habitats amounts to about 2.8–7.1 Tmol of fixed carbon per annum contrasting with estimates of 4,000–4,700 Tmol of fixed carbon per annum in all aquatic habitats (Field *at al.* 1998, Raven 2009, Buitenhuis *et al.* 2013), *i.e.* 0.07–0.15% of the total. Estimates of anoxy-

genic photosynthesis is based on S^{2-} oxidation in the global S cycle; this includes chemolithotrophy and excludes other inorganic electron donors such as Fe and also does not include use of organic carbon as electron donors, which can be regarded as a recycling process for already fixed organic carbon. In marine habitats almost all oxygenic primary productivity is by marine phytoplankton because the area occupied by marine macrophytes and marine angiosperms is such a small proportion of the surface area of the global ocean. Terrestrial oxygenic primary production (oxygenic photolithotrophy) is about 4,700–5,300 T mol(C) per year based on Field *et al.* (1998), Raven (2009), Edwards *et al.* (2015), and Rafique *et al.* (2016). Nearly all oxygenic primary productivity on land can be attributed to embryophytes; predominantly tracheophytes.

Although the estimates of global net primary production (NPP) show a range of values, there seem to be no estimates of how much respiratory CO_2 production is spared by photoheterotrophy involving ion-pumping rhodopsins, BChl and Chl, on a global scale. Dissolved organic carbon (DOC) in the global ocean that is used as an electron and carbon source by the abundant photoheterotrophic bacteria (Kolber *et al.* 1991, 2001) is in effect recycled back into organic carbon in cells. This sparing of respiration of organic carbon from reaching the CO_2 redox state by photoheterotrophic recycling of fixed carbon is discussed by Schmidt *et al.* (2015), Selosse *et al.* (2017), and Stoecker *et al.* (2017), for ion-pumping rhodopsins in bacteria and BChl in aerobic anoxygenic bacteria. Schmidt *et al.* (2015), Selosse *et al.* (2017), and Stoecker *et al.* (2017) also deal with eukaryotic oxygenic photosynthetic organisms that acquire organic carbon in parallel with phagotrophy in mixotrophic algae and in ciliates and Rhizaria that are photosynthetic through symbiosis with microalgae, or kleptoplast. In photosynthetically competent embryophytic land plants dissolved organic carbon is acquired mainly *via* fungal symbionts, in carnivorous plants through trapping animals then dissolving their tissues by extracellular digestion, and sometimes by ingestion of organic particles even in walled cells (Schmidt *et al.* 2015, Selosse *et al.* 2017, Stoecker *et al.* 2017).

Conclusions

A range of biologically produced photochemically active pigment–protein complexes absorbing radiation in the range 350–1050 nm are at the basis of almost all food webs on the Earth today, and may have been involved prior to 3.5 billion years ago (Ga). The ion-pumping rhodopsins use light absorbed by retinal to absorb energy from blue and green light to pump ions across the cell membranes. Chlorophylls have absorption bands in the blue and red (some just extending into the near infrared), and bacteriochlorophylls have absorption bands in the blue and red (Q_X and Q_X–Q_Y) and far red (Q_Y). Absorbed photons energize redox reactions and proton transport powering ADP phosphorylation, then oxidation of an external reductant and autotrophic assimilation of carbon dioxide. Anoxygenic photosynthesis involves external electron donors of a lower redox potential than water and a single photoreaction, while later-evolving oxygenic photosynthesis with two photoreaction centres in series, and water as the electron donor.

Two redox active Chls occur today, Chl *a* and Chl *d*; these two, usually with one or more of Chl *b*, Chl *c*, and Chl *f*, function as light-harvesting pigments. Chls *a* and *b*, Chls *c*, and MgDVP, absorb in the blue and, to lesser extent, the red, and Chls *d* and *f* in the blue plus near infrared (NIR). The additional light-harvesting chlorophylls modify the absorption spectrum of the organism so that, especially with Chls *c* and MgDVP, there is an increase in blue absorption relative to that in the red. The ecological distribution of the various chlorophylls does not provide clear confirmation of, for example, particular occurrence of Chls *c* and MgDVP deep in clear oceanic waters with lowest radiation attenuation in the blue. The occurrence of divinyl Chl *a* and Chl *b* which yield bathochromic shifts in their Soret (blue) bands, in the Chl *a/b*-containing *Prochlorococcus*, may be related to the generally deep open ocean habitat of these cyanobacteria. An additional factor is the size of the organisms, or dense populations of microorganisms; the package effect means that larger aggregations of pigments in larger organisms decreases the photon harvesting benefit and energy costs of increments in the pigment content.

The existence of bacteriochlorophylls raises important and unresolved issues as to the evolution of Chl *vs.* BChl. BChls occur in anoxygenic photosynthetic bacteria, with a small contribution to global primary productivity as anaerobic anoxygenic photosynthetic bacteria in anoxic habitats with often low photosynthetically usable photon fluxes (Table 2). However, anoxygenic bacteria are widespread and often abundant and so they should not be neglected (Kolber *et al.* 1990, 1991; Blankenship *et al.* 1995) despite their small contribution to global net primary productivity (Table 2). They often turn up in unexpected habitats: BChls occur in aerobic surface waters of marine and inland water habitats. The organisms found in these waters mostly do not carry out net primary production (only anaplerotic fixation of CO_2), but the photon absorption by BChl in these osmo-organotrophic organisms generate ion gradients and ATP that can decrease the loss of organic carbon in respiration during growth and maintenance through photo-osmo-organotrophic recycling of fixed carbon. A similar sparing of respiration can occur in the osmo-organotrophs with ion-pumping rhodopsins. Whether the PS bacteria, which possess either a PSI-like or a PSII-like system, evolved before the cyanobacteria has been discussed. BChl can harvest visible light but the possession of a variety of Q_Y bands, enable PS bacteria to

harvest far red radiation up to 1050 nm. MgDVP although present as a metabolite in photosynthetic bacteria does not appear to be incorporated into BChl–protein complexes.

Two things emerge from the present considerations. The first is that photosynthetic organisms often do not behave as expected from our reading of most textbooks (but *see* Kirk 2011) and our knowledge of the real diversity of photosynthesis is limited. The vast majority of microorganisms are not culturable. New organisms with novel pigmentation and photochemistry are being found all the time and usually accidentally and not always in exotic habitats. Even routine laboratory procedures can mask the presence of interesting organisms, for example the routine use of 750 nm as a blank for Chl assay effectively masks the presence of BChl. Very few researchers are familiar at the laboratory bench with both oxygenic and anoxygenic photosynthetic organisms, even excluding organisms that use rhodopsins. The second is that the characteristics of organisms are often incidental not Panglossian: the spandrels argument of Gould and Lewontin (1979). In the present considerations, just because far red radiation is a convenient selection agent for isolating anoxygenic photosynthetic bacteria does not mean that they are necessarily growing using primarily far red radiation in nature. Similarly, Chls and BChls are measured using the Q_Y band absorption maxima *in solvent* but that does not mean that oxygenic organisms are primarily using red light and photosynthetic bacteria are using NIR or far red in their natural habitats. Similarly, just because the Q_Y absorption band of Chl *c* of the Cryptophyta, Haptophya, and most Ochrophyta (but not Eustigmatopyceae) is readily recognised *in vivo* and *in solvent* that does not mean that absorption of 630 nm light is their major function *in vivo* [*see* discussion above on the role of the Soret (Q_X) band of MgDVP and Chl *c*]. In many marine habitats the red/far-red absorption characteristics of photosynthetic organisms are not relevant in terms of natural selection and are incidental as far as absorption of light is concerned because in that particular environment red/far-red radiation is absent. A definite role of the Q_Y bands is in defining the energetics of photochemistry.

A generalisation drawn from the present study is that both accessory chlorophylls and bacteriochlorophylls have an important role in widening the blue absorption band. This is of particular advantage in deeper water where blue light is still available but wavelengths longer than about 600 nm have been eliminated and so are not available for absorbtion by the Q_X–Q_Y and Q_Y bands of chlorophyll and bacteriochlorophylls.

References

Agusti S., Phlips E.J.: Light absorption by cyanobacteria: implications of the colonial growth form. – Limnol. Oceanogr. **37**: 434-441, 1992.

Akimoto S., Shinoda T., Chen M. *et al*.: Energy transfer in the chlorophyll *f*-containing cyanobacterium, *Halomicronema hongdechloris*, analyzed by time-resolved fluorescence spectroscopies – Photosynth. Res. **125**: 115-122, 2015.

Albarracín V.H., Kraiselburd I., Bamann C. *et al.*: Functional green-tuned proteorhodopsin from modern stromatolites. – PLoS ONE **11**: e0154962, 2016.

