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1 Oxygenic Photosynthesis in Cyanobacteria

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1.1 INTRODUCTION

Oxygenic photosynthesis started about 3 billion years ago, when ancient cyanobacteria-like organisms evolved an apparatus capable of capturing and utilizing visible solar radiation (300–700 nm). By using electrons extracted from H_2O, the reduction of CO_2 to energy-rich carbohydrates with concomitant release of O_2 had become possible (for recent reviews on evolution of photosynthesis, see Refs. [1–7]). The unique advent of O_2 released by the first cyanobacteria and its subsequent accumulation in the Earth's atmosphere was, undoubtedly, the *biological Big Bang* [8] for the evolution of the whole biosphere. It created an aerobic condition and the requisite background for the development and sustenance of aerobic metabolism and more-advanced forms of life [9–13]. Another great input of cyanobacteria is the evolutionary event of *endosymbiosis* [14]. Cyanobacteria are the photosynthetic ancestors of plastids in algae and plants (for reviews, see [5,15,16]).

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Cyanobacteria (formerly classified as "blue-green algae") are one of the largest and versatile groups of prokaryotes of enormous biological importance. About 20%–30% of global primary photosynthetic productivity originates from cyanobacteria [17]. This corresponds to the yearly fixation of about 20–30 Gt of CO_2 into biomass and release of about 50–80 Gt of O_2 in the atmosphere by these oxygenic prokaryotes [18,19]. In addition, many cyanobacteria can fix atmospheric N_2 into a biologically accessible form and thereby play a key role in the nitrogen cycle of biosphere [20,21]. Cyanobacteria are highly adaptable; they exhibit wide ecological tolerance and gliding mobility: they can be found almost in any environment, including extreme ones (e.g., benthos, plankton, cold and hot deserts, antarctic dry valleys, tropical rain forests) [22,23]. Although all existing cyanobacteria (except recently discovered oceanic unicellular N_2-fixing cyanobacteria from UCYN-A group [24], discussed in Section 1.3.1) have the ability to perform oxygenic photosynthesis (they use H_2O as electron donor), some are able to grow as anaerobic photoautotrophs using H_2S as an alternative electron donor [25]. This represents unique additional capability of anoxygenic photosynthesis in these organisms, while anoxygenic photobacteria are not able to utilize H_2O as a substrate and produce O_2.

The mechanism of oxygenic photosynthesis in cyanobacteria remarkably resembles that of oxygenic eukaryotes (algae and higher plants). This allows us to use cyanobacteria as a suitable model to study different aspects of oxygenic photosynthesis and its regulation that is often difficult to study in higher plants or algae. Similar to all photosynthetic eukaryotic organisms, cyanobacteria share the use of unique reaction centers (RCs), photosystem I (PSI) and photosystem II (PSII), to drive light-induced electron transfer from H_2O to $NADP^+$ (the oxidized form of nicotinamide adenine dinucleotide phosphate); its reduced form, NADPH, is used to power the synthesis of carbohydrates. Like algae and plants, cyanobacteria have two light reactions that work in series, as known from experiments referred to as the Emerson's enhancement effect (see, e.g., [26,27]), and from antagonistic effects of light I (absorbed by PSI) and light II (absorbed by PSII) on specific components of electron transfer (see, e.g., [28,29]).

Like all other oxygenic photosynthesizers, cyanobacteria contain the photosynthetic pigment *chlorophyll* (Chl) *a* [30] (for an overview on why Chl *a* was chosen by nature, see [31]). In addition to Chl *a*, most cyanobacteria contain *carotenoids* (Cars) [32,33] and *phycobilins* (phycocyanin, allophycocyanin, and, in some species, phycoerythrin) [34]. Phycobilins are not present in plants, but in cyanobacteria they are organized in large light-harvesting multiprotein complexes called *phycobilisomes* (PBSs) [35–41]. The ultrastructure of PBSs may vary among cyanobacteria and is dependent on the growing conditions. There are some cyanobacteria, e.g., prochlorophytes, that contain Chl *b* in addition to Chl *a* [42], while Chl *d* is known to be dominant in an apparently widespread *Acaryochloris*-like organisms [43–46]. Moreover, some cyanobacteria can be transformed to contain Chl *b*, thereby representing their great flexibility [47].

Cyanobacterial cells are surrounded by two membranes: an outer one, which forms *the cell wall* (made of murein), and an inner one, *the cytoplasmic membrane*, which separates *the cytoplasm* from *the periplasm* (see Figure 1.1 and its legend). The light reaction of oxygenic photosynthesis takes place in the so-called *thylakoid membranes* that occur in pairs; the space between the pair is called *the lumen*, and the space between two pairs is contiguous with *the cytoplasm*. One of the major differences between cyanobacteria and photosynthetic eukaryotes is that in cyanobacteria respiratory and photosynthetic redox-active protein complexes share a *common* thylakoid membrane (see [48] and Figure 1.1). The thylakoid membrane in cyanobacteria does not form grana as it does in plants and algae. Moreover, there is even a cyanobacterium *Gloeobacter violaceus* that lacks thylakoids, and the photosynthetic pigments are associated with the cytoplasmic membrane [49]. Nevertheless, despite some minor differences in the composition of the redox-active complexes, the photosynthetic electron transport chain of cyanobacteria is very similar to that of plants and algae. In all oxygenic organisms (both prokaryotic and eukaryotic), the result of the light-driven electron transport is the oxidation of H_2O coupled with evolution of O_2, reduction of $NADP^+$ to NADPH, and phosphorylation of ADP to ATP (see Figure 1.2).

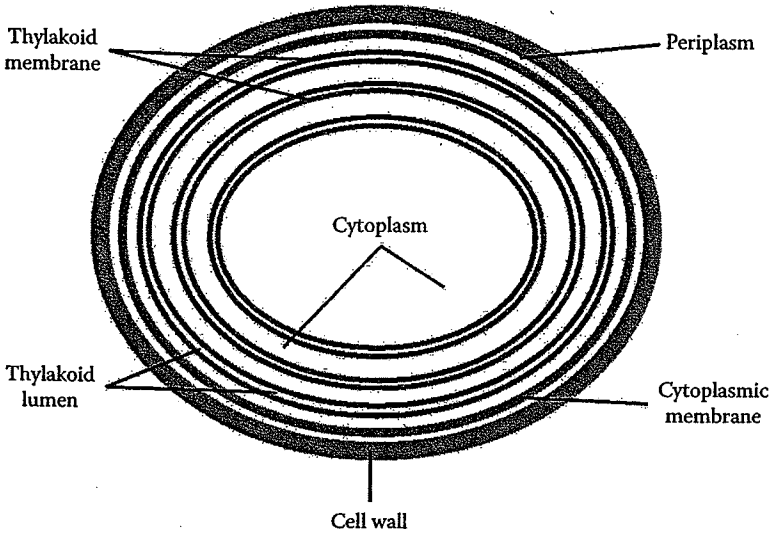

FIGURE 1.1 **(See color insert.)** A schematic outline of the intracellular membranes and compartments in a cyanobacterial cell. The thylakoid membranes (green) contain chlorophyll *a* and perform both photosynthetic and respiratory electron transport, while the cytoplasmic membrane system (yellowish), which contains carotenoids, is involved only in respiration. As a consequence of photosynthetic and respiratory electron transport in thylakoid membranes, protons are brought into the thylakoid lumen, the space between a pair of thylakoid membranes. The resulting proton gradient across the thylakoid membrane is utilized for the synthesis of ATP. (Modified and adapted from Vermaas, W.F.J., *Encyclopedia of Life Sciences (ELS)*, John Wiley & Sons, Ltd, London, U.K., 2001. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.)

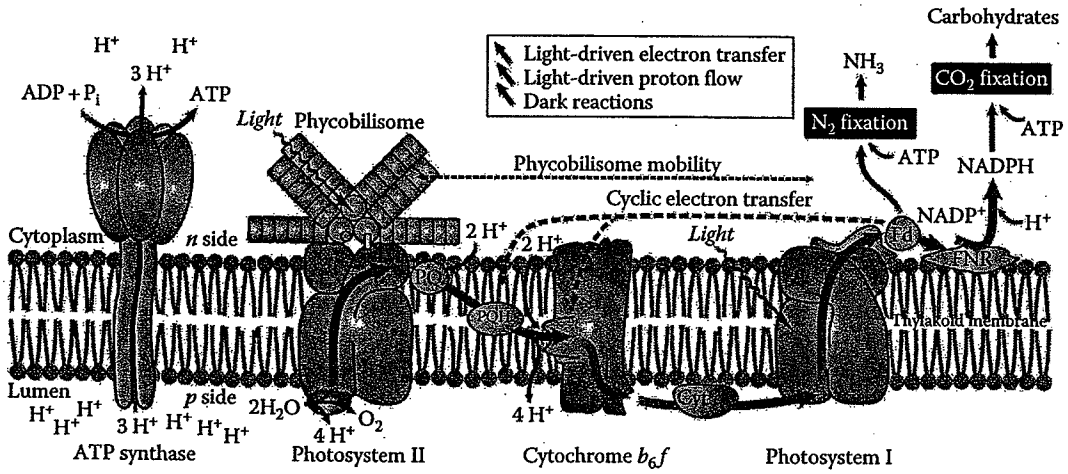

FIGURE 1.2 **(See color insert.)** A schematic representation of the protein complexes involved in light-induced electron and proton transfer reactions of oxygenic photosynthesis in cyanobacteria. The arrows indicating the light-driven electron transfer and proton flow as well as some dark reactions are colored individually, as shown in the figure. Looking at the abbreviated components from the left of the diagram: PQ, plastoquinone; PQH_2, plastoquinol; Cyt c_6, cytochrome c_6 (also known as Cyt c_{553}); Fd, ferredoxin; FNR, ferredoxin-NADP reductase. Note that although the diagram does not show PBSs that are attached to PSI, PBSs can be redistributed to PSI due to their mobility (indicated by black dashed arrow). Also note that cyanobacteria use Cyt c_6 (as shown) or plastocyanin (not shown) to transfer electrons from Cyt b_6f to PSI. For the sake of simplicity, respiratory complexes (type 1 *NADPH dehydrogenase* that oxidizes NADPH to $NADP^+$; *Succinate dehydrogenase* that oxidizes succinate to fumarate and reduces PQ to PQH_2; and a *(terminal) oxidase* that reduces O_2 to water) are not shown. For further details, see text.

The structure of the O_2-evolving apparatus in the cyanobacterial membranes is highly conserved throughout evolution. Many fundamental questions of oxygenic photosynthesis that are often difficult to approach in plants or other eukaryotic photosynthetic organisms are therefore investigated in cyanobacterial model systems. Cyanobacteria show rapid growth in nature and under laboratory culture conditions; they owe a large part of their evolutionary success to their tremendous metabolic flexibility. The simplicity of a single cell system and ease to manipulate them genetically as compared to the multicellular higher plant models has also contributed to cyanobacteria becoming important model systems to study responses to abiotic stress.

In this chapter, we provide a basic introduction to the light-induced reactions of photosynthesis in cyanobacteria, on the two photosystems, their structure and function leading to NADP production, and ATP synthesis. A glimpse of our views on evolution of cyanobacteria is also presented. More detailed information on the photosynthetic and respiratory processes in cyanobacteria and on the historical discoveries in this field can be obtained from the extensive available literature (e.g., see [48,50–59]).

1.2 OVERVIEW OF PHOTOSYNTHETIC ENERGY CONVERSION IN CYANOBACTERIA

1.2.1 The Light-Induced Reactions and Photosynthetic Electron Transport Chain

The thylakoid membrane in most cyanobacteria is the site of the photosynthetic light reactions (see Figures 1.1 and 1.2). However, whereas in algae and plants the thylakoid membrane is located in a special organelle (chloroplast), in cyanobacteria the membrane is within the cytoplasm [48].

The initial event in photosynthetic light reactions of cyanobacteria begins with the absorption of light (photons) by large antenna systems, PBSs, attached to the cytoplasmic surface of photosynthetic membrane. PBSs are made of the *phycobiliproteins* that covalently bind phycobilins (open-chain tetrapyrroles) in a special geometric arrangement (Figure 1.2; for further details, see Section 1.3.4 and [38,60–62]). Phycobilins deliver the energy of absorbed light (excitation energy) (discussed in Section 1.4.1) to the large pigment-protein RC complexes, PSII and PSI (for details, see Section 1.3.3; for recent reviews, see [63–67] and references therein), integrated into the thylakoid membrane. Cyanobacteria contain relatively low amount of PSII complexes as compared to PSI (the PSI/PSII ratio may vary from ~3 up to 5.8) [68–71], and PBSs are primarily associated with PSII (as the external antenna). However, under certain conditions, PBSs are redistributed to PSI, thereby regulating the efficiency of excitation energy transfer between the two photosystems [70,72,73]. In a similar way, Chl *a*-/Chl *b*-containing membrane-integral light-harvesting complexes (LHCs) in plants show an energy equilibration between the photosystem complexes [74]; however, LHCs are absent in thylakoids of cyanobacteria. Normally, the PBS system covers absorption in the wavelength range of 300–700 nm. However, *Acaryochloris*-like cyanobacteria with Chl *d*-dominated photosynthetic antenna system do extend the absorption wavelength range up to 775 nm [43,75].

