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REVIEW

Non-*a* chlorophylls in cyanobacteria

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Abstract

In cyanobacteria and chloroplasts, chlorophyll *a* (Chl *a*) is not always the single type of Chl used in oxygenic photosynthesis. Rather, there is a series of non-*a* Chls, namely, *b*-type Chls, *c*-type Chls, Chl *d*, and Chl *f*. Plenty of reviews published over the past decades commented on these Chls in chloroplasts while only few analogously dealt with cyanobacteria. The review article takes an effort to span the gap. Cyanobacterial *b*-type and *c*-type Chls are exclusively antenna pigments; they absorb near-red and blue light, respectively, and facilitate waste-less energy input to reaction centers. Chl *d* and possibly Chl *f* partake in both antennae and reaction centers; they empower constitutive usage of far-red light or participate in the adaptive mechanism of far-red light photoacclimation.

Additional key words: absorption spectrum; CBP protein; photoadaptation; photosynthetic apparatus; phycobilisome; primary donor.

Introduction

In cyanobacteria, as in chloroplasts, chlorophyll *a* (Chl *a*) not always represents the only one Chl involved in the light phase of oxygenic photosynthesis. Rather, there are several non-*a* Chls: *b*-type Ch1s, *c*-type Chls, Chl *d*, and Chl *f*.

The high adaptability of cyanobacteria permits them to assimilate radiant energy within various regions of light spectrum. Corresponding mechanisms include State 1 ↔ State 2 transition (Allen 1992), complementary chromatic adaptation (Grossman *et al*. 1993), and far-red (> 700 nm) light photoacclimation (FaRLiP, *see* below). Most distributed and apparently the eldest photoadaptation strategy is based on individual absorption properties of non-*a* Chls.

Chl *b*, number one in a series of cyanobacterial non-*a* Chls, was encountered in *Prochloron didemni*, the unicellular symbiont of colonial ascidians inhabiting low latitude marine environments (Lewin 1975, Newcomb and Pugh 1975). This genus and similarly pigmented free-living or symbiotic prokaryotes have been provisionally termed green cyanobacteria (Pinevich *et al*. 2012, Partensky *et al*. 2018) by semblance with green algae to highlight their shared Chl *b* presence with chloroplasts.

Chls inventory in ancestral cyanobacteria and primordial chloroplasts is far from being reliably reconstructed. While Chl *a* is considered to be the evolutionary progenitor and metabolic precursor of other Chls (Kobayashi *et al*. 2013), the hypotheses on the evolution of Chl *b* biosynthesis gene imply either a vertical inheritance or a lateral transfer event (Tomitani *et al*. 1999). In the first case, ancestral cyanobacteria should contain Chls *a* and *b* (assuming the loss of a gene for Chl *b* biosynthesis in most of the descendent cyanobacteria). In the second case, the gene should originate in one of cyanobacterial lineages. It has to be revealed of how and when 3,8-divinyl Chl *b*, *c*-type Chls, and Chls *d* and *f* were acquired by cyanobacteria and chloroplasts.

Ample data published over the past decades touched on non-*a* Chls in chloroplasts. At the same time, there is a scarcity of compilations, from the past seven years, bearing a relation to *b*- and *c*-type Chls, Chl *d*, and Chl *f* in cyanobacteria (*e.g*., Pinevich *et al*. 2012, Miyashita *et al*. 2014, Biller *et al*. 2015, Allakhverdiev *et al*. 2016, Averina *et al*. 2018, Larkum *et al*. 2018). Herein, we review a handful of target information especially focusing on these pigments in a relatively small known to date number of cyanobacterial strains possessing them.

Chlorophylls: general features

Chls, or Mg-chelating cyclic tetrapyrrol pigments (Fig. 1), intensively absorb light in visible and far-red regions (Fig. 2). It is noteworthy that *in vivo* absorption spectra for apoprotein-bound Chls are nearly always different from the spectra for Chls dissolved in organic solvents. In particular, 'red' peak (the Q_y vector of energy transition in long-wavelength area) is positioned at shorter wavelengths.

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Abbreviations: Chl – chlorophyll; FaRLiP – far-red light photoacclimation; PBP – phycobiliprotein; PBS – phycobilisome; Phe – pheophytin; RC – reaction center.
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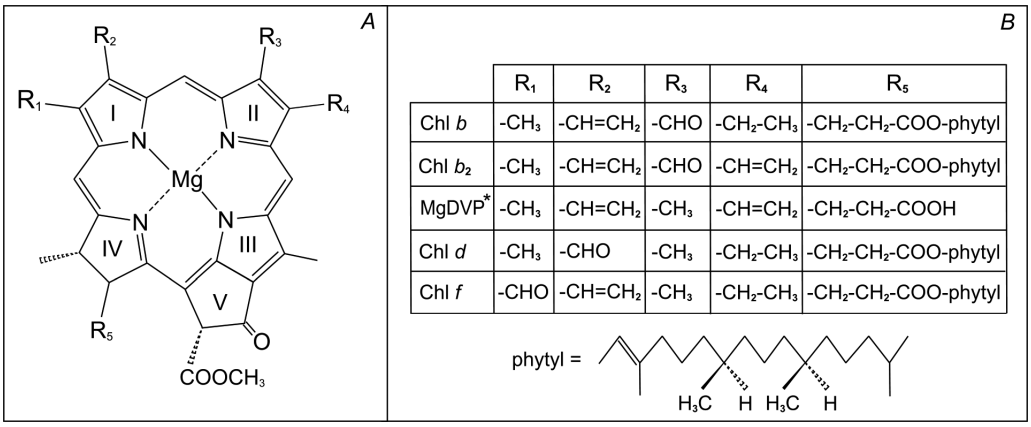

