Minimizing an Electron Flow to Molecular Oxygen in Photosynthetic Electron Transfer Chain: An Evolutionary View

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Recruitment of H₂O as the final donor of electrons for light-governed reactions in photosynthesis has been an utmost breakthrough, bursting the evolution of life and leading to the accumulation of O₂ molecules in the atmosphere. O₂ molecule has a great potential to accept electrons from the components of the photosynthetic electron transfer chain (PETC) (so-called the Mehler reaction). Here we overview the Mehler reaction mechanisms, specifying the changes in the structure of the PETC of oxygenic phototrophs that probably had occurred as the result of evolutionary pressure to minimize the electron flow to O₂. These changes are warranted by the fact that the efficient electron flow to O₂ would decrease the quantum yield of photosynthesis. Moreover, the reduction of O₂ leads to the formation of reactive oxygen species (ROS), namely, the superoxide anion radical and hydrogen peroxide, which cause oxidative stress to plant cells if they are accumulated at a significant amount. From another side, hydrogen peroxide acts as a signaling molecule. We particularly zoom in into the role of photosystem I (PSI) and the plastoquinone (PQ) pool in the Mehler reaction.

Keywords: photosystems, evolution, plastoquinone, phylloquinone, oxygen, reactive oxygen species

INTRODUCTION

Mehler reaction is the major source of reactive oxygen species (ROS), such as O₂•⁻ and H₂O₂, in chloroplasts. During the Mehler reaction, O₂ molecules serve as an alternative electron acceptor from the photosynthetic electron transfer chain (PETC), being a safety valve to release surplus electrons and thus alleviating the PETC over-reduction. This reaction also contributes to building up of ΔpH across the thylakoid membrane and produces a signaling messenger, H₂O₂, which is capable of initiating various signaling pathways (Ivanov et al., 2012). However, an efficient electron flow to O₂ would decrease the photosynthetic quantum yield. Moreover, ROS, if not neutralized efficiently, lead to oxidative damage. Thus, the PETC evolution could have been guided toward minimizing and/or taking strong control over the Mehler reaction.
Most of the PETC components were proposed as sites of \( \text{O}_2^{**} \) photoproduction, the first step of the Mehler reaction. Among them, there are water-soluble and water-exposed components (Figure 1, open circles) and the components situated in hydrophobic zones (Figure 1, closed circles). The former produce \( \text{O}_2^{**} \) in water bulk phases, e.g., stroma, while the latter produce \( \text{O}_2^{**} \), which can be detected outside the membrane when diffused there or can be detected within the thylakoid membranes (Kozuleva et al., 2011). The value of \( E_m \) \( (\text{O}_2/\text{O}_2^{**}) \) in water is \(-160 \text{ mV}\), while in hydrophobic zones of proteins and membranes it is more negative, approximately \(-550 \text{ mV}\) (Wardman, 1990). Only few components in PETC possess enough negative \( E_m \) for \( \text{O}_2 \) reduction within a thylakoid membrane. Numerous experiments unambiguously demonstrated that photosystem I (PSI) is the major site of \( \text{O}_2^{**} \) photoproduction (Kozuleva and Ivanov, 2016). \( \text{O}_2^{**} \) generation by other components was shown under the disturbed PETC function. The second step of the Mehler reaction is \( \text{H}_2\text{O}_2 \) production via \( \text{O}_2^{**} \) dismutation in stroma as catalyzed by superoxide dismutase. Apart from \( \text{O}_2^{**} \) dismutation, another mechanism was shown to operate in the thylakoid membranes (Mubarakshina et al., 2006). It involves \( \text{O}_2^{**} \) reduction by the plastoquinone (PQ) pool, namely, by plastoquinol (PQH\(_2\)) (Borisova-Mubarakshina et al., 2019). Thus, the Mehler reaction proceeds at a variety of sites, still leading to \( \text{O}_2^{**} \) and subsequent \( \text{H}_2\text{O}_2 \) production.