Conversion of solar energy into chemical forms of energy is the result of the two photochemical RCs (PSII and PSI) acting in tandem. Delivery of excitation energy to the RC-Chl *a* molecules, referred to as P680 (special Chl *a*-complex in PSII; for alternative definition of P680, see [76]) and P700 ("heterodimeric" Chl *a*/*a*′-complex in PSI), initiates the energy conversion process. Due to the redox-active cofactors embedded into a protein matrix of both photosystems (see Sections 1.3.3.1 and 1.3.3.2, and references therein), the photochemical acts within RCs involve fast, sequential electron transfers that result in stabilized charge separation, stepwise "extraction" of electrons from water and their transfer to $NADP^+$. Figure 1.3 illustrates the linear (noncyclic) electron transfer pathway in a way that all redox-active cofactors that make this transfer possible are arranged according to their redox potentials. This arrangement, known as *the Z-scheme*, was proposed by Hill and Bendall in 1960 ([77]; for historical perspective on the evolution of the Z-scheme over the last 50 years, see [78]).

The primary photochemical reaction in PSII involves formation of the singlet excited state of P680, P680* (Figure 1.3), delocalized among the ensemble of four RC Chl *a* molecules, either

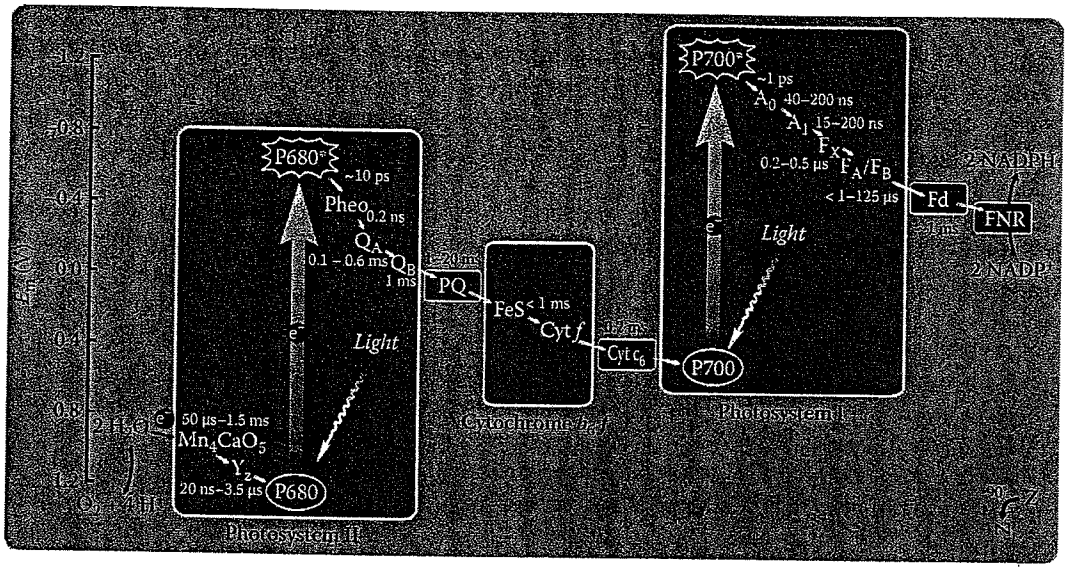

FIGURE 1.3 The Z-scheme of oxygenic photosynthesis in cyanobacteria representing the energetics of linear electron transfer from water to $NADP^+$ plotted on redox midpoint potential (E_m, at pH 7) scale. The two white upward arrows symbolize the transition of the RC Chl *a* molecules (P680 in PSII and P700 in PSI) from the ground to the (singlet) excited state (P*) attained mostly after excitation energy transfer from their respective light-harvesting antenna systems and to a lesser extent by direct absorption of photon ($h\nu$) (see Sections 1.3.4 and 1.4.1). The numbers 680 and 700 are the wavelengths (in nm) of the red absorption maxima for the Chl *a* molecules of the RCs of PSII and PSI. The diagram also shows half-times of several electron transfer steps. In all likelihood, the "bottleneck" reaction is at the PQ/PQH_2 level (1–20 ms). Abbreviations of the components involved in the electron transfer (from the left of the diagram): Mn_4CaO_5, tetra-nuclear manganese-calcium cluster with five oxygen atoms; Y_Z, redox-active tyrosine residue; Pheo, pheophytin; Q_A, primary quinone electron acceptor of PSII; Q_B, secondary quinone electron acceptor of PSII; PQ, a pool of mobile PQ molecules; FeS, an iron-sulfur protein (known as Rieske FeS protein); Cyt *f*, cytochrome *f*; A_0, a special Chl *a* molecule; A_1, a phylloquinone molecule; F_X, F_A, F_B, iron-sulfur clusters. Other abbreviations are as in Figure 1.2. For further details, see text.

upon excitation energy transfer from antenna molecules or upon absorption of a photon with a wavelength of <680 nm. The photochemistry-driving energy per each photon absorbed by PSII is equal to the energy of a 680 nm photon (E_{680}), i.e., 1.83 eV. This results in stable and directed charge separation (see Section 1.4.1 and references therein) between the Chl *a* molecules and the nearby pheophytin (Pheo) molecule, followed by the formation of the radical pair $P680^{\bullet+}Pheo^{\bullet-}$ with less than 10% energy loss from E_{680} [79,80]. The created cation radical $P680^{\bullet+}$, which has one of the highest known oxidizing potential in nature (~1.25 V) [81,82], is strong enough to energetically drive the sequential oxidation of water, *via* a redox-equivalent-accumulating catalyst, a Mn_4CaO_5 cluster, which links the one-electron photochemistry with the four-electron oxidation chemistry of two water molecules. The result of water oxidation is the evolution of molecular oxygen and the release of protons into the thylakoid lumen (Figure 1.2). The free energy stored by PSII due to the transfer of one electron from water to the mobile electron acceptor plastoquinone (PQ) is about 50% of E_{680} [79,80]. The electron transfer in PSII and its composition is further discussed in Section 1.3.3.1. Photosynthetic water splitting is briefly outlined in Section 1.4.2 and in more details in Chapter 2.

PSI, which has some similarities to PSII, captures (upto) <700 nm light energy (E_{700} = 1.77 eV) to drive the redox reactions of the electron transfer in that system (Figure 1.3). The redox potential for the primary electron donor P700 in cyanobacteria was estimated to be 400–450 mV, while in higher plants it has a slightly higher value (~470 mV) [83,84]. Although, this oxidizing potential is not high

enough to extract electrons directly from water, it is enough to drive transmembrane electron transfer between the external electron donor (cytochrome c_6 (Cyt c_6) and/or plastocyanin (PC)) in the thylakoid lumen and acceptor (ferredoxin (Fd)) in the cytoplasm (Figures 1.2 and 1.3). We will come back to the structural organization of PSI and the electron transfer pathways in Section 1.3.2.2.

The integral membrane cytochrome b_6f (Cyt b_6f) complex plays a key role in mediating the photo-induced electron transfer between the two photosystems and in increasing the number of protons pumped across the membrane into the lumen (in addition to that associated with the water-splitting PSII (Figure 1.2)). It is a large multi-subunit protein with several prosthetic groups, which has high structural and functional similarity between those from cyanobacteria and plants. Structure and function of this complex has thoroughly been discussed in reviews [85–90] and is not included in our chapter. The mobile lipophilic electron carrier PQ, in the membrane, connects PSII with Cyt b_6f, and the mobile soluble electron carrier Cyt c_6 (also known as Cyt c_{553}) in the thylakoid lumen connects Cyt b_6f with PSI [91–93]. Under copper-replete conditions, many cyanobacterial species substitute the iron-containing Cyt c_6 by the copper-containing redox carrier, PC [94]. Interestingly, in the absence of both Cyt c_6 and PC, *Synechocystis* sp. PCC 6803 still shows photoautotrophic growth indicating the high flexibility of this prokaryotic photoautotroph to cope with stress [95]. We note that cyanobacteria share the use of PQ pool, Cyt b_6f complex, and PC/Cyt c_6 for both photosynthetic and respiratory electron transport pathways (the latter is not discussed in this chapter) (for further details, see [48,96]). Finally, production of NADPH from NADP is catalyzed by the membrane-associated flavoprotein ferredoxin-$NADP^+$ reductase (FNR) (see Figure 1.2 and Section 1.4.3; for recent reviews, see [97,98]).

Photosynthetic electron transfer, energized by the two photosystems, also involves light-induced proton flow (Figure 1.2)), which establishes a proton electrochemical potential difference ($\Delta\psi$) across the thylakoid membrane (the cytoplasmic side being called the *n* (negative) side; and the luminal side being called the *p* (positive) side). This proton gradient, more precisely *the proton motive force* (PMF), which includes membrane potential gradient, is utilized by the ATP synthase for the phosphorylation of ADP to ATP. This occurs when the protons return to the cytoplasm through the protein complexes of the ATP synthase (for further details, see Section 1.4.4 and [99–102]). Under certain conditions, cyclic electron flow occurs from the reducing side of PSI, through PQ pool and/or Cyt b_6f complex and back to PSI (depicted in Figure 1.2) [103–105]. This cyclic electron flow increases proton pumping into the lumen, thereby increasing the synthesis of ATP.

Thus, the light-driven electron transport from H_2O to $NADP^+$ catalyzed by PSII and PSI results in the formation of the energy-rich compounds NADPH and ATP and leads to the evolution of O_2. The energy stored in NADPH and ATP is subsequently used to drive the reactions of CO_2 fixation. This production of energy-rich carbohydrates by the metabolic C-3 or the Calvin–Benson cycle does not directly require light (reviewed in [106–109]; it is not discussed further in this chapter). For a background in CO_2 fixation and concentration mechanism in cyanobacteria, see [110]. We also note here that in cyanobacteria, ATP can also be utilized for N_2 fixation and other cell processes.

1.2.2 Time Sequence of Light Reactions: From Picoseconds to Milliseconds

Here we will discuss the time sequence of events of photosynthetic light reactions that lead to evolution of O_2 and production of NADPH in cyanobacteria and other oxygenic photosynthesizers.

Photosynthetic electron transfer from water to $NADP^+$ is like a *bucket brigade* from one intermediate to the other. One can also imagine this process as a *relay race*. It begins simultaneously by charge separation at P680 (in PSII) and at P700 (in PSI), and the process is over almost simultaneously within a few ps (see a Z-scheme in Figure 1.3; most of the times given are essentially half-times for single-electron transfers). In PSII, P680 is oxidized and Pheo is reduced; and in PSI, P700 is oxidized and a specific Chl *a* molecule A_0 (first stable electron acceptor) is reduced [65,80,111–115]. Light energy is, thus, converted to chemical energy! Within ~200 ps, the electron on reduced Pheo (in PSII) moves to Q_A (a tightly bound primary quinone electron acceptor of PSII),

and the electron on reduced A_0 (in PSI) moves to A_1 (phylloquinone of PSI) and to F_X within 200 ns (the first iron-sulfur cluster of PSI) (see [67,116] and references therein). In PSII this is followed by reduction of $P680^{\bullet+}$ by Y_Z (redox-active tyrosine residue) within the time range of 20 ns–35 μs [67,81,117]. Then, in the 200 μs range, several steps occur: an electron on the reduced Q_A moves to Q_B (secondary quinone acceptor loosely bound to PSII), and the oxidized Y_Z is reduced by the Mn_4CaO_5 cluster in the so-called oxygen-evolving complex (OEC) [118]; if Cyt c_6/PC was in the reduced state, then during this time (~200 μs), $P700^{\bullet+}$ would also be reduced (see, e.g., [119]).

The Q_B has a very long life, and a proton from His-252 on the D1 protein stabilizes its negative charge [120–122]. There is a "two-electron gate" at the Q_B-site [123]. After a second light reaction, electrons arriving from the excited P680, *via* Pheo, and Q_A reduce Q_B^- to Q_B^{2-}; this occurs in 400–600 μs; however, the reaction is "slow" because of electrostatic repulsion between negative charges on Q_A^- and Q_B^- [124]. The negative charge on Q_B^{2-} is further stabilized by a proton, arriving, *via* several amino acids, from a bicarbonate ion (hydrogen carbonate), bound on the non-heme-iron (NHI) between Q_A and Q_B (see [125] and references cited in [122]). As discussed in Section 1.4.2, oxygen evolution is a period four clock. After four light reactions, oxygen is evolved (from two H_2O) and two molecules of mobile PQ are reduced to plastoquinol (PQH_2). These last reactions (1) the last step of oxygen evolution and (2) reduction of PQ to PQH_2 in addition the electron flow from reduced F_X to Fd in PSI all take place in the ms time range (see [67,116] and references therein).

Overall the slowest reactions of electron transfer from water to $NADP^+$ involve (1) formation of PQH_2 from PQ, (2) uptake of protons from the stromal side (the *n* side), (3) diffusion of PQH_2 to the Cyt b_6f complex, and (4) the release of protons to the luminal side (the *p* side). These aforementioned processes take ~20 ms and are the *bottleneck* reactions of the entire electron transfer (see, e.g., [126,127]). Still, it is difficult to decipher which of the steps is the slowest because this depends upon other conditions of the system. Further, the time taken for the reduction of $NADP^+$ to NADPH depends upon various conditions and the status of the enzyme FNR. Apparently, in continuous strong light, the entire process of electron transfer from water to $NADP^+$ requires about ~500 ms, when all the PSII and PSI electron acceptors are reduced (see, e.g., [128]). This time is also seen by the appearance of the peak "P" in Chl *a* fluorescence transient as in *Acaryochloris marina* [129]. However, superimposition of other phenomena, such as *state changes*, and the redox status of the PQ pool (due to overlap of respiratory and photosynthesis reactions) do not allow us to observe this time through Chl *a* fluorescence measurements in most cyanobacteria. For reviews on the relation of Chl *a* fluorescence transient and photosynthesis, we refer readers to reviews [130–132].