	R_1	R_2	R_3	R_4	R_5
Chl *b*	$-CH_3$	$-CH=CH_2$	-CHO	$-CH_2-CH_3$	$-CH_2-CH_2-COO$-phytyl
Chl b_2	$-CH_3$	$-CH=CH_2$	-CHO	$-CH=CH_2$	$-CH_2-CH_2-COO$-phytyl
MgDVP*	$-CH_3$	$-CH=CH_2$	$-CH_3$	$-CH=CH_2$	$-CH_2-CH_2-COOH$
Chl *d*	$-CH_3$	-CHO	$-CH_3$	$-CH_2-CH_3$	$-CH_2-CH_2-COO$-phytyl
Chl *f*	-CHO	$-CH=CH_2$	$-CH_3$	$-CH_2-CH_3$	$-CH_2-CH_2-COO$-phytyl

Fig. 1. Non-*a* chlorophylls. (*A*) General molecular structure. Pyrrol rings, carbon atom numbering, and radical orientations are according to the IUPAC/IUBMB (International Union of Pure and Applied Chemistry/International Union of Biochemistry and Molecular Biology) system. (*B*) Table showing R radicals (1 to 5) in different chlorophylls. *Asterisk* means that the C17–C18 position of MgDVP contains a double bond. Chl – chlorophyll; MgDVP – Mg-3,8-divinyl protochlorophyllide (*c*-type chlorophyll). Modified from Chen (2014), Allakhverdiev *et al*. (2016), and Larkum *et al*. (2018).

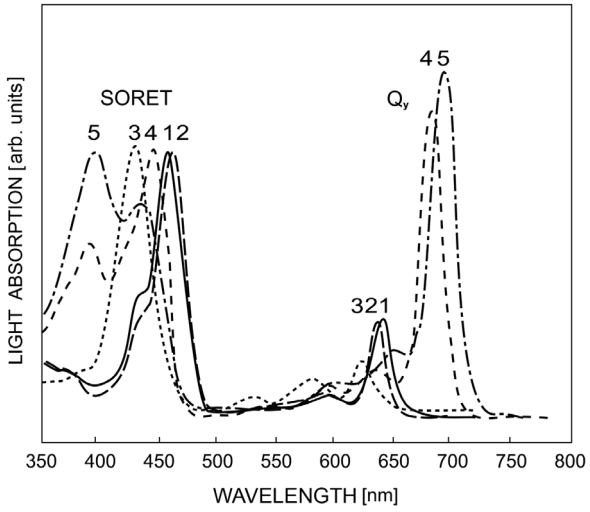

Fig. 2. Absorption spectra of non-*a* chlorophylls. Soret – Soret bands (absorption 'blue' maxima in the short-wavelength area); Q_y – Q_y bands (absorption 'red' maxima, Q_y vectors of energy transition in the long-wavelength area). For comparison, Soret band maxima are arbitrarily scaled to a common height. 1 – chlorophyll *b* (the Q_y band maximum is 645 nm, in acetone); 2 – chlorophyll b_2 (the Q_y band maximum is 644 nm, in diethyl ether); 3 – *c*-type chlorophyll (the Q_y band maximum is 625 nm, in 100% acetone); 4 – chlorophyll *d* (the Q_y band maximum is 688 nm, in 100% acetone); 5 – chlorophyll *f* (the Q_y band maximum is 698 nm, in acetone). Modified from Jeffrey *et al*. (1997), Li *et al.* (2012), and Allakhverdiev *et al*. (2016).

Chls are designated alphabetically in agreement with the order of their discovery (the absence of 'Chl *e*' is because of unfounded reports of the presence of this pigment in some green algae; *see* Larkum *et al*. 2018).

Chl *a* is a sole Chl in chloroplasts (which are also termed the primary plastids) of red algae and glaucophytes, while in primary plastids of green algae and terrestrial plants this pigment is attended with Chl *b*. The so-called secondary plastids (degenerative eukaryotic endosymbionts containing a primary plastid as most prominent rudiment; Keeling 2004) contain, in addition to Chl *a*, either Chl *b* (in euglenophytes, chlorarachniophytes, and 'green' dinoflagellates) or *c*-type Chls (in cryptophytes, dinoflagellates, haptophytes, and heteroconts) (*see* Kobayashi *et al*. 2013).

Functionally, Chls subdivide into major and accessory ones. The former are incorporated in photosynthetic reaction centers (RCs), while the latter play an antenna role. RCs possess, besides Chl molecules performing primary photochemistry, a small number of Chl molecules which participate in RC core antennae. These alone cannot supply enough excited state energy for phototrophy (even in bright sunlight, their photon absorption rate is several orders of magnitude slower than the turnover rate of RCs; *see* Hunter *et al*. 1989). The potential bottleneck is dilated with a help of additional light-harvesting complexes (LHCs) that (*1*) contain large number of Chl or phycobiliprotein (PBP) molecules; (*2*) depending on a type of photoadaptation, absorb quanta in different regions of light spectrum, and (*3*) redistribute excitation energy between RCI and RCII (Blankenship and Chen 2013).