Allakhverdiev S.I., Kreslavski V.D., Zharmukhamedov S.K.: Chlorophylls *d* and *f* and their role in primary photodynthetic processes of cyanobacteria. – Biochemistry-Moscow **81**: 201-212, 2016.

Allen M.B.: Distribution of the chorophylls. – In: Vernon L.P., Seeley G.R. (ed.): The Chlorophylls: Physical, Chemical and Biological Properties. Pp. 511-519. Academic Press, New York and London 1996.

Aronoff S.: The chlorophylls – an introductory survey. – In: Vernon L.P., Seeley G.R. (ed.): The Chlorophylls: Physical, Chemical and Biological Properties. Pp. 3-20. Academic Press, New York and London 1966.

Atamna-Ismaeel N., Finkel O.M., Glaser F. *et al.*: Microbial rhodopsins on leaf surfaces of terrestrial plants. – Environ. Microbiol. **14**: 140-146, 2012.

Atamna-Ismaeel N., Sabehi G., Sharon I. *et al.*: Widespread distribution of proteorhodopsins in freshwater and brackish ecosystems. – ISME J. **2**: 656 -662, 2008.

Bamberg E., Tittor J., Oesterhelt D.: Light-driven proton or chloride pumping by halorhodopsin. – P. Natl. Acad. Sci. USA **90**: 639-643, 1993.

Battistuzzi F.U., Feijao A., Hedges S.B.: A genomic timescale of prokaryote evolution: insights into the origin of methanogenesis, phototrophy, and the colonization of land. – BMC Evol. Biol. **4**: 44, 2004.

Battistuzzi F.U., Hedges S.B.: A major clade of prokaryotes with ancient adaptations to life on land. – Mol. Biol. Evol. **26**: 335-343, 2009.

Baumann C., Bamberg E., Waxhveitl J.: Proteorhodopsin. – Biochim. Biophys. Acta **1837**: 614-625, 2014.

Beardall J., Allen D., Bragg J.: Allometry and stoichometry of unicellular, colonial and multicellular phytoplankton. – New Phytol. **181**: 295-309, 2009.

Beer-Romero P., Gest H.: *Heliobacillus mobilis*, a peritrichously flagellated anoxyphototroph containing bacteriochlorophyll *g*. – FEMS Microbiol. Lett. **41**: 109-114, 1987.

Behrendt L., Brejnrod A., Schliep M. *et al.*: Chlorophyll *f*-driven photosynthesis in a cavernous cyanobacterium. – ISME J. **9**: 2108-2111, 2015.

Béjà O., Spudich E.N., Spudich J.L. *et al.*: Proteorhodopsin phototrophy in the ocean. – Nature **411**: 786-789, 2001.

Beraldi-Campesi H.: Early life on land and the first terrestrial ecosystems. – Ecol. Process. **2**: 1, 2013.

Bieliwski J.P., Dunn K.A., Sabehi G. *et al.*: Darwinian adaptation of proteorhodopsin to different light intensities in the marine environment. – P. Natl. Acad. Sci. USA **101**: 14824-14829, 2004.

Bína D., Gardian Z., Herbstová M. *et al.*: Novel type of red-shifted chlorophyll *a* antenna complex from *Chromera velia* II. Biochemistry and spectroscopy. – BBA-Bioenergetics **1837**: 802-810, 2014.

Binzer T., Sand-Jensen K.: Importance of structure and density of macroalgae communities (*Fucus serratus*) for photosynthetic production and light utilisation. – Mar. Ecol. Prog.

Ser. **235**: 53-62, 2002
Björn L.O., Papageorgiou G.C., Blankenship R.F. *et al.*: A viewpoint: why chlorophyll *a*? – Photosynth. Res. **99**: 85-98, 2009.
Björn L.O.: Why are plants green – relationships between pigment absorption and photosynthetic efficiency. – Photosynthetica **10**: 121-129, 1976.
Blank C.E., Sánchez-Baracaldo P.: Timing of morphological and ecological innovations in the cyanobacteria – a key to understanding the rise in atmospheric oxygen. – Geobiology **8**: 1-23, 2010.
Blankenship R.E., Madigan M.T., Bauer C.E. (ed.): Anoxygenic Photosynthetic Bacteria. Pp. 1331. Kluwer Academic Publications, Dordrecht – Boston – London 1995.
Blankenship R.E., Tiede D.M., Barber J. *et al.*: Comparing photosynthetic and photovoltaic efficiencies and recognising the potential for improvement. – Science **332**: 805-809, 2011.
Bogachev A.V., Bertsova Y.V., Verkhovsakaya M.L. *et al.*: Real-time kinetics of electrogenic Na^+ transport by rhodopsin from the marine flavobacterium *Dokdonia* sp. PRO95. – Sci. Rep. **6**: 21397, 2016.
Boichenko V.A., Pinevich A.V., Stadnichuk I.N.: Association of chlorophyll *a/b*-binding Pcb proteins with photosystems I and II in *Prochlorothrix hollandica*. – BBA-Bioenergetics **1767**: 801-806, 2007.
Borra C., Brunett C. *et al*.: Phylogenetic position of *Crustomastix stigmata*, sp.nov., and *Dolichmastix tenuilepis* in relation to the Mamiellaes (Prasiophyceae, Chlorophyta). – J. Phycol. **38**: 1024-1039, 2002
Bowmaker J.K., Dartnall H.J.: Visual pigments of rods and cones in a human retina. – J. Physiol. **298**: 501-511, 1980.
Brindefalk B., Ekman M., Ininbergs K. *et al.*: Distribution and expression of microbial rhodopsins in Baltic Sea and adjacent waters. – Environ. Microbiol. **18**: 4442-4455, 2016.
Brockmann H. Jr., Lipinski A.: Bacteriochlorophyll *g*. A new bacteriochlorophyll from *Heliobacterium chlorum*. – Arch. Microbiol. **136**: 17-19, 1983.
Bryant D.B., Frigaard N.-U.: Prokaryotic photosynthesis and phototrophy illuminated. – Trends Microbiol. **14**: 488-496, 2006.
Buitenhuis E.T., Hasioka T., Le Quéré R.: Combined constraints on global ocean production using observations and models. – Glob. Change Biol. **27**: 847-858, 2013.
Bumba L. Prášil O., Vácha F.: Antenna ring around trimeric photosystem I in chlorophyll *b* containing cyanobacterium *Prochlorothrix hollandica*. – BBA-Bioenergetics **1708**: 1-5, 2005.
Burke D.H., Alberti M., Hearst J.E.: *bchFNBH* bacteriochlorophyll synthesis genes of *Rhodobacter capsulatus* and identification of the third subunit of light-independent protochlorophyllide reductase in bacteria and plants. – J. Bacteriol. **175**: 2414-2422, 1993.
Burns B.P, Goh F., Allen M., Neilan B.A.: Microbial diversity of extant stromatolites in thehypersaline marine environment of Shark Bay, Australia. – Environ. Microbiol. **6**: 1096-1101, 2004.
Butterfield N.J.: Proterozoic photosynthesis – a critical review. – Paleontology **58**: 953-972, 2015.
Cardona T.: Reconstructing the origin of oxygenic photosynthesis: Do assembly and photoactivation recapitulate evolution? – Front. Plant Sci. **7**: 257, 2016.
Chen M.: Chlorophyll modifications and their spectral extension in oxygenic photosynthesis. – Annu. Rev. Biochem. **83**: 317-340, 2014.
Chen M., Blankenship R.E.: Expanding the solar spectrum used by photosynthesis. – Trends Plant Sci. **16**: 427-431, 2011.
Chen M., Eggink L., Hoober J.K. *et al.*: Influence of structure on binding of chlorophylls to peptide ligands. – J. Am. Chem. Soc. **127**: 2052-2053, 2005.
Chen M., Hiller R.H., Howe C.J. *et al.*: Unique origin and lateral transfer of prokaryotic chlorophyll *b* and chlorophyll *d* light-harvesting systems. – Mol. Biol. Evol. **22**: 21-28, 2005.
Chen M., Schliep M., Willows R. *et al.*: A red-shifted chlorophyll. – Science **329**: 1318-1319, 2010.
Chen M., Li Y., Birch D., Willows R.D.: A cyanobacterium that contains chlorophyll *f* – a red-absorbing photopigment. – FEBS Lett. **586**: 3249-3254, 2012.
Chen M., Scheer H.: Extending the limits of natural photosynthesis and implications for technical light harvesting. – J. Porphyr. Phthalocyan. **17**: 1-15, 2013.
Chisholm S.W., Frankel S.L., Goericke R. *et al.*: *Prochlorococcus-marinus* nov. gen. nov. sp. – an oxyphototrophic marine prokaryote containing divinyl chlorophyll-*a* and chlorophyll-*b*. – Arch. Microbiol. **157**: 297-300, 1992.
Choi A.R., Shi L., Brown L.S. *et al.*: Cyanobacterial light-driven proton pump, *Gloeobacter* rhodopsin: complementarity between rhodopsin-based energy production and photosynthesis. – PLoS ONE **9**: e110643, 2014.
Claire M.W., Sheets J., Cohen M. *et al.*: The evolution of solar flux from 0.1 nm to 160 μm: quantitative estimates for planetary studies. – Astrophys. J. **757**: 95, 2012.
Cockell C.S., Kaltenegger L., Raven J.A.: Cryptic photosynthesis – extrasolar planetary oxygen without a surface biological signature. – Astrobiology **9**: 623-636, 2009.
Cockell C.S., Raven J.A.: Ozone and life on the Archaean Earth. – Philos. T. Roy. Soc. A **365**: 1889-1907, 2008.
Courties A., Riedel T., Rapaport A. *et al.*: Light-driven increase in carbon yield is linked to maintenance in the proteobacterium *Photobacterium angustum* S14. – Front. Microbiol. **6**: 688, 2015.
Crossett R.N., Drew E.A., Larkum A.W.D.: Chromatic adaptation in benthic marine algae. – Nature **207**: 547-548, 1965.
Dring M.J.: Chromatic adaptation of photosynthesis in benthic marine algae: an examination of its ecological significance using a theoretical model. – Limnol. Oceanogr. **26**: 271-284, 1981.
Durako M.J.: Leaf optical properties and photosynthetic leaf absorptances in several Australian seagrasses. – Aquat. Bot. **87**: 83-89, 2007.
Duysens L.N.M.: The flattening of absorption spectrum of suspensions, compared to that of solutes. – Biochim. Biophys. Acta **19**: 1-12, 1956.
Edwards D., Cherns L., Raven J.A.: Could land-based early photosynthesis ing ecosystems have bioengineered the planet in mid-Palaeozoic times? – Palaeontology **58**: 803-837, 2015.
Engqvist M.K.M., McIsaac R.S., Dollinger P. *et al.*: Directed evolution of *Gloeobacter violaceous* rhodopsin spectral properties. – J. Mol. Biol. **427**: 205-220, 2015.
Enríquez S., Agustí S., Duarte C.M.: Light Absorption by marine macrophytes. – Oecologia **98**: 121-129, 1994.
Falkowski P.G., Dubinsky Z., Wyman K.: Growth-irradiance relationships in phytoplankton. – Limnol. Oceanogr. **30**: 311-321, 1985.
Falkowski P.G., Raven J.A.:Aquatic Photosynthesis, 2nd Ed. Pp. 481. Princeton University Press, Princeton 2007.
Fawley M.W.: Photosynthetic pigments of *Pseudoscourfieldia*

