Running title

Photosynthesis at Different Levels of the Organization

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The book is written by Russian and international authorities in the field of photosynthesis research. It is dedicated to investigations of the problems of photosynthesis at different levels of organization: molecular, cellular and organismal. Book describes the multiple roles of various reactive oxygen species in photosynthetic organisms. Further, we have presented here a discussion of the structure and function of water oxidation complex (WOC) of PS II, and a possible role of Mn-bicarbonate complex in WOC. Other important topics in this book are: the structural and functional organization of the pigment-protein complexes, the structure and regulation of chloroplast ATP-synthase, the participation of molecular hydrogen in microalgae metabolism, the current concepts on the evolution and the development of photosynthetic carbonic metabolism, and the adaptive changes of photosynthesis at increased CO_2 concentrations, as well as the photosynthetic machinery response to low temperature stress. The material available in this book is a unique report on the state of this trend in modern science. This book will be helpful not only for biophysicists, biochemists and experts in plant physiology, but also for a wider group of biologists; in addition, it is expected to be used in ongoing and future research work in the field. Lastly, and most importantly, it will serve to educate undergraduate, graduate and post-graduate students around the World.

Preface

Existence of life on the Earth is supported by photosynthetic organisms which provide production of organic substances and oxygen evolution. In general, photosynthesis includes primary light reactions and secondary dark reactions. Light reactions begin with absorption of photons by light harvesting photosynthetic pigments, resulting in the formation of their singlet exited states. This process is followed by excitation energy transfer from one pigment molecule to the other. Then, charge separation occurs in the photosynthetic reaction centers. Excited electrons are transferred via the photosynthetic electron transport chain (ETC), providing production of the reducing power in the form of reduced nicotinamide adenine dinucleotide phosphate (NADPH). The ETC of oxygenic photosynthetics contains two photochemical systems — PS II (water-plastoquinone oxido-reductase) and PS I (plastocyanin-ferredoxin oxido-reductase) — which transfer electrons from water to NADP, using one more complex, the cytochrome-b6f-complex. The source of electrons in this case is water molecules which are decomposed by water-oxidizing complex (WOC) of the PS II. In anoxygenic phototrophs, external hydrogen compounds are a source of the electrons, and the light is absorbed in a single photosystem. During the electron transfer from water to NADP, protons are transferred from the stroma side (the positive (p) side) to the lumen side (the negative (n) side), and when this proton gradient is dissipated through the ATP-synthase, ATP is produced.

The next stage includes biochemical processes of fixation and reduction of CO_2 in photosynthetic carbon metabolism with using NADPH, and ATP. To date, the known metabolic pathways of carbon in photosynthesis can be classified into the 3-hydroxypropionat bicycle; the reductive citrate cycle, i.e., the Arnon cycle; C_3 or the reductive pentose phosphate cycle, i.e., the Benson-Bassham-Calvin cycle; C_4 or cooperative photosynthesis; Crassulacean acid metabolism (CAM); C_3/C_4 photosynthesis; and C_4-CAM photosynthesis. Some of them, for example the 3-hydroxypropionat bicycle and the Arnon cycle, are specific to anoxigenic phototrophs, others, such as C_4, CAM, and so on, have been in the evolution of higher plants. The most important way of carbon in photosynthesis — the Benson-Bassham-Calvin cycle — is widespread in phototrophic organisms of different taxa. Eventually, fixation and reduction of CO_2 during photosynthesis leads to the formation of sugars and other organic compounds.

The present book has 8 chapters written mainly by the researchers of the Institute of Basic Biological Problems of the Russian Academy of Sciences (formerly the Institute of Photosynthesis). The each chapter describes photosynthesis at different levels of organization: molecular, cellular, and organismic. Among discussed problems in this book are: the structural and functional organization of the pigment-protein complexes; the evolutionary origin of the water-oxidizing complex of PS II; the hydrogen photoproduction coupled with photosynthesis; the structure and regulation of chloroplast ATP synthase; the formation, decay and signaling of reactive oxygen species in oxygen-evolving photosynthetic organisms during exposure to oxidative stress; the strategy of adaptation of photosynthetic carbon metabolism; the adaptive changes of photosynthesis under enhanced CO_2 concentration, and the photosynthetic machinery response to low temperature stress.

The material presented here reflects, mainly, the research interests and views of the authors. We do not claim to have produced all-inclusive views of the entire field. The book is intended for a broad range of researchers and students, and all who are interested in learning the most important global process on our planet — the process of photosynthesis.

Chapter 1

The Multiple Roles of Various Reactive Oxygen Species (ROS) in Photosynthetic Organisms[a]

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Abstract. This chapter provides an overview on recent developments and current knowledge about monitoring, generation and the functional role of reactive oxygen species (ROS) – H_2O_2, $HO_2^{\bullet}$, $HO^{\bullet}$, OH^-, $^1O_2$ and $O_2^{-\bullet}$ – in both oxidative degradation and signal transduction in photosynthetic organisms including a summary of important mechanisms of nonphotochemical quenching in plants. We further describe microscopic techniques for ROS detection and controlled generation. Reaction schemes elucidating formation, decay and signaling of ROS in cyanobacteria as well as from chloroplasts to the nuclear genome in eukaryotes during exposure of oxygen-evolving photosynthetic organisms to oxidative stress are discussed that target the rapidly growing field of regulatory effects of ROS on nuclear gene expression.

Keywords: photosynthesis, plant cells, reactive oxygen species, ROS, oxidative stress, signaling systems, chloroplast, cyanobacteria, nonphotochemical quenching, CALI, sensors

Abbreviations:
Ala — delta-aminolevulinic acid
Asc — ascorbate
APX — ascorbate peroxidase
CALI — chromophore-activated laser inactivation

[a]This Chapter was published as a review in Biochim. Biophys. Acta (Schmitt F.J., Renger G., Friedrich T., Kreslavski V.K., Zharmukhamedov S.K., Los D.A., Kuznetsov V.V., Allakhverdiev S.I. Reactive oxygen species: Re-evaluation of generation, monitoring and role in stress-signaling in phototrophic organisms. Biochim. Biophys. Acta, 2014, 1837: 835-848); A modified and edited form of this review is reprinted here, in the form of a chapter, with the permission of Elsevier.

Cars — carotenoids
CHO — Chinese hamster ovary
COX — cytochrome c oxidase
DCF— 2',7'-dichlorofluorescein
DHA—dehydroascorbate
DHAR — DHA reductase
EF-G — elongation factor G
EPR — electron paramagnetic resonance
ETC — electron transfer chain
Fd — ferredoxin
Fur — ferric uptake repressor
GFP — green fluorescent protein
GR — glutathione reductase
GS — glutathione
GSH — reduced glutathione
GSSG — glutathione disulphide
H_2DCF-DA — 2',7'-dichlorodihydrofluorescein diacetate, acetyl ester
Hik — Histidin kinase
HOCl — hypochloric acid
Hsfs — heat stress transcription factors
ISC — inter system crossing
LHC — light harvesting complex
LP — lipid peroxidas
MAPK — mitogen-activated protein kinase
MDHA — monodehydroascorbate radical
MDHAR —MDHA reductase
MPO — myeloperoxidase
Naph — naphthalene
NBT — nitroblue tetrazolium
NOX — NADPH oxidase
NPQ — nonphotochemical quenching
OS — oxidative stress
PA — photosynthetic apparatus
PAHs — polyaromatic hydrocarbons
PBS — phosphate buffered saline
PhyB — phytochrome B
PPFD — photosynthetic photon flux density
PQ — plastoquinone
Prx — peroxiredoxins
PS — photosystem
PTOX — plastid terminal oxidase
RBOHs — respiratory burst oxidase homologs
RFP — red fluorescent protein
RL — red light

ROS — reactive oxygen species
RRP — response regulator protein
RS — redox-sensitive proteins
RsS — redox-sensitive sensors
SA — salicylic acid
SOD — superoxide dismutase
t-APX — APX bound to the thylakoid membrane
TF — transcription factors
WOC — water-oxidizing complex
WT — wild type
YFP — yellow fluorescent protein

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Acknowledgments
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1. Introduction

About 3 billion years ago the atmosphere started to transform from a reducing to an oxidizing environment as evolution developed oxygenic photosynthesis as key mechanism to efficiently generate free energy from solar radiation (Buick, 1992; Des Marais, 2000; Xiong and Bauer, 2002; Renger, 2008; Rutherford et al., 2012; Schmitt et al., 2014a). Entropy generation due to the absorption of solar radiation on the surface of the Earth was retarded by the generation of photosynthesis, and eventually a huge amount of photosynthetic and other organisms with rising complexity developed at the interface of the transformation of low entropic solar radiation to heat. The susbequent release of oxygen as a “waste” product of photosynthetic water cleavage

led to the present day aerobic atmosphere (Kasting and Siefert, 2002; Lane, 2002; Bekker et al., 2004), thus opening the road for a much more efficient exploitation of the Gibbs free energy through the aerobic respiration of heterotrophic organisms (for thermodynamic considerations, see (Nicholls and Ferguson, 2013; Renger, 1983).