The evolution of various photosynthetic complexes has been a subject of several recent reviews (Jagannathan et al., 2012; Rutherford et al., 2012; Pierella Karlusich and Carrillo, 2017; Orf et al., 2018). Here, we briefly summarize the structural changes which could have happened in PETC to control and minimize an electron flow to \( \text{O}_2 \). The general evolutionary trends could include: (i) kinetic control, making the forward reactions faster than the competing electron flow to \( \text{O}_2 \), (ii) redox tuning of cofactors, disabling spontaneous exergonic reactions with \( \text{O}_2 \), and (iii) shielding of cofactors with protein environment, restricting \( \text{O}_2 \) accessibility (Rutherford et al., 2012).

**PHOTOSYSTEM I**

All secondary electron acceptor cofactors of PSI were proposed as the sites of \( \text{O}_2\)\( ^{**} \) photoreduction. The terminal FeS clusters \( \text{F}_X/\text{F}_B \) are inevitably oxidized by \( \text{O}_2 \) in the absence of ferredoxin (Fd). The role of intermediate cofactor \( \text{FeS} \) cluster \( \text{F}_X \) was claimed in Takahashi and Asada (1988) based on experiments showing that the primary \( \text{H}_2\text{O}_2 \) photoproduction site was a \( \text{PsaA}/\text{PsaB} \) heterodimer, which harbors \( \text{F}_X \). However, the \( \text{PsaA}/\text{PsaB} \) heterodimer also binds two phylloquinone (PhQ) molecules at the \( \text{A}_1 \) sites and they could also contribute to \( \text{H}_2\text{O}_2 \) photoproduction. For the first time, the role of PhQs was proposed by Kruk with coauthors (Kruk et al., 2003) since adding PhQ to quinone-depleted thylakoid membranes re-established the \( \text{O}_2 \) uptake at a single light flash. This result still does not rule out that \( \text{FeS} \) clusters reduce \( \text{O}_2 \) by electrons from \( \text{P}_{700} \) via PhQ re-incorporated to the \( \text{A}_1 \) sites. The PhQ involvement in \( \text{O}_2 \) photoreduction in intact PSI under steady-state illumination was

![Figure 1](image-url)
ET and contributes to both alleviating PETC over-reduction and preventing charge recombination (Kozuleva and Ivanov, 2016). Both PhQs in PSI have one of the most negative $E_m$ in the PETC (−671 and −840 mV for PhQ$_A$ and PhQ$_B$, respectively; Figure 1A), which allows phyllosemiquinones to reduce O$_2$ even in the hydrophobic zones of the thylakoid membranes, where $E_m$ (O$_2$/O$_2^*$) is close to −550 mV (see above). Due to a longer lifetime, PhQ$_A^*$ gets higher chances to react with O$_2$, although the more negative $E_m$ of PhQ$_B$/PhQ$_B^*$ provides a larger $−ΔG$ in reaction with O$_2$. However, the particular impact of each PhQ as well as clarifying the F$_X$ role is still open questions.

FERREDOXIN AND FNR

In bacterial type Fd, two 4Fe-4S clusters are partially exposed to solvent and accessible for O$_2$ attacks (Jagannathan et al., 2012). After binding the ancestral Fd to RC, the organisms recruited another Fd, where a single 2Fe–2S cluster is shielded by a protein.

A long-lasting controversy on the role of Fd in the Mehler reaction was solved nearly a decade ago. In the absence of NADP$^+$, which is the major electron sink for Fd, O$_2$ inevitably oxidizes the reduced Fd (Fd$^–$). In the presence of NADP$^+$, simultaneously with its photo-reduction, the electron flow to O$_2$ was shown to be significant in high light; however, the contribution of Fd was almost negligible relative to that of the membrane-bound PETC components (Kozuleva and Ivanov, 2010). These results reveal a low reactivity of Fd$^–$ toward O$_2$, which enables Fd to fulfill the function of stromal hub-donating electrons to multiple enzymes and proteins, including ferredoxin-NADP$^+$ reductase (FNR) (Hanke and Mulo, 2013).