marina and select green flagellates and coccoid ultraphytoplankton: implications for the systematics of the Micromonadophyceae (Chlorophyta). – J. Phycol. **28**: 26-31, 1992.

Feng S., Powell S.M., Wilson R. *et al.*: Light-stimulated growth of proteorhodopsin-bearing psychrophilic *Psychoflexus torquis* is salinity dependent. – ISME J. **7**: 2206-2213, 2013.

Feniouk B.A., Junge W.: Proton translocation and ATP synthesis by the F_oF_1 –ATPase of purple bacteria. – In: Hunter N., Daldal F., Thurnauer M.C., Beatty J.T. (ed.): The Purple Phototrophic Bacteria. Pp. 475-493. Springer, Dordrecht 2009.

Ferrera I., Sánchez O., Kolářová E. *et al.*: Light enhances the growth rates of natural populations of aerobic anoxygenic phototrophic bacteria. – ISME J. **11**: 2391-2393, 2017.

Field C.B., Behrenfeld M.J., Randerson J.T. *et al.*: Primary production of the biosphere: integrating terrestrial and oceanic components. – Science **281**: 237-240, 1998.

Finkel Z.V., Beardall J., Flynn K.J. *et al.*: Phytoplankton in a changing world: cell size and elemental stoichiometry. – J. Plankton Res. **32**: 118-137, 2010.

Fork D.C., Amesz J.: Action spectra and energy transfer in photosynthesis. – Annu. Rev. Plant Phys. **20**: 305-328, 1969

Fork D.C., Larkum A.W.D.: Light harvesting in the green alga *Oestreobium* sp., a coral symbiont adapted to extreme shade. – Mar. Biol. **103**: 381-385, 1989.

French C.S.: The quantum yield of hydrogen and carbon dioxide accumulation in purple bacteria. – J. Gen. Physiol. **20**: 711-735, 1937.

Frigaard N.-U., Chew A.G.M., Li H. *et al.*: *Chlorobium tepidum*: insights into the structure, physiology, and metabolism of a green sulphur bacterium derived from the complete genome sequence. – Photosynth. Res. **78**: 93-117, 2003.

Frigaard N.-U., Larsen K.L., Cox R.P.: Spectrochromatography of photosynthetic pigments as a fingerprinting technique for microbial phototrophs. – FEMS Microbiol. Ecol. **20**: 69-77, 1996.

Frigaard N.-U., Martinez A., Mincer T.J. *et al.*: Proteorhodopsin lateral gene transfer between marine planktonic Bacteria and Archaea. – Nature **439**: 847-850, 2006.

Frost-Christensen H., Sand-Jensen K.: The quantum efficiency of photosynthesis in macroalgae and submerged angiosperms. – Oecologia **91**: 377-384, 1992.

Fuhrman J.A, Schwalbach M.S., Stingl U.: Proteorhodopsins: an array of physiological roles? – Nat. Rev. Microbiol. **6**: 488-494, 2008.

Fuchs B.M., Spring S., Teeling H. *et al.*: Characterisation of a marine gamma proteobacterium capable of aerobic anoxygenic photosynthesis. – P. Natl. Acad. Sci. USA **108**: 2891-2896, 2007.

Ganapathy S., Venselaar H., Chen Q. *et al.*: Retinal-based proton pumping in the near-infrared. – J. Am. Chem. Soc. **139**: 2338-2344, 2017.

Gao K., Ai H.: Relationship of growth and photosynthesis with colony size in an edible cyanobacterium, Ge-Xian-Mi Nostoc (Cyanophyceae). – J. Phycol. **40**: 523-526, 2004.

Garcia-Chaves M.C., Cottrell M.T., Kirchman D.L. *et al.*: Single-cell activity of freshwater aerobic anoxygenic phototrophic bacteria and their contribution to biomass production. – ISME J. **10**: 1579-1588, 2016.

Gaudana S.B., Zarzycki J., Moparthi V.K. *et al.*: Bioinformatic analysis of the distribution of inorganic carbon transports and prospective targets for bioengineering to increase C_i uptake by cyanobacteria. – Photosynth. Res. **126**: 99-109, 2015.

Gloag R.S., Ritchie R.J., Chen M. *et al.*: Chromatic photoacclimation, photosynthetic electron transport and oxygen evolution in the Chlorophyll *d*-containing oxyphotobacterium *Acaryochloris marina* Miyashita. – BBA-Bioenergetics **1767**: 127-135, 2007

Goericke R., Repeta D.J.: Chlorophylls *a* and *b* and divinyl chlorophylls *a* and *b* in the open subtropical North Atlantic Ocean. – Mar. Ecol. Prog. Ser. **101**: 307-313, 1993.

Goericke R., Repeta D.J.: The pigments of *Prochlorococcus marinus*: the presence of divinylchlorophyll *a* and *b* in a marine procaryote. – Limnol. Oceanogr. **37**: 425-433, 1992.

Gómez I., Huovinen P.: Morpho-functional patterns and zonation of South Chilean seaweeds: the importance of photosynthetic and bio-optical traits. – Mar. Ecol. Prog. Ser. **422**: 77-91, 2011.

Gómez-Consarnau L., Akram N., Lindell K. *et al.*: Proteorhodopsin phototrophy promotes survival of marine bacteria during starvation. – PLoS Biol. **8**: e1000358, 2010.

Gómez-Consarnau L., González J.M., Coll-Lladó M. *et al.*: Light stimulates growth of proteorhodopsin-containing marine Flavobacteria. – Nature **445**: 210-213, 2007.

Gould S.J., Lewontin R.C.: The spandrels of San Marco and the Panglossian paradigm: a critique of the adaptionist programme. – P. Roy. Soc. B-Biol Sci **205**: 581-598, 1979.

Govindjee R., Balashov S.P. Ebrey T.G.: Quantum efficiency of the photochemical cycle of bacteriorhodopsin. – Biophys. J. **58**: 597-606, 1990.

Govindjee, Shevela D., Björn L.O.: The evolution of the Z-scheme of photosynthesis: a perspective. – Photosynth. Res. **133**: 5-15, 2017.