From the very first moment this interaction with oxygen generated a new condition for the existing organisms starting an evolutionary adaptation process to this new oxydizing environment. Reactive oxygen species (ROS) became a powerful selector and generated a new hierarchy of life forms from the broad range of genetic mutations represented in the biosphere. We assume that this process accelerated the development of higher, mainly heterotrophic organisms in the sea and especially on the land mass remarkably.

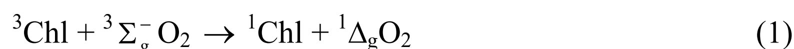
The efficient generation of biomass and the highly selective impact of ROS lead to a broad range of options for complex organisms to be developed in the oxydizing environment. The direct, mostly deleterious impact of ROS on the biosphere is thereby just a minor facet in the broad spectrum of consequences. Important and more complex side effects are for example given by the fact that the molecular oxygen led to generation of the stratospheric ozone layer, which is the indispensable protective shield against deleterious UV-B radiation (Worrest and Caldwell, 1986). ROS lead to new complex constraints for evolution that drove the biosphere into new directions – by direct oxidative pressure and by long range effects due to environmental changes caused by the atmosphere and the biosphere themselves as energy source for all heterotrophic organisms.

For organisms that had developed before the transformation of the atmosphere the pathway of redox chemistry between water and O_2 by oxygenic photosynthesis was harmful, due to the deleterious effects of ROS. O_2 destroys the sensitive constituents (proteins, lipids) of living matter. As a consequence, the vast majority of these species was driven into extinction, while only a minority could survive by finding anaerobic ecological niches. All organisms developed suitable defence strategies, in particular the cyanobacteria, which were the first photosynthetic cells evolving oxygen (Zamaraev and Parmon, 1980).

The ground state of the most molecules including biological materials (proteins, lipids, carbohydrates) has a closed electron shell with singlet spin configuration. These spin state properties are of paramount importance, because the transition state of the two electron oxidation of a molecule in the singlet state by ${}^3\Sigma_g^- O_2$ is "spin-forbidden" and, therefore, the reaction is very slow. This also accounts for the back reaction from the singlet to the triplet state.

In contrast to this majority of singlet ground state molecules the electronic configuration of the O_2 molecule in its ground state is characterized by a triplet spin multiplicity described by

the term symbol ${}^3\Sigma_g^- O_2$. This situation drastically changes by two types of reactions which transform ${}^3\Sigma_g^- O_2$ into highly reactive oxygen species (ROS): i) Electronic excitation leads to population of two forms of singlet O_2 characterized by the term symbols ${}^1\Delta_g$ and ${}^1\Sigma_g^+$. The ${}^1\Sigma_g^+$ state with slightly higher energy rapidly relaxes into ${}^1\Delta_g O_2$ so that only the latter species is of physiological relevance (type I). ii) Chemical reduction of ${}^3\Sigma_g^- O_2$ (or ${}^1\Delta_g O_2$) by radicals with non-integer spin state (often doublet state) leads to formation of $O_2^{-\bullet}$, which quickly reacts to $HO_2^\bullet$ and is subsequently transferred to H_2O_2 and $HO^\bullet$ (*vide infra*) (type II). In plants, the electronic excitation of ${}^3\Sigma_g^- O_2$ occurs due to close contact to chlorophyll triplets that are produced during the photoexcitation cycle (Schmitt et al., 2014a) (see Figure 1, Figure 2). Singlet oxygen is predominantly formed via the reaction sensitized by interaction between a chlorophyll triplet (^{3}Chl) and ground state triplet ${}^3\Sigma_g^- O_2$:



$$ {}^3\text{Chl} + {}^3\Sigma_g^- O_2 \rightarrow {}^1\text{Chl} + {}^1\Delta_g O_2 \qquad (1) $$

^{3}Chl can be populated either via intersystem crossing (ISC) of antenna Chls or via radical pair recombination in the reaction centers (RCs) of photosystem II (PS II) (for reviews, see (Vass and Aro, 2008; Renger, 2008; Rutherford et al., 2012; Schmitt et al., 2014a). Alternatively, ${}^1\Delta_g O_2$ can also be formed in a controlled fashion by chemical reactions, which play an essential role in programmed cell death upon pathogenic infections (e.g. by viruses).

Figure 2 schematically illustrates the pattern of one-electron redox steps of oxygen forming the ROS species $HO^\bullet$, H_2O_2 and $HO_2^\bullet/O_2^{-\bullet}$ in a four step reaction sequence with water as the final product. The sequence comprises the water splitting, leading from water to $O_2 + 4\,H^+$ and the corresponding mechanism *vice versa* of the ROS reaction sequence. The production of ${}^1\Delta_g O_2$ is a mechanism next to that.

In biological organisms, the four-step reaction sequence of ROS is tamed and energetically tuned at transition metal centers, which are encapsulated in specifically functionalized protein matrices. This mode of catalysis of the "hot water redox chemistry" avoids the formation of ROS. In photosynthesis, the highly endergonic oxidative water splitting ($\Delta G° = + 237.13$ kJ/mol, see Atkins, 2014) is catalyzed by a unique Mn_4O_5Ca cluster of the water-oxidizing complex (WOC) of photosystem II and energetically driven by the strongly oxidizing cation radical $P680^{+\bullet}$ (Klimov et al., 1978; Rappaport et al., 2002) formed via light-induced charge separation (for review, see Renger, 2012).

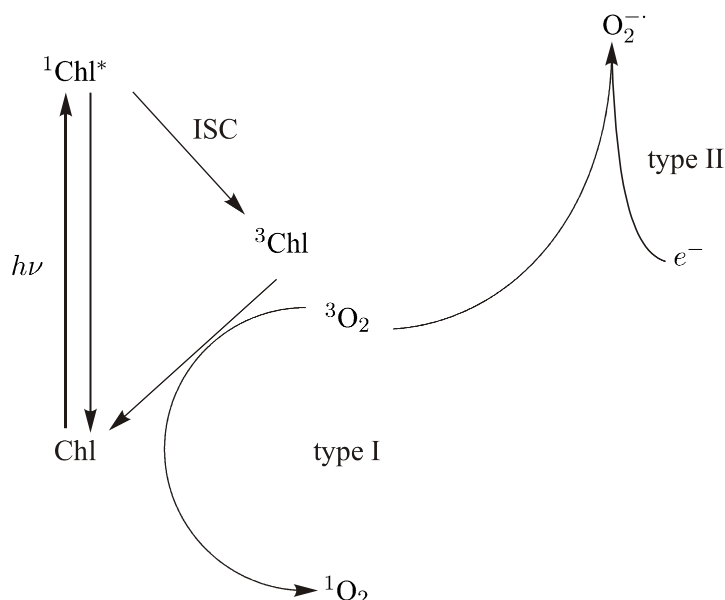


Figure 1. Production of ROS by interaction of oxygen with Chlorophyll triplet states (type I) to $^1O_2$ or chemical reduction of oxygen to $O_2^{-\bullet}$ (type II)

Corespondingly, the highly exergonic process in the reverse direction is catalyzed by a binuclear heme iron-copper center of the cytochrome oxidase (COX), and the free energy is transformed into a transmembrane electrochemical potential difference for protons (for a review, see Renger, 2011), which provides the driving force for ATP synthesis (for a review, see Junge, 2008). In spite of the highly controlled reaction sequences in photosynthetic WOC and respiratory COX, the formation of ROS in living cells cannot be completely avoided The excess of ROS under unfavorable stress conditions causes a shift in the balance of oxidants/antioxidants towards oxidants, which leads to the intracellular oxidative stress (Kreslavski et al., 2012b). Formation of ROS (the production rate) as well as decay of ROS (the decay rate) with the latter one determining the lifetime, both bring about the concentration distribution of the ROS pool (Kreslavski et al., 2013a). The activity of antioxidant enzymes, superoxide dismutase (SOD), catalase, peroxidases, and several others, as well as the content of low molecular weight antioxidants, such as ascorbic acid, glutathione, tocopherols, carotenoids, anthocyanins, play a key role in regulation of the level of ROS and products of lipid peroxidation (LP) in cells (Apel and Hirt, 2004; Pradedova et al., 2011, Kreslavski et al., 2012b).

