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REVIEW

Electron Transport in Chloroplasts: Regulation and Alternative Pathways of Electron Transfer

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Abstract—This work represents an overview of electron transport regulation in chloroplasts as considered in the context of structure-function organization of photosynthetic apparatus in plants. Main focus of the article is on bifurcated oxidation of plastoquinol by the cytochrome b_6f complex, which represents the rate-limiting step of electron transfer between photosystems II and I. Electron transport along the chains of non-cyclic, cyclic, and pseudocyclic electron flow, their relationships to generation of the trans-thylakoid difference in electrochemical potentials of protons in chloroplasts, and pH-dependent mechanisms of regulation of the cytochrome b_6f complex are considered. Redox reactions with participation of molecular oxygen and ascorbate, alternative mediators of electron transport in chloroplasts, have also been discussed.

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INTRODUCTION

Oxygenic photosynthesis is the most important process of the Earth biosphere, which provides production of molecular oxygen (O_2) and fixation of CO_2 driven by the sunlight energy absorbed by light-harvesting pigments of plants, algae, and cyanobacteria. Photosynthetic apparatus of these organisms contains two photosystems (PS), the pigment–protein complexes PSI and PSII, cytochrome b_6f complex, and ATP synthase complex CF_0–CF_1, which catalyzes formation of ATP from ADP and orthophosphate P_i. Transfer of two electrons from the water-oxidizing complex of PSII to $NADP^+$ (terminal electron acceptor in PSI) ensures reduction of $NADP^+$ to NADPH. ATP and NADPH, as the high energy products of the “light stages” of photosynthesis, are used in the reactions of the Calvin–Benson cycle (CBC) for CO_2 fixation [1, 2].

Structural and functional organization of the plant photosynthetic apparatus is well studied [3-21]. At the same time, some questions remain unclear, related to regulation of photosynthetic processes and acclimation of the photosynthetic apparatus to changes in environmental conditions. This review briefly examines structural organization of the photosynthetic apparatus of oxygenic organisms and main regulation mechanisms of the electron and proton transport, which ensure high efficiency of light energy conversion in chloroplasts. The first part of the article describes the processes of non-cyclic, cyclic, and pseudocyclic electron transfer, their role in generation of the trans-thylakoid difference in electrochemical potentials of hydrogen ions ($\Delta\tilde{\mu}_{H^+}$), and also discusses the mechanisms of pH-dependent regulation of the cytochrome b_6f complex functioning in chloroplasts. The second part examines the processes related to participation of molecular oxygen (O_2)

Abbreviations: Asc, MDHA, DHA, three redox forms of ascorbate (fully reduced, semiquinone, and completely oxidized); CBC, Calvin–Benson cycle; CET, cyclic electron transport; EPR, electron paramagnetic resonance; ETC, electron transport chain; ISP, iron-sulfur protein, part of PSI; Fd, ferredoxin; FNR, ferredoxin-NADP reductase; NDH-1, NAD(P)H-dehydrogenase of chloroplasts type 1; P_{700} and P_{680}, primary electron donors in PSI and PSII; Pc, plastocyanin; PGR5 and PGRL1, proteins involved in cyclic electron transfer around PSI; PSI and PSII, photosystem I and photosystem II; PQ, plastoquinone; PQH_2, plastoquinol; PTOX, plastid (plastoquinol) terminal oxidase; ROS, reactive oxygen species.

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and ascorbate (Asc) as mediators in electron transfer in chloroplasts.

STRUCTURAL AND FUNCTIONAL ORGANIZATION OF THE PHOTOSYNTHETIC APPARATUS OF PLANTS. ELECTRON TRANSPORT CHAIN

In plants, the processes of light-induced electron transport and transmembrane proton transfer occur in chloroplasts, the energy-transducing organelles of the plant cell [18-21]. The chloroplast is separated from the cytoplasm by the envelope, which consists of two adjacent membranes – the outer and the inner one. Under the envelope, in the stroma, there are lamellae membranes. Under normal physiological conditions, grana are formed from the lamellae membranes, which are arranged as the appressed stacks of flattened vesicles (thylakoids) with diameter of ~350-600 nm. Individual thylakoids of the grana protrude into the stroma as the intergranular thylakoids. Thylakoid membranes are densely filled with photosynthetic protein complexes, which make up to ~70-80% of the total membrane mass. The pigment–protein electron transport complexes are incorporated into the thylakoid membranes. The stroma contains RNA, DNA molecules, ribosomes, starch grains, as well as enzymes that ensure absorption of CO_2 in the CBC.

A diagram illustrating interaction of the electron transport complexes is shown in Fig. 1. The energy of light quanta, absorbed by the pigments of the light-harvesting