Chl *a* usually represents a major cyanobacterial Chl (except *Acaryochloris marina* in which bulk and major Chl is Chl *d*, *see* below). Typically, cyanobacteria contain phycobilisome (PBS) as a non-chlorophyllous LHC, and lack accessory Chls, although a minority of strains produce *b*- and *c*-type Chls, Chl *d*, and Chl *f*. These have been shown to participate in LHCs while Chl *d*, and possibly Chl *f*, also can be a key component of RC complexes.

b-type chlorophylls: participation in light-harvesting antenna complexes

In comparison to *a*-type Chls, *b*-type Chls are 'green shifted', *i.e.*, their Q_y band is displaced for *ca*. 20 nm to near-red region (662 → 645 nm, in 100% acetone; Jeffrey

et al. 1997).

Possession of accessory *b*-type Chls is the specific trait for a combined group of PBS-lacking cyanobacteria (Goericke and Repeta 1992, van der Staay *et al*. 1998, Velichko *et al*. 2012). These are represented by unicellular species *Prochloron didemni* (Lewin 1975) and *Prochlorococcus marinus* (Chisholm *et al*. 1988), and filamentous species *Prochlorothrix hollandica* (Burger-Wiersma *et al*. 1989) and *P. scandica* (Velichko *et al*. 2012) not closely related to one another. The unicellular species *Acaryochloris thomasi* RCC1774 is similar to these cyanobacteria in that it contains Chl *b* (at the Chls *a*/*b* molecular ratio of 6.25), and differs from them in that it contains a PBS (*see* below). Additionally, this strain is dissimilar from other members of the genus *Acaryochloris* (*see* below) in that it lacks Chl *d* (Partensky *et al*. 2018).

Chl *b* supposedly originates from 3,8-divinyl Chl *b* in enzymatic reaction catalyzed by C8-vinyl reductase (Helfrich *et al*. 1999). An alternate biosynthetic route is assumed to use Chl *a* oxygenase reaction (Tanaka *et al*. 1998; Fig. 3).

P. marinus contains accessory 3,8-divinyl Chls *a* and *b* which are also termed Chls a_2 and b_2 (Goericke and Repeta 1992). Chl b_2 displays nearly the same Q_y band position with Chl *b* (644 nm, in diethyl ether; *see* Jeffrey *et al*. 1997) but it more intensely absorbs short-wavelength light than its monovinyl counterpart. Only *P. marinus* NIES-2086 is known to possess both *b*-type Chls (Komatsu *et al*. 2016).

LHCs in *P. didemni*, *P. hollandica*, and *P. marinus* are remarkably similar in structure to one another. They consist of highly hydrophobic six-domain 28–36 kDa proteins belonging to the CBP (Chl-binding protein; previous designation – Pcb, prochlorophyte Chl *b* protein) superfamily. The CBP proteins can bind Chls *a* and *b*, Chls a_2 and b_2, as well as *c*-type Chls and Chl *d* (Chen *et al*. 2008, Averina *et al*. 2018). Importantly, they are dissimilar from three-domain proteins of the CAB (Chls *a*/*b* protein) superfamily typical for the chlorobionts (Chlorophyceae, Euglenophyceae, and Viridiplantae; La Roche *et al*. 1996). Rather, they are similar to the members of CP43/IsiA family (Burnap *et al*. 1993). In particular, the CP43 (PsbC) protein participates in RCII core antenna while the IsiA (CP43') protein represents an iron stress-induced component of RCII peripheral antenna. Six-domain proteins CBP, CP43, and IsiA vary in the length of peripheral loop connecting integral spirals V and VI (Herbstová *et al*. 2010). The CBP proteins aggregate with each other to produce multimeric supercomplexes embedded in thylakoid membrane (Bibby *et al*. 2001).

In *P. didemni*, ten CBP subunits associate with dimeric RCII core to form a supercomplex (*ca*. 20 × 30 nm in size, 1.5 mDa molecular mass) that provides for a nearly threefold increase in the size of PSII antenna (Bibby *et al*. 2003a).

The CBP proteins of *P. hollandica* are CBPA (32 kDa), CBPB (33.5 kDa), and CBPC (38 kDa), correspondingly (van der Staay and Staehelin 1994). The CBPA and CBPB proteins are highly similar to those in *P. didemni* and *P. marinus* (Nikolaitchik and Bullerjahn 1998), while the CBPC protein has a different amino acid composition than