The exact mechanisms of neutralization and the distribution of ROS have not been clarified so far. Especially the involvement of organelles, cells and up to the whole organism, summarizing the complicated network of ROS signalling (see chap. 6 and 7) are still far from being completely understood (Swanson and Gilroy, 2010; Kreslavski et al., 2012b, Kreslavski et al., 2013a).

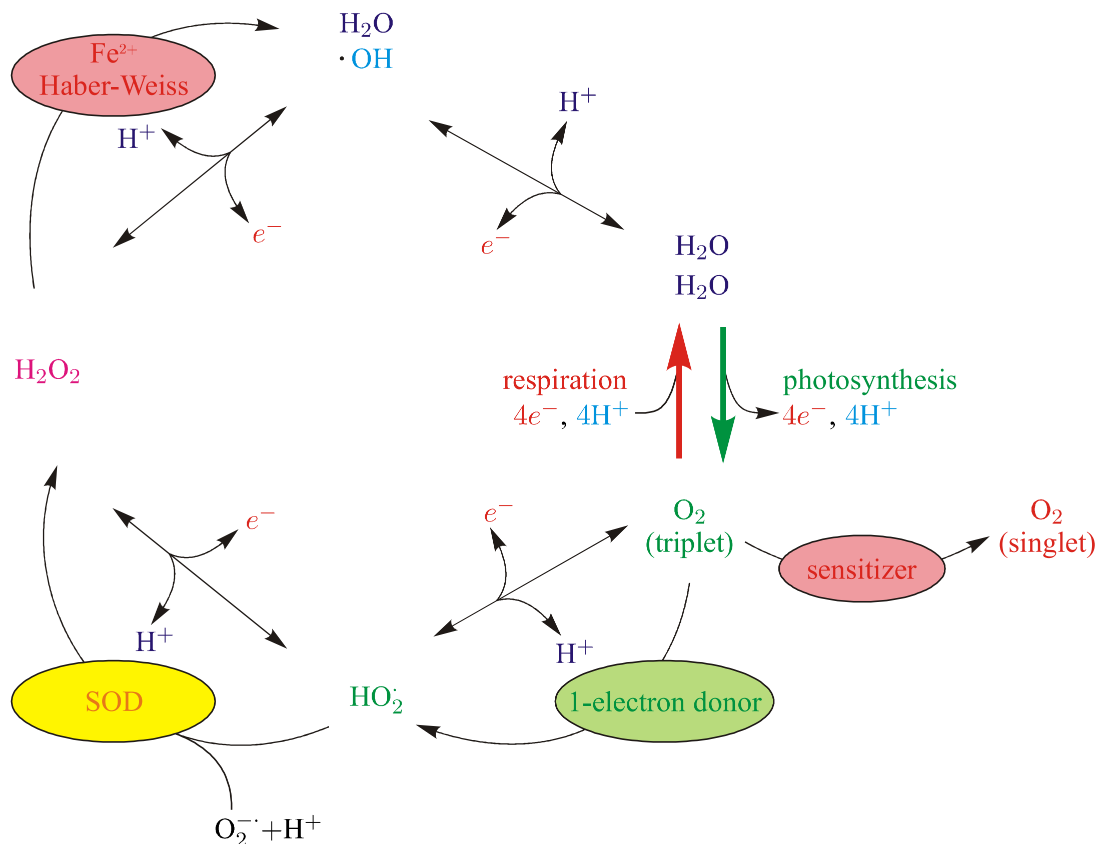


Figure 2. Scheme of ROS formation and water redox chemistry (water-water cycle, for details, see text)

Photosynthetic organisms growing under variable environmental conditions are often exposed to different types of stress like harmful irradiation (UV-B or high-intensity visible light), heat, cold, high salt concentration and also infection of the organisms with pathogens (viruses, bacteria) (Gruissem et al., 2012). Under these circumstances, the balance between oxidants and antioxidants within the cells is disturbed. This imbalance leads to enhanced population of ROS including singlet oxygen ($^1\Delta_gO_2$), superoxide radicals ($O_2^{-\bullet}$ or $HO_2^{\bullet}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($HO^{\bullet}$). Other highly reactive oxygen species like atomic oxygen or ozone are either not formed or play a role only under very special physiological conditions and will not be considered here. In this sense, the term ROS is used in a restricted manner. In addition to ROS, also reactive nitrogen- and sulfur-based species play an essential role in oxidative stress (OS) developed within the cells (Fryer et al., 2002; Benson, 2002). However, this interesting subject is beyond the scope of this chapter.

It is obvious that ROS exert deleterious effects. Oxidative destruction by ROS is known and has been studied for decades. However, ROS also act as important signaling molecules with regulatory functions, which have been unraveled only recently. ROS were found to play a key role in the transduction of intracellular signals and in control of gene expression and activity of antioxidant systems (Apel and Hirt, 2004; Desikan et al., 2001; Desikan et al., 2003; Mori and

Schroeder, 2004; Galvez-Valdivieso and Mullineaux, 2010; Foyer and Shigeoka, 2011). Being implicated in reactions against pathogens, (e.g. by respiratory bursts) and by the active participation in signaling, ROS have a protective role in plants (Bolwell et al., 2002; Dimitriev, 2003).

ROS contribute to acclimation and protection of plants, regulate processes of polar growth, stromatal activity, light-induced chloroplast movements, and plant responses to biotic and abiotic environmental factors (Mullineaux at al., 2006; Pitzschke and Hirt, 2006; Miller et al., 2007; Swanson and Gilroy, 2010; Vellosillo, 2010). In animals, recent studies have established that physiological H_2O_2 signaling is essential for stem cell proliferation, as illustrated in neural stem cell models, where it can also influence subsequent neurogenesis (Dickinson and Chang, 2011). This chapter will describe generation and decay of ROS and their monitoring in cells including novel microscopic techniques. Additionally the rapidly growing field of regulatory effects and pathways of ROS will be described although a complete description of the multitude of roles of ROS from nonphotochemical quenching (NPQ) to genetic signaling is impossible. However, this chapter provides an overview about the existing knowledge aiming to include the most important original literature and reviews. The book chapter is based on the review of (Schmitt et al., 2014a), however, it is significantly broadened to cover the fields that were not mentioned in (Schmitt at al., 2014a).

2. Generation, Decay and Deleterious Action of ROS

The interaction between chlorophyll triplets (^3Chl) and triplet ground state of molecular oxygen ($^3\Sigma_g^- O_2$): $^3Chl + {}^3\Sigma_g^- O_2 \rightarrow {}^1Chl + {}^1\Delta_g O_2$ is the predominant reaction forming singlet oxygen ($^1\Delta_g O_2$) in photosynthetic organisms (see Figure 1). ^3Chl is populated either via intersystem crossing (ISC) of antenna Chls or via radical pair recombination in the reaction centers of photosystem II (PSII) (for reviews, see (Renger, 2008; Rutherford et al., 2012)). Alternatively, ROS can also be formed by direct reduction of oxygen, most probably at PS I and by controlled chemical reactions, which play an essential role in programmed cell death upon pathogenic (e.g. viral) infections. The general water-water cycle which is mostly responsible for the subsequent formation of $O_2^{-\bullet}$ or $HO_2^{\bullet}$, H_2O_2 and $HO^{\bullet}$ is shown in Figure 2.

Under optimal conditions, only small amounts of ROS are generated in different cell compartments. However, exposure to stress can lead to a drastic increase of ROS production and sometimes to inhibition of cell defense systems (Desikan et al., 2001; Nishimura and Dangl,

2010). As a consequence of unfavorable conditions, oxidative stress is developed due to the generation of ROS via both the sensitized $^1\Delta_gO_2$ formation and the reductive pathways leading to production of $O_2^{-\bullet}$, H_2O_2 and $HO^\bullet$ radicals (see Figure 2).

Rapid transient ROS generation can be observed and is called "oxidative burst" (Bolwell et al., 2002). In this case, a high ROS content is attained within time periods from several minutes up to hours. Oxidative bursts occur during many plant cell processes, especially photosynthesis, dark respiration and photorespiration.