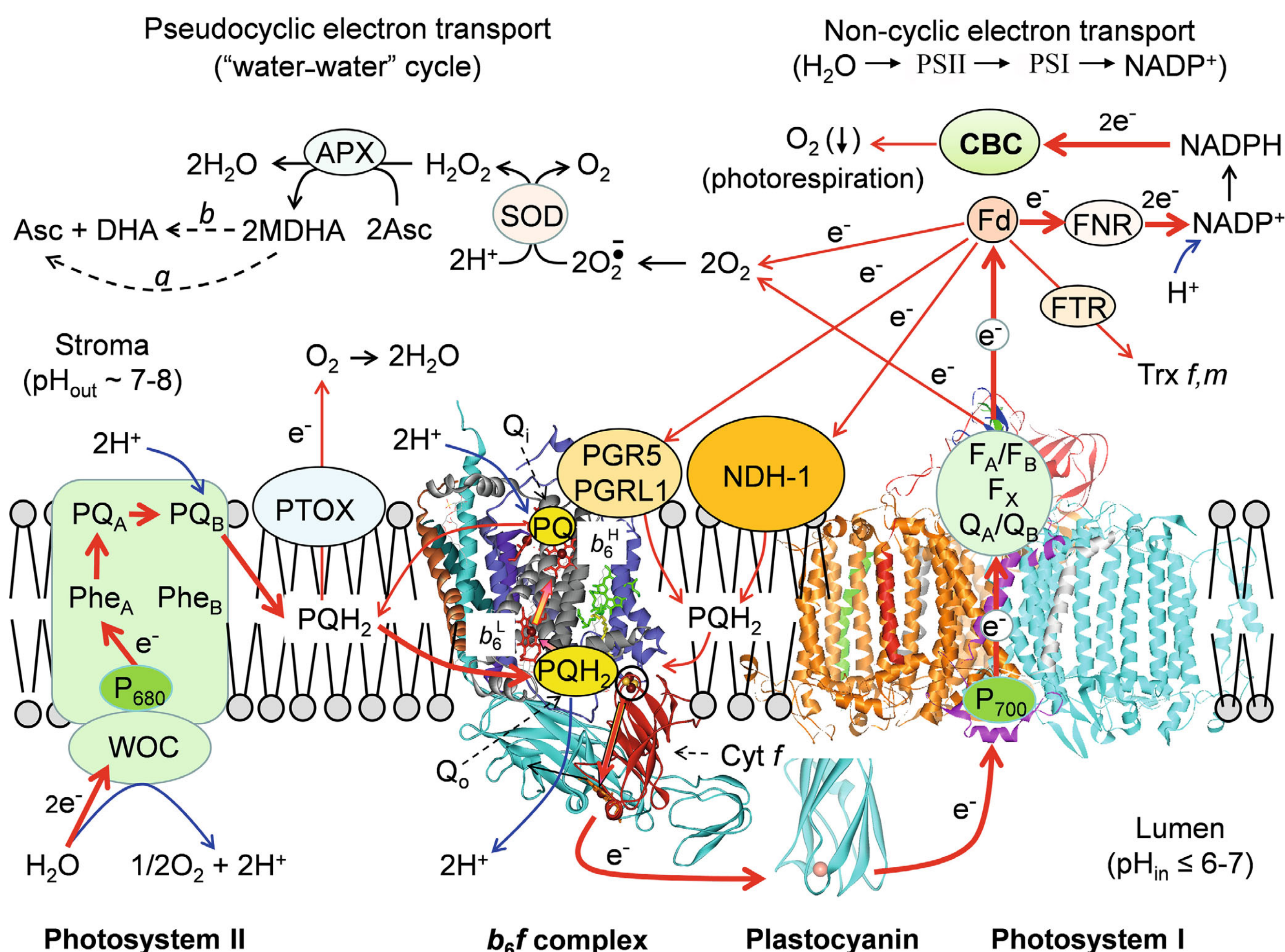

Fig. 1. Scheme illustrating interaction between the electron transport complexes (Photosystem I, Photosystem II, and the cytochrome b_6f complex) embedded in the thylakoid membrane and the mobile electron carriers (ferredoxin, Fd; plastoquinone, PQ; plastoquinol, PQH_2; plastocyanin, Pc). F_X, F_A, and F_B are the iron-sulfur centers of PSI; Q_A and Q_B are the phylloquinone molecules associated with PSI; PQ_A and PQ_B are the plastoquinone molecules associated with PSII; APX, ascorbate peroxidase; FNR, ferredoxin-NADP reductase; FTR, ferredoxin thioreductase; NDH-1, NAD(P)H-dehydrogenase of chloroplasts type 1; PTOX, chloroplast (plastid) terminal oxidase; CBC, Calvin–Benson cycle; SOD, superoxide dismutase; Asc, MDHA and DHA are fully reduced, semiquinone (monodehydroascorbate) and oxidized (dehydroascorbate) forms of ascorbate, respectively; Trx *f*,*m*, isoforms *f* and *m* of thioredoxin. Explanation of other symbols and abbreviations is given in the main text of the article. Red arrows indicate main paths of the electron transfer, blue arrows indicate transfer of hydrogen ions. The arrows marked as *a* and *b* indicate two pathways of the Asc formation from MDHA.

antennas of PSI and PSII, migrates to the reaction centers, in which charge separation occurs, and electron transfer along the photosynthetic electron transport chain (ETC) is initiated [6-17]. Coordinated functioning of PSI and PSII accomplishes oxidation of water in the oxygen-evolving complex of PSII ($2H_2O \rightarrow O_2 + 4e^- + 4H^+$) and provides reduction of $NADP^+$ to NADPH with the help of PSI ($NADP^+ + 2e^- + H^+ \rightarrow NADPH$). The cytochrome b_6f complex and the mobile electron carriers, plastoquinol (PQH_2) and plastocyanin (Pc), facilitate communication between the low-mobility membrane-embedded protein complexes PSII and PSI.

Electron transfer is coupled with generation of the trans-thylakoid difference in the electrochemical potentials of hydrogen ions ($\Delta\tilde{\mu}_{H^+}$). As a result of water decomposition by the oxygen-evolving complex of PSII and due to the work of the b_6f complex, the stroma becomes alkalized, and hydrogen ions accumulate in the lumen. Since the thylakoid membranes have relatively low permeability to hydrogen ions and charged molecules, they able to maintain $\Delta\tilde{\mu}_{H^+}$, which allows the membrane-embedded ATP synthase complexes (CF_0–CF_1) to ensure formation of ATP from ADP and orthophosphate P_i [3-5]. In chloroplasts, the pH difference, $\Delta pH = pH_{out} - pH_{in}$, where pH_{out} and pH_{in} are pH values of the stroma and lumen, respectively, provides main contribution to $\Delta\tilde{\mu}_{H^+}$ [22, 23].

Photosystem II (PSII) functions as an oxidoreductase, oxidizing water and reducing plastoquinone (PQ) to plastoquinol (PQH_2) [6, 7, 9-11]. In photosynthetic reaction centers of PSII, energy from the excited light-harvesting pigments migrates to the primary electron donor, which consists of an ensemble of four chlorophyll *a* molecules ($Chl_{D1}/P_{D1}/P_{D2}/Chl_{D2}$). The primary electron donor, known as P_{680}, transfers the electron to the pheophytin (Phe) through the chlorophyll Chl_{D1}, from which it goes to the plastoquinone PQ_A, tightly bound to PSII ($P^*_{680} \rightarrow Chl_{D1} \rightarrow PheA \rightarrow PQ_A$). PQ_A^- reduces the second plastoquinone molecule PQ_B ($PQ_A^-PQ_B \rightarrow PQ_APQ_B^-$). After accepting the second electron, the PQ_B^{2-} molecule becomes protonated by the hydrogen ions from the stroma ($PQ_B^{2-} + 2H^+_{out} \rightarrow PQ_BH_2$) and then dissociates into the lipid phase of the membrane in exchange for another oxidized PQ molecule ($PQ_BH_2 + PQ \rightarrow PQ_B + PQH_2$). Further step of electron transfer along the ETC involves the PQH_2 diffusion to the cytochrome b_6f complex (plastoquinol–plastocyanin oxidoreductase). In this complex, a two-electron (bifurcation) oxidation of PQH_2 into PQ occurs, leading to the reduction of Cyt *f*, which then reduces Pc, which serves as an electron donor for PSI. Two hydrogen ions absorbed from the stroma during the PQH_2 formation ($PQ + 2e^- + 2H^+_{out} \rightarrow PQH_2$) are released into the lumen during the oxidation of PQH_2 by the cytochrome b_6f complex.

Photosystem I (PSI). In plants, PSI is a monomeric complex that includes light-harvesting pigments and electron carriers; PSI in cyanobacteria is, as a rule, a trimeric supercomplex [6, 7]. Excitation of P_{700}, the primary electron donor of PSI, leads to the charge separation in PSI and formation of the oxidized form of P_{700} (P^+_{700}), which accepts an electron from the reduced plastocyanin (Pc^-). From PSI, the electron is transferred to ferredoxin (Fd) [6-8]. At the acceptor side of PSI, electron carriers are structured in the form of two quasi-symmetric branches. From P_{700}, the electron proceeds (through Chl *a* and phylloquinone molecules) to the iron-sulfur acceptor F_X and further, through the redox centers F_A and F_B, to the ferredoxin located in the stroma ($F_X \rightarrow F_A \rightarrow F_B \rightarrow Fd$). Two molecules of the reduced ferredoxin (Fd^-) mediate reduction of $NADP^+$ to NADPH by the ferredoxin-NADP reductase (FNR). Thus, due to the joint work of PSII and PSI, the non-cyclic transfer of electrons from water to $NADP^+$ occurs, ensuring formation of NADPH molecules, which are consumed mainly in the CBC reactions.

At the level of the Fd pool, electron flow can branch out. In addition to the non-cyclic electron transport from PSI to $NADP^+$, Fd is involved in the electron transfer around PSI (cyclic electron transport, CET), when the electron from Fd returns to the plastoquinone pool of chloroplasts [24-31]. Figure 2 demonstrates possible CET pathways along which electrons from the acceptor side of PSI could return to the pool of plastoquinone molecules. One of them suggests that CET includes hypothetical protein FQR (ferredoxin-quinone reductase), existence of which was postulated previously [24]. At present time, there are compelling reasons to believe that the role of FQR is performed by the proteins PGR5 and PGRL1, associated with the cytochrome b_6f complex [28-30]. In addition, electron transfer from the reduced Fd to the plastoquinone pool is possible with participation of the minor NADPH dehydrogenase complex type 1 (NDH-1), which forms a supercomplex with PSI [31-35].

Oxidation of plastoquinol in the cytochrome b_6f complex. Q-cycle. The cytochrome complex b_6f is the link in the electron transport chain that governs interactions between PSII and PSI. Oxidation of PQH_2 by the b_6f complex is the slowest step in the electron transfer chain between PSII and PSI [36-41]. The rate-determining factor in this section of the ETC is turnover of plastoquinone ($PQ \rightarrow PQH_2 \rightarrow PQ$), which includes formation of PQH_2 in PSII and interaction of PQH_2 with the b_6f complex. In a wide range of conditions (pH, temperature), reduction of PQ to PQH_2 in PSII and its diffusion along the membrane to the b_6f complex was experimentally proven to occur faster than actual oxidation of PQH_2 within the cytochrome complex [37, 38, 40, 41].