Graham J.E., Wilcox L.W., Graham L.E. *et al.*: Algae. 3rd Edition. eBook; www.lijmpress.com/algae.html, 2016.

Granick S.: Evolution of heme and chlorophyll. – In: Bryson C., Vogel H.J. (ed.): Evolving Genes and Proteins. Pp. 67-88. Academic Press, New York, 1965.

Greene R.M., Gerard V.A.: Effects of high frequency light fluctuations on growth and photoacclimation of the red alga *Chondrus crispus.* – Mar. Biol. **105**: 337-344, 1990.

Guo Z., Zhang H., Lin S.: Light-promoted rhodopsin expression and starvation survival in the marine dinoflagllate *Oxyrrhis marina.* – PLoS ONE **9**: e114941, 2014.

Harada J., Mizoguchi T., Tsukatani Y. *et al.*: A seventh bacterial chlorophyll driving a large light-harvesting antenna. – Sci. Rep-UK **2**: 671, 2012.

Harel A., Karkar S., Cheng S. *et al.*: Deciphering primordial cyanobacterial genome functions from protein network analysis. – Curr. Biol. **25**: 628-634, 2015.

Harvey W.H.: A Manual of the British Algae. Pp. 52. John van Voorst, London 1849.

Havosi F.I.: Spectral relation of core pigments in goldfish. – J. Gen. Physiol. **68**: 65-80, 1976.

Haxo F.T., Blinks L.R.: Action spectra of marine algae. – J. Gen. Physiol. **33:** 389-422, 1950.

Hegemann P., Oesterbelt D., Steiner M.: The photocycle of the chloride pump halorhodopsin. I: Azide-catalysed deprotonation of the chromophore is a side reaction of photocycle intermediates inactivating the pump. – EMBO J. **4**: 2347-2350, 1985.

Hellingwerf K.J. de Vrij W., Konings W.N.: Wavelength dependence of energy transduction in *Rhodopseudomonas sphaeroides*: action spectrum for growth. – J. Bacteriol. **151**: 534-541, 1982.

Herbstová M., Litvín R., Gardian Z. *et al.*: Localization of Pcb

antenna complexes in the photosynthetic prokaryote *Prochlorothrix hollandica*. – BBA-Bioenergetics **1797**: 89-97, 2010.

Ho M., Gan F., Shen G. *et al.*: Far-red light photoacclimation (FaRLiP) in *Synechococcus* sp. PCC 7335: I. Regulation of FaRLiP gene expression. – Photosynth. Res. **131**: 173-186, 2017.

Ho M.-Y., Shen G., Canniffe D.P. *et al.*: Light-dependent chlorophyll *f* synthase is a highly divergent paralog of PsbA of photosystem II. – Science **353**: 886-887, 2016.

Hohmann-Marriott M.F., Blankenship R.E.: Evolution of photosynthesis. – Annu. Rev. Plant Biol. **62**: 515-548, 2011.

Hoogewerf G.J, Jung D.O., Madigan M.T.: Evidence for limited species diversity of bacteriochlorophyll *b*-containing purple non-sulphur anoxygenic phototrophs in freshwater habitats. – FEMS Microbiol. Lett. **218**: 359-364, 2003.

Horath T., Bachofen R.: Molecular characterisation of an endolithic microbial community in dolomite rock in the Central Alps (Switzerland). – Environ. Microbiol. **58**: 290-306, 2009.

Hubas C., Jesus B., Passarelli C. *et al.*: Tools providing new insight into coastal anoxygenic purple bacterial mats. – Res. Microbiol. **162**: 858-868, 2011.

Hughes J.L., Smith P., Pace R. *et al.*: Charge separation in photosystem II core complexes induced by 690-730nm excitation at 1.7 K. – BBA-Bioenergetics **1757**: 841-851, 2006.

Hunter C.N., Coomber S.A.: Cloning and oxygen-regulated expression of the bacteriochlorophyll biosynthesis genes *bch,E, B, A* and *C* of *Rhodobacter spheroids.* – J. Gen. Microbiol. **134**: 1491-1497, 1988.

Itoh S., Ohno T., Noji T. *et al.*: Harvesting far-red light by chlorophyll *f* in photosystems I and II of unicellular cyanobacterium strain KC1. – Plant Cell Physiol. **56**: 2024-2034, 2015.

Janke C., Scholz F., Becker-Baldus J. *et al.*: Photocycle and vectorial proton transfer in a rhodopsin from the eukaryote proton transfer in a rhodopsin from the eukaryote *Oxyrrhis marina.* – Biochemistry **52**: 2750-2763, 2013.

Jiao N., Zhang Y., Zeng Y. *et al.*: Distinct distribution pattern of abundance and diversity of aerobic anoxygenic phototrophic bacteria in the global ocean. – Environ. Microbiol. **9**: 3091-3099, 2007.

Johnston D.T., Wolfe-Simon F., Pearson A. *et al.*: Anxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth's middle age. – P. Natl. Acad. Sci. USA **106**: 16925-16929, 2009.

Jones H.G.: Plants and Microclimate. A Quantitative Approach to Environmental Plant Physiology. 3rd Edition. Pp. 527. Cambridge University Press, Cambridge 2013.

Kaňa R., Prášil O., Mullineaux C.C.: Immobility of phycobilins in the thylakoid lumen of as cryptophyte suggests that protein diffusion in the lumen is very restricted. – FEBS Lett. **583**: 670-674, 2009.

Kandori H.: Ion-pumping microbial rhodopsins. – Front. Mol. Biosci. **2**: 52, 2015.

Kang I., Oh H.M., Lim S.I. *et al.*: Genome sequence of *Fulvimarina pelagi* HTCC2506(T), a Mn(II)-oxidising alphaproteobacterium possessing an aerobic anoxygenic photosynthetic gene cluster and xanthorhodopsin. – J. Bacteriol. **192**: 4798-4799, 2010.

Kantz T.S., Theriot E.C., Zimmer E.A. *et al.*: The Pleurastrophyceae and Micromonadophyceae: a cladistic analysis of nuclear ribosomal RNA sequence data. – J. Phycol. **26**: 711-721, 1990.

Kato H.E., Inoue K., Kandori H. *et al.*: The light-driven sodium ion pump: a new player in rhodopsin research. – Bioessays **38**: 1274-1282, 2016.

Key T., McCarthy A., Campbell D.A. *et al.*: Cell size trade-offs govern light exploitation strategies in marine phytoplankton. – Environ. Microbiol. **12**: 95-104, 2009.

Kiang N.Y., Segura A., Tinetti G. *et al.*: Spectral signatures of photosynthesis. II. Coevolution with other stars and the atmosphere on extrasolar worlds. – Astrobiology **7**: 252-274, 2007b.

Kiang N.Y., Siefert J., Govindjee *et al.*: Spectral signatures of photosynthesis. I. Review of Earth organisms. – Astrobiology **7**: 222-251, 2007a

Kirchman D.L., Hanson T.E.: Bioenergetics of photoheterotrophic bacteria in the oceans. – Env. Microbiol. Rep. **5**: 188-199, 2013.

Kirk J.T.O. A theoretical analysis of the contribution of algal cells to the attenuation of light within natural waters. I. General treatment of suspensions of pigmented pigmented cells. – New Phytol. **75**: 11-20. 1975a.

Kirk J.T.O. A theoretical analysis of the contribution of algal cells to the attenuation of light within natural waters. II. Spherical cells. – New Phytol. **75**: 21-36.1975b.

Kirk J.T.O. A theoretical analysis of the contribution of algal cells to the attenuation of light within natural waters. III. Cylindrical and spheroidal cells. – New Phytol. **76**: 341-258. 1976.

Kirk J.T.O.: – Light and Photosynthesis in Aquatic Ecosystems. 3rd Edition. Pp. 649. Cambridge University Press, Cambridge UK, 2011.

Klamt S., Grammel H., Straube R. *et al.*: Modelling the electron transport chain of purple non-sulfur bacteria. – Mol. Syst. Biol. **4**: 156, 2008.

Klughammer C., Schreiber U.: Apparent PS II absorption cross-section and estimation of mean PAR in optically thin and thick suspensions of *Chlorella.* – Photosynth. Res. **123**: 77-92, 2015.

Koehne B., Elli G., Jennings R.C. *et al.*: Spectroscopic and molecular characterization of a long wavelength absorbing antenna of *Ostreobium* sp. – BBA-Bioenergetics **1412**: 94-107, 1999.

Koh E.Y., Atamna-Ismaeel N., Martin A. *et al.*: Proteorhodopsin-bearing bacteria in Antarctic sea ice. – Appl. Environ. Microb. **76**: 5918-5925, 2010.