Studies using advanced imaging techniques, e.g. a luciferase reporter gene expressed under the control of a rapid ROS response promoter in plants (Miller et al., 2009), or a new H_2O_2/redox state-GFP sensor in zebrafish (Niethammer et al., 2009; see chapter 4, "Monitoring of ROS"), revealed that the initial ROS burst triggers a cascade of cell-to-cell communication events that result in formation of a ROS wave. This wave is able to propagate throughout different tissues, thereby carrying the signal over long distances (Mittler et al., 2011). Recently, the auto-propagating nature of the ROS wave was experimentally demonstrated. Miller *et al.* (Miller et al., 2009) showed by local application of catalase or an NADPH oxidase inhibitor that a ROS wave triggered by different stimuli can be blocked at distances of up to 5-8 cm from the site of signal origin. The signal requires the presence of the NADPH oxidase (the product of the *RbohD* gene) and spreads throughout the plant in both the upper and lower directions.

The lifetime of $^1\Delta_gO_2$ in aqueous solution is about 3.5 μs (Egorov et al., 1989). On the other hand, the lifetime is significantly shortened in cells due to the high reactivity of $^1\Delta_gO_2$, which rapidly attacks all relevant biomolecules (pigments, proteins, lipids, DNA), thus leading to serious deleterious effects. Values in the order of 200 ns were reported for $^1\Delta_gO_2$ in cells (Gorman and Rogers, 1992) so that the species can diffuse up to 10 nm under physiological conditions (Sies and Menck, 1992), thus permitting penetration through membranes (Schmitt et al., 2014a). Distances up to 25 nm have been reported (Moan, 1990) suggesting that $^1\Delta_gO_2$ can permeate through the cell wall of *E. coli*. The singlet oxygen chemistry significantly depends on the environment, solvent conditions and the temperature (Ogilby and Foote, 1983). Higher values of up to 14 μs lifetime and 400 nm diffusion distance in lipid membranes suggest that $^1\Delta_gO_2$ can indeed diffuse across membranes of cell organelles and cell walls (Baier et al., 2005). But as most proteins are prominent targets (Davies, 2003) with reaction rate constants in the range of 10^8-10^9 $M^{-1}s^{-1}$ the potential of $^1\Delta_gO_2$ to work directly as a messanger is rather limited (Wilkinson et al., 1995). Among the canonical amino acids, only five (Tyr, His, Trp, Met and Cys) are primarily attacked by a chemical reaction with $^1\Delta_gO_2$, from which Trp is unique by additionally exhibiting a significant physical deactivation channel that leads to the ground state

$^3\Sigma_g^- O_2$ in a similar way as by quenching with carotenoids. The reaction of $^1\Delta_g O_2$ with Trp primarily leads to the formation of peroxides, which are subsequently degraded into different stable products. One of these species is N-formylkynurenine (Gracanin et al., 2009). This compound exhibits optical and Raman spectroscopic characteristics that might be useful for the identification of ROS generation sites (Kasson and Barry, 2012). The reactivity of Trp in proteins was shown to markedly depend on the local environment of the target (Jensen et al., 2012). Detailed mass spectrometric studies revealed that a large number of oxidative modifications of amino acids are caused by ROS and reactive nitrogen species (Galetskiy et al., 2011).

The wealth of studies on damage of the photosynthetic apparatus (PA) by $^1\Delta_g O_2$ under light stress and repair mechanisms is described in several reviews and book chapters on photoinhibition (Li et al., 2012; Vass and Aro, 2008; Adir et al., 2003, Allakhverdiev and Murata, 2004; Nishiyama et al., 2006; Murata et al., 2007; Li et al., 2009; Goh et al., 2012, Allahverdiyeva and Aro, 2012). Such high reactivity leads to an extensive oxidation of fundamental structures of PS II where oxygen is formed in the water-oxidizing complex. $^1\Delta_g O_2$ is directly involved in the direct damage of PS II (Mishra et al., 1994, Hideg et al., 2007; Triantaphylidès at al., 2008; Triantaphylidès at al., 2009; Vass and Cser, 2009), destroying predominantly the D1 protein, which plays a central role in the primary processes of charge separation and stabilization in PS II. The resulting photoinhibition of PS II (Nixon et al., 2010) leads to dysfunction of D1 and high turnover rates during the so called D1-repair cycle. D1 by far exhibits the highest turnover rate of all thylakoid proteins and underlies complex regulatory mechanisms (Loll et al., 2008).

Carotenoids play a pivotal role in ^{3}Chl suppression and quenching (Frank et al., 1993; Pogson et al., 2005). In addition, NPQ developed under light stress also reduces the population of ^{3}Chl in antenna systems as well as PSII of plants (Ruban et al., 1994; Härtel et al., 1996; Carbonera et al., 2012) (see chapter 3). The interaction between $^1\Delta_g O_2$ and singlet ground state carotenoids does not only lead to photophysical quenching, but also to oxidation of carotenoids by formation of species that can act as signal molecules for stress response (Ramel et al., 2012). Likewise, lipid (hydro)peroxides generated upon oxidation of polyunsaturated fatty acids by $^1\Delta_g O_2$ can act as triggers to initiate signal pathways, and propagation of cellular damage (Galvez-Valdivieso and Mullineaux, 2010; Triantaphylides and Havaux, 2009). Detailed studies of the damage of the PA by $^1\Delta_g O_2$ are additionaly found in (Li et al., 2012; Allakhverdiev and Murata, 2004; Allakhverdiyeva and Aro, 2012; Goh et al., 2012; Wakao et al., 2009; Nishiyama at al., 2006).

Among all ROS, the $O_2^{-\bullet}$ /H_2O_2 system is one of the key elements in cell signaling and other plant functions (see Figure 1). $O_2^{-\bullet}$ and H_2O_2 are assumed to initiate reaction cascades for the generation of "secondary" ROS as necessary for long-distance signaling from the chloroplasts to or between other cell organelles (Baier and Dietz, 2005; Sharma et al., 2012; Bhattacharjee, 2012).

The initial step in formation of redox intermediates of the H_2O_2/O_2 system in all cells is the one-electron reduction of O_2 to $O_2^{-\bullet}$ (see Figure 2). $O_2^{-\bullet}$ and H_2O_2 are mainly formed in chloroplasts, peroxisomes, mitochondria and cell walls (Bhattacharjee, 2012). Enzymatic sources of $O_2^{-\bullet}$ / H_2O_2 generation have been identified such as cell wall-bound peroxidases, aminooxidases, flavin-containing oxidases, oxalate and plasma membrane NADPH oxidases (Bolwell et al., 2002; Mori and Schroeder, 2004; Svedruzic at al., 2005). In particular, sources of ROS in the apoplast are oxidases bound to the cell wall, peroxidases, and polyamino oxidases (Minibayeva et al., 2009b, Minibayeva et al., 1998).

The major source of $O_2^{-\bullet}$/H_2O_2 production in chloroplasts is the acceptor side of photosystem I (PS I) (Asada, 1999; Asada, 2006). The exact mechanism of O_2 reduction is still a matter of discussion. It was assumed that O_2 mainly is reduced by transfer of electrons from reduced ferredoxin (Fd) to O_2 via ferredoxin-thioredoxin reductase (Gechev et al., 2006) although this assumption was challenged since a long time (Asada et al., 1974; Goldbeck and Radmer, 1984). New findings showed that reduced Fd was only capable of low rates of O_2 reduction in the presence of $NADP^+$ with contribution to the total O_2 reduction not exceeding 10% (Kozuleva and Ivanov, 2010; Kozuleva et al., 2014). NADPH oxidase (NOX) is considered to be involved into ROS production both in animal and plant cells (Sagi and Fluhr, 2001; Sagi and Fluhr, 2006) according to the reaction $NADPH + 2\ O_2 \rightarrow NADPH^+ + 2\ O_2^{-\bullet} + H^+$.

Under conditions of limited NADPH consumption due to impaired CO_2 fixation rates via the Calvin-Benson cycle in photosynthetic organisms, some components of the electron transport chain (ETC) will stay reduced and can perform ${}^3\Sigma_g^- O_2$ reduction to $O_2^{-\bullet}$. It is suggested that H_2O_2 formation takes place in the plastoquinone (PQ) pool, but with a low rate (Ivanov et al., 2007), studies on mutants of *Synechocystis* sp. PCC 6803 lacking phylloquinone (*menB* mutant) show the involvement of phylloquinone in O_2 reduction (Kozuleva et al., 2014).

Recent literature suggests very short lifetimes for $O_2^{-\bullet}$ radicals in the μs regime (1 μs half-life is published in (Sharma et al., 2012), while 2-4 μs are found in (Gechev et al., 2006) - which is about one order of magnitude longer than that of ${}^1\Delta_g O_2$ (*vide supra*). $O_2^{-\bullet}$ radicals are rapidly transformed into H_2O_2 via the one-electron steps of the dismutation reaction catalyzed by

the membrane-bound Cu/Zn-superoxide dismutase (SOD) (see Figure 2) (Asada, 1999; Asada, 2006).