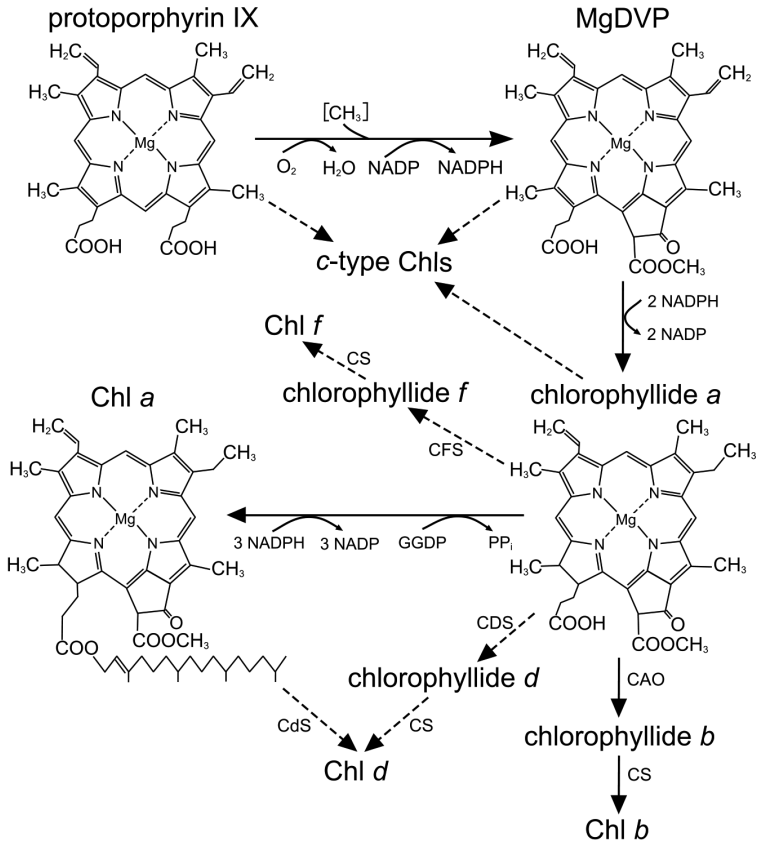

Fig. 3. Final reactions in the biosynthesis of chlorophylls *a*, *b*, *c*-type, *d*, and *f*. *Dashed arrows* indicate biochemically feasible conversions. Chl – chlorophyll; MgDVP – Mg-3,8-divinyl protochlorophyllide (*c*-type chlorophyll); CAO – chlorophyll *a* oxygenase; CDS – chlorophyllide *d* synthase; CdS – chlorophyll *d* synthase; CFS – chlorophyllide *f* synthase; CS – chlorophyll synthase; GGDP – geranylgeranyl diphosphate; NADP(H) – oxidized and reduced nicotinamide adenine dinucleotide phosphate, respectively; PP_i – inorganic pyrophosphate. Modified from Schliep *et al*. (2013).

that in other PBS-lacking cyanobacteria (van der Staay *et al*. 1998, Garczarek *et al*. 2000). PSI and PSII oligomers are assumed to be encircled by their respective antenna supercomplexes (Bibby *et al*. 2003a, Boichenko *et al*. 2007). Alternately, the CBPA and CBPB proteins are supposed to form an antenna that dynamically interacts with either PS, while the CBPC protein-containing domain of LHC preferentially interacts with PSI (Herbstová *et al*. 2010).

PSI and PSII in low light-adapted (LL) deep-water *P. marinus* strains (Coleman and Chisholm 2007) possess individual peripheral antennae (Bibby *et al*. 2003b). Here, the CBPC proteins constitute the 18-meric supercomplex encircling PSI trimer, while the CBPB proteins produce an octameric ring around PSII dimer (Bibby *et al*. 2001, Dekker and Boekema 2005). At the same time, in high light-adapted (HL) surface-water strains (Coleman and Chisholm 2007), only the genes encoding the CBPA and CBPC proteins are transcribed, while the CBPB protein is regulated similarly with the IsiA protein – both are induced by iron stress (Bibby *et al*. 2003b). In other words, CBP supercomplexes in HL- and LL-strains specify two contrasting adaptive strategies (Chen *et al*. 2005b, Biller *et al.* 2015).

c-type chlorophylls: participation in light-harvesting antenna complexes

The so-called '*c*-type Chls' is a set of structurally related molecules – Chls c_1, c_2, and c_3 being most common. They have been investigated in marine algae, primarily in diatoms (Zapata *et al*. 2006). However, in the strict sense of the term, *c*-type Chls are not true Chls (*see* Fig. 1). Namely, they have a trait of porphyrins (double bond in C17–C18 position, 22 π electrons), on the one hand, and a trait of chlorophyllides (carboxyl residue in C17 position is not phytilated, with the exception of Chl c_3; Zapata *et al*. 2006), on the other hand. Despite *c*-type Chls weakly absorb light in long-wavelength area (the Q_y band at *ca*. 628 nm; *see* Fig. 2), they have a pronounced Soret band (absorption 'blue' maximum) lying close to that of Chl *a* (445–450 nm *vs*. 430.3 nm, in 100% acetone; *see* Jeffrey *et al*. 1997). Biosynthetic pathway for *c*-type Chls has not been yet elucidated: they can be equally proposed to derive from: (*1*) Mg-protoporphyrin IX, (*2*) Mg-C3,C8-divinyl phaeoporphyrin a_5 monomethyl ester (divinyl protochlorophyllide, MgDVP), and (*3*) chlorophyllide *a* (Schliep *et al*. 2013; Fig. 3).

c-type Chls have been found in *P. didemni* (Larkum *et al*. 1994) and *A. marina* (Miyashita *et al*. 1997); a negligible amount of this pigment has been also detected in *P. marinus* (Chisholm *et al*. 1988). In particular, *P. didemni* contains the accessory MgDVP which is similar to Chls c_2 and c_3 in that it contains vinyl group in C8 position. At the same time, this pigment differs from *c*-type Chls proper (Chen 2014) in that it has propionyl group in C17 position instead of acryl group. The content of accessory MgDVP in *P. didemni* is 4–15% of total Chl amount, and this pigment is thought to participate in LHC together with Chls *a* and *b* (Larkum *et al*. 1994).