Kolber Z.S., van Dover C.L., Niederman R.A. *et al.*: Bacterial photosynthesis in surface waters of the open ocean. – Nature **407**: 177-179, 1991.

Kolber Z.S., Plumley F.G., Lang A.S. *et al.*: Contribution of photoheterotrophic bacteria to the carbon cycle in the ocean. – Science **292**: 2492-2495, 2001.

Kolber Z.S., van Dover C.L., Niederman R.A. *et al.*: Bacterial photosynthesis in surface waters of the open ocean. – Nature **407**: 177-179, 2000.

Kotabová E., Jarešová J., Kaňa R. *et al.*: Novel type of red-shifted chlorophyll *a* antenna complex from *Chromera velia.* I. Physiological relevance and functional connection to photosystems. – Biochim. Biophys. Acta **1837**: 734-743, 2014.

Krauss S., Fichtinger B., Lammer H. *et al.*: Solar flares as a proxy for the young Sun: Satellite observed thermosphere response to an X17.2 flare of Earth's upper atmosphere. – Ann. Geophys. **30**: 1129-1141, 2012.

Kübler J.E., Raven J.A.: Nonequilibrium rates of photosynthesis and respiration under dynamic light supply. – J. Phycol. **32**: 963-969, 1996.

Kühl M., Fenchel T.: Bio-optical characteristics and the vertical

distribution of photosynthetic pigments and photosynthesis in an artificial cyanobacterial mat. – Microb. Ecol. **4**: 94-103, 2000.

Kume A., Akitsu T., Nasahara K.N.: Leaf color is fine-tuned on the solar spectra to avoid strand direct solar radiation. – J. Plant Res. **129**: 615-624, 2016.

Kume A.: Importance of the green color, absorption gradient, and spectral absorption of chloroplasts for the radiation energy balance of leaves. – J. Plant Res. **130**: 501-514, 2017.

La Roche J., van der Staay G.W.M., Partensky F. *et al.*: Independent evolution of the prochlorophyte and green plant chlorophyll *a/b* light harvesting proteins. – P. Natl. Acad. Sci. USA **93**: 15244-15248, 1996.

Lange O.L., Kidron G.J., Budel B. *et al.*: Taxonomic composition and photosynthetic characteristics of the `Biological Soil Crusts' covering sand dunes in the Western Negev Desert. – Funct. Ecol. **6**: 519-527, 1992.

Larkum A.W.D.: The Evolution of Chlorophylls. – In: Scheer H. (ed.): .Chlorophylls. Pp. 367-383. CRC Publ., Boca Raton 1991.

Larkum A.W.D.: Light-harvesting systems in algae. – In: Larkum A.W.D., Douglas S.E., Raven J.A. (ed.): Photosynthesis of Algae. Pp. 277-304. Kluwer Acad. Publ., Dordrecht 2003.

Larkum A.W.D.: The evolution of chlorophylls and photosynthesis. – In: Grimm B., Porra R.J., Rüdiger E., Scheer H. (ed.): Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications. Advances in Photosynthesis and Respiration, Vol. 25. Pp. 261-282. Springer, New York 2006.

Larkum A.W.D.: Evolution of the reaction centers and photosystems. – In: Renger G. (ed.): Primary Processes of Photosynthesis: Principles and Apparatus, Vol. 2. Pp. 489-521. Royal Society of Chemistry, Cambridge 2008

.Larkum A.W.D. and Barrett J.: Light Harvesting Processes **in** Algae. Advances in Botanical Research 10, 1-219. Academic Press, New York, 1983.

Larkum A.W.D., Scaramuzzi C., Cox G.C. *et al.*: Light-harvesting chlorophyll *c*-like pigment in *Prochloron.* – P. Natl. Acad. Sci. USA **91**: 678-683, 1994.

Larkum A.W.D, Lockhart P.J., Howe C.J.: Shopping for plastids. – Trends Plant Sci. **12**: 189-195, 2007.

Latasa M., Scharek R., Le Gall F. *et al.*: Pigment suites and taxonomic group in Prasinophyceae. – J. Phycol. **40**: 1149-1155, 2004.

Leliaert F., Tronholm A., Lemieux C. *et al.*: Chloroplast phylogenomic analysis reveal the deepest-branching lineage of the Chlorophyta, Palmophyllophyceae class nov. – Sci. Rep. **6**: 25367, 2016.

Lenton T.M., Daines S.J.: Matworld – the biogeochemical effects of early life on land. – New Phytol. **215**: 531-537, 2017.

Li X., Koblížek M., Feng F. *et al.*: Whole-genome sequence ofa freshwater aerobic anoxygenic phototroph, *Porphyrobacter* sp. strain AAP82, isolated from the Huguangyan Maar Lake in Southern China. – Genome Announc. **1**: e00034-13, 2013.

Li Y-Q., Scales N., Blankenship R.E. *et al.*: Extinction coefficient for red-shifted chlorophylls: Chlorophyll *d* and chlorophyll *f*. – BBA-Bioenergetics **1817**: 1292-1298, 2012

Lichtenberg M., Kühl M.Y.: Pronounced gradients of light, photosynthesis and O_2 consumption in the tissue of the brown alga *Fucus serratus*. – New Phytol. **207**: 559-569, 2015.

Litchman E.: Growth rates of phytoplankton under fluctuating light. – Freshwater Biol. **44**: 223-235, 2000.

Loughlin P., Lin Y., Chen M.: Chlorophyll *d* and *Acayochloris marina*: current status. – Photosynth. Res. **116**: 277-293, 2013.

Loughlin P.C., Willows R.D., Chen M.: *In vitro* conversion of vinyl to formyl groups in naturally occurring chlorophylls. – Sci. Rep. **4**: 6069, 2014.

Lüning K., Dring M.R.: Action spectra and spectral quantum yield of photosynthesis in marine macroalgae with thin and thick thalli. – Mar. Biol. **87**: 119-129, 1985.

Lüning K.: Seaweeds. Their Environment, Biogeography, and Ecophysiology. Pp. 527. John Wiley & Sons, New York 1990.

Lyell C.: On fossil rain-marks of the Recent, Triassic and Carboniferous periods. – J. Geol. Soc. **7**: 338-347, 1851.

Man D., Wang W., Sabehei G. *et al.*:. Diversification and spectral tuning in marine proteorhodopsin. – EMBO J. **22**: 1725-1731, 2003.

Mareš J., Hrouzek P., Kaňa R. *et al.*: The primitive thylakoid-less cyanobacterium *Gloeobacter* is a common rock-dwelling organism. – PLoS ONE **8**: e66323, 2013.

Marchetti A., Schruth D.M., Durkin C.A. *et al.*: Comparative metatranscriptomics identifies molecular basis for the physiological response phytoplankton to varying iron availability. – P. Natl. Acad. Sci. USA **109**: E317-E325, 2012.

Markager S.: Light absorption and quantum yield for growth in five species of marine macroalga. – J. Phycol. **29**: 54-63, 1993.

Markager S., Sand-Jensen K.: Light requirement and depth zonation of marine macroalgae. – Mar. Biol. Prog. Ser. **88**: 83-92, 1992

Marosvölgyi M.A., van Gorkum H.J.: Cost and color of photosynthesis. – Photosynth. Res. **103**: 105-109, 2010.

Mathusamy S., Baltar F., González J.M. *et al.*: Dynamics of metabolic activities and gene expression in the roseobacter clade bacterium *Phaeobacter* sp. strain med153 during growth with thiosulfate. – Appl. Environ. Microbiol. **80**: 6933-6942, 2014.

Matsunoto-Yagi A., Mukohata Y.: Two possible roles of bacteriorhodopsin; a comparative study of strains of *Halobacterium halobium* differing in pigmentation. – Biochem. Bioph. Res. Co. **78**: 237-243, 1977.

Mauzerall D.: Why chlorophyll? – Ann. NY Acad. Sci. **206**: 483-494, 1973.

Meeks J.C.: Chlorophylls. – In: Stewart W.D.P. (ed.): Algal Physiology and Biochemistry. Pp. 161-175. Blackwell, Oxford 1974.

Merbs S.L., Nathans J.: Absorption spectra of human cone pigments. – Nature **356**: 433-435, 1992.

Michel H., Oesterhelt D.: Electrochemical proton gradient across the cell membrane of *Halobacterium halobium*: effect of *N,N'*-dicyclohexylcarbodiimide, relation to adenosine triphosphate, adenosine diphosphate and phosphate concentration, and influence of the potassium gradient. – Biochemistry **19**: 4607-4614, 1980.

Milo R.: What governs the reaction centre excitation wavelengths of photosystems I and II. – Photosynth. Res. **101**: 59 -67, 2009.