The Fd affinity to its redox partners, i.e., PSI acceptor side, was also raised to ensure the competition with O$_2$ for electrons. However, this is not entirely the case of FNR. Although a semiquinone form of FAD prosthetic group in FNR can react with O$_2$ (Massey, 1994), so far there are no reliable experimental data demonstrating that FNR is involved in O$_2$ photoreduction in the thylakoid membranes (Kozuleva and Ivanov, 2016). The FNR of oxygenic phototrophs possesses ~10 times higher catalytic activity than the bacterial FNR (Pierella Karlusich and Carrillo, 2017), with affinity remaining roughly the same. The high catalytic activity is likely achieved through conformational changes caused by NADP$^+$ binding to FNR, which greatly facilitate both the Fd$^–$ oxidation (Batie and Kamin, 1984) and the liberation of the oxidized Fd from the complex (Mulo and Medina, 2017). This enhancement in the FNR catalytic activity most possibly decreased the chances for both the FAD semiquinone (Q$^*$) oxidation by O$_2$ and the formation of Fd:FNR$^*$ complex in the absence of NADP$^+$.

PLASTOQUINONE POOL

O$_2^*$ photoproduction by PQ$^*$ in the PQ pool was demonstrated (Khorobrykh and Ivanov, 2002; Vetoshkina et al., 2017). However, the maximal O$_2^*$ production rates observed in the pool were 10 times lower than in the PSI.

proposed based on comparing O$_2$ photoreduction as a function of irradiance in the wild-type PSI with that in the mutant PQ-containing PSI (Kozuleva et al., 2014). The authors concluded that the PhQ$_B$ at the A$_1$ sites are the major contributor to O$_2^*$ generation.

From an evolutionary point of view, the terminal cofactor F$_B$ can be one of the sites where the Mehler reaction should have been taken under control. This cofactor possesses negative $E_m$, allowing for the efficient reduction of both Fd and O$_2$. However, Fd is a mobile protein, diffusing to and out of PSI and leaving F$_m$– transiently open to O$_2$. If F$_B$– is oxidized by O$_2$ efficiently, it would be insufficient in a steady-state reduction of Fd. However, the electron lives mostly on F$_A$ not F$_B$, because of a positive shift of $E_m$ (F$_A$/F$_A^*$) relative to (F$_B$/F$_B^*$) (Figure 1A; Fischer et al., 1997; Shinkarev et al., 2000). F$_A$ is embedded deeper in the protein, which shields it from O$_2$. This feature allows keeping of electrons for Fd and avoiding any wasteful electron leakage to O$_2$. The PsAC protein carrying F$_A$ and F$_B$ is homologous to mobile ferredoxins in anoxygenic phototrophs (Jagannathan and Golbeck, 2009). It is widely accepted that, during evolution, the ancestral mobile Fd was tightly bound to the ancestral homodimeric reaction center (RC). This binding resulted in an elongation of the ET chain in the RC that could have aimed at stabilizing the charge separation state and minimizing the charge recombination, which could lead to $^{3}$’P$_{700}$ and, hence, $^{1}$’O$_{2}$ formation (Orf et al., 2018). However, that binding probably provided an additional protein shielding for F$_X$, which was the terminal cofactor in the ancestral RC, and for F$_A$, limiting O$_2$ diffusion and preventing unproductive electron leakage (Jagannathan et al., 2012). The protein shielding of these FeS clusters, being potentially capable of catalyzing H$_2$O$_2$ decomposition into a highly reactive HO$^*$ (Snyrchová et al., 2006), could have additionally protected the PSI acceptor side from HO$^*$ formation.