Chlorophyll *d*: participation in light-harvesting antenna complexes and reaction centers

Chl *d* contains formyl group in C3 position instead of vinyl group of Chl *a* (*see* Fig. 1). The relatively small substitution has brought to pronounced change of light absorption: the Q_y band is displaced for *ca*. 30 nm to far-red area (665 → 688 nm, in 100% acetone; Li *et al*. 2012).

Chl *d* was firstly found in *A. marina* MBIC 110017 isolated from a symbiotic association of this cyanobacterium with the West Pacific ascidian *Lissoclinum patella* (Miyashita *et al*. 1996). Here, Chl *d* comprises the majority of Chl molecules, while Chl *a* represents only 1–10%, depending on light regime (Miyashita *et al*. 1997, Mimuro *et al*. 2004, Lin *et al*. 2013a). Additionally, Chl *d*-containing strains were obtained from symbiotic associations of *A. marina* with the ascidians *Diplosoma* spp. (Kühl *et al*. 2005), *Cystodytes dellechiajei* (Martínez-García *et al*. 2011), and *Lissoclinum fragile* (López-Legentil *et al*. 2011).

Besides the type strain MBIC 110017, the species *A. marina* is represented by a series of low latitude endo- and epyzoic strains – Awaji-1 (Murakami *et al*. 2004), CCMEE 5410 (Miller *et al*. 2005), MBIC 10697 (Swingley *et al*. 2005), HICR 111A (Mohr *et al*. 2010), MPGRS1 (Larkum *et al*. 2012), CRS (Behrendt *et al*. 2013), and Ssball 1 (Lin *et al*. 2013b).

According to metagenomics data, operational taxonomic units (OTUs) assembling the tags most similar to those of *A. marina* are widespread on coral reefs. In such niches, they comprise *ca*. 5% of cyanobacterial and *ca*. 2% of total bacterial sequences, correspondingly (Behrendt *et al*. 2011). The tags similar to *A. marina* tags were obtained from the ascidians *Didemnum molle*, *Lissoclinum patella*, *L. punctatum*, and *L. timorense*, as well as from the sponge *Neopetrosia exigua* (Ohkubo and Miyashita 2012). Additionally, *Acaryochloris*-similar sequences were detected in microbial communities of Antarctic rocks (de los Ríos *et al*. 2007), Mayan pyramids (McNamara *et al*. 2006), and the Andes' microbial mats (Fleming and Prufert-Bebout 2010). Finally, *Acaryochloris* tags were obtained from red algal crusts in geographically distant places, such as the Red Sea and Australian Great Barrier reef, as well as in coastal zones of Croatia and Spain (Behrendt *et al*. 2014). However, high similarity of environmental 16S rDNA with *A. marina* 16S rDNA does not guarantee that the former belonged to Chl *d*-containing strains. For example, Chls *a*- and *b*-containing cyanobacterium *A. thomasi* RCC1774 (Partensky *et al*. 2018) densely clusters with *A. marina* although it lacks Chl *d* discriminating this unicellular genus.

Unlike *A. marina* that contains Chl *d* as main Chl, unicellular cyanobacteria *Chroococcidiopsis thermalis* PCC 7203, *Synechococcus* sp. PCC 7335 (Gan *et al*. 2014), and *Synechocystis* sp. CALU 1173 (Averina *et al*. 2018) adaptively produce a minor amount of accessory Chl *d* when subjected to far-red light illumination (the adaptive response termed far-red light photoacclimation, FaRLiP; Gan *et al*. 2015). Filamentous strains that exhibit this property include *Chlorogloeopsis fritschii* PCC 6912 (Airs

et al. 2014), *Chlorogloeopsis* sp. PCC 9212, *Fischerella thermalis* PCC 7521, *Calothrix* sp. PCC 7507 (Gan *et al*. 2015), and *Leptolyngbya* sp. JSC-1 (Gan *et al*. 2014).

Similar to Chls *b* and *c*, Chl *d* is formed in the common biosynthetic pathway ultimately leading to individual porphyrins and Chls (Bauer *et al*. 1993, Schliep *et al*. 2013; Fig. 3). Taking into account that Chl *d* differs from Chl *a* by formyl group in C3 position instead of vinyl group, the former pigment is suggested to originate from the latter pigment. Alternately, Chl *d* may be produced in reactions of a separate terminal biosynthetic branch (Loughlin *et al*. 2013). The conversion of Chl *a* in Chl *d* is more plausible: thus, experiments with $^{18}O_2$ or $H_2{}^{18}O$ demonstrated that oxygen atom in formyl group originates from dioxygen molecule (Schliep *et al*. 2010). Although Chl *d* synthase has not been yet identified, a candidate enzyme may be P450-type cytochrome (Chen and Blankenship 2011, Yoneda *et al*. 2016).

Chl *d* is not only the LHC pigment in *A. marina* LHC – it also partially replaces Chl *a* in RCI and RCII (Itoh *et al*. 2007). In this respect, Chl *d* functionally differs from *b*- and *c*-type Chls (which are exclusively antenna pigments), and is similar to Chl *f* (which participates in LHCs and possibly in RCs; *see* below).

The LHC of *A. marina* channels energy to both PSI and PSII (Schiller *et al*. 1997, Chen *et al*. 2005c,d). This membrane-embedded photosynthetic antenna is build of six-domain proteins belonging to the CBP superfamily (*see* above). As many as 18 CBP subunits encircle a trimer of PSI complexes, while a tetramer of PSII complexes is flanked by CBP octamers (Chen *et al*. 2005a,b). In iron-starved cells, the CBPC proteins substitute for the CBPA proteins; similarly, low-light conditions induce transcription of the genes encoding adaptive CBP proteins (Swingley *et al*. 2005, Chen *et al*. 2008).