Three forms of SODs exist in plants containing different metal centers, such as manganese (Mn-SOD), iron (Fe-SOD), and copper-zinc (Cu/Zn-SOD) (Bowler et al., 1992; Alscher et al., 2002), from which Cu/Zn-SOD is the dominant form. The non-enzymatic $O_2^{-\bullet}$ dismutation reaction is very slow (Foyer and Noctor, 2009; Foyer and Shigeoka, 2011). Earlier literature suggested generally a low reactivity of $O_2^{-\bullet}$ radicals indicating that the exact mechanisms of the $O_2^{-\bullet}$ reaction pathways in living cells might need further elucidation (see Halliwell and Gutteridge, 1985 and references therein). In earlier studies, Halliwell (Halliwell, 1977) pointed out that $O_2^{-\bullet}$ is a moderately reactive nucleophilic reactant with both oxidizing and reducing properties. The negative charge of the $O_2^{-\bullet}$ radical leads to an inhibition of its electrophilic properties in presence of molecules with many electrons, while molecules with a low electron number might be oxidized. $O_2^{-\bullet}$ oxidizes enzymes containing [4Fe-4S] clusters (Imlay, 2003), while cytochrome c is reduced (Cord et al., 1977).

Among the amino acids, mainly histidine, methionine, and tryptophan can be oxidized by $O_2^{-\bullet}$ (Dat et al., 2000). These radicals interact quickly with other radicals due to the spin selection rules. For example, superoxide interacts with radicals like nitric oxide and with transition metals or with other superoxide radicals (dismutation). As an example, Fe(III) is reduced by $O_2^{-\bullet}$, then H_2O_2 interacts with Fe^{2+} (Fenton reaction), in effect forming $HO^{\bullet}$, which is the most reactive species among all ROS (see also Figure 2). This reaction is particularly mentioned due to its importance for the generation of highly reactive $HO^{\bullet}$ from long-lived H_2O_2 which might act as long distance messenger. Further information about various reaction rate constants of $O_2^{-\bullet}$ at different conditions, concentrations and pH are found in (Rigo et al., 1977; Fridovich, 1983; Löffler et al., 2007).

Within the chloroplasts, H_2O_2 is reduced to H_2O by ascorbate (Asc) via a reaction catalyzed by soluble stromal ascorbate peroxidase (APX) (Asada, 2006; Noctor et al., 1998) or APX bound to the thylakoid membrane (t-APX). As shown in Figure 3, the Asc oxidized to the monodehydroascorbate radical (MDHA) is regenerated by reduction of MDHA either directly by Fd or by NAD(P)H catalyzed by MDHA reductase (MDHAR). The MDHA radical always decays partially into dehydroascorbate (DHA), which is reduced by DHA reductase (DHAR). In that step, reduced glutathione (GSH) is oxidized to glutathione disulfide (GSSG). The reduction of GSSG to GSH occurs from NAD(P)H by glutathione reductase (GR) (Noctor and Foyer, 1998; Asada, 2006).

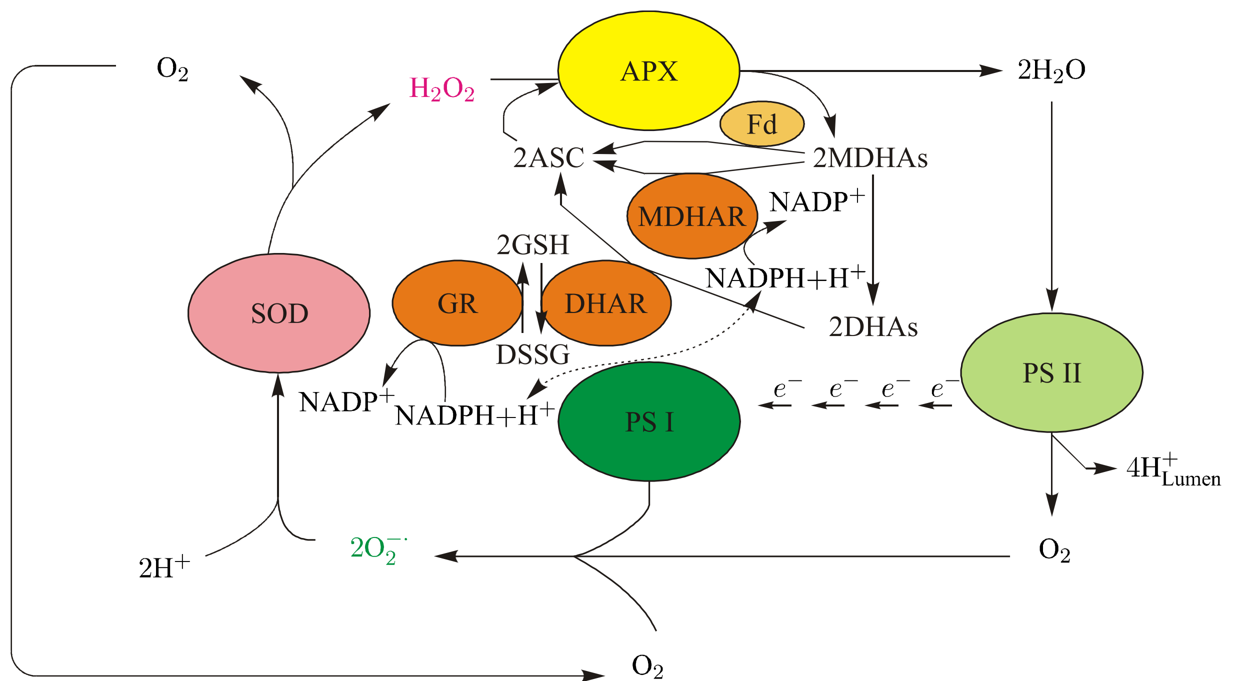


Figure 3. Scheme of pseudocyclic "H_2O-H_2O" electron transport (for details, see text)

The result of the reaction sequence of O_2 reduction to $O_2^{-\bullet}$ at the acceptor side of PS I, followed by dismutation of $O_2^{-\bullet}$ by SOD, and the reduction of H_2O_2 by t-APX is the reduction of one O_2 molecule to two H_2O molecules. This four-electron reduction process counterbalances the oxidation of two H_2O molecules to one O_2 molecule at the donor side of PS II so that no net change in the overall turnover of O_2 is obtained, as is schematically illustrated in Figure 3. Therefore, this "water-water cycle" is referred to as pseudocyclic electron transport (for details, see (Foyer and Shigeoka, 2011; Asada, 1999; Asada, 2006)). It has to be kept in mind that this pseudocyclic electron transport can be coupled to the formation of a transmembrane pH difference, ΔpH.

Figure 2 indicates that H_2O_2 could also be generated by oxidation of two H_2O molecules. In fact, formation of H_2O_2 has been reported to take place at a disturbed water-oxidizing complex (WOC) under special circumstances (Ananyev at al, 1992; Klimov et al., 1993; Pospisil, 2009). However, under physiological conditions, this process is negligible if taking place at all. Accordingly, H_2O_2 production at PS II occurs via the reductive pathway at the acceptor side under conditions where the PQ pool is over-reduced (Ivanov et al., 2007).

H_2O_2 is the ROS with the longest lifetime, which is in the order of 1 ms (Henzler and Steudle, 2000; Gechev and Hille, 2005). This is mostly supported as the molecule is neutral and therefore can pass lipophilic regions of the cell especially membranes including water channels like aquaporins (Bienert et al., 2007). Therefore, it can travel over large distances and play a central role in signaling of stress (see chapter 5 ff., "Signaling").

Even at high light, no substantial amounts of $^1\Delta_gO_2$ and H_2O_2 are accumulated, when the electron flow through the pseudocyclic ETC (*vide supra*) increases and sufficient amounts of $NADP^+$ are present in the cell. At high light intensity and conditions of saturating CO_2 assimilation, the rate of electron flow increases. This leads to its redistribution, i.e. the rate of electron flow to $NADP^+$ decreases and, concomitantly, the rate of electron transfer through the pseudocyclic electron transport increases (Asada, 1999).