1.3 PHOTOSYNTHETIC UNITS OF CYANOBACTERIA

1.3.1 Photosynthetic Reaction Centers: Evolutionary Perspective

In every photosynthetic organism, the primary events of energy conversion involve the so-called *photosynthetic unit* (reviewed in [133]). This concept includes a certain RC protein complex performing transmembrane charge separation and the light-harvesting pigment-containing system delivering the energy of the captured photons to the RC. All photosynthetic RCs (both prokaryotic and eukaryotic) share structural similarities; they all contain an integral membrane-protein complex of homodimeric or heterodimeric nature to which pigments (Cars and Chls) and redox-active cofactors (such as Chls, quinones, or iron-sulfur clusters) are bound [64,66,134,135]. However, the differences in the nature of the terminal electron acceptors allow classification of all existing RCs into two types (for reviews, see [1,7,136,137]): *FeS-type RCs* and *Q-type RCs*. Those that have iron-sulfur clusters as the terminal acceptor (e.g., the RC of green sulfur bacteria and PSI of cyanobacteria and oxygenic eukaryotes) belong to the FeS-type RCs (also called *type I RCs*), while those with quinones as final acceptor belong to the Q-type RCs (or *type II RCs*) (e.g., the RCs of purple bacteria and PSII of cyanobacteria and other oxygenic organisms) (Figure 1.4). Although structural

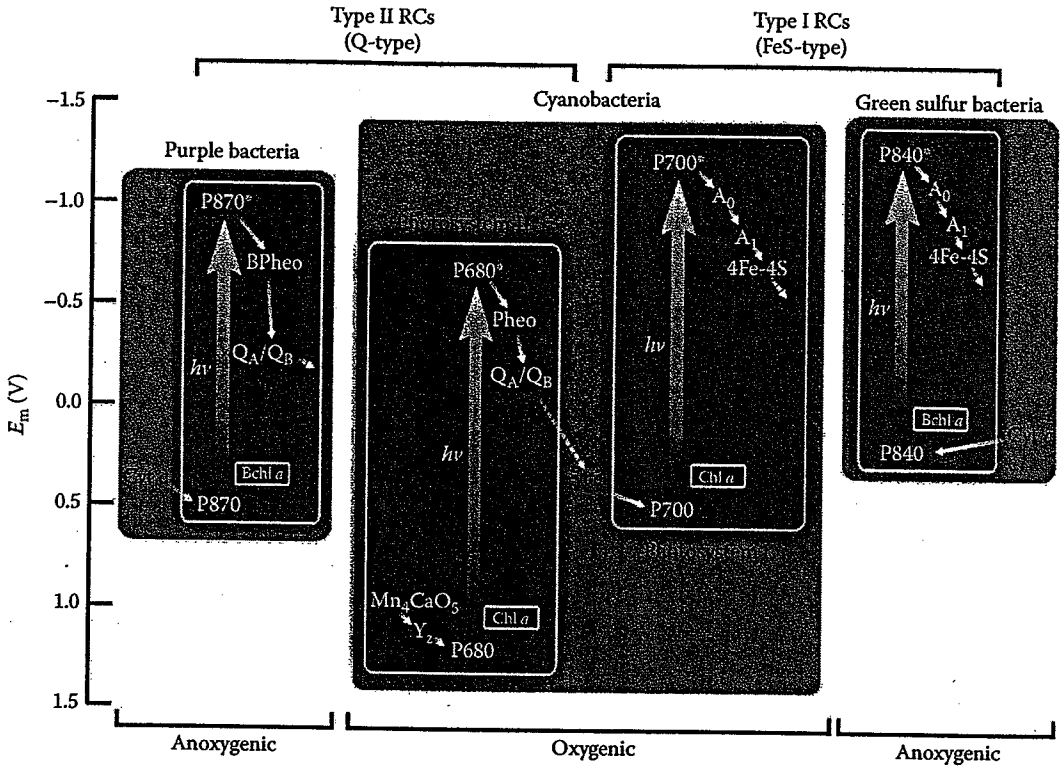

FIGURE 1.4 Photosynthetic RCs in anoxygenic (purple bacteria and green sulfur bacteria) and oxygenic (cyanobacteria) organisms. For each RC the electron donors, as well as the electron acceptors, are shown and plotted on the redox midpoint potential scale (E_m, at pH 7). Depending on the final electron acceptors (quinones (Q_A/Q_B) or iron-sulfur clusters (4Fe-4S)), the RCs are classified as Q- or FeS-type (also called as type II and type I RC, respectively). The numbers after P represent the long-wavelength absorption maxima of the RC pigments and are inversely related to the absorbed energy (length of straight white arrows). For the sake of simplicity, some redox components of the electron transfer chain are omitted (indicated by dashed arrows). Cyt *c* in purple bacteria symbolizes all the four different forms of cytochrome *c* used by these bacteria. A_0 denotes an electron acceptor: bacteriochlorophyll (in green sulfur bacteria) or chlorophyll (in PSI of cyanobacteria). Other specific abbreviations are BPheo, bacteriopheophytin; 4Fe-4S, RC-associated iron-sulfur centers: F_X, F_A, and F_B; Q_A/Q_B, the primary (Q_A) and secondary (Q_B) quinone electron acceptors. See text and [7,56,134] for further details. (Based on the data in Hohmann-Marriott, M.F. and Blankenship, R.E., *Annu. Rev. Plant Biol.*, 62, 515, 2011; Govindjee and Shevela, D., *Front. Plant Sci.*, 2, 28, 2011; Wraight, C., Reaction centers, electron flow, and energy transduction, in *Photosynthesis*, Govindjee, Ed., Academic Press, New York, p. 17, 1982.)

protein and cofactor similarities between the two types of RCs strongly support the idea that they all have a common evolutionary origin, there is presently no clear agreement on whether the earliest photosynthetic RC was the type I (similar to homodimeric RC of current green sulfur bacteria *Chlorobiaceae*), the type II (similar to one of purple bacteria), or an intermediate between these two types (called *type 1.5*) (see e.g., [1,66,138–144]).

The evolutionary origin of direct ancestors of the O_2-evolving cyanobacteria is even more mysterious and not yet resolved. We know that oxygenic cyanobacteria (as well as all other O_2-evolving organisms) have both types of RCs (PSII and PSI), whereas all anoxygenic photosynthetic bacteria have just one of these types (either type I or type II RC) (Figure 1.4). This indicates that the origin of oxygenic photosynthesis begins with the origin of the functionally linked RCs (PSII and PSI) in a direct ancestor of O_2-evolving cyanobacteria-like organisms. Two different hypotheses have been proposed to explain how both type I and II RCs ended up in the first cyanobacteria (for details, see [1,3,7,11,144]). Briefly, *the selective loss hypothesis* assumes that the two types of RCs evolved

separately in one ancestor of cyanobacteria and that the anoxygenic bacteria with just one RC are derived from this organism by a loss of either type I or type II RCs. Later, two RCs in a primitive cyanobacterium became linked and achieved the ability to oxidize water and evolve O_2 and to reduce $NADP^+$. According to *the fusion hypothesis*, type I and type II RCs developed separately in distinct anoxygenic bacteria and later were brought together in one cyanobacteria-like organism by a large-scale lateral gene transfer.

What is unique in cyanobacterial flexibility is that it may reflect their position in evolutionary history. Examples are shown by Vermaas et al. [145], who observed that electrons from PSII could be used by an oxidase in the absence of PSI, and by Wang et al. [146], who reported that several PSI-minus mutants of *Synechocystis* sp. PCC 6803 were able to evolve O_2 in the light in the presence of glucose for up to 30 min. On the other hand, some "anoxygenic" cyanobacteria among the so-called UCYN-A group of oceanic unicellular N_2-fixing cyanobacteria have been recently discovered [24,147]. These cyanobacteria are not able to perform oxygenic photosynthesis because they completely lack a functional PSII apparatus, although PSI was found to be intact (it is not known yet, however, how PSI functions in the absence of PSII in these organisms). These two "opposite" examples clearly reveal global importance of water-splitting PSII for oxygenic photosynthesis.

How and when the ability to oxidize water was added to type II RC remains a mystery. Undoubtedly, the development of a strongly oxidizing RC (PSII), together with the invention of the catalytic site for water oxidation (Mn_4CaO_5-protein complex) that is capable of collecting and storing oxidizing equivalents, formed the central stage in the transition from anoxygenic to oxygenic photosynthesis [3,148–150].

1.3.2 Primary Reaction Center Pigments in Cyanobacteria

Which invention was required for the type II RC (primitive PSII) to become so highly oxidizing? It is assumed that the evolutionary development of a specific protein environment of the RC that contained a photoactive pigment with a redox potential (E_m) higher (more positive) than +0.82 V for oxidation of H_2O (at pH 7.0) was that "invention" in a direct progenitor of cyanobacteria [1,31,150]. Unfortunately, we do not know the E_m value of the RC photoactive pigment in these ancient organisms. What we know is that in modern water-oxidizing photoautotrophs, the E_m value of the RC photoactive Chl *a* (cation radical $P680^{\bullet+}$) is about +1.25 V [81,82] and that this value exceeds the oxidizing power of Chl *a* (Chl $a^{\bullet+}$) *in vitro* (in acetonitrile) by about 0.4 V [151]. This clearly indicates that such energetics (E_m value) for P680 *in vivo* (in PSII) is achieved not only due to the chemical nature of Chl *a* but to a great extent due to the specific structural arrangement of the surrounding protein matrix of the PSII RC [80,152,153]. Although the basic principles of the photosynthetic RCs are very similar and highly conserved throughout evolution, there are no other natural RCs that contain photoactive pigments (cation radicals) with such strong oxidizing potential as $P680^{\bullet+}$ of PSII. Thus, the E_m of $P680^{\bullet+}$ is at least 0.5 V above the cation radicals in the RCs of all anoxygenic bacteria that contain bacteriochlorophyll (BChl) *a* (Figure 1.4) and other forms of BChl (*b* and *g*) [154]; for an overview of possible scenarios for the evolution of Chls and BChls, see [11,56,150,155–158]). The evolutionary replacement of BChl *a* by Chl *a* in oxygenic photosynthetic organisms must have been "inspired" by the unique physicochemical property of Chl *a* to form a sufficiently stable radical pair $P680^{\bullet+}Q_A^{\bullet-}$ [153]. Such functional compatibility of Chl *a* with neighboring cofactors of electron transfer and protein surroundings makes this pigment to be unique and essential in the RCs of all water-splitting photosynthesizers [31,153].

Are photoactive RC pigments in oxygenic organisms always a Chl *a*-complex? For many years this was believed to be true. However, the unique role of Chl *a* for P680 became a matter of debate after 1996, when Miyashita et al. [43] discovered the Chl *d*-dominant O_2-evolving cyanobacterium *A. marina*. This marine cyanobacterium was found to contain more than 95% Chl *d* and only trace amount of Chl *a* (~3% of the total Chl) [43]. Such an unusual pigment composition results in a

unique constitution of the photosystems in cyanobacteria from the genus *Acaryochloris*. Thus far, these cyanobacteria are the only known organisms that perform oxygenic photosynthesis by using Chl *d* as the RC photopigment for both photosystems (PSI and PSII) [159,160]. Thus, the photoactive RC pigment of PSI, P700, which is Chl *a*/Chl *a'* heterodimer in all oxygenic photosynthesizers, was shown to be replaced by a Chl *d*/Chl *d'* heterodimer in *A. marina* [161]. Since this pigment shows a flash-induced absorbance difference maximum at ~740 nm, the primary donor of PSI is termed P740 [159], corresponding to P700 in other O_2-evolving organisms. The E_m of P740/P740$^{\bullet+}$ was found to be +335 mV [159], which is 70–120 mV lower than the E_m of P700/P700$^{\bullet+}$ of the usual cyanobacterial Chl *a*-containing PSI [83]. It is still an open question whether the special Chl pair (P_{D1}/P_{D2}) of the photoactive pigment in *Acaryochloris* PSII RC is a Chl *d*/Chl *d* homodimer [160,162,163] or a Chl *a*/Chl *d* heterodimer [164–166]. At the same time, there is an agreement that the primary electron acceptor of PSII in *A. marina* is Pheo *a*, not Pheo *d* [162,167,168]. However, not all RC Chls *a* are substituted by Chl *d* in photosystems of this unusual cyanobacterium (reviewed in [163]) indicating that Chl *a* is still the unique RC photoactive pigment for driving oxygenic photosynthesis (for a viewpoint on why Chl *a* is unique among the other Chl species for serving RCs of oxygenic organisms, see [31]). Despite this, the Chl *d*-containing *A. marina* provides an interesting system to further explore the energetics of the primary reactions of photosynthesis and water-splitting reaction by PSII (see e.g., [166,168–172]).