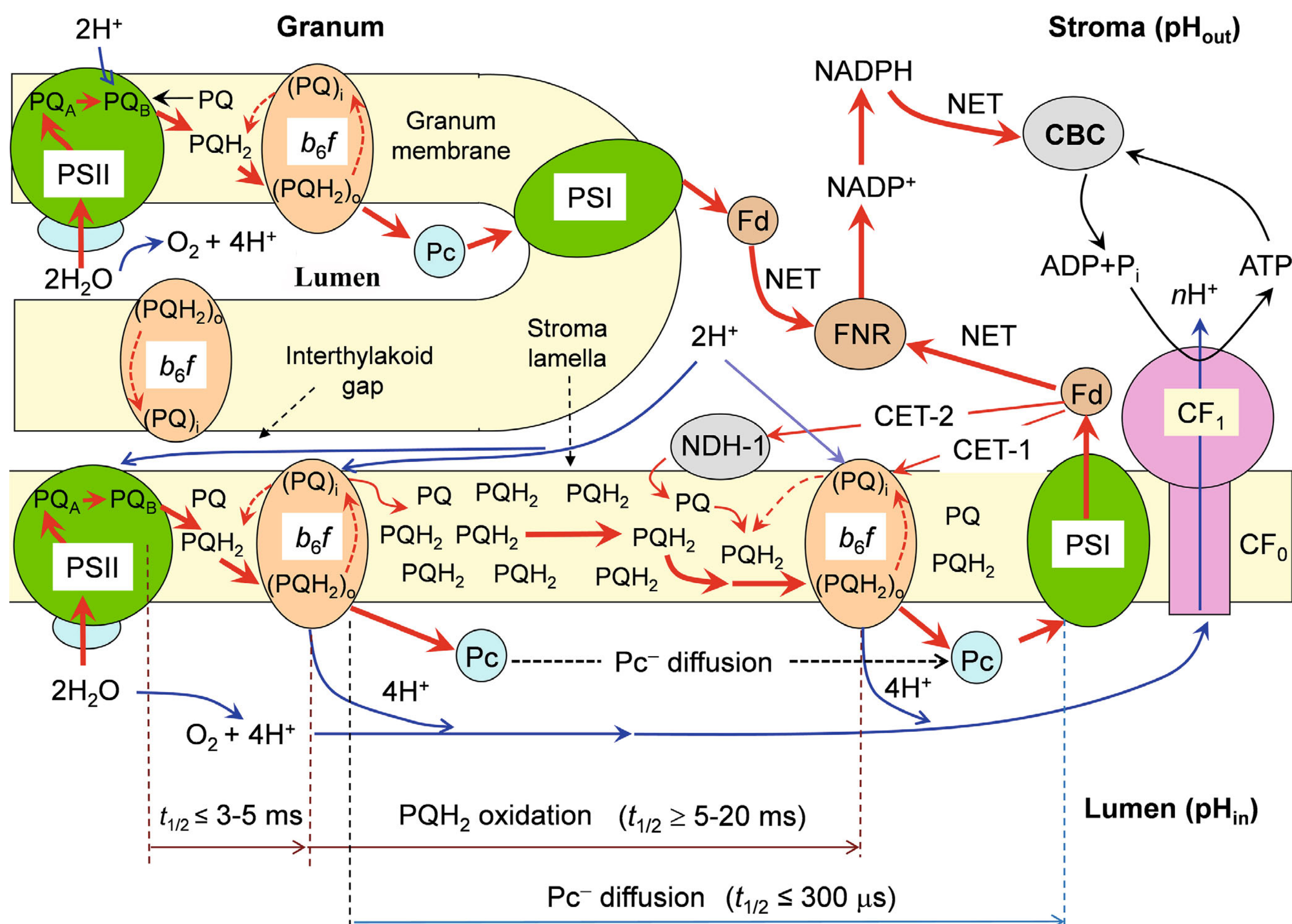

Fig. 2. Scheme of localization of the electron transport complexes in the membranes of granal and stroma-exposed intergranal thylakoids. The arrows labelled NET, CET-1, and CET-2 designate different paths of electron transfer at the acceptor side of PSI. NET stands for non-cyclic electron transfer associated with $NADP^+$ reduction. CET-1 is the pathway for cyclic electron transfer around PSI with suspected involvement of the proteins PGR5 and PGRL1, associated with the cytochrome b_6f complex. CET-2, cyclic electron transfer involving NADP dehydrogenase complex type 1 (NDH-1).

The cytochrome b_6f complex is organized as a dimeric complex consisting of two identical protein fragments [12-17, 42]. Oxidation of PQH_2 occurs at the quinol-binding sites of the dimeric complex (Fig. 3, Q_o catalytic sites). Each of the Q_o centers is located near the lumenal side of the thylakoid membrane, between the low-potential heme b_6^L and the Fe_2S_2 cluster of the high-potential iron-sulfur protein (ISP), often called the Rieske protein. Catalytic functions of the monomers are carried out by four redox centers: the Fe_2S_2 cluster of the ISP, two hemes of the cytochrome b_6 (b_6^L and b_6^H), and cytochrome *f*. According to the Mitchell Q-cycle mechanism [42-46], oxidation of PQH_2 is a bifurcated process; two electrons donated by the PQH_2 molecule are transferred along the different chains: one electron goes to the oxidized Fe_2S_2 cluster of the ISP, the second electron is transferred to the low-potential heme b_6^L. At the same time, two protons of the PQH_2 molecule dissociate into the lumen. In the *high-potential* electron transfer chain, the ISP is oxidized by the heme *f*, from which the electron proceeds to plastocyanin and then to the oxidized center P_{700}^+ (ISP → f → Pc → P_{700}). The second electron donated by PQH_2 is transferred along the *low-potential* chain of the b_6f complex, which includes two cytochrome b_6 hemes and heme c_n. This electron arrives at the PQ molecule located at the Q_i center ($b_6^L \rightarrow b_6^H \rightarrow$ PQ). According to the modified Q-cycle model, the second electron arrives at the Q_i center from the PSI acceptor site. After the double reduction of PQ and arrival of two protons from the stroma ($PQ + 2e^- + 2H^+_{out} \rightarrow PQH_2$), the reduced PQH_2 molecule dissociates from the Q_i center and returns to the catalytic center Q_o (see [12-17, 42-45] for more details). In the end, it turns out that two protons are transferred into the thylakoid ($H^+/e^- = 2$) per one electron transferred to the CBC from PSI (PSI → $NADP^+$) [46].

Plastocyanin diffusion in the lumen. The cytochrome complex reduces Pc molecule. Diffusing inside the lumen, Pc^- transfers an electron to PSI. The diffusion of Pc^- and its oxidation by PSI occurs faster (at room