The structure of RCI in *A. marina* has been investigated in detail. The scaffold PsaA/PsaB heterodimer is 86% similar to that in most of cyanobacteria. The primary donor P740 is represented by Chls *d*/*d*' special pair (*d*' stands for C13^2-allomer of Chl *d*; *see* Fig. 1). It interacts with two intrinsic Chl *a* molecules and two phylloquinone molecules, and with 97 Chl *d* molecules of RC core antenna (Hu *et al*. 1998). Redox potential of primary donor (P740∗) is –439 mV (Hu *et al*. 1998), *i.e*., nearly the same value as that of Chl *a* special pair (P700∗) in most of cyanobacteria (Tomo *et al*. 2007). The primary acceptor is one of two intrinsic Chl *a* molecules (Hu *et al*. 1998).

The structure of RCII in *A. marina* has not been yet clarified. The role of Chl *d* special pair as primary donor is questionable because, in this case, excited state energy would not drive the water-oxidizing complex (Allakhverdiev *et al*. 2016). In its turn, the use of Chl *a* special pair P680 (as in most of cyanobacteria) addresses a problem of uphill transfer of excited state from light-harvesting Chl *d*. Data obtained in experiments with thylakoid membrane preparations indicate that primary donor could be Chl *d* special pair P713 (Tomo *et al*. 2007); the analysis of purified RCII is in support of this possibility (Itoh *et al*. 2007). At the same time, calculations performed by Renger and Schlodder (2008) indicated the primary donor to be Chls *a*/*d* heterodimer.

In well-substantiated model by Allakhverdiev *et al*. (2016), RCII contains two pheophytin (Phe) *a* molecules and six Chl molecules (including at least four Chl *d* molecules). The Chl *d* (d_{D1}) molecule of functional branch is supposed to be primary acceptor while the quasisymmetrically positioned Chl *d* (d_{D2}) molecule – to reside on nonfunctional branch. Two remaining Chl *d* molecules (d_z) are suggested to perform an antenna role. The RCII secondary acceptor is possibly Phe *a* rather than Phe *d*.

Despite uncertain identity of primary donor, energy absorbed by LHC is sufficient to drive the four-step process of water oxidation (the so-called B. Kok's clock) as demonstrated in algae acclimating to far-red light without a help of red-shifted Chls (Wolf *et al*. 2018).

Chlorophyll *f*: participation in light-harvesting antenna complexes (and possibly in reaction centers)

Although Chl *f* structurally differs from Chl *a* in only C2 position of the molecule (formyl group instead of methyl group; Fig. 1), this relatively small substitution results in *ca*. 40-nm shift of the Q_y band towards far-red region (665 → 698 nm, in 100% acetone; Li *et al*. 2012). Thus, Chl *f* is a most red-shifted Chl known to date (Chen *et al*. 2010).

The synthesis of bulk Chl *f* is stimulated by far-red light (although a negligible amount of pigment is also produced in white light; Ho *et al*. 2016a). Mechanism of Chl *f* biosynthesis may be like that of Chl *b* because, in both cases, methyl group is converted to formyl group (Chen 2014, Larkum *et al*. 2018). Namely, Chl *f* can be suggested to originate *via* one of two alternative biosynthetic pathways (*see* Fig. 3): (*1*) Chl *a* is site-specifically oxidized to Chl *f*, and (*2*) C2-methyl group of chlorophyllide *a* is oxidized before the phytylation reaction (Chen *et al*. 2010, Ho *et al*. 2016a, Miyashita *et al*. 2014). Chl *f* 'oxidizing' synthase is encoded by the *psbA4* gene (in order not to confuse this gene with paralogue gene encoding the D1 protein of PSII, it was suggested that the *psbA4* gene and the PsbA4 protein product be renamed *chlF* and ChlF, respectively; Ho *et al*. 2016a). These and supporting data (Murray 2012, Cardona *et al*. 2015) indicate that the *chlF* gene could be a progenitor of the *psbA* gene family, and that Chl *f* very possibly appeared before the origin of oxygenic photosynthesis (Ho *et al*. 2016a).

Chl *f* is a minor pigment (*ca*. 10% of Chl *a*) in several unicellular cyanobacteria – *Aphanocapsa* sp. KC1 (Miyashita *et al.* 2014), the NSW Jenolan limestone caves strain (Behrendt *et al*. 2015), *Synechococcus* sp. PCC 7335 (Gan *et al*. 2015), and *Synechocystis* sp. CALU 1173 (Averina *et al*. 2018). Additionally, Chl *f* has been detected in filamentous strains *Chlorogloeopsis fritschii* PCC 6912 (Airs *et al*. 2014), *Chlorogloeopsis* sp. PCC 9212 (Gan *et al*. 2015), *C. fritschii* CALU 759 (Averina *et al*. 2018), *Halomicronema hongdechloris* C2206 (Chen *et al*. 2012), and *Leptolyngbya* sp. JSC-1 (Gan *et al*. 2014).