1.3.3 Cyanobacterial Photosystems: Structure and Function

1.3.3.1 Photosystem II

1.3.3.1.1 General Structural Organization

PSII is a large multimeric pigment-protein complex that exists as a dimer with a total weight of ~700 kDa. Figure 1.5 shows general arrangement of cyanobacterial dimeric PSII based on the recent PSII crystal structure from *Thermosynechococcus vulcanus* at 1.9 Å resolution [125]. Each monomer of PSII from cyanobacteria comprises 17 integral membrane-protein subunits, 3 peripheral protein subunits on the luminal side of the complex, and close to 90 cofactors (Figures 1.5 and 1.6) [63,64,67,125,173–176].

All redox cofactors required for photochemical charge separation and for water splitting are located on the D1 (PsbA) and D2 (PsbD) polypeptides that form the D1/D2 heterodimer. Each polypeptide has five transmembrane α-helices (TMHs) (Figure 1.5A). The D1 and D2 proteins show sequence homology with the L and M subunits of the photosynthetic RC of anoxygenic purple bacteria [177]. The D1/D2 heterodimer of cyanobacteria coordinates 6 Chl *a* molecules (among which are the pair of P_{D1}/P_{D2} and 2 accessory Chls (Chl_{D1} and Chl_{D2}) now included in the symbol P680), 2 Pheo *a* molecules ($Pheo_{D1}$ and $Pheo_{D2}$), 2 or 3 quinones (Q_A on the D2 side and Q_B on the D1 side; the third quinone Q_c identified in PSII crystal structure at 2.9 Å resolution [178] was not seen in the recent PSII structure at 1.9 Å resolution [125]), at least 2 β-Cars and 1 NHI (between Q_A and Q_B) with an associated (bi)carbonate ion (HCO_3^-/CO_3^{2-}) [125,174]. Although the symmetrically related cofactors located on the D2-branch do not participate in electron transfer through PSII ("inactive" branch) (Figure 1.6), some of them are known to play protective roles against photo-induced damage of PSII. In fact, the overall structure and arrangement of the cofactors on the reducing side of the D1/D2 heterodimer closely resembles that of their counterparts from purple bacteria [179]. The only clear exception here is that in PSII, the NHI is bound to (bi)carbonate and not to Glu as in anoxygenic bacterial RC (recently reviewed in [73,122]) and that the Q_B site is slightly larger and in a closer contact with the cytoplasmic surface than in anoxygenic bacteria.

Two redox-active Tyr residues, Y_Z (D1-Tyr161) and Y_D (D2-Tyr161), are located on the electron-donor side of the D1/D2 heterodimer (see Figure 1.6). The Pheo *a* molecules (discovery of Pheo is reviewed in [180]) and the Tyr residues on D1 and D2 are homologous. However, they are not

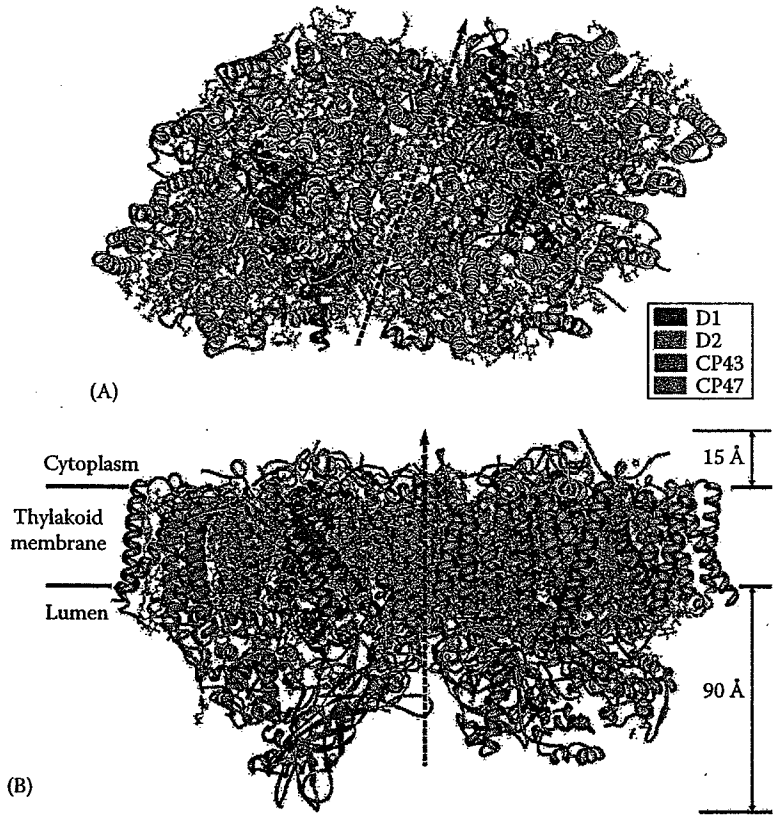

FIGURE 1.5 **(See color insert.)** Overall structure of the cyanobacterial PSII dimer from *T. vulcanus*. (A) View of the dimer from the cytoplasmic side. (B) Side-on view (perpendicular to the membrane normal). The PSII core proteins D1, D2, CP43, and CP47 are colored individually, as shown in the figure, whereas others are colored in light gray. PSII extends to ~15 Å on the cytoplasmic side but to a much larger distance, ~90 Å, on the lumen side. Approximate boundary between the monomeric subunits of the homodimer is indicated by dashed arrows. See text for further details. The PSII model was generated with *RCSB Protein Workshop Viewer* using x-ray crystallographic coordinates deposited at Protein Data Bank (PDB) with ID 3ARC. (By permission from Macmillan Publishers Ltd. *Nature*, Umena, Y. et al., Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å, 473, 55, 2011. Copyright 2011.)

equivalent, since the electron transfer of PSII proceeds only through the $Pheo_{D1}$ and Y_Z on D1 protein (Figure 1.6). Nevertheless, although Y_D (located on D2) is not involved in electron flow of PSII, it plays an important role in the redox processes in PSII (see e.g., [181–183]), and it is probably also involved in the photoactivation of the OEC [184].

The D1 protein not only holds the redox-active cofactors of the "active" electron transfer branch (Figure 1.6) but also provides most of the ligands to the catalytic site of oxidative water splitting [185], a cluster of four Mn atoms, one Ca atom, and five bridging oxygen atoms (the Mn_4CaO_5 cluster) [125,186]. Together with its protein ligands [185] and at least one Cl^- ion as cofactor (two Cl^- ions according to [125]), the Mn_4CaO_5 cluster forms a functional unit, the OEC (also called the water-oxidizing complex). The Mn_4CaO_5 cluster is surrounded by three extrinsic proteins on the lumenal side of PSII: PsbO (33 kDa), PsbV (also known as cytochrome c_{550} (Cyt c_{550}); 17 kDa) and PsbU (12 kDa) (Figure 1.6). The latter two smaller proteins are present only in the cyanobacterial OEC; in case of higher plants, they are substituted by PsbP (23 kDa) and PsbQ (17 kDa). PsbO is often called the *Mn-stabilizing protein* for its key role in stabilization of the Mn_4CaO_5 cluster and hence the O_2-evolving activity. These three extrinsic proteins are highly important for shielding the

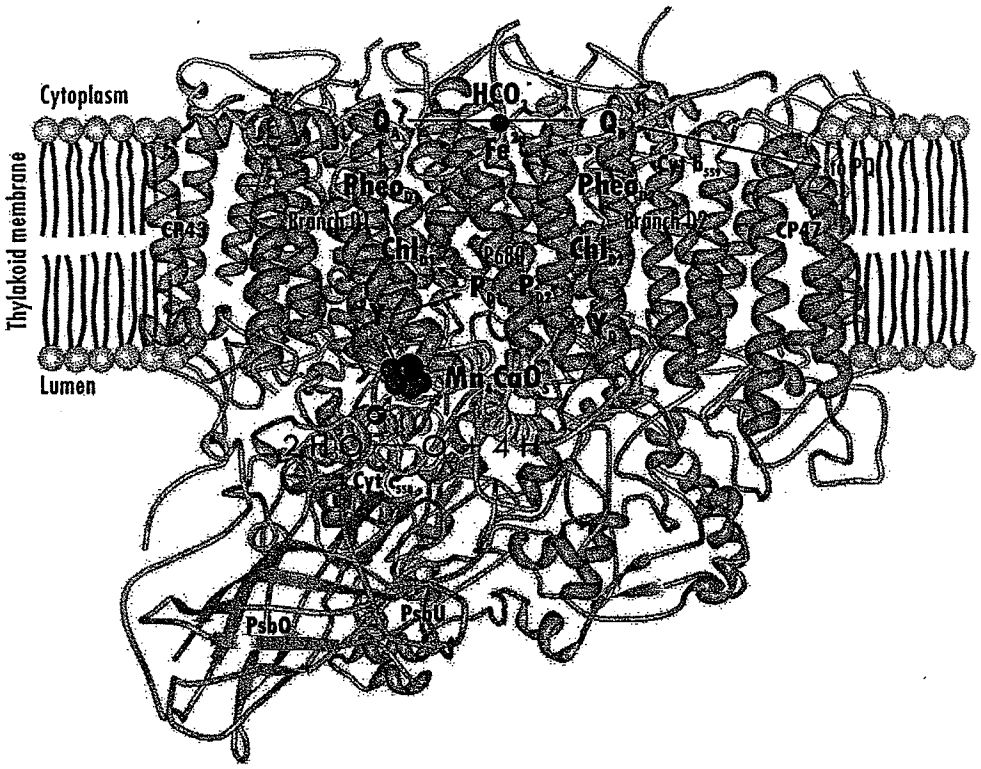

FIGURE 1.6 **(See color insert.)** Schematic arrangement of electron transfer cofactors in cyanobacterial PSII monomer. Figure shows side-on view from the direction parallel to the membrane plane. All cofactors (dark blue labels) of the monomer are arranged in two branches on the D1 and D2 protein subunits (see Figure 1.5). The light-induced single electron transfer occurs mainly on the D1 protein of the PSII RC (so-called active branch). The direction of electron transfer is indicated by dark blue arrows. The location of some protein subunits is shown (black labels). Note that primary electron donor P680 (traditional definition) refers to a pair of Chl *a* molecules (P_{D1} and P_{D2}), and two accessory Chls (Chl_{D1} and Chl_{D2}). For further details and abbreviations, see text. The protein background of PSII monomer was generated with the *RCSB Protein Workshop viewer* using coordinates deposited at PDB under ID 3KZI.

Mn_4CaO_5 cluster and for the optimization of water oxidation at physiological concentrations of Ca^{2+} and Cl^- ions (for recent reviews, see [187–189]).

The D1-D2 heterodimer is closely associated with two internal antenna subunits, the Chl *a*-containing proteins CP47 (PsbB) and CP43 (PsbC) (Figures 1.5 and 1.6), which bind 16 and 13 Chls *a* molecules, respectively [174]. These Chls funnel excitation energy from light-harvesting antenna system (PBSs) to PSII RC Chls. However, pigments in CP43 and CP47 are not only Chls but also Cars (reviewed in [190]). The CP47 and CP43 proteins are structurally homologous, each having large membrane-extrinsic loops interacting with the extrinsic subunits on the lumenal side. Both proteins are indispensable for establishing the water-splitting site. CP43 contributes a ligand (Glu354) to the first coordination sphere of the Mn_4CaO_5 cluster [125,191], while the large loop of CP47 is known to be essential for stabilization of the entire OEC [192].

In addition to the aforementioned proteins of the PSII RC, there are also 13 small membrane-intrinsic protein subunits, referred to as *low molecular weight* (LMW) *proteins* (PsbE, PsbF, PsbH, PsbI, PsbJ, PsbK, PsbL, PsbM, PsbT, PsbX, PsbY, PsbZ, and Ycf12) (for reviews, see [175,193]. Among them, only PsbZ has two TMHs, whereas all others have just one TMH. Two of the LMW

proteins, namely, PsbE (or α-subunit) and PsbF (or β-subunit), provide His ligands for the high-potential heme of cytochrome b_{559} (Cyt b_{559}) (Figure 1.6). The Cyt b_{559} and the nearby β-Car (not shown in Figure 1.6) are located on the D2 side. Their function is to protect the system against photo-induced damage [193,194].

Cyanobacterial PSII complex is known to have the highest content of lipids as essential cofactors among the others membrane-bound photosynthetic complexes. Thus, in total, 25 lipids per PSII monomer were revealed by x-ray structural models at 3.0 Å [173] and 2.9 Å [178] resolution. Lipids are mainly bound at the interface of the D1/D2 heterodimer and the antenna proteins CP43 and CP47, playing a significant role in the structure and function of PSII (for a review, see Ref. [195]).

All of the aforementioned protein subunits and cofactors of PSII have been physically seen in the latest x-ray structures of dimeric PSII complexes from thermophilic cyanobacteria at 1.9 Å [125] (also see Figure 1.5) and 2.9 Å [178] resolution. The crystal structure of cyanobacterial monomeric PSII complexes is also available, though at a lower resolution (3.6 Å) [196].