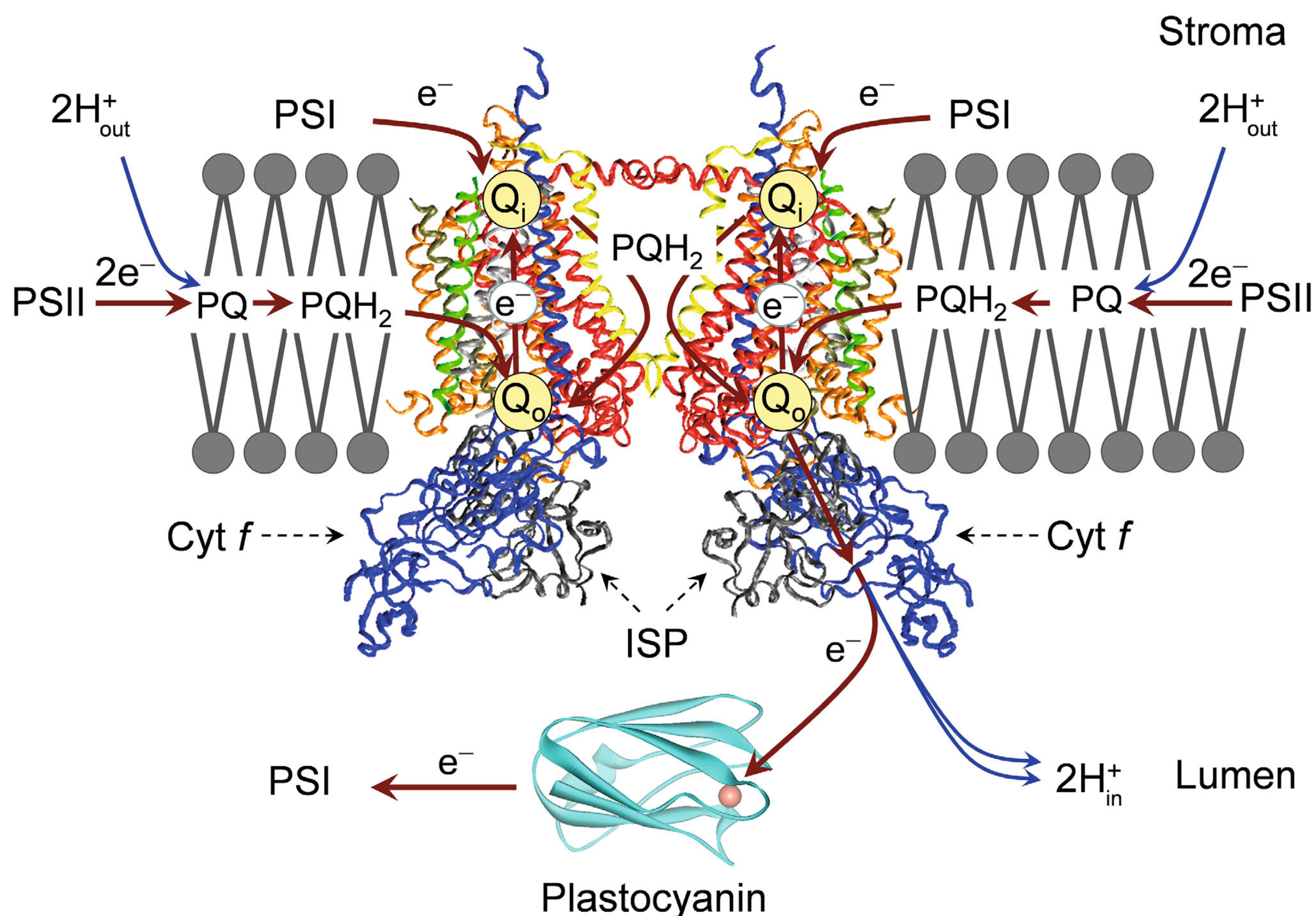

Fig. 3. Dimeric cytochrome b_6f complex. The image was constructed using the Accelrys DV visualizer software package (http://www.accelrys.com) according to the PDB data (PDB ID 1Q90).

temperatures $\tau_{1/2} < 300$ μs) than the diffusion of PQH_2 from PSII to the b_6f complex and oxidation of PQH_2 by the b_6f complex ($\tau_{1/2} \geqslant$ 4-20 ms) [36-41]. Under certain conditions (for example, in dark-adapted chloroplasts), steric restrictions could prevent movement of the Pc molecules within the narrow (~4-5 nm) lumen gap [47]. Width of the lumen gap can increase upon the chloroplast illumination, and then lateral diffusion of Pc^- inside the lumen would not limit transfer of the electrons from the b_6f complexes to PSI [47].

Apart from the processes described above, alternative electron transfer reactions can occur in chloroplasts, among which a special role belongs to the so-called pseudocyclic electron transfer, when molecular oxygen acts as the final acceptor of the electron donated by PSI (the Mehler reaction [48-51]). Reduction of O_2 to water can also be catalyzed by the chloroplast (plastid) terminal oxidase (PTOX), which oxidizes PQH_2 [52-56]). It should be noted that the PTOX content in mature chloroplasts is very low – only one PTOX complex per 100 PSII complexes [57]. The NDH-1 content is approximately three times lower than the PTOX content [57, 58].

Redox reactions involving ascorbate also play a special role in the metabolism of plant cells, providing detoxification of reactive oxygen species (ROS) [59]. Alternative electron transfer pathways are discussed in more detail below.

LATERAL HETEROGENEITY OF THYLAKOID MEMBRANES AND ALTERNATIVE PATHWAYS OF PHOTOSYNTHETIC ELECTRON TRANSFER

Photosynthetic protein complexes are unevenly distributed between the granal and intergranal (stromal) thylakoids [18-21, 60-63]. Granal thylakoids are enriched with PSII complexes; majority of the PSI and ATP synthase complexes are concentrated in the intergranal thylakoids, at the edges and ends of the grana domains exposed to the stroma. The cytochrome complexes are distributed approximately evenly along the lamellar membranes, from which thylakoids of the grana and stroma are formed [60-63]. Heterogeneous distribution of the complexes is caused by steric restrictions: ATP synthases and PSI complexes have protein fragments that significantly protrude from the membrane, thereby preventing compact arrangement of these complexes in the appressed thylakoids of grana.

Structural and functional properties of thylakoids could be associated with the lateral heterogeneity of the thylakoid membranes. The cytochrome complexes localized in the granal and stroma-exposed thylakoids can participate in the electron transfer along different pathways: the “granal” b_6f complexes are included in the chain of non-cyclic (“linear”) electron transfer from PSII to PSI and further to $NADP^+$ (PSII → PQ → b_6f → Pc → PSI → → $NADP^+$), the “stromal” complexes could be included in the cyclic electron transport chain around PSI (PSI → → Fd → PQ → b_6f → Pc → PSI).

Interaction between the remote low-mobility protein complexes is mediated by the diffusion of mobile electron carriers – plastoquinone and plastocyanin. High density of the protein complexes in the thylakoid membrane limits mobility of plastoquinone, and poses steric restrictions that impede movement of plastocyanin in the narrow gap of the lumen, thereby limiting the rates of the diffusion-controlled stages of electron transfer [64]. Note that, despite the steric restrictions, diffusion of PQH_2 along the thylakoid membrane does not limit *per se* the rate of electron transfer between photosystems. As mentioned above, in a wide range of experimental conditions (pH, temperature), formation of PQH_2 in PSII and its diffusion occur faster than actual oxidation of PQH_2 after its binding to the catalytic center Q_o of the cytochrome b_6f complex [37, 38]. Despite the fact that many PSII and PSI complexes are at a distance from each other, a significant portion of the b_6f complexes located in grana are positioned close to PSII. Close arrangement of these complexes minimizes the average distance traveled by the plastoquinone pool molecules, ensuring rapid exchange between the PQH_2 and PQ molecules formed as a result of the PSII functioning (formation of PQH_2) and oxidation of PQH_2 by the b_6f complex. Thus, due to the high mobility of plastoquinol in the membrane and rapid diffusion of Pc inside the lumen [38, 40], effective electron transfer from PSII to PSI and further to $NADP^+$ (non-cyclic electron transport) is ensured.

The cytochrome b_6f complexes located in the intergranal thylakoids close to PSI complexes, could be directly included in the cyclic electron transport (CET) chain around PSI. Efficient functioning of CET could be facilitated by formation of the supercomplex consisting of the electron transport complexes b_6f and PSI [27]. Various pathways of CET are possible. PGR5 and PGRL1 proteins, which operate together with the b_6f complex, function as the electron transfer mediators involved in CET [28-30].

Another CET pathway around PSI is realized with the help of the minor NAD(P)H dehydrogenase complex type 1, which is an analogue of the similar complex in mitochondria [31-33]. NDH-1 acts as an oxidoreductase, oxidizing ferredoxin and reducing plastoquinone [34, 35]. CET around PSI mediates $\Delta\tilde{\mu}_{H^+}$ formation and, consequently, can support the ATP synthesis. In this case, however, no reduction of $NADP^+$ occurs. Coexistence of the linear and cyclic electron flows allows to maintain proper stoichiometry between the ATP and NADPH molecules, which is necessary for optimal functioning of the CBC (ATP/NADPH = 3/2) [1, 2].