Binding of the ancestral Fd to the ancestral homodimeric RC resulted in RC asymmetry through locating the FA cluster closer to one of the quinones (PhQ$_A$), bringing about a negative shift in $E_m$ (PhQ$_B$/PhQ$_B^*$) (Rutherford et al., 2012). The difference in $E_m$ between PhQ$_A$ and PhQ$_B$ is up to 170 mV (Ptushenko et al., 2008). Rutherford with coauthors presented an elegant hypothesis explaining the benefit of this asymmetry as it eliminates $^{3}$’P$_{700}$ (and hence $^{1}$’O$_{2}$) formation under the conditions of the Fd pool over-reduction (Rutherford et al., 2012). In line with this hypothesis, PhQ$^*$ oxidation by O$_2$ sustains a forward
While anoxygenic phototrophs use menaquinone (MQ) and ubiquinone (UQ), the oxygenic ones recruited PQ, a representative of a “more recent” group of quinones (Schoepf-Cothenet et al., 2009). MQ was probably the first quinone in ancient photosynthetic membranes. The rationale for replacing MQ with PQ in clear: the \( E_m \) values of (Q/QH) and (Q/QH) are ~100 mV (Kishi et al., 2017) and ~180 mV (Bergdoll et al., 2016), more negative for MQ than for PQ (Figure 1B). This means that PQ\(^{•−}\) and the PQ pool itself in the reduced state are more stable in the presence of O\(_2\). Furthermore, \( pK_a \) (Q\(^*/\)QH) for PQ is higher than for MQ, providing an easier protonation and, hence, a higher stability of plastosemiquinone (Hasegawa et al., 2017).

A possible rationale for choosing PQ instead of UQ in the PETC of oxygenic phototrophs is still vague. Firstly, the O\(_2\)^{•−}\- generation by free UQ\(^{•−}\) in the mitochondria was discovered as early as in 80-s (Turrens et al., 1985). This reaction has long been considered as an important source of O\(_2\)^{•−}\ in animal cells. On the contrary, PQ\(^{•−}\) in photosynthetic systems has little impact on O\(_2\)^{•−}\- production, as stated above. Secondly, PQH\(_2\) is more efficient as an antioxidant than UQH\(_2\) (Borisova-Mubarakshina et al., 2019), e.g., in lipid peroxidation prevention (Kruk et al., 1997). A consequence of higher antioxidant activity of PQH\(_2\) is its higher ability to reduce O\(_2\)^{•−}\ to H\(_2\)O\(_2\). It was shown that PQ pool in the thylakoid membrane (presumably PQH\(_2\)) is indeed oxidized by O\(_2\)^{•−}\ (Borisova-Mubarakshina et al., 2018). Therefore, despite the low O\(_2\)^{•−}\-generating activity, the contribution of the PQ pool to the Mehler reaction can be essential due to the production of H\(_2\)O\(_2\) from O\(_2\)^{•−}\. We hypothesize that ensuring the efficient transformation of O\(_2\)^{•−}\, which is generated by PSI, to H\(_2\)O\(_2\) could be one of the evolutionary driving forces for the choice of PQ.

Replacing MQ with PQ as a mobile pool in the thylakoid membrane inevitably affected all of the complexes interacting with quinone. All cofactors in photosystem II (PSII) and cytochrome \( b_{6f} \) complexes have \( 110–150 \) mV more positive \( E_m \) values than in their MQ-based analogs (Schoepf-Cothenet et al., 2009; Bergdoll et al., 2016).

**CYTOCHROME \( b_{6f} \) COMPLEX**

The cytochrome \( b_{6f} \) complex is also considered to be an O\(_2\) photoreduction site (Taylor et al., 2018). The high \( E_m \) values of the \( b_{6f} \) complex cofactors are a consequence of MQ replacement with PQ (Bergdoll et al., 2016). Among its ET cofactors, the \( b_L \) heme possesses one of the lowest \( E_m \), ~130 mV (Alric et al., 2005). Thermodynamically, this heme can hardly reduce O\(_2\) since \( E_m \) (O\(_2\)/O\(_2\)^{•−}\) in the membrane is close to ~550 mV (Figure 1B, see above). The fast ET from \( b_L \) to \( b_H \) decreases the possibility of a \( b_L \) reaction with O\(_2\).