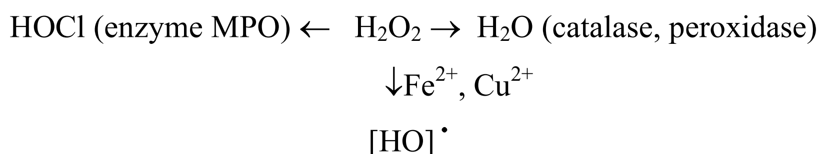
H_2O_2 can also participate in the control of $^1\Delta_gO_2$ formation, when an excess of H_2O_2 induces oxidation of the primary electron acceptor of PS II, thus leading to activation of the electron transport. As a result, production of $^1\Delta_gO_2$ is diminished due to reduced probability of ^{3}Chl population. Accordingly, pseudocyclic electron transport can function as a relaxation system to permit a decline of $^1\Delta_gO_2$ generation (Galvez-Valdivieso and Mullineaux, 2010). Such effects can result in autoinhibited reaction patterns and lead to spatiotemporal osciallations of the ROS distribution e.g. ROS waves.

The steady-state level of cellular H_2O_2 depends on the redox status of the cell (Karpinski et al., 2003; Mateo et al., 2006). Light-induced ROS generation in plants is mainly determined by the physiological state of the PA (Foyer and Shigeoka, 2011; Asada, 1999). Under physiological conditions, the H_2O_2 content in the cell is usually less than 1 μM. At elevated concentration, H_2O_2 inhibits several enzymes by oxidative cross-linking of pairs of cysteine residues. At about 10 μM, H_2O_2 inhibits CO_2 fixation by 50%, which is mainly due to the oxidation of SH groups of Calvin cycle enzymes (Foyer and Shigeoka, 2011).

H_2O_2 can block the protein synthesis in the process of PS II repair (Nishiyama et al., 2001; Nishiyama et al., 2004; Nishiyama et al., 2011; Murata et al., 2012). This effect of H_2O_2 has been analyzed in the cyanobacterium *Synechocystis* sp. PCC 6803. It was shown that the translation machinery is inactivated with the elongation factor G (EF-G) being the primary target (see chap. 5.1). Due to that oxidation the protein de novo synthesis is completely blocked via the stop of protein translation. This process has been studied in deep detail and it is understood today mainly as a protective mechanism that avoids an expensive *de novo* synthesis of proteins in a highly oxidizing environment. Further details on this general type of H_2O_2 signalling are found in chapter 5 (signalling).

Elimination of H_2O_2 is tightly associated with scavenging of other ROS in plant cells. Both, H_2O_2 production and removal are precisely regulated and coordinated in the same or in different cellular compartments (Foyer and Noctor, 2005; Karpinski et al., 2003; Mateo et al., 2006; Ślesak et al., 2007; Pfannschmidt et al., 2009). The mechanisms of H_2O_2 scavenging are regulated by both, non-enzymatic and enzymatic antioxidants.

The biological toxicity of H_2O_2 appears through oxidation of SH groups and can be enhanced, if metal catalysts like Fe^{2+} and Cu^{2+} take part in this process (Fenton reaction) (see above and Figure 2). The enzyme myeloperoxidase (MPO) can transform H_2O_2 to hypochloric acid (HOCl), which has high reactivity and can oxidize cysteine residues by forming sulfenic acids (Dickinson and Chang, 2011):



Thus, H_2O_2 takes part in formation of reactive species like $HO^{\bullet}$ via several pathways.

Both $O_2^{-\bullet}$ and H_2O_2 are capable to initiate the peroxidation of lipids, but since $HO^{\bullet}$ is more reactive than H_2O_2, the initiation of lipid peroxidation is mainly mediated by $HO^{\bullet}$ (Bhattacharjee, 2012; Miller et al., 2009).

Different defense systems have been developed to protect cells from deleterious effects of ROS. The underlying response mechanisms are either leading to diminished generation or enhanced scavenging of ROS. De novo synthesis of antioxidant enzymes (SOD, catalase, ascorbate peroxidase, glutathione reductase) and/or activation of their precursor forms take place and low-molecular antioxidants (ascorbate, glutathione, tocopherols, flavonoids) are also accumulated (Foyer and Noctor, 2005; Hung et al., 2005).

The antioxidant defense system contains many components (Pradedova et al., 2011). Essentially, three different types are involved: i) systems/compounds preventing ROS generation, primarily by chelating transition metals which catalyze $HO^{\bullet}$ radical formation, ii) radical scavenging by antioxidant enzymes and metabolites, and iii) components involved in repair mechanisms. Treatment of mature leaves of wheat plants with H_2O_2 was shown to activate leaf catalase (Sairam and Srivasteva, 2000).

The $HO^{\bullet}$ radical is the most reactive species known in biology. $HO^{\bullet}$ is isoelectronic with the fluorine atom and characterized by a midpoint potential of + 2.33 V at pH 7 (for comparison, the normal reduction potential of fluorine is + 2.85 V). In cells, the extremely dangerous $HO^{\bullet}$ radical can be formed by reduction of H_2O_2 via the Haber-Weiss reaction (Haber and Weiss, 1934) catalyzed by Fe^{2+} (Kehrer, 2000). $HO^{\bullet}$ radicals immediately attack proteins and lipids in the immediate environment of the site of production, thus giving rise to oxidative degradation (Halliwell, 2006). Cells cannot detoxify $HO^{\bullet}$ radicals and, therefore, a protection can only be achieved by suppression of H_2O_2 formation in the presence of Fe^{2+} using metal

binding proteins like ferritins or metallothioneins (Hintze and Theil, 2006). On the other hand, $HO^\bullet$ radicals can be produced in programmed cell death as part of defense mechanisms to pathogenic infections (Gechev et al., 2006).

It has to be mentioned that the $HO^\bullet$ radical is not the only possible product of the reaction between H_2O_2 and Fe^{2+}. New calculations on the electronic structure and ab initio molecular dynamics simulations have shown that the formation of the ferri-oxo species $[Fe^{IV}(O^{2-})(H_2O)_5]^{2+}$ is energetically favored by about 100 kJ/mol compared to the generation of the $HO^\bullet$ radical (Yamamoto et al., 2012). Therefore, in future mechanistic studies, the species $[Fe^{IV}(O^{2-})(H_20)_5]^{2+}$ should be taken into account for mechanistic considerations on the oxidative reactions of H_2O_2 in the presence of Fe^{2+}.

3. Non-photochemical Quenching in Plants and Cyanobacteria

Due to its important role in ROS surpression, non-photochemical quenching (NPQ) in plants and cyanobacteria has to be mentioned. During evolution, cyanobacteria and plants have developed various mechanisms of acclimation, in particular regulatory pathways for defense to stress induced by unfavorable environmental factors. These defense mechanisms include the decrease of the rate of ROS generation, the increase of the rate of ROS scavenging, the acceleration of the repair of damaged cell structures but also the important mechanisms of NPQ of superfluous excitation energy by carontenoids (Cars) or other NPQ mechanisms.

Photosynthetic organisms have evolved quite different mechanisms for sensing of light and response to stress, which operate in markedly different time domains and light intensities. The fastest response is the annhiliation process of excess energy in light harvesting systems dur to processes of non-photochemical quenching (NPQ) and the induction of NPQ processes due to acidification of the thylakoid lumen by formation of a transmembrane pH difference (ΔpH). This effect is designated qE (for review, see (Ruban et al., 2012)). A regulation of excitation energy funnelling to PS I and PS II in oxygen-evolving organisms occurs via a phenomenon designated "state transitions" which comprises reversible phosphorylation/dephosphorylation of light harvesting complexes II (see (Iwai et al., 2010) and references therein). For an analyse of the hierarchy of light induced kinetic steps in the PS II by measurement of single flash induced transient quantum yield and modelling with a PS II reaction scheme see also (Belyaeva et al., 2008, Belyaeva et al., 2011, Belyaeva et al., 2014) and references therein.

The relative content of different ROS depends on the mode of stress. For example, high light stress primarily leads to $^1\Delta_gO_2$, while chilling or drought stress affect the rate of CO_2 fixation via the Calvin-Benson cycle (Calvin, 1989; Benson, 2002), thus resulting in a retardation of electron transfer through the linear electron-transport chain (ETC) and over-reduction of many components of the ETC (Asada, 1999; Foyer and Noctor, 2005). Then, even under comparatively "normal" high light conditions, the excitation energy absorbed by the Chl molecules is not completely depleted by the photochemical quenching processes, which results in a rise of Chl fluorescence and increased risk of formation of excited Chl triplet states and subsequent generation of ROS (see Figure 1). Therefore, various mechanisms of NPQ are triggered, for example the light-induced and pH-dependent xanthophyll cycle (Härtel et al., 1996; Demmig-Adams et al., 1996), the photo-switchable orange carotenoid protein (OCP) in cyanobacteria (Wilson A. et al., 2008; Wilson et al., 2010; Boulay et al., 2010, Stadnichuk et al., 2013) or the the PsbS subunit of PSII in higher plants, which is an independently evolved member of the LHC protein superfamily acting as a luminal pH sensor (Niyogi et al., 2013; Schmitt et al., 2014b).