1.3.3.1.2 Electron Transfer Pathway and Function of PSII

The time sequence of the light-induced reactions within PSII is discussed in Section 1.2.2, and the electron transfer pathway is shown in Figure 1.6. An important point here is to realize that among the 4 RC Chl *a* molecules that form P680 and are mentioned earlier, Chl_{D1} is the Chl molecule where the very first light-induced charge separation begins, followed by the transfer of the positive charge to P_{D1} soon thereafter and formation of the $P_{D1}^{\bullet+}Pheo_{D1}^{\bullet-}$ pair (see, e.g., [197] and Section 1.4.1 for primary photochemistry). Each electron passes rapidly (see Section 1.2.2 for time sequence) from $Pheo^{\bullet-}$ to a permanently bound Q_A, leading to the stabilized radical ion pair $P_{D1}^{\bullet+}Pheo_{D1}Q_A^{\bullet-}$, before finally arriving at the loosely bound Q_B in the Q_B-pocket. The resulting $P_{D1}^{\bullet+}$ ($P680^{\bullet+}$) serves as the driving force for oxidative splitting of two H_2O molecules to O_2 and four protons. The electrons from water are transferred to $P_{D1}^{\bullet+}$ *via* the Mn_4CaO_5 cluster and the redox-active Y_Z (see Figure 1.6). Transfer of the second electron reduces Q_B^- to Q_B^{2-}, and the reduced Q_B^{2-} picks up two protons, ultimately, from the cytoplasmic side of the medium, yielding PQH_2 (Figure 1.3) [121]. A bicarbonate ion, bound to the NHI between Q_A and Q_B, plays a key role in this protonation event (reviewed in [122,198]). Upon protonation, PQH_2 leaves the PSII complex and diffuses in the membrane to the Cyt b_6f complex. Thereafter, another PQ molecule from the PQ pool immediately fills the empty Q_B-pocket of PSII.

Thus, PSII functions as a water:plastoquinone oxidoreductase (see recent reviews, see [65,67,199] and relevant chapters in [200]; it utilizes light energy to remove electrons from H_2O (water oxidation) and adds these electrons, as well as protons, to PQ (reduction of PQ pool). The role of the OEC in this process is indispensable: it couples the successive one-electron oxidations of $P_{D1}^{\bullet+}$ ($P680^{\bullet+}$) to the four-electron oxidation of water to molecular oxygen (for further details, see Section 1.4.2 and Chapter 2 and references therein).

1.3.3.2 Photosystem I

1.3.3.2.1 General Structural Organization

Cyanobacterial PSI is the largest photosynthetic membrane-bound protein complex; its oligomeric form predominantly exists as a trimer and has a molecular weight of ~1100 kDa (for recent overviews, see [63,201,202] and relevant chapters in [203]). The structure from the thermophilic cyanobacterium *T. elongatus* was determined at 2.5 Å resolution (see Figure 1.7 and Refs. [204,205]). Under certain environmental conditions, especially under high light intensities, PSI in cyanobacteria can also become a monomer (as it always exists in higher plants) [206,207]. Each monomeric PSI complex consists of 12 protein subunits that harbor 127 non-covalently bound cofactors (96 Chls *a*, 22 β-Cars, 2 phylloquinones, 3 [4Fe-4S] clusters, and 4 lipids) [208,209].

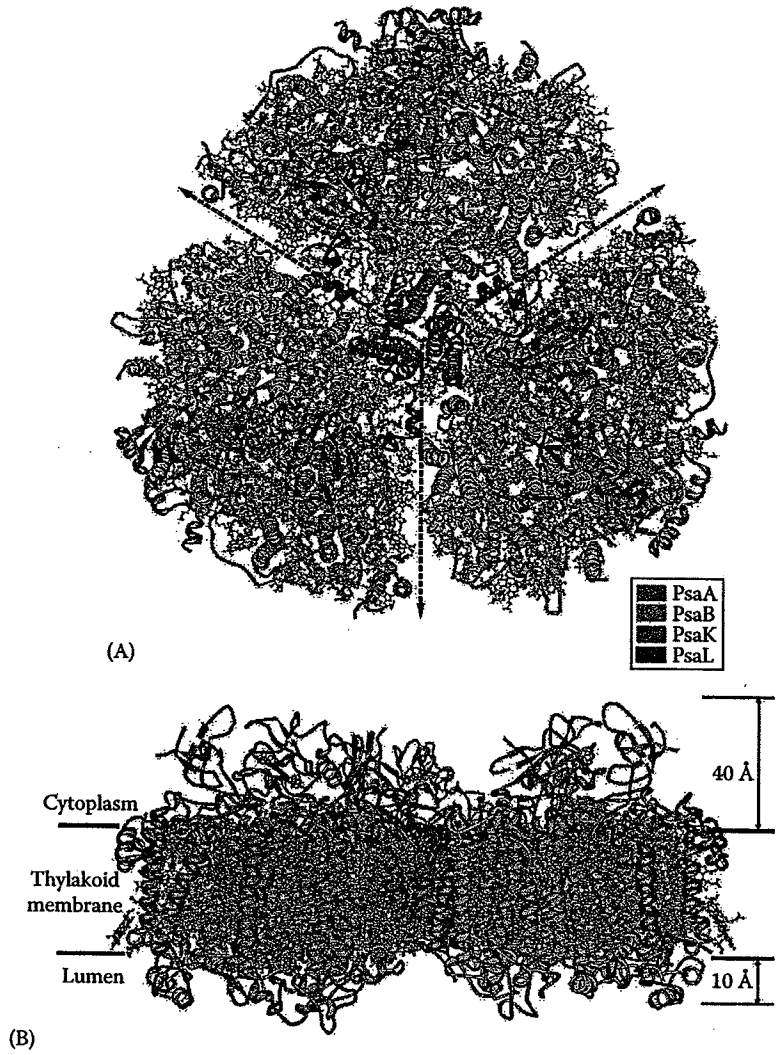

FIGURE 1.7 **(See color insert.)** Overall structure of the cyanobacterial PSI trimer from *T. elongatus*. (A) View of the trimer from the cytoplasmic side. (B) Side-on view (from the direction perpendicular to the membrane normal). PSI core proteins PsaA, PsaB, PsaK, and PsaL are colored individually, as shown in the figure, whereas the others are colored in light gray. PSI extends to ~40 Å on the cytoplasmic side but to a lesser distance, ~10 Å, on the lumen side. Approximate boundary between monomeric RCs is indicated by dashed arrows. For details, see text. The PSI model was generated with the *RCSB Protein Workshop viewer* using coordinates from PDB with ID 3PCQ. (By permission from Macmillan Publishers Ltd. *Nature*, Jordan, P. et al., Three-dimensional structure of cyanobacterial photosystem I at 2.5 A resolution, 411, 909, 2001. Copyright 2001; *Nature*, Chapman, H.N. et al., Femtosecond X-ray protein nanocrystallography, 470, 73, 2011. Copyright 2011.)

Two main protein subunits, PsaA and PsaB (the PsaA/PsaB heterodimer), form the core of PSI. Although these proteins are larger (each has 11 TMHs) than the core components of PSII (D1 and D2) and the anoxygenic RCs, they are homologous. The similarities of the TMHs arrangements are thought to indicate an evolutionary evolvement of PSI and PSII from a common ancestor [142]. Not all, but the majority of cofactors of the electron transfer chain of PSI are coordinated by the PsaA and PsaB. These cofactors are the primary electron donor (P700) that is the "special pair" of Chl *a* and Chl *a'* heterodimer, P_A and P_B, according to a nomenclature suggested by Redding and van der Est [210]; the

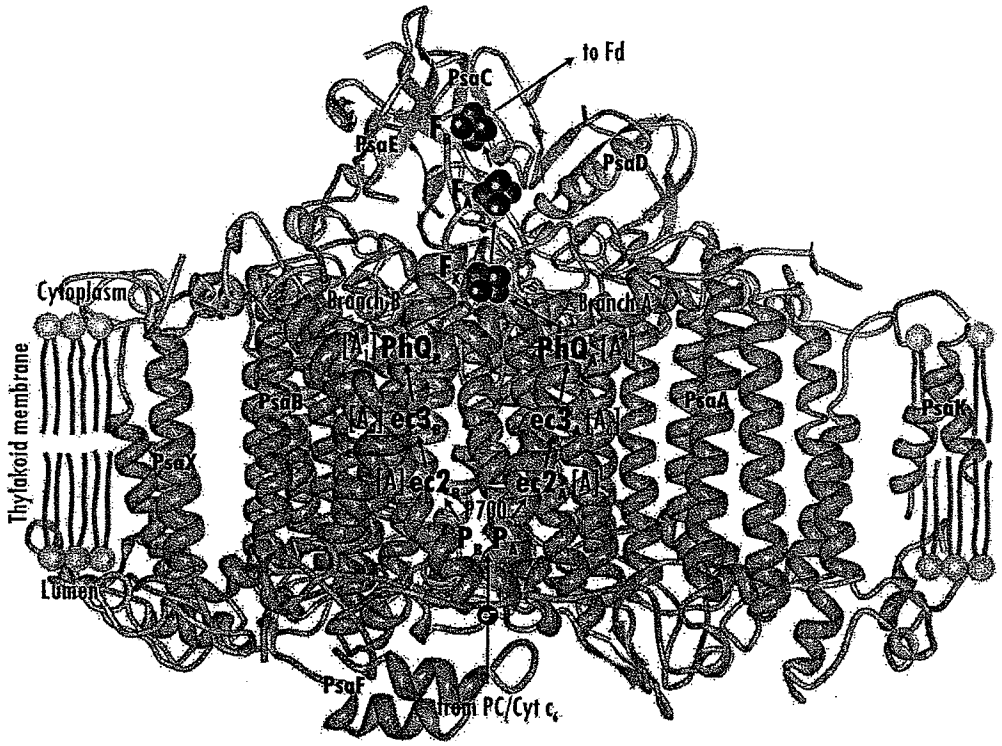

FIGURE 1.8 **(See color insert.)** Schematic arrangement of electron transfer cofactors in cyanobacterial PSI monomer. This figure is a side view of the monomer from the direction of the membrane exposed periphery of PSI along the membrane plane into the center of the trimer. As in PSII, the electron transfer cofactors (dark blue labels) in PSI are organized in two parallel branches denoted as A and B (named after the protein subunits PsaA and PsaB, respectively; see Figure 1.7). The arrows indicate the direction of the electron transfer and the two possible electron transfer pathways with almost equal probability (for overviews of bidirectional electron transfer in PSI and its possible advantages for photosynthetic organism, see [210,214]). The electron transfer cofactors of two branches are indicated according to the nomenclature suggested by Redding and van der Est [210], while in brackets we show the commonly used (traditional) names that refer to the spectroscopic signatures of these cofactors. Note that the primary electron donor P700 (P_A and P_B) is used for a "special pair" of Chl *a* and Chl *a'* heterodimer. The location of some protein subunits is indicated by black labels. For further details and cofactor abbreviations, see text. The protein background of PSI monomer was modeled by the *RCSB Protein Workshop viewer* using coordinates deposited at PDB with ID 1JB0. (By permission from Macmillan Publishers Ltd. *Nature*, Jordan, P. et al., Three-dimensional structure of cyanobacterial photosystem I at 2.5 A resolution, 411, 909, 2001. Copyright 2001.)

initial electron acceptor, A, that consists of two Chls *a* ($ec2_A$ and $ec2_B$); the first stable electron acceptor A_0 that is also formed by two Chls *a* ($ec3_A$ and $ec3_B$); two phylloquinone molecules A_1, PhQ_A and PhQ_B; and the first [4Fe-4S] cluster termed as F_X (see Figure 1.8). Moreover, most of the antenna Chls of PSI (79 of the 90) as well as most of the Cars are bound to the PsaA/PsaB heterodimer. This represents a unique feature of PSI to form strong structural and functional cohesiveness of the RC and the integral antenna system. Another important function of PsaA and PsaB is that they are involved in the docking of the mobile electron donors to P700 (Cyt c_6/PC) on the lumenal side of PSI [211].

The PsaA/PsaB heterodimer is surrounded by seven small membrane-integral protein subunits (PsaF, PsaI, PsaJ, PsaK, PsaL, PsaM, and PsaX), each containing from 1 up to 3 TMHs. Four of the subunits (PsaF, PsaJ, PsaK, and PsaX) are located at the membrane exposed surface of the PSI trimer (Figures 1.7 and 1.8) and are involved in the stabilization of the core-antenna system of PSI. Other three proteins (PsaI, PsaL, and PsaM) are located in the interface of the neighboring

monomers in the trimeric PSI complex, thereby forming "trimerization domain" [209]. With the exception of one subunit, PsaX, which is not found in higher plants [212], all other cyanobacterial protein subunits are present in higher plants.

Three proteins (PsaC, PsaD, and PsaE) on the cytoplasmic side do not contain TMHs (Figures 1.7 and 1.8). They form the docking site of PSI for the mobile electron acceptor of PSI, Fd. PsaC is the most important among these proteins, because it binds the [4Fe-4S] clusters F_A and F_B, the two terminal cofactors of the electron transfer chain of PSI. This protein has high sequence homology and identical structure in cyanobacteria and higher plants [204,212].

1.3.3.2.2 Electron Transfer Pathway and Function of PSI

The electron transfer chain in PSI is arranged in two quasi-symmetrical branches (A and B) that contain 6 Chls and 2 phylloquinones A_1 (Figure 1.8). Both branches are found to be active [213,214]. However, the electron transfer in cyanobacteria takes place mostly on the branch A [215,216], while in photosynthetic eukaryotes, branch B is thought to be more active than A [217–219].