In several studies, PQ\(^{•−}\) at the quinol-oxidizing (Q\(_o\)) site of the complex is considered as the electron donor to O\(_2\). However, the concerted oxidation of PQH\(_2\) diminishes the PQ\(^{•−}\) lifetime. If semiquinone is produced, it is either quickly oxidized by \( b_L \) heme or reduced by it, if the heme is pre-reduced. The dimer organization of the \( b_{6f} \) complex was proposed to lower the chances of O\(_2\)^{•−}\- generation at the Q\(_o\) site (Rutherford et al., 2012). In the \( b_{1c} \) complex, a spin–spin complex state between the semiquinone and the Rieske cluster was shown to suppress O\(_2^•\)\- generation (Bujnowicz et al., 2019). This keeps up well with the experimental observations that PQ\(^{•−}\) can reduce O\(_2\) once it leaves the Q\(_o\) pocket (Forquer et al., 2006), becoming a part of the pool (see above). It was demonstrated that O\(_2^•\)\- production by the isolated \( b_{6f} \) complexes was 10 times higher than the one by the isolated \( b_{1c} \) complexes (Baniulis et al., 2013). This can be explained by an easier liberation of semiquinone from the Q\(_o\) site in the former case. It is important that, in vivo, such PQ\(^•\)\- would appear at the luminal side of the thylakoid membrane. The lumen pH determines the protonation of PQ\(^•\). Since PQH\(_2^•\) has a lower chance to reduce O\(_2\), the lumen pH can regulate the O\(_2^•\)-production there.

The appearance of semiquinone at the quinone-reducing site (Q\(_o\)) of the \( b_{1c} \) complex from purple bacteria was shown (Drachev et al., 1989). There are still no reliable data on semiquinone formation at the Q\(_o\) site of the \( b_{6f} \) complex. The double reduction of PQ occurs there when the second electron is transferred to the \( b_H \) heme (Ivanov, 1993). The residence of the first electron at the \( b_H \) heme can be a result of the \( e_r \) heme situated in close vicinity to the \( b_{6f} \) complex.

**PHOTOSYSTEM II**

Three major tasks could have been solved during the evolution of PSII: (i) the existence of highly oxidizing P680\(^•\), (ii) dealing with charge recombination leading to \(^1\)O\(_2\) production, and (iii) stabilization of Q\(_B\)\- waiting for the second electron (Rutherford et al., 2012). O\(_2^•\)\- production in PSII was shown many times (Pospíšil, 2012). Phoehphytin (Pheo), QA, QB, and cytochrome \( b_{559} \) were suggested as the sites of O\(_2\) reduction to O\(_2^•\), based presumably on the experiments with PSII complexes with disrupted function, e.g., after modifications of the water-oxidizing complex.

Although Pheo\(^−\) possesses \( E_m \), ~610 mV (Rappaport et al., 2002), negative enough to reduce O\(_2\) even in hydrophobic media (Figure 1C), its lifetime is rather short (300 ps) such that it prevents the electron leakage to O\(_2\). This reaction with QA\(^−\) (Ivanov and Khorobrykh, 2003; Pospíšil, 2012) is thermodynamically unfavorable due to a more positive \( E_m \) (QA/QA\(^−\)), ~70 mV (Brinkert et al., 2016), than \( E_m \) (O\(_2\)/O\(_2^•\)). However, the binding of HCO\(_3^−\) to non-heme Fe situated between the QA and the QB shifts \( E_m \) (QA/QA\(^−\)) to ~145 mV, making the electron leakage from QA\(^−\) to O\(_2\) more probable. In contrast to QA, QB undergoes two sequential reduction steps, meaning that QA\(^−\) lives for a longer time waiting for the second electron. However, QA\(^−\) is thermodynamically stable due to the positive \( E_m \) potentials (Causmaecker et al., 2019).