Mimuro M., Hirayani K., Uezono K. *et al.*: Uphill energy transfer in a chlorophyll d-dominated oxygenic photosynthetic prokaryote, *Acaryochloris marina.* – Biochim. Biophys. Acta **456**: 27-34, 2007.

Miyashita H., Adachi K., Kurazo N. *et al.*: Pigment composition of a novel oxygenic photosynthetic prokaryote containing chlorophyll *d* as a major chlorophyll. – Plant Cell Physiol. **38**: 274-281, 1997.

Miyashita H., Ikemoto H., Kurano N. *et al.*: *Acaryochloris marina* Gen. et Sp. Nov. (Cyanobacteria), an oxygenic photosynthetic prokaryote containing Chl *d* as a major pigment.

– J. Phycol. **39**: 1247-1253, 2003.
Miyashita H., Ikemoto H., Kurano N. *et al.*: Chlorophyll *d* as a major pigment. – Nature **383**: 402-403, 1996.
Mohr R., Voβ B., Schliep M. *et al.*: A new chlorophyll *d*-containing cyanobacterium: evidence for niche adaptation in the genus *Acaryochloris*. – ISME J. **4**: 1456-1469, 2010.
Morel A., Bricaud A.: Theoretical results concerning light absorption in a discrete medium, and application to specific absorption of phytoplankton. – Deep Sea Res. **28**: 1375-1393, 1981.
Morel A., Bricaud A.: Inherent optical properties of algal cells including phytoplankton: theoretical and experimental results. – Can. Bull. Fish. Aquat. Sci. **214**: 521-559, 1986.
Mulkidjanian A.Y., Koonin E.V., Makarova K.S. *et al.*: The cyanobacterial genome core and the origin of photosynthesis. – P. Natl. Acad. Sci. USA **103**: 13126-13131, 2006.
Muyzer G., Stams A.J.M.: The ecology and biotechnology of sulphate-reducing bacteria. – Nat. Rev. Microbiol. **6**: 441-454, 2008.
Niedzwiedzki D.M., Liu H., Chen M. *et al.*: Excited state properties of chlorophyll *f* in organic solvents at ambient and cryogenic temperatures. – Photosynth. Res. **121**: 25-34, 2014.
Nieuwenburg P., Clark R.J. Chen M. *et al.*: Explanation of proposed "uphill energy transfer" in chlorophyll *d*, the major pigment of *Acaryochloris marina*. – Photochem. Photobiol. **77**: 628-637, 2003.
Nicholls D.G., Ferguson S.J.: Bioenergetics 4. Pp. 419. Academic Press, Amsterdam 2013.
Nishio J.N.: Why are higher plants green? Evolution of the higher plant photosynthetic pigment complement. – Plant Cell Environ. **23**: 539-548, 2000.
Nutman A.P., Bennett V.C., Friend C.R.L. *et al.*: Rapid emergence of life shown by discovery of 3,700-million-year-old microbial structures. – Nature **537**: 535-538, 2016.
Oesterhelt D., Hegemann P., Tittor J.: The photocycle of the chloride pump halorhodopsin. II: Quantum yields and a kinetic model. – EMBO J. **4**: 2351-2356, 1985.
Oesterhelt D., Stoeckenius W.: Rhodopsin-like protein from the purple membrane of *Halobacterium halobium.* – Nature New Biol. **233**: 149-152, 1970.
Ohashi S., Miyashita H., Okada N. *et al.*: Unique photosystems in *Acaryochloris marina*. – Photosynth. Res. **98**: 141-149, 2008.
Ohkubo S., Miyashita H.: A niche for cyanobacteria producing chlorophyll *f* within a microbial mat. – ISME J. **11**: 2368-2378, 2017.
Öquist G.: Adaptations in pigment composition and photosynthesis by far red radiation in *Chlorella pyrenoidosa.* – Physiol. Plantarum **22**: 516-528, 1969.
Ort D.R., Merchant S.S., Alric J. *et al.*: Redesigning photosynthesis to sustainability meet global food and bioenergy demand. – P. Natl. Acad. Sci. USA **112**: 8529-8536, 2015.
Palovaara J., Akram N., Baltar F. *et al.*: Stimulation of growth of proteorhodopsin phototrophy involves regulation of central metabolic pathways in marine planktonic bacteria. – P. Natl. Acad. Sci. USA **111**: E3650-E3658, 2014.
Pan H., Slapeta J., Carter D. *et al.*: Phylogenetic analysis of the light-harvesting system in *Chromera velia*. – Photosynth. Res. **111**: 19-28, 2012.
Pazderník M.: Light harvesting complexes and chromatic adaptation of Eustigmatophyte alga *Trachydiscus minutus.* MSc Thesis, University of Southern Bohemia, České Budějovice 2015.
Pettai H., Oja V., Freiberg A. *et al.*: Photosynthetic activity of far-red light in green plants. – BBA-Bioenergetics **1708**: 311-321, 2005b.
Pettai H., Oja V., Freiberg A. *et al.*: The long-wavelength limit of plant photosynthesis. – FEBS Lett. **579**: 4017-4019, 2005a.
Pinhassi J., deLong E.F., Béjà,O. *et al.*: Marine bacterial and archael ion-pumping rhodopsins: genetic diversity, physiology, and ecology. – Microbiol. Mol. Biol. R. **80**: 929-954, 2016.
Pirie N.W.: The size of small organisms. – P. Roy. Soc. B-Biol. Sci. **160**: 149-166, 1964.
Pirie N.W.: On being the right size. – Annu. Rev. Microbiol. **27**: 119-166, 1973.
Poorter L., Oberbauer S.T., Clark D.B.: Leaf optical properties along a vertical gradient in a tropical rain forest canopy in Costa Rica. – Am. J. Bot. **82**: 1257-1263, 1995.
Poorter L., Kwant R., Hernández R., Medina E., Werger M.J.A.: Leaf optical properties in Venezuelan cloud forest trees. –Tree Physiol. **20**: 519-526, 2000.
Price D.C., Chan C-X., Yoon H-S. *et al.*: *Cyanophora paradoxa* genome elucidates origin of photosynthesis in algae and plants. – Science **335**: 843-847, 2012.
Přibyl P., Eliáš M., Cepák V. *et al.*: Zoosporogenesis, morphology, ultrastructure, pigment composition and phylogenetic position of *Trachydiscus minutus* (Eustigmatophyceae, Heterokontophyta). – J. Phycol. **48**: 231-242, 2012.
Rafique R., Zhao F., de Jong R. *et al.*: Global and regional variability and change in terrestrial ecosystems in net primary productivity and NDVI: a model-data comparison. – Remote Sens.-Basel **8**: 177, 2016.
Raven J.A.: A cost-benefit analysis of photon absorption by photosynthetic unicells. – New Phytol. **98**: 583-625, 1984.
Raven, J.A. Evolution of plant life forms. – In: Givnish T (ed.): On the Economy of Plant Form and Function. Pp. 421-492. Cambridge University Press, Cambridge 1986a.
Raven J.A. Physiological consequences of extremely small size for autotrophic organisms in the sea. – In: Platt T, Li W.K.W. (ed.): Photosynthetic Picoplankton. Pp. 1-70. Department of Fisheries and Oceans, Ottawa 1986b.
Raven J.A.: The bigger the fewer: size, taxonomic diversity and the range of chlorophyll(ide) pigments in oxygen evolving marine photolithotrophs. – J. Mar. Biol. Assoc. UK **76**: 211-217, 1996
Raven J.A.: Small is beautiful. The picophytoplankton. – Funct. Ecol. **12**: 503-513. 1998.
Raven J.A.: Picophytoplankton. – Prog. Phycol. Res. **13**: 33-106, 1999.
Raven J.A.: Astrobiology. Photosynthesis in watercolours. – Nature **448**: 418, 2007.
Raven J.A.: Functional evolution of photochemical energy transformation in oxygen-producing organisms. – Funct. Plant Biol. **36**: 505-515, 2009a.
Raven J.A.: Contribution of anoxygenic and oxygenic phototrophy and chemolithotrophy to carbon and oxygen fluxes in aquatic environments. – Aquat. Microb. Ecol. **56**: 177-192, 2009b.
Raven J.A.: Evolution and palaeophysiology of the vascular system and other means of long distance transport. – Philos. T. R. Soc. B **373**: 20160497, 2018.
Raven J.A., Smith F.A.: H^+ transport in the evolution of photosynthesis. – Biosystems **14**: 95-111, 1981.
Raven J.A., Cockell C.S.: Influence on photosynthesis of starlight, moonlight, planetlight and light pollution (Reflections

on photosynthetically active radiation in the universe). – Astrobiology **6**: 668-675, 2006.

Raven J.A., Hurd C.J.: Ecophysiology of photosynthesis in macroalgae. – Photosynth. Res. **113**: 105-125, 2012.