In this context, the large ΔpH across the thylakoid membrane (with acidic luminal pH) that builds up under extreme light due to the limited capacity of the F_0F_1-ATPase system is the most immediate biochemical signal for triggering NPQ mechanisms, and it is responsible for the most rapidly responding energy-(ΔpH)-dependent NPQ component (Schmitt et al., 2014b; Müller et al., 2001; Szabo et al., 2005). At acidic luminal pH, the pH-sensing PsbS protein of plants undergoes conformational changes (Bergantino et al., 2003) and most likely triggers a rearrangement of PSII supercomplexes in grana (Müller et al., 2001). NPQ is induced by reducing the semi-crystalline ordering and increasing the fluidity of protein organization in the membrane (Goral et al., 2012).

Low lumenal pH also triggers the xanthophyll cycle (Härtel et al., 1996; Demmig-Adams et al., 1996) by activating of pH-dependent xanthin deepoxidases. In the violaxanthine cycle of plants and green or brown algae, the violaxanthin deepoxygenase converts violaxanthin via antheraxanthin to xeaxanthin, whereas diatoms and many eucaryotic algae perform the diadinoxanthin cycle. Xanthin deepoxygenases associate with thylakoid membranes at low pH to act on their substrate (Müller et al., 2001). The mechanism by which zeaxanthin deactivates excited Chl molecules more efficiently than violaxanthin is still not completely understood. All carotenoids with more than ten conjugated C=C bonds have an excited singlet S1 state low enough to accept energy from excited Chl. However, the S1 state cannot be populated by one-photon absorption, but it can be reached upon rapid internal conversion from the S2 state. In vitro determination of the energy levels of the S1 state of zeaxanthin and violaxanthin showed

that both pigments have an S1 state suitable for direct quenching of excited Chl through singlet–singlet energy transfer. Experimental evidence suggests that violaxanthin is implicated in direct quenching of LHCII, since its particularly short fluorescence lifetime of 10 ps was found in femtosecond transient absorption experiments in intact thylakoids.

Cyanobacteria contain the photoswitchable orange carotenoid protein (OCP) containing 3'-hydroxyechinenone as cofactor (Wilson A. et al., 2008; Wilson et al., 2010; Boulay et al., 2010, Stadnichuk et al., 2013, Kirilovsky and Kerfeld, 2013; Maksimov et al., 2014a; Maksimov et al., 2015). The fluorescence decay curves of phycobilisomes (PBS) interacting with activated OCP are characterized by short decay components with $(170\ ps)^{-1}$ at strongest NPQ by OCP. PBS, which are strongly interacting with OCP, are lacking excitation energy transfer to the terminal emitter of the PBS antennae indicating that OCP quenches mainly the transfer from allophycocyanin in the PBS (Maksimov et al., 2014a). This fact was interpreted as intermolecular interaction between the OCP and its binding site in the PBS core induced by blue light. Detailed spectroscopic studies and investigations of OCP mutants unraveled most probable H-bonds between two residues, Trp-298 and Tyr-203 and an oxygen localized at the beta-ring of 3'-hydroxyechinenone as the most important interaction to stabilize the orange form of OCP. Light absorption and switching into the red form releases these bonds which leads to major structural changes and a red shift of the echinenone absorption spectrum. Binding of OCP in its red form to the PBS core and the resulting spatial proximity and spectral resonance then efficiently quenches the excited states in the PBS antenna (Kirilovsky and Kerfeld, 2013; Leverenz at al., 2014; Maksimov et al., 2015).

Conclusively, Cars play a pivotal role (for reviews on the key role of Cars in photosynthesis, see (Frank and Gogdell, 1993; Polivka and Sundström, 2004, Pogson et al., 2005) for NPQ developed under light stress (for reviews, see (Ruban et al., 2012)) thus effectively reducing the population of ^{3}Chl in antenna systems as well as PS II of plants (Carbonera et al., 2012). Cars, in addition, act as direct ROS scavengers. The interaction between $^1\Delta_gO_2$ and singlet ground state Cars does not only lead to photophysical quenching, but also to oxidation of Cars by formation of species that can act as signal molecules for stress response (Ramel et al., 2012).

Conformational changes of pigment-protein complexes are typically induced under high light conditions leading to the depletion of excited singlet states by internal conversion and interaction with quenching groups in the protein backbone. Recently, such conformational changes were artificially introduced by freezing of PBS of cyanbacteria and it was shown that this can reduce the fluorescence quantum yield of the PBS by 90 % (Maksimov et al., 2013).

Light harvesting complexes containing phycobiliproteins are not prone to triplet formation since phycocyanobilins (linear tetrapyrrols) do not undergo inter-system crossing. Therefore, PBS must not necessarily be quenched by carotenoids at high light conditions. Instead of this also decoupling mechanisms can occur that have been extensively studied for PBS and the rod-shaped phycobiliprotein antenna of the cyanobacterium A. marina including the EET processes on a molecular level (Schmitt et al., 2006; Theiss et al., 2008; Theiss et al., 2011; Schmitt, 2011). It was found that the phycobiliprotein antenna of A. marina decouples from the PSII under cold stress (Schmitt et al., 2006).

To assess the state of the PA and in mechanisms of NPQ in PS II under stress, the methods of variable and delayed fluorescence are often applied that allow the determination of important parameters from fluorescence induction curves, such as F_v, F_m, F_0 reflecting: a) the amount of photochemical quenching; b) the amount of nonphotochemical quenching and c) the yield of constant fluorescence, independent from photochemical reactions (as described in Keslavski et al., 2013a). The ratio (F_v/F_m) reflects the quantum efficiency of PS II in leaves and photosynthesizing cells.

In some cases, however, this ratio is not suitable for assessment of the stress state of the PA. For example (Liu et al., 2009) investigated the heterogeneity of PS II in the soybean leaves. Heterogeneity was changed, whereas the F_v/F_m ratio remained identical for all stress (heat) treatments.

Another parameter, which may be calculated from the fluorescence induction curves, is the photochemical quantum yield of PS II, which characterizes the state of the PA in leaves adapted to light. This parameter allows evaluation of the effectivity of PS II under physiological conditions and appears to be more sensitive to many types of stressors, than the fluorescence ratio of F_v/F_m (Strasser et al., 2000; Liu et al., 2009). Coefficients of photochemical and non-photochemical quenching and the size of light-harvesting antennae of PSII during the stress conditions are calculated from such data.

The methods for assessment of photosynthetic activity and stress acclimation of PA in cyanobacteria and symbiotic microalgae have some specificity and are described in details in (Biel et al., 2009).

Fluorescence methods (variable fluorescence and delayed fluorescence of Chl a) were successfully used to demonstrate that PAHs negatively influence the activity of PS II (Marwood et al., 2001; Kummerova et al., 2006, 2007, 2008), in particular decreasing the number of active reaction centers (Singh-Tomar and Jajoo, 2013). It is suggested that the negative influence of PAHs on PS II of leaves is linked to the generation of oxidative stress in chloroplasts. The

method of delayed light emission was recently successfully applied to detect effects of several PAHs on PS II photochemistry also (Kreslavski et al., 2014b).

Lately, a measurement of the induction curves of the photoinduced increase in Chl fluorescence (OJIP) is becoming a popular tool in studies of photosynthesis, since this increase is very sensitive to environmental stresses such as heat (Strasser, 2000).

In spite of the historically successful applications of OJIP curves as transient photoinduced Chl fluorescence the method of thermoluminescence is adequate for a detailed characterization of the PS II state of both acceptor and donor side and detecting early stress symptoms (Gilbert et al., 2004; Maslenkova, 2010). It is known that the temperature range of the thermoluminometer not only allows to analyze the different thermoinduced radical pair recombination of PS II in the lower temperature region but also chemiluminescence from lipid peroxidation in the higher temperature region. Thus, both the extend of oxidative stress and photochemical activity in plant cells and leaves can be assessed by fast method without using any chemicals.

The analysis of the prompt fluorescence kinetics of Chl a yields information about EET in antenna complexes and charge separation and ET steps leading to the formation of the radical ion pairs $P680^{+\bullet}Phe^{-\bullet}$ and $P680^{+\bullet}Q_A^{-\bullet}$ in PS II. Monitoring of the light-induced changes of the relative fluorescence quantum yield gives information about the processes of ET to the secondary plastoquinone acceptor Q_B of PS II. It is therefore of high interest, to analyse both simultaneoulsy, prompt fluorescence kinetics with sub-ns resolution and flash induced transient fluorescent yield changes with μs resolution simultaneously, in order to analyse EET and primary ET steps in the PS II together with formation and decay of fluorescence quenchers or chemical sensitizers like ROS. The technique described above would be well suited to permit this novel means of biophysical experimentation, and thus provide unprecedented information on the functional properties of biological systems.