Distribution of the b_6f complexes between the granal and intergranal thylakoids depends on the functional state of the photosynthetic apparatus. Changes in the chloroplast architecture could lead to redistribution of the electron flows between the non-cyclic and cyclic pathways. Lateral movement of some b_6f complexes from the granal to the stromal regions of the thylakoid membranes would lead to increase in the relative contribution of CET to the functioning of chloroplasts. It is assumed that such redistribution of the b_6f complexes could indeed occur, for example, due to the light-induced changes in the distance between the neighboring granal thylakoids [65].

Two ferredoxin isoforms and alternative electron flows. Taking into account localization of b_6f complexes in different regions of chloroplasts, it is of note that there are several isoforms of ferredoxin (at least two fractions, minor (Fd1) and major (Fd2)), which differ slightly in physicochemical properties (for example, in standard redox potential values) and some functional properties [66-70]. The Fd1 and Fd2 proteins have similar amino acid sequences, but are present in different quantities in the chloroplasts of C3 plants. For example, in *Arabidopsis* and pea the Fd1 and Fd2 fractions account for 10% and 90%, respectively, of the total pool of ferredoxin molecules [66]. The ratio between the fractions depends on the plant acclimation conditions: practically no expression of Fd1 is observed in the plants grown under low light; under conditions that stimulate CET (high light intensity, drought), Fd1 expression increases significantly [68, 69].

As an example illustrating the difference in the functioning of Fd1 and Fd2, let us consider the results of experiments with the class B bean chloroplasts (chloroplasts with damaged outer membrane, lacking ferredoxin) presented in Fig. 4 using the kinetic data from Gins et al. [70]. These chloroplasts retained membrane-bound ferredoxin-NADP reductase, but lost ferredoxin molecules located in the stroma. Addition of $NADP^+$, a physiological electron acceptor, did not affect the kinetics of electron transfer, as assessed from the light-induced changes in the electron paramagnetic resonance (EPR) signal from the oxidized P_{700}^+ centers [70]. Both forms of ferredoxin, Fd1 and Fd2, were active as electron transfer mediators. In both cases, far-red light (λ_{max} = 707 nm), which predominantly excites PSI, caused noticeable oxidation of P_{700}. However, under the white light illumination (WL), which excites both photosystems, addition of Fd1 or Fd2, which interacts with FNR, affected kinetics of the P_{700} redox transformations

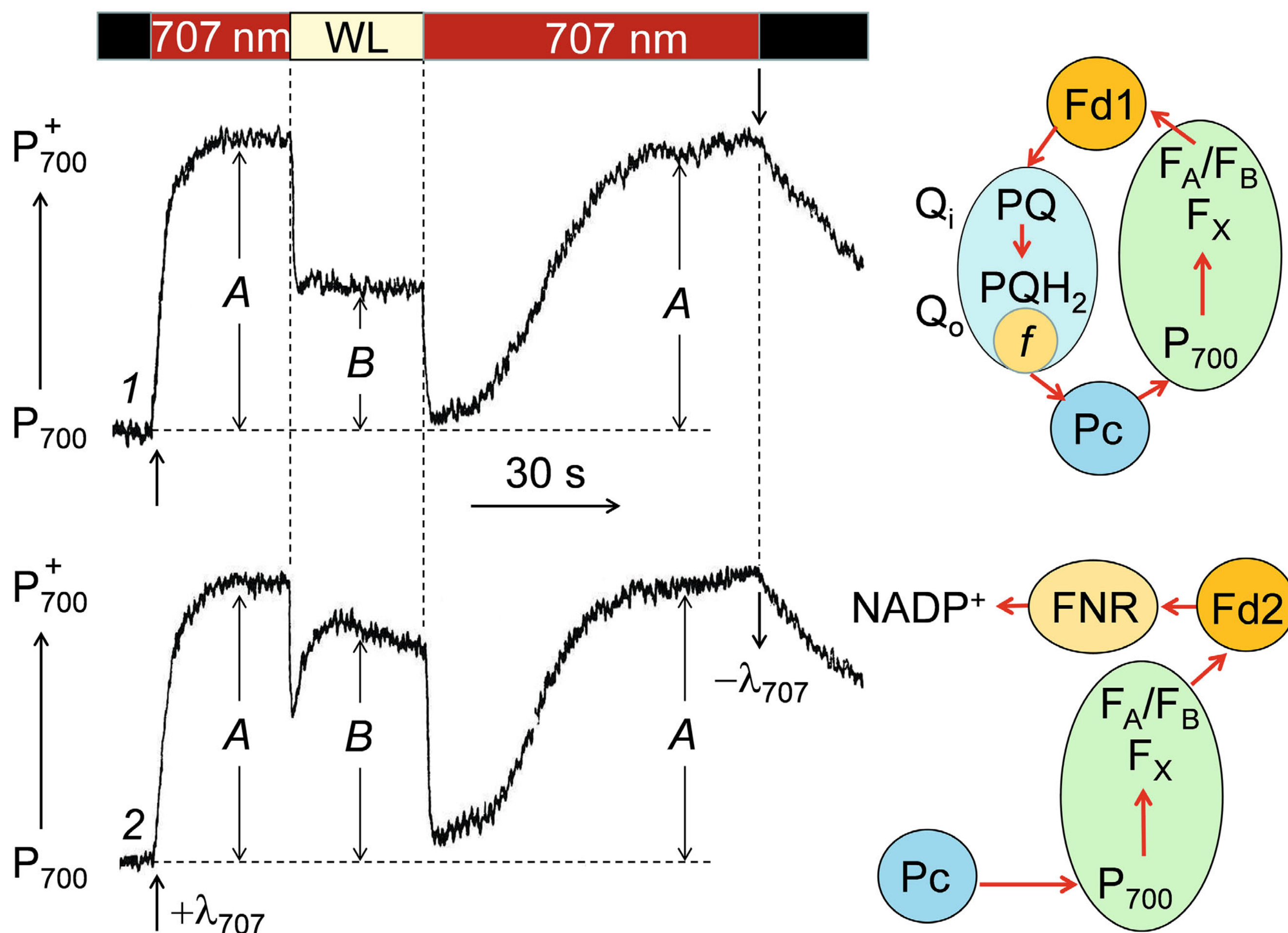

Fig. 4. Influence of two isoforms of pea ferredoxin, Fd1 and Fd2, on the kinetics of P^+_{700} EPR signal amplitude from the isolated class B chloroplasts of beans (*Vicia faba*) , induced by the far-red light (λ_{max} = 707 nm) and white light (WL) in the presence of 2 mM $NADP^+$. Ferredoxin input: *1*) 60 µm Fd1, *2*) 60 µm Fd2. The figure was constructed using kinetic curves from [70].

in different ways. Fd2 more efficiently catalyzed the "linear" electron transfer from PSI to FNR and then to $NADP^+$. This is supported by the fact that white light caused a stronger increase in the EPR signal from P^+_{700} (Fig. 4, parameter *B*) in the presence of Fd2 than in the case of Fd1 addition. Fd1 exhibited significant activity as an electron carrier in the CET chain around PSI. Intensity of the P^+_{700} signal under the white light illumination was lower in the presence of Fd1 than in the case of Fd2. This difference could be caused by acceleration of the electrons outflow from PSI to $NADP^+$ through Fd2, as well as by the fact that Fd1 catalyzed the cyclic transfer of electrons around PSI, returning electrons to PSI, thereby reducing concentration of P^+_{700}. It was also demonstrated that the addition of antimycin, the CET inhibitor, accelerated photooxidation of P_{700}. The effect of antimycin was more noticeable in the case of Fd1 than Fd2. This indicates higher activity of Fd1 as a mediator of CET around PSI. It has been suggested in the literature that variations of the expression of different Fd isoforms allow plants to optimize the use of solar energy and avoid excessive reduction of electron transport chain carriers under unfavorable environmental conditions [68, 69].