Raven J.A., Ralph P.J.: Enhanced biofuel production using optimality, pathway modification and waste minimization. – J. Appl. Phycol. **27**: 1-31, 2015.

Raven J.A., Beardall J.: The ins and outs of CO_2. – J. Exp. Bot. **67**: 1-13, 2016.

Raven J.A., Kübler J.E., Beardall J.: Put out the light, then put out the light. – J. Mar. Biol. Assoc. UK **80**: 1-25, 2000.

Raven J.A., Wolstencroft R.D.: Constraints on photosynthesis on Earth and Earth-like planets. – In: Norris, R.P., Stooman, F.H. (ed.): Bioastronomy: Life among the Stars. Proceedings of the 213th Symposium of the International Astronomical Union. Hamilton Island, Great Barrier Reef, Australia. Pp. 305-308. Astronomical Society of the Pacific, San Francisco, USA, 2002.

Raven J.A., Beardall J., Flynn K.J., Maberly S.C.: Phagotrophy in the origins of photosynthesis in eukaryotes and as a complementary mode of nutrition in phototrophs: relation to Darwin's Insectivorous Plants. – J. Exp. Bot. **60**: 3975-3987, 2009.

Raven J.A., Beardall J., Larkum A.W.D., Sanchez-Baracaldo P.: Interaction of photosynthesis with genome size and function. – Philos. T. Roy. Soc. B **368**: 20120264, 2013a.

Raven J.A., Donnelly S.: Brown Dwarfs and Black Smokers: the potential for photosynthesis using radiation from low-temperature black bodies. – In: de Vera J.-P., Seckbach J. (ed.): Habitats of other Planets and Satellites, Cellular Origin, Life in Extreme Habitats and Astrobiology. Pp. 267-284. Springer, Dordrecht 2013b.

Raven J.A., Beardall, J., Giordano M.: Energy cost of carbon dioxide concentrating mechanisms in aquatic organisms. – Photosynth. Res. **121**: 111-124, 2014.

Raven J.A., Beardall J., Sánchez-Baracaldo P.: The possible evolution and future of CO_2 concentrating mechanisms. – J. Exp. Bot. **68**: 3701-3716, 2017.

Reimers J.R., Cai Z.-L., Kobayashi R. *et al.*: Assignment of the Q-bands of the chlorophylls: coherence loss *via* Qx - Qy Mixing. – Sci. Rep-UK **3**: 2761, 2013.

Rexroth S., Mullineaux C.W., Ellinger E. *et al.*: The plasma membrane of the cyanobacterium *Gloeobacter violaceous* contains segregated bioenergetics domains. – Plant Cell **23**: 2379-2390, 2011.

Ritchie R.J.: Fitting light saturation curves measured using PAM fluorometry. – Photosynth. Res. **96**: 201-215, 2008.

Ritchie R.J.: The use of solar radiation by a photosynthetic bacterium, *Rhodopseudomonas palustris*: Model simulation of conditions found in a shallow pond or flatbed reactor. – Photochem. Photobiol. **89**: 1143-1162, 2013

Ritchie R.J.: Photosynthesis in an encrusting LÍichen (*Dirinaria picta* (Sw.) Schaer.ex Clem., Physiaceae) and its symbiont, *Trebouxia sp,* using PAM fluorometry. – Int. J. Plant Sci. **175**: 450-466, 2014.

Ritchie R.J., Runcie J.W.: Photosynthetic electron transport in an oxygenic photosynthetic bacterium *Afifella* (*Rhodopseudomonas*) *marina* measured using PAM fluorometry. – Photochem. Photobiol. **89**: 370-383, 2013.

Ritchie R.J., Runcie J.W.: A portable reflectance-absorptance-transmittance meter for photosynthetic work on vascular plant leaves. – Photosynthetica **52**: 614-626, 2014.

Ritchie R.J., Mekjinda N.: Measurement of photosynthesis using PAM technology in a purple sulphur bacterium *Thermochromatium tepidum* (Chromatiaceae). – Photochem. Photobiol. **91**: 350-358, 2015.

Ritchie R.J., Larkum A.W.D., Ribas I.: Could photosynthesis function on Proxima Centauri b? – Int. J. Astrobiol. **2017**: 1-30, 2017

Rosing M.T., Frei R.: U-rich Archaean sea-floor sediments from Greenland – indications of > 3700 Ma oxygenic photosynthesis. – Earth Planet. Sc. Lett. **217**: 237-244, 2004.

Rowan K.S.: Photosynthetic Pigments of Algae. Pp. 334. Cambridge University Press, Cambridge 1989.

Runcie J.W., Gurgel,C.F., Mcdermid K.J.: *In situ* photosynthetic rates of tropical marine macroalgae at their lower depth limit. – Eur. J. Phycol. **43**: 377-388, 2008.

Sabehi G., Kirkup B.C., Rozenberg M.: Adaptation and spectral tuning in divergent marine proteorhodopsins from the eastern Mediterranean and the Sargasso Sea. – ISME J. **1**: 49-55, 2007.

Sánchez-Baracaldo P., Pisani D., Raven J.A. *et al.*: Early photosynthetic eukaryotes inhabited low-salinity habitats. – P. Natl. Acad. Sci. USA **114**: E7727-E7746, 2017.

Sánchez-Baracaldo P., Ridgwell P., Raven J.A.: A neoproterozoic transition in the marine nitrogen cycle. – Curr. Biol. **24**: 652-657, 2014.

Sánchez-Baracaldo P.: Origin of marine planktonic cyanobacteria. – Sci. Rep.-UK **5**: 17418, 2015.

Saw J.H.W., Schatz M., Brown M.V. *et al.*: Cultivation and complete genome sequencing of *Gloeobacter kilaueensis* sp. nov., from a lava cave in Kīlauea Caldera, Hawai'i. – PLoS ONE **8**: e76376, 2013.

Seatae P., Bunthawi, S., Ritchie R.J.: Environmental persistence of chlorine from prawn farm discharge monitored by measuring the light reactions of photosynthesis of phytoplankton. – Aquacult. Int. **22**: 321-338, 2014.

Selosse M.-A., Charpin M., Not F.: Mixotrophy everywhere on land and in the water: the *grand écourt* hypothesis. – Ecol. Lett. **20**: 246-263, 2017.

Senge M.O., Smith K.M.: Biosynthesis and Structures of the Bacteriochlorophylls. – In: Blankenship R.E., Madigan M.T., Bauer C.E. (ed): Anoxygenic Photosynthetic Bacteria. Pp. 137-151. Kluwer Academic Publishers, Dordrecht 1995.

Shih P. M., Hemp J., Ward L.M. *et al.*: Crown group Oxyphotobacteria postdate the rise of oxygen. – Geobiology **15**: 19-29, 2017.

Scheer H.: An overview of chlorophylls and bacteriochlorophylls: biochemistry, biophysics, functions and applications – In: Scheer H. (ed.): Chlorophylls and Bacteriochlorophylls. Pp. 1-26. Springer, Dordrecht 2006.

Scheer H.: Structure and occurrence of chlorophylls. – In: Scheer H. (ed.): Chlorophylls and Bacteriochlorophylls. Pp. 3-30. CRC Press, Boca Raton 1991.

Schirrmeister B.E., Sánchez-Baracaldo P., Wacey D.: Cyanobacterial evolution during the Precambrian. – Int. J. Astrobiol. **15**: 187-204, 2016.

Schliep M., Cavigliasso G., Quinnell R.G. *et al.*: Formyl group modification of chlorophyll *a*: a major evolutionary mechanism in oxygenic photosynthesis. – Plant Cell Environ. **36**: 521-527, 2013.

Schliep M., Crossett B., Willows R.D. *et al.*: O-18 labeling of chlorophyll *d* in *Acaryochloris marina* reveals that chlorophyll *a* and molecular oxygen are precursors. – J. Biol. Chem. **285**: 28450-28456, 2010.