Chl *f* is generally assumed to play an antennal role (Chen and Blankenship 2011, Allakhverdiev *et al*. 2016, Nürnberg *et al*. 2018). Chl *f* molecules are proposed to comprise two separate pools associated with PSI and PSII,

respectively, and transfer excitation energy to Chl *a* in RCI and RCII (Tomo *et al*. 2014, Itoh *et al*. 2015). However, spectral properties of Chl *f* are unfavorable for this process because the pigment weakly absorbs 400–700 nm light. More importantly, Chl *f* should keep to the Stokes' law (*i.e.*, excited state transfer from pigment with a lower wavelength absorption maximum to pigment with a higher wavelength absorption maximum). Nevertheless, in reality, energy exchange between Chls *f* and *a* does not contradict to the Carnot's (second) principle of thermodynamics, and uphill excitation transfer is possibly attained due to: (*1*) long lifetime of Chl *f* in excited state, (*2*) spatial proximity of Chl *f* to Chl *a*, (*3*) favorable Boltzmann's statistics (k_BT) of inter-Chls resonance at physiological temperatures, and (*4*) specific conjugation of Chls *a* and *f* to apoproteins (Niedzwiedzki *et al*. 2014, Itoh *et al*. 2015, Allakhverdiev *et al*. 2016, Larkum *et al*. 2018). The role of Chl *f* as excitation energy intermediate carrier, rather than excitation energy trap, has been extensively demonstrated in spectrometry experiments with *H. hongdechloris*, and *via* mathematic modeling by Schmitt *et al*. (2018).

The involvement of Chl *f* in primary photochemistry remains debatable (Allakhverdiev *et al*. 2016). However, pioneering data by Nürnberg *et al*. (2018) obtained in experiments with far-red light grown *Chroococcidiopsis thermalis* implied that Chl *f* may promote charge separation in RCI and RCII. Namely, Chl *f* (745-nm maximum *in situ*), and Chl *f* and/or Chl *d* (727-nm maximum *in situ*) may prove to be primary donors in PSI and PSII, respectively, because in far-red light they are more redox active than P700 and P680. Additionally, in far-red light-adapted PSI and PSII, Chl *f* molecules act as linkers to shorter wavelength antenna pigments, and as longer wavelength small antenna system (Nürnberg *et al*. 2018).

Eco-physiological aspects of non-*a* chlorophylls

The majority of cyanobacteria use visible light in the range of 400–700 nm, with excited state being ultimately entrapped by Chl *a* (the pigment has 430-nm Soret band and 662-nm Q_y band, in 100% acetone; Jeffrey *et al*. 1997). The LHC of such strains (PBS) is built of phycobiliproteins (PBP) – hydrophilic proteins which covalently bind non-porphyrin ('linear') tetrapyrrol chromophores. Importantly, PBS can be remodeled for a purpose of preferential absorption of light at either left or right side (500 and 650 nm, respectively) of 'green window'. This bioenergetics strategy is termed the complementary chromatic adaptation (Grossman *et al*. 1993).

Cyanobacteria, which constitutively or adaptively synthesize Chls *d* and *f*, have an access to both 'green window' (due to the peak absorbance of PBPs) and 'far-red window' (due to the peak absorbance of red-shifted Chls). For example, *A. marina* employs PBS-like LHC in addition to Chl *d*-containing LHC (Chen *et al*. 2009). The former antenna significantly differs from 'standard' PBS (MacColl 1998): it represents a rod-like stack of ApcA/ApcB subunits heterotrimers interlinked with the CpcA and the CpcB colorless polypeptides. Additionally, the indispensable 'anchor' polypeptide ApcE is missing, and thus the attachment of PBS-like LHC to thylakoid membrane is difficult to explain. Regardless, both antenna types ensure the harvesting of ambient light, and excitation energy is effectively funneled to RCII (Hu *et al*. 1999, Petrášek *et al.* 2005, Loughlin *et al*. 2013).

As far as PBS-lacking cyanobacteria are concerned, they can, to a certain extent, use energy within 'green window'. In fact, their LHCs containing *b*- and *c*-type Chls partially substitute for PBS.

***b*-type chlorophylls: waste-less migration of excited state energy towards reaction centers**. According to data obtained in experiments with chloroplasts, Chl *b* molecules improve the resonance between Chl *a* molecules. In other words, they create an effective barrier against wasteful fluorescence emission by Chl *a* molecules – for this purpose, minimum molecular ratio of Chl *a* to Chl *b* should be 1.4 (Swenberg *et al*. 1976). Thus, in algae and higher plants, the ratio equals, on the average, 2.5 (Green and Durnford 1996). It is approximately same value as in *P. hollandica* (van der Staay and Staehelin 1994). *P. marinus* which contains Chls a_2 and b_2 instead of monovinyl counterparts displays an exceptionally high 11–15 molecular ratio of these pigments (Partensky *et al*. 1997).

It is commonly considered that wasteful dissipation of energy by LHC is lowered with an increase of pigment heterogeneity (*see* Fleming *et al*. 2012, Kondo *et al*. 2017). In particular, elaborate topology of Chl *b* molecules ensures an effective functioning of Chls *a*/*b* complexes. It should be reminded that the CBP proteins (which bind Chls *b* and b_2) are similar to the CP43/IsiA proteins. Therefore, it can be proposed that the supplement of *b*-type Chls to ancestral CP43/IsiA-containing LHCs might have improved the effectiveness of these antenna compared to modern – not too efficient – Cp43/IsiA containing LHCs (Burnap *et al*. 1993).