ELECTRON TRANSPORT REGULATION AT THE LEVEL OF b_6f COMPLEX

PQH_2 oxidation stage limiting electron transfer between PSII and PSI. There is evidence that in a wide range of experimental conditions (pH, temperature) electron transfer between PSII and PSI is limited not by the PQH_2 diffusion from PSII to b_6f complex, but by the electron transfer from PQH_2 to the Fe_2S_2 cluster of the Rieske protein that occurs after formation of the PQH_2–ISP complex. This conclusion, previously made by studying the P_{700} redox transformations kinetics in chloroplasts of spinach and beans [37, 38], recently received additional confirmation in the experiments with *Arabidopsis* mutants, in which the grana diameter varied widely (from 370 to 1600 nm). In the study by Höhner et al. [40], the characteristic time of PQH_2 formation in PSII and its diffusion to the b_6f complex was shown

to be ~3.2÷3.6 ms in all cases. This time is significantly less than that for the total oxidation of PQH_2, regardless of grana diameter. These results convincingly prove that the limiting stage of the electron transfer from PSII to the b_6f complex is PQH_2 oxidation in the catalytic center Q_o but not the PQH_2 diffusion along the thylakoid membrane [37, 38].

After the ISP reduction, its mobile domain containing the Fe_2S_2 cluster shifts to the cytochrome *f* and donates the electron to the cytochrome *f* heme. From the cytochrome *f* the electron is transferred to Pc. After oxidation of ISP, his labile domain returns to its original position. The movement of the mobile domain does not limit the total electron transfer rate: significant displacements of the ISP redox center occur relatively quickly as compared to the PQH_2 oxidation rate by Fe_2S_2. At room temperatures, the electron transfer from ISP_{red} to Cyt *f* proceeds with the characteristic time of ~2-4 ms [71, 72], which is less than the times of PQH_2 semi-oxidation and cytochrome *f* reduction ($\tau_{1/2}$ > 5-20 ms [36-41]). This means that the PQH_2 oxidation rate is ultimately determined by the stage of electron transfer from PQH_2 to the oxidized Fe_2S_2 cluster after formation of the substrate–enzyme complex PQH_2–ISP_{ox}.

pH-Dependent regulation of electron transfer in chloroplasts. Two main mechanisms are known for the pH-dependent inhibition of electron transfer between the PSII and PSI caused by the decrease in the lumen pH (pH_{in}): (i) slowdown of the PQH_2 oxidation by the cytochrome b_6f complex [12-15, 73-76] and (ii) attenuation of the PSII photochemical activity due to phenomenon known as non-photochemical quenching (NPQ) of chlorophyll excitation [77-79]. The effect of pH_{in} on the PQH_2 oxidation rate happens due to the negative feedback mechanism: oxidation of PQH_2 is accompanied by the release of protons into the lumen, acidification of the lumen ($pH_{in}\downarrow$) inhibits oxidation of PQH_2. According to the "proton-gated" model [80, 81], the PQH_2 deprotonation stimulates electron transfer to the oxidized Rieske protein (ISP_{ox}); slowdown of the PQH_2 deprotonation caused by pH_{in} decrease should inhibit oxidation of PQH_2. There is every reason to believe that the proton is transferred to the histidine residue of the ISP, which is a ligand for one of the Fe_2S_2 cluster ions, and this occurs simultaneously with the transfer of the electron to the Fe_2S_2 cluster of the ISP (see [12-16, 42, 44] for more details). The pK_a value of the ISP protonated group depends on the redox state of the Fe_2S_2 cluster [82]. Two processes – PQH_2 deprotonation (proton transfer to the histidine residue of ISP) and electron transfer to the Fe_2S_2 cluster of the ISP – could be considered as coupled processes that are interconnected and occur almost simultaneously [83-87]. The deprotonated state of ISP is a necessary condition for the occurrence of the proton transfer from PQH_2 to ISP. ISP deprotonation is associated with the proton exit into the lumen; probability of this process depends on pH_{in}. Protonation/deprotonation of the ISP depends on the effective value of the pK_a of the protonated ISP group and is controlled by pH_{in} [12, 14]. Oxidation of ISP after the electron transfer to heme *f* is accompanied by the decrease in pK_a, which should stimulate deprotonation of ISP [82] and, accordingly, contribute to oxidation of PQH_2. However, with a sufficiently strong acidification of the lumen ($pH_{in} \leqslant pK_a$), ISP deprotonation would be hindered, and, therefore, the flow of electrons through the cytochrome b_6f complex would decrease. A simple mathematical model, based on the fact that the electron transfer through the cytochrome complex is controlled by the processes of ISP protonation/deprotonation, adequately describes pH dependence of the electron transfer through the b_6f complex [12, 14]. The alternative hypothesis describing participation of a water molecule as the primary proton acceptor in the ubiquinol oxidation in the cytochrome bc_1 complex was suggested in the study of Postila et al. [88].

The phenomenon of photosynthetic control. The pH-dependent regulation of electron transport is the basis of a phenomenon called "photosynthetic control" [89-92]. Essence of this phenomenon is that the electron flow between the photosystems PSII and PSI correlates with the "phosphate potential", $P = [ATP]/([ADP] \times [P_i])$, where [ATP], [ADP], and $[P_i]$ denote concentrations of ATP, ADP, and P_i, respectively. The ratio of ATP/ADP can vary depending on the physiological state of the plant cell and interactions of the photosynthetic apparatus with mitochondria and other metabolic systems [93-96]. In the state of "photosynthetic control" ("state 4" according to the terminology coined by Chance and Williams [89]), exhaustion of the pools of ADP and/or P_i molecules leads to the decrease in the synthesis of ATP and transmembrane proton flow through the ATP synthase (CF_0–CF_1 complex); simultaneously lumen pH decreases significantly ($pH_{in} < 6$), which slows down operation of the cytochrome complex. In the "state 3", when an intensive ATP synthesis occurs, the outflow of protons from lumen to stroma accelerates, and, therefore, such strong acidification of the lumen, which could significantly slow down the electron transfer, does not occur ($pH_{in} \geqslant$ 6-6.5). This allows for an effective ATP synthesis and, at the same time, high rate of electron transport is maintained [74-76, 90-92].

Increase of the stroma pH (pH_{out}) due to the proton translocation from the stroma to lumen can also affect the rate of the photosynthetic ETC functioning. Increase in pH_{out} up to 7.8-8.0 promotes activation of the CBC reactions [1]. This would lead to acceleration of the NADPH consumption and, accordingly, to the faster outflow of electrons from PSI. Experiments on the injections of protonophores (uncouplers) into the leaves, which equalized pH inside (lumen, pH_{in}) and outside (stroma, pH_{out}) of the thylakoids, confirmed

the above notion on the pH-dependent regulation of electron transport in chloroplasts [97, 98].

ALTERNATIVE WAYS OF ELECTRON TRANSFER IN CHLOROPLASTS

In addition to the electron transport processes involving reduction of $NADP^+$ and CET around PSI, described above, chloroplasts can host other redox reaction, among which molecular oxygen and ascorbate play crucial roles in the functioning of the photosynthetic apparatus.

Interaction of O_2 with chloroplasts. Molecular oxygen (O_2) is an active participant in metabolic processes in the plant cell. O_2 molecules serve as electron acceptors interacting with the chloroplast ETC. At the same time, active forms of oxygen may be generated: superoxide radicals ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and a very toxic $OH^{\bullet}$ radical [51]. In plants, formation of $O_2^{\bullet-}$ occurs as a result of one-electron reduction of O_2 due to its interaction with the photosynthetic ETC. The main source of electrons for the ROS formation is the acceptor region of PSI, which contains low-potential electron carriers. Such electron donors can be represented by phylloquinone PhQ and low-potential iron-sulfur centers F_A, F_B, F_X, as well as ferredoxin [99-102]. The electron from PSI is transferred to O_2 molecule, which is reduced to the superoxide radical ($O_2 + e^- \rightarrow O_2^{\bullet-}$, the Mehler reaction [48, 49]). The superoxide radical ($O_2^{\bullet-}$) is then reduced to hydrogen peroxide and O_2 in the reaction catalyzed by superoxide dismutase ($2O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2$) [51]. Quantitative estimates of the Mehler reaction contribution to the ROS production are ambiguous. Most authors consider that this contribution is small, no more than ~10%; according to other, the electron flow to O_2 measure up to 40% of the total flow of electrons donated by PSII (for review, see [49-51] and the literature cited therein). Nevertheless, even a relatively small electron flow from PSI to O_2 could be essential for the maintenance of optimal energy balance in chloroplasts and protection of the photosynthetic apparatus of plants against oxidative stress. Examples illustrating the effects of electron outflow from PSI to O_2 include the experiments with injections of methyl viologen – an artificial mediator of electron transport – into a leaf, which significantly accelerates photooxidation of P_{700}^+, as well as experiments with varying O_2 content in the medium around the leaf, or in the suspension of cyanobacterial cells [103-106].