Recent data suggest that the primary charge separation in PSI may begin not from P700, as it was initially thought, but from the A/A_0 pair (Figure 1.8), followed by the generation of a primary $A^{\bullet+}A_0^{\bullet-}$ radical pair, rapid reduction by P700 and the formation of the subsequent radical pair $P700^{\bullet+}A_0^{\bullet-}$ [220–222]. The oxidized $P700^{\bullet+}$ is then reduced by the electron provided by Cyt c_6/PC. The electron available at the $A_0^{\bullet-}$ moves though the remaining intermediates across the membrane to reduce water-soluble Fd. For its important function to power the electron transfer from Cyt c_6/PC to Fd by using energy of light, PSI may be called as light-driven plastocyanin:ferredoxin oxidoreductase.

1.3.4 Light-Harvesting Complexes: Phycobilisomes

In Sections 1.3.3.1 and 1.3.3.2, we have already mentioned membrane-bound antenna systems associated with the two photosystems in cyanobacteria. For further information on these integral (core) antennas and their structures, see [38,61,133]. Here, we briefly focus on a distinctive feature of cyanobacteria—the giant multidimensional extraneous antenna system on the cytoplasmic side of their thylakoid membranes, the PBSs (Figure 1.2), which give the specific blue-green color to cyanobacteria (for overviews on PBSs, see [38,61,62,223]). However, cyanobacteria are not the sole photosynthetic organisms that have PBSs; red algae also employ the PBSs for harvesting sunlight (see, e.g., [40,224,225]).

PBSs are organized into 3 core cylinders (two in the base and one on the top) and 6 (sometimes 8 or 10) peripheral stacked disk rods (Figure 1.2). The core cylinders, and the peripheral rods of the PBSs, are formed by water-soluble proteins, the *phycobiliproteins*, which contain covalently bound (*via* thioester bonds) open-chain tetrapyrroles, the *phycobilins*. In most cyanobacteria, phycobilins include *phycocyanins* (with absorption maxima in the 615–640 nm range) located in the peripheral rods, and *allophycocyanins* (with absorption at 650–655 nm) located in the core rods (see Figure 1.9A). There are some cyanobacteria that, in addition to phycocyanins and allophycocyanins, contain *phycoerythrins* (with absorption at 495 and/or at 565–575 nm) in their PBSs (see, e.g., [60,226–228]).

The absorption of light by phycobilins in the wavelength range 495–655 nm gives cyanobacteria an advantage at ocean depths where mainly green light is available. Excitation energy transfer is efficient and the cascade of energy transfer starts at the outer rods downhill toward the phycobilins localized at the core cylinders that absorb at longer wavelength [62]. The terminal long-wavelength allophycocyanins of the core cylinders interact with Chls *a* of internal antenna subunits of PSII, CP43 and CP47 (see Figures 1.5 and 1.6 and Section 1.3.3.1). One of these allophycocyanins, namely, allophycocyanin B (with absorption maxima at 670 nm) [229], is located on the PBS core-membrane linker protein ApcE, also called an "anchor" polypeptide for its mediating function with thylakoid membrane and/or the RCs [223,230]. Cyanobacterial PBSs are much larger in size than the photosystems. Thus, their most abundant hemidiscoidal morphological form normally has a diameter in the range of 300–800 Å [133,231]. The size of PBSs may vary depending on the light conditions: under

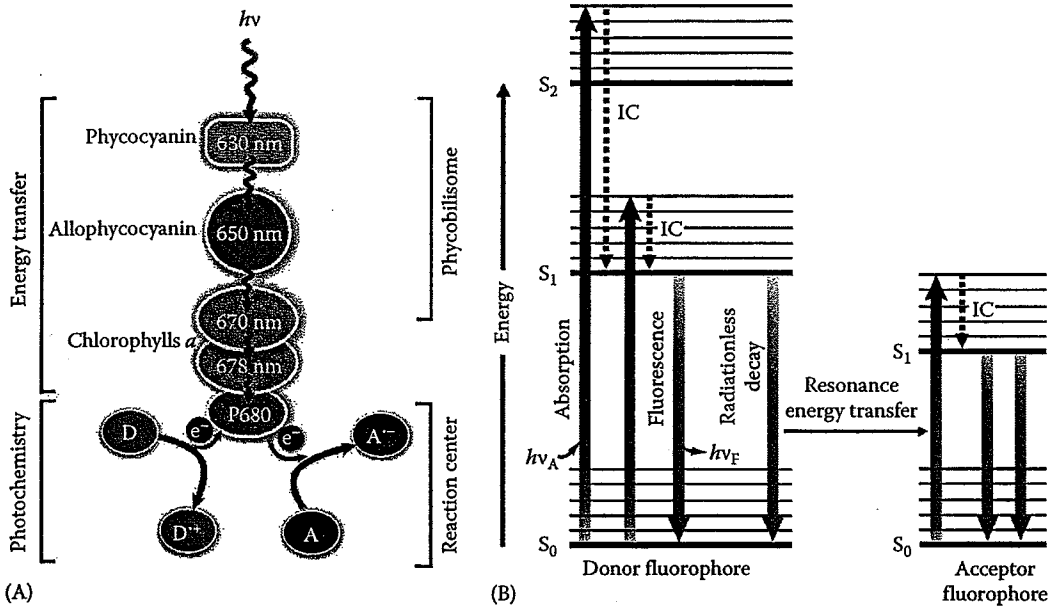

FIGURE 1.9 Excitation energy transfer in cyanobacteria. (A) Energy transfer steps in PBSs including primary photochemistry (charge separation) at the PSII RC of cyanobacteria. The energy of absorbed photon ($h\nu$) passes through a number of phycobilin pigments (phycocyanin and allophycocyanin) in PBSs and Chl *a* molecules until it reaches the RC Chls *a* (P_{D1}). The excited P_{D1} donates its electron to an acceptor (A) leading to a primary charge separation and formation of $P_{D1}^{\bullet+}$ and $A^{\bullet-}$ ($Pheo^{\bullet-}$). The electron vacancy in $P_{D1}^{\bullet+}$ is filled by the electron from an electron donor (D). The wavelength numbers (nm) represent pigments corresponding to the long wavelength absorption maxima of these molecules. (B) Perrin–Jablonski diagram illustrating the transfer of excitation energy between antenna molecules by Förster Resonance Energy Transfer (FRET). Absorption of energy in the form of electromagnetic radiation (photon) by an antenna molecule induces a very fast (10^{-13} s) transition from the lowest vibration level (only a few vibrational energy levels are shown) of a ground electronic singlet state (S_0) to an excited electronic states (S_1 or S_2). The magnitude of the absorbed energy ($h\nu_A$) determines which vibrational level of S_1 (or S_2) becomes populated. In the next 10^{-13} s, due to the process called internal conversion (IC), the antenna molecule relaxes to the lowest vibrational level of the first excited singlet state (S_1). One of the routes by which molecule can return to S_0 is fluorescence—photon emission (with the magnitude $h\nu_F$) that occurs between states S_1 and S_0. In most cases, emitted light will have a longer wavelength and therefore lower energy than the absorbed radiation. However, because of the proximity of other antenna molecules with a near (or the same) energy levels, the excited singlet state energy has a very high probability to be transferred to a neighboring antenna molecule *via* FRET. Since the S_1 state of Chl *a* is energetically lower than that of phycobilins, excitation energy is rapidly localized on the Chl *a* molecules. See text for further details.

low light intensities, PBSs increase in size, whereas they decreased in size under high light intensities (in some extreme cases, the outer rods may even disappear and only core allophycocyanins remain) [61].

For a long time, PBSs were thought to be the light-harvesting antennas of only PSII [62]. However, numerous investigations clearly revealed that effective excitation energy transfer may occur directly from PBSs to PSI RC (see e.g., [70,232,233]), indicating that PBSs are mobile complexes and that depending on the light conditions, they can be attached either to PSII or to PSI [72]. In a few cyanobacterial species, phycobiliproteins act as extrinsic antenna system as phycobiliproteins aggregates and are not organized into PBSs. The representatives of such PBS-lacking cyanobacteria are the Chl *d*-dominating cyanobacterium *A. marina* [171,234,235] and Chl *b*-containing cyanobacterium *Prochlorococcus marinus* [236–238].

The light-harvesting PBSs are highly important for photoautotrophic growth and directly mirror the physical parameters of the environment, especially light. Light can vary with respect to quality

and amount, and the organism senses and responds to the light environment by tuning its physiology. With respect to light harvesting, size, composition, number, and location of PBSs are optimized to maximize yield of physiologically usable light energy while minimizing damage to the photosynthetic apparatus and the cell [239]. During the so-called *state transitions* (also termed as State 1–State 2 (inversely, State 2–State 1) transition), cyanobacteria balance the light excitation between the two RCs on a timescale of seconds to minutes. Upon over-excitation of PSII (State 2), excitation energy channeled to PSI is increased, while upon over-excitation of PSI (State 1), excitation energy channeled to PSII is increased. In higher plants and green algae, state transitions are regulated *via* phosphorylation/dephosphorylation and redistribution of an LHC species within thylakoid membranes and between PSII and PSI [240]. In cyanobacteria, PBSs are required and rpaC has been found essential to establish State 2 (see, e.g., [72,241,242]). In addition, cyanobacteria respond with alterations in the composition of PBSs *via* a long-term physiological process termed *chromatic adaptation* (*acclimation*) upon changes in the quality (light color) of the light environment [243–246]. Cyanobacteria showing maximal rates of photosynthesis in one particular light intensity and quality can also acclimate and operate with less effective light conditions through a process termed *photoacclimation* [247,248]. Finally, physiology of cyanobacteria copes with excess light energy utilizing a number of photoprotective mechanisms [249].

1.4 LIGHT-INDUCED REACTIONS IN CYANOBACTERIA

1.4.1 Light Absorption, Excitation Energy Transfer, and Primary Photochemistry

Three types of pigment molecules, Chls, phycobilins, and Cars, are responsible for the light absorption properties of the cyanobacterial antenna complexes. Membrane-integral antenna complexes of PSII and PSI, together with PBSs, serve the RCs with excitation energy needed for the primary photochemistry processes. Here, we briefly outline the reaction sequence of excitation energy transfer that leads to primary photochemistry in the RCs of cyanobacteria and other oxygenic organisms (for reviews, see [80,183,250]).

The reaction sequence initiated by absorption of photon ($h\nu$) and excitation energy transfer within the PBSs and the RC integral antenna complexes can be represented as follows (also see Figure 1.9A for a simplified schematic drawing of these processes):

$$\text{Pbl} + h\nu \rightarrow \text{Pbl}^* \tag{1.1}$$

$$\text{Pbl}^*\,\text{Pbl} \rightarrow \text{Pbl}\,\text{Pbl}^* \tag{1.2}$$

$$\text{Pbl}^*\,\text{Chl}\ a \rightarrow \text{Pbl}\,\text{Chl}\ a^* \tag{1.3}$$

$$\text{Chl}\ a^*\,\text{Chl}\ a \rightarrow \text{Chl}\ a\,\text{Chl}\ a^* \tag{1.4}$$

where

Pbl represents phycobilins
Chl *a* represents Chls of the RC-integrated antenna complexes
$h\nu$ is a photon (quantum)
the asterisk indicates an electronically excited state

After absorption of photons, antenna pigment molecules go into specific excited states, depending upon the wavelength of light. The light energy is converted into excitation energy of the molecules that absorbed the light. Finally, light energy absorbed by different phycobilins (reaction 1.1) is transferred (reaction 1.2), as shown in Figure 1.9A, to the antenna Chls (reaction 1.3). This is followed by excitation energy transfer among Chl *a* molecules (reaction 1.4). The nature of the excitation energy transfer in

photosynthetic units has been debated for a long time. The *Förster hopping model* and the *delocalized (coherent) exciton model* are two mechanisms for the description of excitation energy transfer. Both models can be derived from quantum mechanics principles and, in fact, the applicability of these theories strongly depend on the interaction energies between different chromophores (pigments) and the protein environment: The Förster theory, the Redfield theory, the Modified Redfield theory, and the Generalized Förster theory are the result of direct application of the known physical concepts, which include the *exciton concept*, to the photosynthetic system [251–253]. Figure 1.9B shows the Perrin–Jablonski diagram illustrating the transfer of excitation energy transfer between antenna molecules by Förster Resonance Energy Transfer (FRET) (also see legend of this figure for description). In general, the Förster theory appears applicable to energy transfer from say phycocyanin to allophycocyanin and then to Chls *a*. The important feature of exciton dynamics is a cooperative mechanism of the excitation energy transfer. Such mechanism has a very clear physical interpretation: due to nonzero coupling energy between Chls in the antenna complexes, molecules lose their individual properties and the system behaves like a "super molecule" with a set of exciton energies which we observe in the optical experiments.

Taking PSII RC complex as an example, the excitation energy ("exciton" in the language of many) from the antenna Chls is trapped by the photoactive accessory pigment (Chl_{D1}) (see Figure 1.6); this is followed by primary charge separation (for simplicity, some steps have been left out):

$$\text{Chl } a^* \; Chl_{D1} \rightarrow \text{Chl } a \; Chl_{D1}^* \tag{1.5}$$

$$Chl_{D1}^* \; P_{D1} \; Pheo_{D1} \rightarrow Chl_{D1}^{\bullet+} \; P_{D1} \; Pheo_{D1}^{\bullet-} \rightarrow Chl_{D1} \; P_{D1}^{\bullet+} \; Pheo_{D1}^{\bullet-} \tag{1.6}$$

where the dot symbolizes a radical (unpaired electron).