The role of a very low potential form of cytochrome \( b_{559} \) (\( E_m \) is ~150 to ~200 mV) in O\(_2\) reduction was also proposed (Khorobrykh, 2019). However, the fraction of this form is extremely small under normal conditions and increases only when the PSII functioning is severely perturbed. The \( b_{559} \) heme is embedded in the hydrophobic zone of the membrane; therefore, O\(_2\) photoreduction by \( b_{559} \) heme is thermodynamically unfavorable.
DISCUSSION

In this review, we briefly summarize some features of the modern PETC, which have evolved at the background of the Mehler reaction. The main site of \( \text{O}_2 \)\(^{-}\) generation is PSI. Several experiments revealed that PhQ could be the major contributor to this process (Kruk et al., 2003; Kozuleva et al., 2011, 2014). The reactivity of the FeS components with \( \text{O}_2 \), especially \( \text{F}_B \) and \( \text{Fd} \), was diminished by redox tuning and protein shielding. The recruitment of a high-potential PQ to the membrane quinone pool instead of a low-potential MQ was driven by the necessity to keep the pool in the reduced state under illumination in the presence of \( \text{O}_2 \). Replacing MQ with PQ triggered a redox tuning of PSII and cytochrome \( \text{b}_6/\text{f} \) complex cofactors, disabling, among other things, efficient \( \text{O}_2 \)\(^{-}\) generation in these complexes. The only MQ-based cofactor preserved in the modern PETC is PhQ, which is likely to be the main site of \( \text{O}_2 \)\(^{-}\) generation.

The stromal production of \( \text{O}_2 \)\(^{-}\) via \( \text{Fd} \) greatly increases if the \( \text{NADP}^+ \) recovering in the Calvin–Benson–Bassham cycle is retarded, e.g., due to closed stomata. In the stroma, \( \text{H}_2\text{O}_2 \) is produced from \( \text{O}_2 \)\(^{-}\) under catalysis by superoxide dismutase. \( \text{O}_2 \) reduction by PhQ\(^{-}\) can account for \( \text{O}_2 \)\(^{-}\) appearance within the thylakoid membrane (Kozuleva et al., 2011); however, a significant part of \( \text{O}_2 \)\(^{-}\) formed by PhQ\(^{-}\) still likely diffuses outside the membrane. Nevertheless, the increasing irradiance resulted in both a larger \( \text{O}_2 \)\(^{-}\) production just within the thylakoid membrane and a larger \( \text{H}_2\text{O}_2 \) production via \( \text{O}_2 \)\(^{-}\) reduction by PQH\(_2\), i.e., by the mechanism different from dismutation (Borisova-Mubarakshina et al., 2012).

Thus, in chloroplasts, \( \text{H}_2\text{O}_2 \) is produced via two distinct reactions in two distinct chloroplast compartments. We believe that this observation may be important for the understanding of \( \text{H}_2\text{O}_2 \)-mediated signal transduction. The stromal \( \text{H}_2\text{O}_2 \), which might be considered as a messenger of \( \text{NADP}^+\)/\( \text{NADPH} \) status, can oxidize thioredoxins (Hofmann, 2010; Netto and Antunes, 2016). Therefore, a temporary \( \text{H}_2\text{O}_2 \) accumulation in the stroma can affect the expression of chloroplast genes and/or the translation aimed at the fast adaptation of photosynthetic apparatus. \( \text{H}_2\text{O}_2 \) formed by the membrane PQ pool might be considered as a messenger of PETC status. It is important in terms of the PQ pool function as a central hub, of which the redox state represents a signal for both the chloroplast gene expression (Pfannschmidt et al., 2009) and the retrograde signaling pathways from the chloroplast to the nucleus (Pfannschmidt et al., 2003). For example, the PQ pool redox state initiates the changes in the PSII light-harvesting antenna size as a long-term acclimation to light conditions (Escoubas et al., 1995; Frigerio et al., 2007). We demonstrated that it is \( \text{H}_2\text{O}_2 \) rather than the PQ pool reduction state itself that is responsible for the antenna size reduction in high light (Borisova-Mubarakshina et al., 2015, 2019). Therefore, we suppose that a high potential of the PQ pool to form \( \text{H}_2\text{O}_2 \) in high light and under stress conditions could serve as evolutionarily set to signal about the PETC redox state to adjust to the ever-changing environmental conditions.

AUTHOR CONTRIBUTIONS

MK and MB-M designed the concept of the article. All authors contributed to the writing of the first draft and manuscript revision, and approved the submitted version. MK incorporated all inputs from the coauthors, reviewers, and editor.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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