Beside the electron flow to O_2 from the low-potential acceptors of PSI [99-101], production of ROS also involves the reduced ferredoxin [51, 102], the cytochrome b_6f complex, and the redox-active molecules, plastosemiquinone and plastoquinone, located in the thylakoid membrane [51, 107-109]. Contribution of PSII to O_2 reduction is insignificant. When comparing the cytochrome b_6f and bc_1 complexes, it should be noted that the b_6f complex exhibits a noticeably higher (by an order of magnitude) rate of O_2 reduction than the bc_1 complex [107]. It is assumed that this can be explained by the presence of chlorophyll *a* molecule near the PQH_2 binding site in the catalytic center Q_o. The phytyl tail of chlorophyll can pose steric restrictions that prevent the shift of the plastosemiquinone molecule, which is formed after the electron transfer reaction from PQH_2 to the Rieske protein, towards the heme b_6^L. This prolongs lifetime of the redox-active radical (plastosemiquinone) and increases efficiency of the O_2 reduction.

The O_2 reduction under aerobic conditions by the electrons donated by ETC carriers in the region between PSII and PSI, called *chlororespiration*, is well studied [52-56]. In this case the PQH_2 pool is oxidized, which can be assessed, for example, from the measurements of the chlorophyll *a* fluorescence induction after adaptation of the plant leaves to darkness [103, 104]. This process involves chloroplast terminal oxidase, which oxidizes PQH_2 and provides electron transfer to O_2 molecule. Relative contribution of this pathway of O_2 reduction is small as compared to the contribution of the light-induced Mehler reaction [51, 57, 58]. However, chlororespiration emerges, for example, when we evaluate changes in the redox status of chloroplast ETC during the plant adaptation to darkness. This pathway of electron outflow to O_2 explains the relatively slow oxidation (minutes to tens of minutes) of the plastoquinone pool in the darkness. Finally, it is well known that the oxygen uptake can occur in the intact chloroplasts at Rubisco level due to the phenomenon called *photorespiration* (see [1, 51] and the literature cited therein).

Another mechanism for O_2 reduction by plastoquinol was proposed in the works of Boris Nikolaevich Ivanov et al. (see Ivanov et al. [51] for a review). The results of these studies suggest that the redox-active plastosemiquinone molecules (mostly deprotonated form of $PQ^{\bullet-}$), which can form as a result of the comproportionation reaction ($PQH_2 + PQ \leftrightarrow 2PQH^{\bullet} \leftrightarrow 2PQ^{\bullet-} + 2H^+$), can serve as electron donors for O_2 reduction. Reactive radicals $PQ^{\bullet-}$ are oxidized when interacting with O_2. This can also explain the fact that the content of PQH_2 in chloroplasts gradually decreases under aerobic conditions in the darkness [103, 104]. In the works of Ivanov et al. [51, 108, 109] the idea was also proposed and substantiated that, in addition to the reduction of O_2 molecules in the plastoquinone pool by plastosemiquinone molecules, perhaps a more important role is played by the reduction of superoxide anion radicals formed both in this pool and in PSI. According to the authors, this process is involved both in the detoxification of $O_2^{\bullet-}$ and, more importantly, in the production of signal molecules of hydrogen peroxide, which, when formed in this way, serve as messengers that transmit

information to other systems of the chloroplast and the cell about state of the ETC –sensitive sensor of environmental conditions.

Permeability of thylakoid membranes to O_2. Without spending much time on how the changes in O_2 concentration inside the plant cell can affect functioning of other metabolic systems [94-96], we should note some properties of the chloroplast membranes that are important for understanding the features of their interaction with O_2. It has been established that there is a relatively rapid equalization of oxygen concentrations inside the leaf and in the surrounding atmosphere. This was demonstrated using EPR and solid oxygen-sensitive paramagnetic particles that were injected into the leaf with a microsyringe [110]. Such leaf samples retain the ability to release O_2 in the light due to the PSII functioning and to absorb O_2 in the darkness through respiration. At the same time, O_2 concentration inside the leaves, which are in contact with air, remains virtually unchanged in response to turning the light on and switching it off [110].

It should be also noted that the rate of O_2 diffusion through the thylakoid membranes is high, as determined by probing the membranes with lipid-soluble spin probes [111]. Permeability for O_2 of the lipid bilayer of spinach chloroplast thylakoid membranes, measured at 20°C, is 39.5 cm·s^{-1}, which is 20% higher than the permeability coefficient of a water layer of the same thickness as the lipid membrane. High membrane permeability for O_2 can help equalize O_2 concentrations in different compartments of the plant cell. According to the estimates given in Ligeza et al. [110], the trans-thylakoid difference in O_2 concentrations is small, it does not exceed 1 μM. Such good "ventilation" of the interior of plant leaves indicates that significant accumulation of O_2 inside the plant cells, which could arise due to the water oxidation in PSII, does not occur; this would limit the ROS generation.

Good aeration of the plant cell should ensure that the photosynthetic apparatus of chloroplasts would effectively interact with other metabolic systems of the plant cell. Indicative is the fact that when O_2 is removed by incubation of the leaves with an inert gas (N_2 or Ar), concentration of the oxidized P_{700}^{+} centers sharply decreases, when the leaves are illuminated by the light exciting both photosystems [103-105]. One of the explanations for this phenomenon is restriction of the electron outflow from PSI to O_2, which prevents oxidation of P_{700}. Excessive reduction of electron carriers on the acceptor side of PSI, which are unable to accept electrons from P_{700}, would accelerate the charge recombination in PSI, preventing photo-oxidation of P_{700}. Under these conditions, singlet oxygen, a very dangerous form of ROS, can be formed [112]. It could also be assumed that functioning of the respiratory chain of the plant cell mitochondria slows down and/or functioning of other metabolic systems is disrupted during O_2 deficiency. This would decrease consumption of NADPH, the final electron acceptor in PSI, preventing, therefore, the P_{700} oxidation.

Interaction of ascorbate with chloroplasts. A special role is played in plant metabolism by the redox processes involving ascorbate, which can interact with the ETC of chloroplasts and neutralize ROS [59]. Ascorbate content in the plant tissues can be high; in some species its concentration is 20-50 mM, depending on the species and plant cultivation conditions [113-116]. Physiological role of the reactions involving ascorbate is associated with establishing redox homeostasis in the plant cells and with protection of the photosynthetic apparatus from the damage caused by ROS. Ascorbate, together with glutathione, acts as a redox buffer when changes in external conditions (e.g., fluctuations in the intensity and spectral composition of light) are capable of disrupting redox state of the plant cell [59]. Ascorbate prevents inhibition of photosynthetic processes under stress conditions (excess light, lack of moisture, etc.). Chloroplasts possess a complex multi-stage system of biochemical reactions that prevent accumulation of H_2O_2 [51, 59]. Ascorbate is an effective antioxidant; it serves as a ROS scavenger by participating in the enzymatic reduction of H_2O_2 and superoxide radicals; enzymatic oxidation of Asc to monodehydroascorbate (MDHA) in the ascorbate peroxidase reaction catalyzing conversion of H_2O_2 to H_2O could be an example. Ascorbate is an electron donor for the violaxanthin–deepoxidase reaction (violaxanthin → zeaxanthin), which results in the increase of thermal energy dissipation in the PSII light-harvesting antenna (non-photochemical quenching of chlorophyll excitation) [117-119].