Schliep M., Chen M., Larkum T. *et al.*: The function of MgDVP in a chlorophyll *d*-containing organism. – Photosynth. Res. **91**:

263-263, 2007.
Schlodder E., Lendzian F., Meyer J. *et al.*: Long-wavelength limit of photochemical energy conversion in photosystem I. – J. Am. Chem. Soc. **136**: 3904-3918, 2014.
Schmidt S., Raven J.A., Paungfoo-Lonhienne C.: The mixotrophic nature of photosynthetic plants. – Funct. Plant Biol. **40**: 425-438, 2013.
Schobert B., Lanyi J.K.: Halorhodopsin is a light-driven chloride pump. – J. Biol. Chem. **257**: 10306-10313, 1982.
Skelton A.E., Catchpole G., Abbott J.T. *et al.*: Biological origins of color categorization. – P. Natl. Acad. Sci. USA **114**: 5545-5550, 2017.
Slamowitz C.H., Okamoto N., Burri L. *et al.*: A bacterial proteorhodopsin proton pump in marine eukaryotes. – Nat. Commun. **2**: 183, 2011.
SMARTS: Simple Model of Atmospheric Radiative Transfer of Sunshine (SMARTS): http://www.nrel.gov/rredc/smarts/ [Accessed 12/Aug/2011].
Som S.M., Buick R., Hagadorn J.W. *et al.*: Earth's air pressure 2.7 billion years ago constrained to less than half of present levels. – Nat. Geosci. **9**: 448-451, 2016.
Som S.M., Catling D.C., Hornmeijer J.P. *et al.*: Air density billion years ago limited to less than twice modern levels. – Nature **484**: 359 -362, 2012.
Soo R.M., Hemp J., Parks D.H. *et al.*: On the origins of oxygenic photosynthesis and aerobic respiration in cyanobacteria. – Science **355**: 1436-1440, 2017.
Soo R.M., Skennerton C.T., Sekiguchi Y. *et al.*: An expanded genomic representation of the phylum cyanobacteria. – Genome Biol. Evol. **6**: 1031-1045, 2014.
Sparks W.B., DasSarma S., Reid I.N.: Evolutionary competition between primitive systems: existence of an early purple Earth? – In: Bulletin of the American Astronomical Society, Vol. 38. Pp. 901. University of Maryland Biotechnology Institute, Maryland 2007.
Stoecker D.K., Hansen P.J., Caron D.A. *et al.*: Mixotrophy in the marine plankton. – Annu. Rev. Mar. Sci. **9**: 311-335, 2017.
Stomp M., Huisman J., Stal L.J. *et al.*: Colorfull niches of phototrophic microorganisms shaped by vibrations of the water molecules. – ISME J. **1**: 271-282, 2007.
Suomivuori C-M., Gamiz-Hernandez A.P., Sundholm D. *et al.*: Energetics and dynamics of a light-driven sodium-pumping rhodopsin. – P. Natl. Acad. Sci. USA **114**: 7043-7048, 2017.
Telfer A., Pascal A., Barber J. *et al.*: Electron transfer reactions in photosystem I and II of the chlorophyll *d* containing cyanobacterium, *Acaryochloris marina*. – Photosynth. Res. **91**: 143-143, 2007.
Thapper A., Madedor F., Mokvist F. *et al.*: Defining the far-red limit of photosystem II in spinach. – Plant Cell **21**: 2381-2401, 2009.
Tice M.M., Lowe D.R.: Photosynthetic microbial mats in the 3,416-Myr-old ocean. – Nature **431**: 549-552, 2004.
Tomitani A., Okada K., Miyashita H. *et al.*: Chlorophyll *b* and phycobilins in the common ancestor of cyanobacteria and chloroplasts. – Nature **400**: 159-162, 1999.
Tomkins A.G., Bowlt L., Genge M. *et al.*: Ancient micrometeorites suggestive of oxygen-rich Archaean upper atmosphere. – Nature **533**: 235-238, 2016.
Toms T., Shinoda T., Chen M. *et al.*: Energy transfer processes in chlorophyll *f*-containing cyanobacteria using time-resolved fluorescence spectroscopy on intact cells. – Biochim. Biophys. Acta **1837**: 1484-1489, 2014.
Trissl H.W.: Modelling the excitiation energy capture in thylakoid membranes. – In: Larkum A.W.D., Douglas S.E. Raven J.A. (ed.): Photosynthesis in Algae. Pp. 245-276. Springer Verlag, Berlin 2003.
Tsukamoto T., Yoshizawa S., Kikukawa T. *et al.*: Implications for light driven chloride ion transport mechanism of *Nonlabens marinus* Rhodopsin 3 by its photochemical characteristics. – J. Phys. Chem. B **121**: 2027-2038, 2017.
Tsunuda S.P., Ewers D.O., Gazzarrini S. *et al.*: H^+-pumping rhodopsin from the marine alga *Acetabularia*. – Biophys. J. **91**: 1471-1479, 2006.
Vásquez-Elizondo R.M., Legaria-Moreno L., Pérez-Castro M.A. *et al*.: Absorptance determinations on multicellular tissues. – Photosynth. Res. **132**: 311-324, 2017.
Vogl K., Tank M., Orf G.S. *et al.*: Bacteriochlorophyll *f*: properties of chlorosomes containing the "forbidden chlorophyll". – Front. Microbiol. **3**: 298, 2012.
Vopel K., Hawes I.: Photosynthetic performance of benthic microbial mats in Lake Hoare, Antarctica. – Limnol. Oceanogr. **51**: 1801-1812, 2006.
Wakao N., Yokoi N., Isoyama N. *et al.*: Discovery of natural photosynthesis using Zn-containing bacteriochlorophyll in an aerobic bacterium *Acidophilium rubrum*. – Plant Cell Physiol. **37**: 889-893, 1996.
Waters E.R.: Molecular adaptation and the origin of land plants. – Mol. Phylogenet. Evol. **29**: 456-463, 2003.
Wellman C.H., Strother P.K.: The terrestrial biota prior to the origin of land plants (embryophytes): a review of the evidence. – Palaeontology **58**: 601-627, 2015.
Wilhelm C., Jakob T.: Uphill energy transfer from long-wavelength absorbing chlorophylls to PSII in *Ostreobium* sp. is functional in carbon assimilation. – Photosynth. Res. **87**: 323-329, 2006.
Williams P.J.leB. , Laurens L.M.L.: Microalgae as biodiesel and biomass feedstocks: review and analysis of the biochemistry, energetics and economics. – Energ. Environ. Sci. **3**: 554-590, 2010.
Willows R.D., Li Y., Scheer H. *et al.*: Structure of chlorophyll *f*. – Org. Lett. **15**: 1588-1590, 2013.
Wolf B.J., Niedzwiedzki D.M., Magdaong N.C.M. *et al.*: Characterizarion of a newly isolated Eustigmatophyte alga capable of ultilizing far-red light as its sole light source. – Photosynth. Res. doi: 10.1007.s11120-017-0401-z, *in press*, 2017.
Wolstencroft R.D., Raven J.A.: Photosynthesis: likelihood of occurrence and possibility of detection on Earth-like planets. – Icarus **157**: 535-548, 2002.
Wraight C.A., Clayton R.K.: The absolute quantum efficiency of bacteriochlorophyll photo-oxidation in reaction centres of *Rhodopseudomonas spheroides.* – Biochim. Biophys. Acta **333**: 246-260, 1974.
Yoshizawa S., Kumagai Y., Kim H. *et al.*: Functional characterisation of flavobacteria rhodopsins reveal a unique class of light-driven chloride pump in bacteria. – P. Natl. Acad. Sci. USA **111**: 6732-6737, 2014.
Yurkov V., Beatty J.T.: Aerobic anoxygenic photosynthetic bacteria. – Microbiol. Mol. Biol. Rev. **62**: 695-724, 1998.
Yutin N., Koonin E.V.: Proteorhodopsin genes in giant viruses. – Biol. Direct **7**: 34, 2012.
Zak E., Norling B., Maitra R. *et al.*: The initial steps of biogenesis of cyanobacterial photosystems occur in plasma membranes. – P. Natl. Acad. Sci. USA **98**: 13443-13448, 2001.
Zapata M., Garrido J.L.: Occurrence of phytylated chlorophyll *c* in *Isochrysis galbana* and *Isochrysis sp.* (Clone T-Iso)

(Prymnesiophyceae). – J. Phycol. **33**: 209-214, 1997.

Zeng Y., Feng F., Liu Y. *et al.*: Genome sequences and photosynthetic gene cluster composition of a freshwater aerobic anoxygenic phototroph, *Sandarakinorhabdus* sp. strain AAP62, isolated from the Shahu Lake of Ningxia, China. – Genome Announc. **1**: e00034-13, 2013a.

Zeng Y., Koblížek M., Feng F. *et al.*: Whole-genome sequence of an aerobic anoxygenic phototroph, *Blastomonas* sp. strain AAP 53, isolated from a freshwater desert lake in inner Mongolia, China. – Genome Announcements 1: e00071-13, 2013b.

Zheng Q., Liu Y., Sun J. *et al.*: Whole-genome sequence of aerobic anoxygenic phototrophic bacterium *Erythrobacter* sp. JL457, isolated from the South China Sea. – Mar. Genom. **21**: 15-16, 2015.

Zhu X.G., Long S.P., Ort D.R.: What is the maximum efficiency with which photosynthesis can convert solar energy into biomass. – Curr. Opin. Biotech. **19**: 153-159, 2008.