***c*-type chlorophylls: harvesting blue light**. An advantage of accessory *c*-type Chls is primarily due to unique spectral properties of these pigments. Although the position of Soret band in *c*-type Chls is close to that in Chl *a* (445–450 nm *vs*. 430.3 nm, in 100% acetone; Jeffrey *et al*. 1997), the relative height and width of this peak are much larger suggesting an enhanced harvesting of blue light. Such physiological strategy proves beneficial in certain environments, especially in deep-water niches penetrated by short-wavelength quanta. Additionally, in semblance with *b*-type Chls, *c*-type Chls are suggested to optimize energy migration to RCs (Larkum *et al*. 2018).

Chlorophyll *d*: constitutive usage of far-red light. Although the intensity of solar radiation at Earth's surface is nearly equal within the ranges of 600–700 nm and 700–800 nm, respectively, ultimate penetration depth of far-red light in aquatic niches is about 10 m (Gan *et al*. 2014). Because long-wavelength quanta are poorer in energy than short-wavelength quanta, photosynthesis in > 700-nm light is metabolically disadvantageous, and thus cyanobacteria do not commonly use far-red light. However, some of them produce red-shifted Chl *d* that extends the range

of PAR to long-wavelength region (Kühl *et al*. 2005). In particular, *A. marina* that constantly produces Chl *d* is often encountered in visible light-depleted marine systems, as well as in continental salt waters poor in visible light. In these niches, *A. marina* produces biofilms or thrives as symbionts on algal or invertebrate hosts (Murakami *et al*. 2004, Kühl *et al*. 2005, Miller *et al*. 2005, Ohkubo *et al*. 2006, Mohr *et al*. 2010, Behrendt *et al*. 2011, Martínez-García *et al*. 2011).

Chlorophylls *d* and/or *f*: adaptive use of far-red light. A supplementary strategy that helps cyanobacteria inhabit not only the niches penetrated by 400–700 nm light, but also those enriched in long-wavelength light, is based on the FaRLiP adaptive response. Cyanobacteria which can adaptively synthesize Chls *d* and/or *f* are encountered in biofilms, microbial mats, and stromatolites (Chen *et al*. 2010, Gan *et al*. 2015, Trampe and Kühl 2016). Additionally, they have been discovered in marine and freshwater ecosystems (Akutsu *et al*. 2011, Averina *et al*. 2018), hot springs (Gan *et al*. 2014, 2015), bogged soil (Airs *et al*. 2014, Gan *et al*. 2015), and karst caves (Behrendt *et al*. 2015).

The involvement of Chls *d* and *f* in FaRLiP has been studied in *Chlorogloeopsis fritschii* PCC 9212, *Chroococcidiopsis thermalis* PCC 7203, *Leptolyngbya* sp. JSC-1, and especially in *Synechococcus* sp. PCC 7335 wild type strain and mutants in the *rfpA*, *rfpB*, and *rfpC* genes (the latter strains are incapable of adaptive Chl *f* synthesis although they produce Chl *d* even in white light; Zhao *et al*. 2015, Ho *et al*. 2016a). The FaRLiP gene cluster embraces 21 genes, in particular the PSI genes paralogues *psaA2*, *psaB2*, *psaF2*, *psaJ2*, *psaI2*, and *psaL2*, and the PSII genes paralogues *psbA3*, *psbA4*, *psbB2*, *psbC2*, and *psbD2*. Products of their expression bind Chls *a*, *d*, and *f* that facilitates waste-less energy migration within LHC, and electron transfer in RCs (Gan and Bryant 2015). FaRLiP-mediated photosynthetic apparatus rearrangements affect the composition of PSI, PSII, and PBS (Gan *et al*. 2014, Gan and Bryant 2015, Gan *et al*. 2015). In particular, resultant PSII heterodimer contains the PsbA3 and PsbA4 subunits encoded by corresponding paralogue genes (Gan *et al*. 2014). Despite the PsbA3 and the PsbA4 subunits being similarly equipped with Chl molecules, total photochemical activity is reduced because the former subunit contains binding sites for electron transporter cofactors, while the latter subunit lacks these (Murray 2012, Cardona *et al*. 2015, Gan *et al*. 2015).

Besides the genes encoding adaptive components of photosynthetic apparatus, the FaRLiP gene cluster codes for the two-component signal system composed of three master control elements – the RfpA phytochrome (sensory receptor), the CheY-like protein RfpC (signal transmitter), and the RfpB protein (response regulator). In detail, far-red light activates histidine kinase RfpA, which in its turn phosphorylates RfpC that finally phosphorylates the transcription factor RfpB (Zhao *et al*. 2015, Ho *et al*. 2016b). The latter protein contains a DNA-binding domain, and operates as positive regulator for the FaRLiP genes.

Conclusion

According to information dealt with in this review, *b*- and *c*-type Chls participate in LHCs of few cyanobacterial genera. In its turn, Chl *d*, and possibly Chl *f*, also participate in RCs. In some strains, antennal Chls *d* and *f* are synthesized during the FaRLiP adaptive response. The reason of *b*- and *c*-type Chls is to facilitate waste-less energy input to RCs and, additionally, to absorb near-red and blue light, respectively. The involvement of Chls *d* and *f* in phototrophy is to empower the use of far-red light. Data on distribution and role of non-*a* Chls in cyanobacteria extend the knowledge on molecular mechanisms and adaptation limits of oxygenic photosynthesis. Taking into account the high adaptability of cyanobacteria, one can expect future discovery of new Chls – those absorbing light at either side of 'green window', and those capable to absorb quanta in infra-red region.

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