There is still a debate as to the definition of P680 and the detailed steps involved in the primary photochemistry; we do not discuss it here (for further details, see Refs. [65,111,254,255]). Thus, the end result of the excitation energy transfer to Chl_{D1} (reaction 1.5), subsequent charge separation and the transfer of the positive charge to P_{D1} is the generation of the charge separated state $(Chl_{D1})\, P_{D1}^{\bullet+}\, Pheo_{D1}^{\bullet-}$ (reaction 1.6). This state is further stabilized by the following reactions on the acceptor side of PSII:

$$Pheo_{D1}^{\bullet-} \; Q_A \rightarrow Pheo_{D1} \; Q_A^{\bullet-} \tag{1.7}$$

$$Q_A^{\bullet-} \; Q_B \rightarrow Q_A \; Q_B^{\bullet-} \tag{1.8}$$

The absorption of the second photon ($h\nu$) initiates a second turnover of the reaction sequences (1.1) through (1.7), leading to the following reaction sequence on the Q_B-site of PSII:

$$Q_A^{\bullet-} \; Q_B^{\bullet-} \rightarrow Q_A \; Q_B^{2-} + 2H^+_{\text{cytoplasm}} \rightarrow Q_A \; Q_B \; H_2 \tag{1.9}$$

$$Q_A \; Q_B \; H_2 + PQ \rightarrow Q_A \; Q_B + PQH_2 \tag{1.10}$$

$$PQH_2 \rightarrow PQ + 2H^+_{\text{lumen}} \tag{1.11}$$

Thus, after the reduction of Q_B to Q_B^{2-}, followed by its protonation with two protons from cytoplasm (reaction 1.9), plastoquinone Q_B forms plastoquinol PQH_2 (reaction 1.10), which then diffuses towards the Cyt b_6f complex finally resulting in delivery of two protons into the lumen (reaction 1.11) and two electrons to the redox-cofactors of the Cyt b_6f complex. As it has been already discussed in Section 1.2.2, reaction (1.11) is the slowest reaction event among the all light-induced reactions of the electron transfer chain of thylakoid membrane.

1.4.2 Light-Induced Water Oxidation

Mechanism of water oxidation in oxygenic organisms is discussed in Chapter 2. Therefore, in this section, we briefly mention the basic principles of this process.

The basis for the understanding of the mechanism of photosynthetic water oxidation, known to be identical in both prokaryotic and eukaryotic O_2-evolving organisms, was set more than 40 years ago. Illuminating dark-adapted algae and chloroplasts by short ("single turnover") saturating flashes, Joliot and coworkers [256] discovered that O_2 evolved with a characteristic periodicity of four. The periodicity of four was readily explained by the four-electron chemistry of water splitting. On the other hand, the fact that the first maximum of O_2 evolution occurred after the third rather than the fourth flash, and that O_2 oscillation was damped after a few cycles, indicated an unexpected level of complexity in the mechanism of water oxidation by PSII. Based on these findings, Kok et al. [257] developed an elegant model of photosynthetic water oxidation (also called as Kok cycle or the "oxygen clock") (see Figure 1.10 and also [258] for various kinetic models of water oxidation). It assumes that each OEC cycles through five different redox states during oxidation of two water molecules, named S_i states ($i = 0, \ldots, 4$), where i is the number of oxidizing equivalents stored within the Mn_4CaO_5 cluster of the OEC. The formation of the four oxidizing equivalents occurs during repeated oxidation (one electron at a time) of the OEC by $P680^{\bullet+}$ *via* a redox-active tyrosine, $Y_Z^{\bullet}$

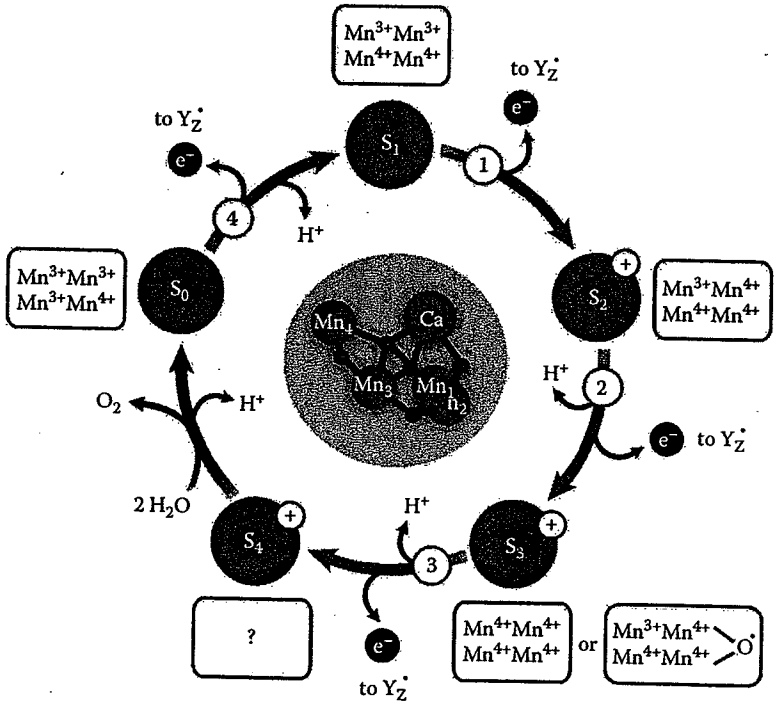

FIGURE 1.10 **(See color insert.)** The Kok cycle (also known as the "oxygen clock") that illustrates the stepwise process of photosynthetic water oxidation by the Mn_4CaO_5 cluster of oxygenic organisms. Blue arrows indicate light-induced S-state transitions and the numbers in circles on the arrows indicate the number of light flashes required for that transition, assuming that in the dark the Mn_4CaO_5 cluster is mostly in the S_1 state. The $S_4 \rightarrow S_0$ transition does not require light and is shown in black. Note that depending on the S-state transition, either the electron or the proton is thought to be removed first. Currently discussed oxidation states of the four Mn ions of the Mn_4CaO_5 cluster in various S states are shown. For further details on photosynthetic water splitting, see text (this chapter), Chapter 2 (this book), and Refs. [266,267,320]. For the original version of the Kok cycle and other models, see [256–258]. The structural model of the Mn_4CaO_5 cluster in the center is as derived from the recent x-ray crystallographic PSII structure.

(see Figures 1.6 and 1.10). In order to explain the maximum O_2 evolution after the third flash, Kok et al. assumed that in long dark-adapted samples, practically all (almost 100%) PSII centers are in the S_1 state, and not in the S_0. Therefore, the first S cycle begins from the S_1 state and is completed after three given flashes, while each next cycle is completed after four flashes. Indeed, later studies showed that the S_0 state is slowly (tens of minutes) oxidized to the S_1 state by the oxidized form of tyrosine D, $Y_D^{\bullet}$, of polypeptide D2 (Figure 1.6) [182,259,260]. The S_2 and S_3 states are reduced within seconds to minutes into the S_1 state by the reduced tyrosine Y_D *via* a fast decay [259,261,262] or a slower decay due to electron donation from the reduced acceptor side quinones [263–265]. The $S_4 \rightarrow S_0$ transition does not require a light flash. Therefore, the S_4 state is thought to spontaneously decay into the S_0 state releasing O_2; this is accompanied by the binding of at least one new substrate water molecule (reviewed in Refs. [67,266,267]). Lifetime measurements of the S_2 and S_3 states clearly indicate that the redox potentials and kinetics within the OEC do not differ between various species of cyanobacteria and higher plants [170,268]. In spite of numerous attempts, the S_4 state has not yet been detected because of its very short lifetime [269–271].

The oxidation state changes in the Mn_4CaO_5 cluster are mostly Mn-based. Several spectroscopic studies have been made to record the oxidation states of Mn ions in each S state (see reviews [67,272–275] and references therein). The results of these studies are summarized in Figure 1.10. Important insight about the structure of the Mn_4CaO_5 complex was provided by x-ray diffraction crystallography studies and extended x-ray absorption fine structure spectroscopy (see e.g., [173,174,186]). Recently, x-ray crystallography investigations on the PSII at 1.9 Å resolution have provided important new structural information about the Mn_4CaO_5 cluster in cyanobacteria (see [125] and Figure 1.10).

1.4.3 Some Comments on Production of the Reducing Power (NADPH) in Cyanobacteria

As mentioned earlier, the cyanobacterial system is not only unique but more flexible than those of higher plants and algae (see Section 1.1). Cyanobacteria are unique in the sense that both the reduction of $NADP^+$ to NADPH (for photosynthesis) and its reverse, the oxidation of NADPH (for respiration) take place on the same thylakoid membrane, although respiration also occurs on cytoplasmic membranes (see, e.g., [48] and Figure 1.1). In addition to PSI, PSII and Cyt b_6f complex (Figure 1.2), needed for the production of NADPH, thylakoid membrane also harbors (1) type 1 NADPH dehydrogenase (NDH-1) that oxidizes NADPH to $NADP^+$; (2) a terminal oxidase that reduces O_2 to H_2O; and (3) succinate dehydrogenase (SDH) that oxidizes succinate to fumarate providing reducing power to the PQ pool [48]. This complicates the kinetics of the production of NADPH. Another uniqueness lies in the fact that, as already mentioned in Section 1.2.1, the number of PSI to PSII is not 1:1 as is the case in higher plants and algae, but ranges from 3 to 5:1 (see, e.g., [68–70])—clearly favoring, in principle, a higher "cyclic" reaction around PSI (see e.g., [103]), over noncyclic electron flow from water to $NADP^+$.

1.4.4 Production of ATP

The basic steps preceding the energy-requiring ATP synthesis from ADP and inorganic phosphate (P_i) are (1) charge separation in both PSII and PSI leading to a negative charge on the thylakoid membrane side facing the cytoplasmic side (the *n* side), and a positive charge on the thylakoid membrane side facing the lumen side (the *p* side); (2) deposition of four protons into the lumen when two H_2O molecules are oxidized to O_2 (see Section 1.4.2); (3) utilization of four electrons available from water oxidation for the conversion of two PQ molecules to two molecules of PQH_2, with the four protons, needed for this reaction, being taken from the cytoplasmic side (see Figure 1.2); this step being followed by proton release into the lumen, while the electrons on PQH_2 are being transferred to the Cyt c_6 (or PC) *via* the Cyt b_6f complex; and (4) in addition to the noncyclic pathway of electron transfer from H_2O to $NADP^+$, and also a cyclic electron

flow around PSI, there is a "Q-cycle" (see, e.g., [198,276]). These cycles also lead to proton translocation from the cytoplasmic side to the lumen side. The sum of the two components (ΔpH and membrane potential, $\Delta\psi$) forms the PMF (see Section 1.2.1). Peter Mitchell ([277]; Nobel Prize in Chemistry in 1978) suggested that dissipation of the PMF through ATP synthase provides energy for ATP synthesis. About 42 kJ of converted light energy in this reaction is stored in each mole of the high-energy phosphate, ATP.

The mechanism of ATP formation is very different from the electron transfer processes described in Section 1.2. Jagendorf and Uribe [278] had observed that if chloroplasts (experiments were not done in cyanobacteria then) were first suspended in an acidic medium and then transferred to an alkaline medium in the presence of ADP and P_i, ATP formation occurred in darkness. Junge and coworkers (reviewed in [100,102]) found that valinomycin that dissipates the electric field inhibited phosphorylation. These experiments clearly support the Mitchell's chemiosmotic hypothesis.

The ATP synthase is shown schematically in Figures 1.2 and 1.11 (for more detailed models and structures, see the figures in [100–102]); this enzyme is ~15 nm long and ~12 nm wide and it has a molecular weight of ~600 kDa. It has two basic parts, one hydrophobic part (F_o) that, is embedded in the thylakoid membrane and another hydrophilic part (F_1) protruding into the stroma (see Figure 1.11A and B). The F_o of cyanobacteria contains several subunits: a (one copy), b (two copies; sometimes b and b′; [279]), and c (10–15 copies), whereas F_1 contains α (three copies), β (three copies), γ (one copy), δ (one copy), and ε (one copy), subunits. The F_o-enzyme part acts as a rotary motor, and most of the membrane-associated subunits rotate (Figure 1.11C), while H^+'s are translocated across the membrane (reviewed in [101]). Mechanical energy in this rotary motion is coupled to the formation of "high-energy phosphate bonds" in ATP at the stator (α, β, and δ) F_1 part of the enzyme (Figure 1.11C). Paul Boyer and John Walker received, in 1997, a Nobel Prize in Chemistry for their explanation of how the ΔpH energy is converted into mechanical energy on F_o followed by this rotation energy being converted into chemical energy, during ATP formation from ADP and P_i on the α and β subunits of F_1 (for historical perspective see [102]).