Ascorbate and its oxidized forms (monodehydroascorbate, MDHA, and dehydroascorbate, DHA) interact with chloroplasts at various sites in the ETC. The average redox potential (E_m') of the Asc/DHA pair is ~60-90 mV [120]. This means that ascorbate (in its fully reduced form) can interact as an electron donor with the chloroplast ETC in the region between PSII and PSI, while its oxidized forms serve as electron acceptors for the electrons donated by PSI. Due to this, ascorbate helps to maintain optimal redox status of the plant cell. Figure 5 shows a diagram demonstrating how the reduced and oxidized forms of ascorbate interact with the chloroplast ETC. The fully reduced form of ascorbate (Asc) can serve as an electron donor on the donor side of PSII and at the plastocyanin section of ETC between PSII and PSI [121, 122]. Ascorbate penetrating into thylakoids is capable of reducing Pc, which in turn, serves as an effective electron donor for PSI. The flow of electrons from Asc to PSI can reach ~50-70% of the non-cyclic electron transport [121]. In one-electron oxidation of Asc, it is converted into MDHA radical, which produces the characteristic doublet EPR signal.

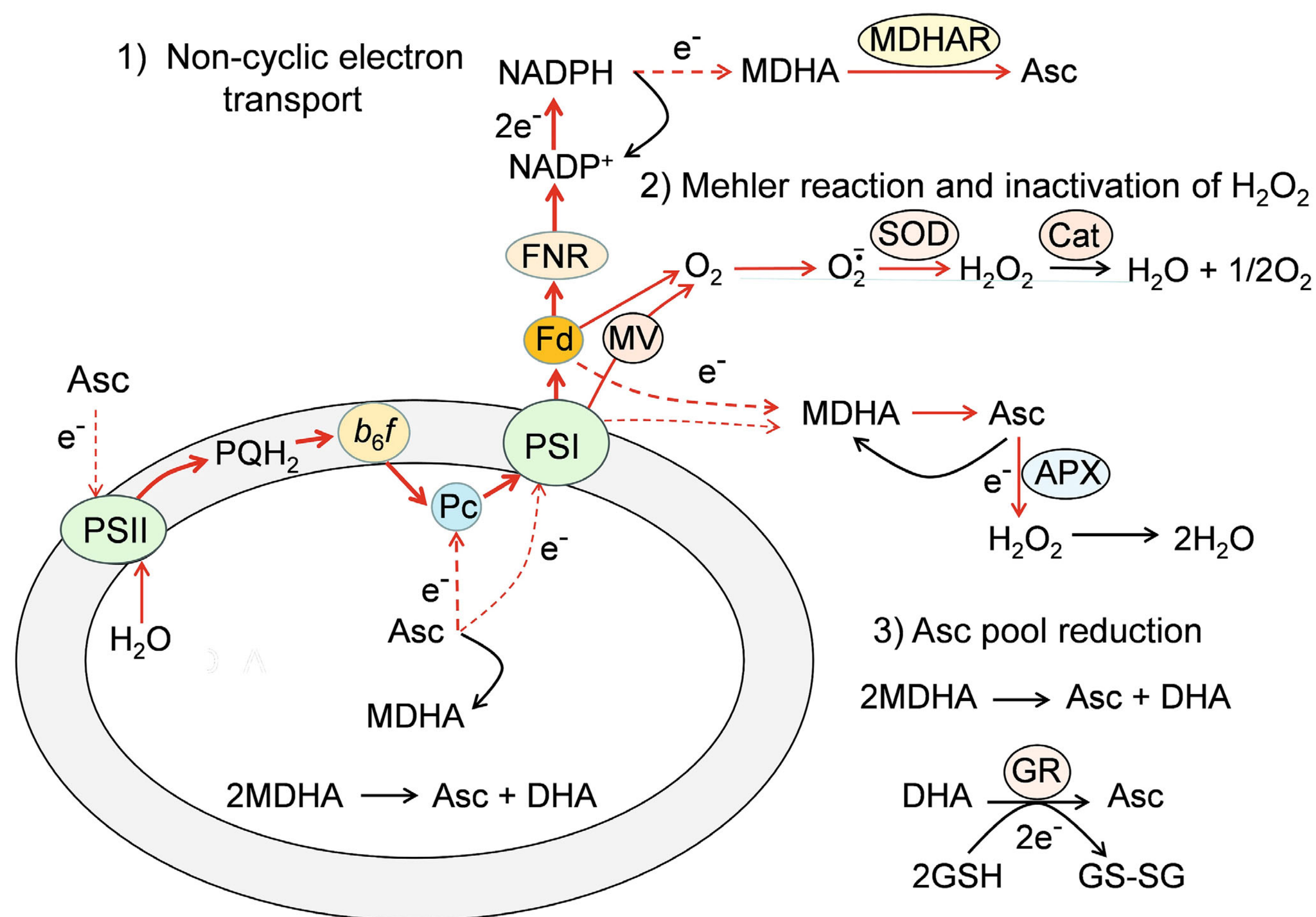

Fig. 5. Interactions of various forms of ascorbate (Asc, MDHA, DHA) with chloroplasts. Designations: APX, ascorbate peroxidase; GR, glutathione reductase; GSH and GS-SG, reduced and oxidized forms of glutathione; Cat, catalase; MV, methyl viologen; MDHAR, MDHA reductase; SOD, superoxide dismutase.

It should be noted that Asc can directly reduce oxidized P^+_{700} centers, which has been clearly demonstrated by the experiments with the isolated PSI complexes [122]. In this case, however, the reduction rate of P^+_{700} is low; the characteristic reduction time of P^+_{700} is ~20-30 s, which is significantly slower as compared to the reduction of P^+_{700} by Pc^-.

Asc oxidation is a reversible process. Reduction of the semiquinone form of MDHA to the fully reduced Asc form occurs via different ways. MDHA can receive an electron directly from PSI [51, 123]. The characteristic rate of electron transfer from PSI to MDHA, leading to formation of the fully reduced form of Asc, is comparable to the rate of electron transfer between photosystems. MDHA molecules can also accept electrons from the reduced ferredoxin (Fd^-) and NADPH [51, 124]. The rate of MDHA reduction depends on Fd^- concentration and, under certain conditions, can be many times higher than the rate of the light-induced reduction of $NADP^+$ by FNR.

Another pathway of the reduced Asc form formation is disproportionation reaction of MDHA radicals (2MDHA ↔ Asc + DHA) [122]. The resulting fully oxidized DHA form can then be reduced to Asc. In this process, an important role is played by the glutathione oxidase reaction, in which reduced glutathione serves as an electron donor [59].

Thus, in the same way as the pseudocyclic electron transport (the "water–water" cycle) and cyclic electron transfer around PSI protect the photosynthetic apparatus from the excessive light energy, reactions involving ascorbate protect the photosynthetic apparatus from the damage under excessive light, promoting energy dissipation into heat and antioxidant protection of the plant cell. Ascorbate can serve as an alternative mediator of electron transfer in chloroplasts: by stimulating the outflow of electrons from PSI and Fd^-, MDHA prevents excessive reduction of carriers at the acceptor site of PSI. On the other hand, reduced ascorbate molecules could compensate for the reduction of photochemical activity of PSII caused by adverse environmental factors and could serve as electron donors in the electron transport chain section between PSII and PSI [125-127].

CONCLUSION

Optimal functioning of the photosynthetic electron transport in chloroplasts is achieved primarily through regulation of the electron transfer in two sections of the electron transport chain: between PSII and cytochrome b_6f complex and at the stage of electron outflow from PSI to the CBC. An important role in these processes is associated with the structural and functional rearrangements of the photosynthetic apparatus, which determine sustainability of chloroplasts and their capability to respond quickly to the changes in external conditions, as well as alternative redox mediators (O_2 and ascorbate), which ensure redox homeostasis of the plant cell and the ETC stability.

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