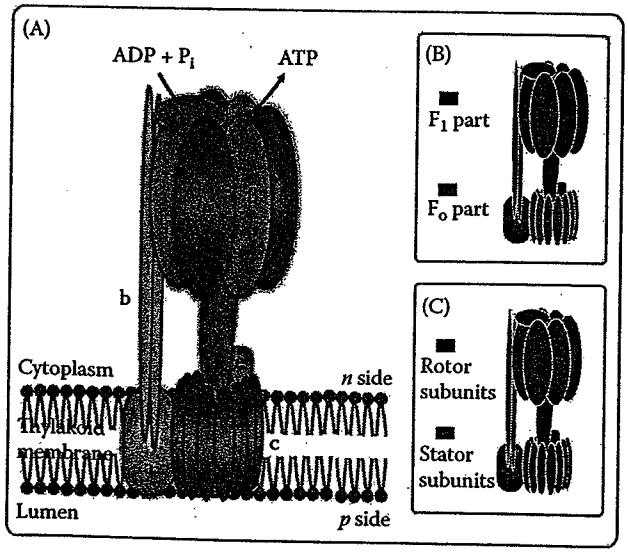

FIGURE 1.11 Schematic representation of ATP synthase and its subunits. (A) Overall subunit scheme of ATP synthase. (B) Schematic view of two basic parts of ATP synthase: a membrane-embedded F_o part and a peripheral (cytoplasmic) F_1 part (shaded individually as shown in the figure). (C) Schematic view of rotor and stator subunits of ATP synthase (shaded differently as shown in the figure).

Protons on the *p* side bind to the "c subunits." Pogoryelov et al. [280] had examined c subunits in several cyanobacteria species; although they had >80% sequence identity, one species had 13 copies; four species had 14 copies and two species had 15 copies. Again, this may be interpreted to show a high degree of flexibility of the cyanobacterial biology. There are many reports that deal with the number of protons needed per ATP produced. Van Walvaren et al. [281] had found this number to be 4 in two cyanobacterial strains (also see [282]).

In summary, the PMF (mainly proton gradient, just mentioned) is used by F_o, particularly the c subunit, to be converted into a mechanical rotation energy (a torque), which is then used by F_1, particularly its α/β unit, that converts this rotation energy into chemical energy, resulting in the formation of ATP from ADP and P_i. Further, both ε and γ subunits are involved in the regulation of this ATP synthase activity [283,284]. For details of mechanism, see Ref. [198].

1.5 COMMENTS ON EVOLUTION

One of the great enigmas in the evolution of life is the question when and how the first cyanobacteria initiated oxygenic photosynthesis and hence became capable of carrying out the thermodynamically and chemically demanding reaction of water oxidation into O_2? This evolutionary mystery remains unsolved. We know that before the event of oxygenic photosynthesis, photosynthetic organisms were anoxygenic (not O_2-producing). For reduction of CO_2 (carbon fixation) an oxygenic phototrophs used electrons from available reductants, such as H_2, H_2S, CH_4, and/or $Fe(OH)^+$ [7,285,286]. Although H_2O was another potential and the most abundant electron donor present in the environment, its utilization as source of electrons for carbon fixation required significantly higher investment in energy than for other electron donors. However, a constantly decreasing supply of H_2 and of other substrates on the surface of the planet, and the presence of an enormous (almost unlimited) H_2O pool, and the necessity of the photobacteria to gain energy for sustaining essential cellular processes may have resulted in constant evolutionary pressure towards the development of photosynthetic apparatus capable of extracting electrons from water. During the period between 3.2 and 2.4 billion years ago (the exact date is not known but is intensively discussed in the literature [157,287–296]), the problem of water splitting was solved: using the energy of sunlight, the emerged photosynthetic machinery in the first cyanobacteria successfully bridged the large potential barrier between water and $NADP^+$ [3,144,148,297,298]. Unlike anoxygenic photosynthetic apparatus, the new water-splitting photosynthetic apparatus contained the following inventions: (i) two types of *functionally linked RCs* (PSI and PSII) each comprising a new photosynthetic pigment, Chl *a*, and the unique RC, where the primary photochemistry takes place (see [3,31,35]; also see Sections 1.3.1 and 1.3.2); (ii) the *catalytic site of water oxidation* (OEC) functioning as a charge-accumulating system coupled to a strongly oxidizing RC (PSII) (see [149] and Section 1.4.2); and (iii) characteristic *light-harvesting antenna complexes* (PBSs) for the capture of light energy and its delivery, in the form of excitation energy, to the RCs (see [299] and Section 1.3.4). Since the metabolic waste product of the water-splitting reaction was O_2, the first oxygenic organisms had the great advantage of being able "to poison" their competitors with "toxic" dioxygen. As result, only those organisms survived that either developed protective mechanisms against O_2 or found O_2-free ecological niches. The origin of cyanobacteria and the levels of atmospheric O_2 is well depicted in the relationship between important events in the evolution of life and photosynthesis (see Figure 1.12A and its legend for further details and references). Most of the successful survived organisms, including cyanobacteria, managed to develop highly efficient respiratory processes which utilized O_2 as the terminal electron acceptor for "biochemical burning" which allowed the release of at least 10–15 times more free energy from organic substances than through anoxygenic processes [13,300]. Geochemical data indicate that already about 2.3 billion years ago, the amount of O_2 in the atmosphere was

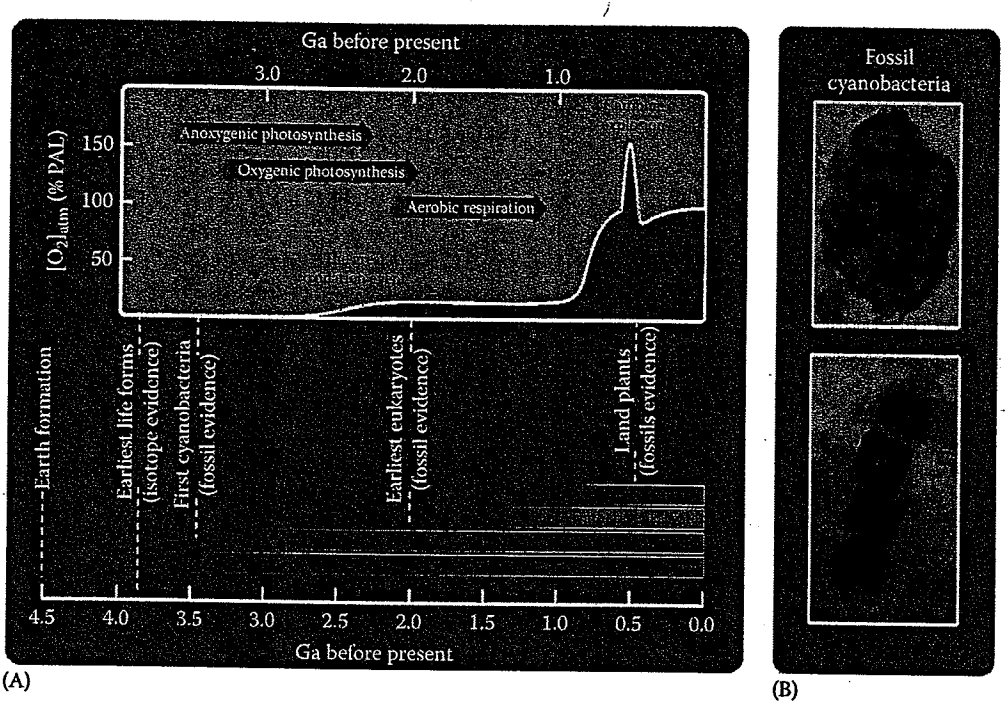

FIGURE 1.12 **(See color insert.)** The role of cyanobacteria in the evolution of life and evolution of metabolic pathways during Earth's history. (A) Schematic view on the relationships between important events in the evolution of life and photosynthesis, origin of cyanobacteria (highlighted in blue), and atmospheric O_2 concentration (in % of present atmospheric level (PAL) of O_2) through geological times in billions of years (Ga). These relationships and the dates in the figure are approximations based on numerous literature data [1,7,9,157,289,290,292, 296,298,302,303]. Only selected events of evolutionary diversification and the emergence of some organisms are shown. There is no firm conclusion as to when oxygenic photosynthesis was invented by primitive cyanobacteria. The earliest known fossil record of cyanobacteria occurring at 3.45 Ga [291,293] has been questioned [286,287]. Although there are other ample indications for the presence of primitive morphological forms of cyanobacteria in stomatolites about 3.5 Ga ago [294,295], they do not rule out the possibility that some of the earliest cyanobacteria behaved like anoxygenic photosynthetic bacteria. Concentration curve of atmospheric O_2 over time is displayed between a lower and an upper limits of PAL values provided in [290]. (B) Two representatives of ancient fossil cyanobacteria from the ~0.85-Ga-old Bitter Springs Chert of central Australia. On the top is a nonmobile colonial chroococcacean cyanobacterium (Coccoidal cyanobacteria), and on the bottom is the filamentous cyanobacterium *Palaeolyngbya* (Oscillatoriaceae). The Oscillatoriaceaen cyanobacteria have changed little or not at all over the last thousands of millions years [292]. The pictures of fossil cyanobacteria were kindly provided to the authors by J. William Schopf. (Based on Blankenship, R.E., *Plant Physiol.*, 154, 434, 2010; Hohmann-Marriott, M.F. and Blankenship, R.E., *Annu. Rev. Plant Biol.*, 62, 515, 2011; Falkowski, P.G., *Science*, 311, 1724, 2006; Raymond, J. and Blankenship, R.E., *Coord. Chem. Rev.*, 252, 377, 2008; Jagendorf, A.T. and Uribe, E., *Proc. Natl. Acad. Sci. USA*, 55, 170, 1966; Dunn, S.D. et al., *Biochemistry*, 40, 187, 2000; Van Walraven, H.S. et al., *FEBS Lett.*, 379, 309, 1996; Olson, J.M., *Photosynth. Res.*, 88, 109, 2006; Brasier, M.D. et al., *Nature*, 416, 76, 2002; Schopf, J.W., *Science*, 260, 640, 1993; Schopf, J.W., *Photosynth. Res.*, 107, 87, 2011.)

high enough to form an ozone layer, which began to absorb a large part of the highly damaging UV radiation from the sun [11,290,301] (Figure 1.12). Consequently, this allowed organisms to make better use of the terrestrial environment and led to a significant increase of genomic and metabolic complexity of life, as we observe it today [9,302,303].

Two representatives of ancient fossil cyanobacteria are shown in Figure 1.12B (also see legend and [292] for further details). Given the high degree of conservation of the photosynthetic apparatus, it is well possible, that the first cyanobacteria which learned how to split water and produce O_2, and thus changed the world, looked very similar to one of these two fossil representatives.

1.6 ABIOTIC STRESS ADAPTATION IN CYANOBACTERIA

Cyanobacteria live in many different environmental conditions that often include extremes of temperature, light, and nutrient status. Clearly, abiotic stress affects light-induced reactions of oxygenic photosynthesis in cyanobacteria. However, cyanobacteria have evolved many strategies for survival and adaptation (for recent review, see [304]). We provide here a glimpse of two of the many abiotic stresses and how cyanobacteria deal with them: nutrient stress and light stress. For a general description of abiotic stress adaptation in plants, see various chapters in [305].

An example of nutrient stress adaptation is the lack or excess of copper. Lack of copper leads to Cyt c_6 (Cyt c_{553}) replacing PC as electron donor to $P700^{\bullet+}$; on the other hand, the presence of copper in the medium leads to induction of the PC gene [306]. There is indeed an exchange of Cyt c_{553} with PC [93]; and copper mediates regulation of the two interchangeable intermediates [94,95]. Another nutrient stress that cyanobacteria experience is iron stress. Falk et al. [307] discussed the production of a CP43′ polypeptide of PSII under iron deficiency conditions. Recently, Ivanov et al. [308] demonstrated that iron stress induces the production of CP43′ and monomerization of PSI trimers and reduces the capacity for state transition. Leonhardt and Strauss [309] described the iron stress operon involved in dealing with electron transport and, thus, how cyanobacteria cope with this stress. Excess light can lead to irreversible photoinhibition and destroy the organism. However, cyanobacteria do tolerate high light and protect themselves by what is termed "non-photochemical quenching" of the first singlet excited state of Chl molecules; this entails de-excitation of the excited state through release of heat. In addition, excess of light in PSII causes the formation of low-fluorescent state II, whereas excess of light in PSI causes the formation of high-fluorescent state I; this indicates that there is reorganization of pigments and PBSs between PSI and II (state transitions). For a description and understanding of these regulatory mechanisms, we refer readers to some of the available literature (see, e.g., [132,310–318]). Recent data suggest that state transitions in cyanobacteria are important physiological adaptation mechanism to maximize the efficiency of light harvesting at very low light intensities, and that they play no role in protection from photoinhibition [72]. For further details on abiotic stress responses in cyanobacteria, see the chapters of this book.

1.7 CONCLUDING REMARKS

There is tremendous need and interest in solving problems of dwindling resources, global climate changes, and sustainability for our future. We need to develop artificial photosynthesis to capture the all abundant solar energy as well as improve photosynthesis efficiency. To achieve this goal, we must exploit the knowledge of natural photosynthesis [319–327] (also see Chapter 2). We believe that cyanobacteria can help us in this respect. We hope to exploit the flexibility of cyanobacteria in learning how to use them to produce hydrogen [328–331] and fix nitrogen [20,21] and for the synthesis of biopharmaceuticals [332,333]. Information provided in this chapter on the structure and function of the antenna system, and the photosystems, and on evolution is crucial, in our opinion, in designing future directions for using cyanobacteria to serve society.

ACKNOWLEDGMENTS

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