A detailed description of Chl a fluorescence as a reporter of the functional state of the PS II is found in (Papageorgiou and Govindjee, 2005). In the following chapter we focus on the direct monitoring of ROS in plant tissue.

4. Monitoring of ROS

In plant cells, ROS are produced in different organelles, predominantly in chloroplasts and peroxisomes, while the contribution from mitochondria is smaller (Foyer and Noctor, 2005).

Imaging of oxidative stress in leaves of *Arabidopsis thaliana* revealed that $^1\Delta_gO_2$ and $O_2^{-\bullet}$ are primarily located in mesophyll tissues, while H_2O_2 was predominantly detected in vascular tissues (Fryer et al., 2002).

The simultaneous formation of several ROS complicates analyses on formation, decay and degradation action of individual species, e.g. $^1\Delta_gO_2$ versus $H_2O_2/O_2^{-\bullet}$. Therefore, suitable species-specific probes are required to monitor the different ROS molecules. In the following, methodologies will be briefly summarized, with especial emphasis on application to cellular systems according to Schmitt et al., 2014a.

Another important approach to study effects of different ROS next to the selection of special assay conditions is given by the use of mutant strains that differ in the generation of individual ROS and/or the content of protection systems/enzymes. This point is of high relevance for studies on specific signaling pathways (see chap. 5 "Signaling of ROS").

$^1\Delta_gO_2$ can be directly monitored via its characteristic phosphorescence with a maximum around 1270 nm (Wessels and Rodgers, 1995) and even singlet oxygen microscopy within the visible spectrum has been reported (Snyder et al., 2004). However, the detection of $^1\Delta_gO_2$ concentration and their time-dependent profiles in biological systems is difficult (for a discussion, see Li et al., 2012), because of the very low quantum yield of the emission, which ranges from 10^{-7} to 10^{-4} depending on the solvent (Schweitzer and Schmidt, 2003). Therefore, detailed analyses require the use of suitable probe molecules, which specifically change their properties due to reaction with $^1\Delta_gO_2$. Likewise, the detection of other ROS ($H_2O_2/O_2^{-\bullet}$) also needs the use of appropriate indicators.

Essentially, two types of probe molecules can be distinguished for monitoring of ROS: spin traps, which interact with ROS giving rise to EPR-detectable species (Hideg et al., 1994; Hideg et al., 2011; Zulfugarov et al., 2011), and fluorophores, which change their emission properties due to interaction with ROS (*vide infra*).

The use of fluorophores offers a most promising tool because it permits the application of recently developed advanced techniques of time- and space-resolved fluorescence microscopy for *in vivo* studies (see (Shim et al., 2012; Schmitt et al., 2013) and references therein).

Two different approaches can be used: a) addition of exogenous fluorescence probes, which penetrate into the cell and change their fluorescence properties due to reaction with ROS, and b) expression of ROS-sensitive fluorescent proteins, mostly variants of the green fluorescent protein (GFP), which act as real-time redox reporters for the use in intact cyanobacteria, algae and higher plants (Schmitt et al., 2014a).

4.1. Exogenous ROS Sensors

Table I gives an overview on exogenous fluorophores that typically change their emission properties due to interaction with ROS.

Since exogenous dyes typically respond in a certain oxidative potential range, appropriate mixtures can permit assays that are selective in a certain range of oxidative potentials (e.g. when both dyes show fluorescence or only one dye shows fluorescence, but the other not). These assays are more selective than those utilizing just a single dye.

In principle, permeability across membranes is necessary for the applicability of exogenous ROS-sensing fluorophores (table 1). For a quantitative analysis, it is necessary to know the reaction mechanism in detail, as well as possible interfering side effects and the cellular localization of these dyes. Generally, the water/octanol partition coefficient could be utilized to quantify membrane permeability of the probes.

Some of these ROS probes can be tuned regarding their properties inside the cell by enzymatic reactions. For instance, the commercially available 2’,7’-dichlorodihydrofluorescein diacetate, acetyl ester (H_2DCF-DA), a fluorescein-based dye, which is virtually non-fluorescent in the reduced state, becomes fluorescent after oxidation and concomitant splitting of the acetate groups by cellular esterases as 2',7'-dichlorofluorescein (DCF). H_2DCF-DA is widely used in (nonphotosynthetic) animal cells.

Figure 4 illustrates the application of CM-H_2DCFDA in monitoring the development of ROS production upon exposure of CHO cells to 440-480 nm light in phosphate buffered saline (PBS). After staining the cells with CM-H_2DCFDA, the fluorescence of the indicator strongly rises upon illumination of the cells with light of 440 nm – 480 nm wavelength due to the light-induced production of ROS and subsequent photooxidation in presence of oxidative compounds. It can be seen that after 6 sec, the lower cell has a higher cytosolic redox potential (higher fluorescence yield) than the upper two cells that show a less intense luminescence. On the other hand, these cells exhibit white “dots” indicating “hot spots” of accumulated DCF and/or higher local ROS activity (Schmitt et al., 2014a).

CM-H_2DCFDA is sensitive to ROS only in the living cell environment (in vivo) which enables the generation of dyes not only sensitive to ROS but also indicating that the ROS are produced inside the cell. Such studies are necessary especially to avoid side effects due to generation of ROS by the applied dyes, monitoring of ROS outside the cells in solution due to inspecific localisation and/or photoxidation of the dye by illumination (Vitali, 2011; for a detailed description see also Dixit and Cyr, 2003).

Table 1. Compilation of ROS-sensitive exogenous fluorescence probes

Compound / reference	Specificity Further information / localizability
CM-H2DCFDA (Dixit and Cyr, 2003)	Unspecific Permeates into animal cells, requires the presence of cellular esterases. Not easily applicable in plants
Singlet oxygen sensor green (SOSG) (Flors et al., 2006)	Highly specific to singlet oxygen. Successfully used for detection of $^1\Delta_gO_2$ in *A. thaliana* leaves
3,3'-diaminobenzidine (DAB) (Thordal-Christensen et al., 1997; Fryer et al., 2002)	Specific to H_2O_2 in presence of peroxidase (and other haem-containing proteins). Generates a dark brown precipitate which reports the presence and distribution of hydrogen peroxide in plant cells. Permeates into plant cells.
Aminophenyl fluorescein (APF)	APF is a cell permeable indicator that can be used to detect hydroxyl radicals ($HO^\bullet$), peroxynitrite ($ONOO^-$) and hypochlorite (OCl^-) production in cells. Shows limited photoxidation (see section “reactive oxygen species” in http://www.interchim.fr/cat/ApoptosisAssays)
hydroxyphenyl fluorescein (HPF)	Specific to hydroxyl radical and peroxynitrite. Minor sensitivity to other ROS. HPF is cell permeable (see section “reactive oxygen species” in http://www.interchim.fr/cat/ApoptosisAssays)
nitroblue tetrazolium (NBT) (Maly et al., 1989; Thordal-Christensen et al., 1997)	Specific to superoxide and with slightly reduced reactivity to hydrogen peroxide
Proxyl fluorescamine (Cohn et al., 2008)	Specific to hydroxyl radicals and superoxide Complementary use as spin trap
Hydroethidine (dihydroethidium) (Gomes et al., 2005)	Unspecific Binds specifically to DNA, marking the nucleus
DPPP (diphenyl-1-pyrenylphosphine) (Gomes et al., 2005)	Unspecific Lipophilic, detects ROS in lipids, blood plasma, tissues and food
MCLA (2-methyl-6-(4-methoxyphenyl) -3,7-dihydroimidazo[1, 2-a] pyrazin-3-one, hydrochloride) (Godrant et al., 2009)	Specific to superoxide or singlet oxygen (see section “reactive oxygen species” in http://www.interchim.fr/cat/ApoptosisAssays)
Trans-1-(2'-Methoxyvinyl)Pyrene	Highly specific to singlet oxygen (see section “reactive oxygen species” in http://www.interchim.fr/cat/ApoptosisAssays)

DCF can be used in plant cells of *A. thaliana* leaves for measuring the ROS production (mainly H_2O_2) upon illumination with UV-A. Figure 5 shows the highly fluorescent DCF after incubation of leaves of *A. thaliana* to PBS containing 500 μM H_2DCFDA. The leaves were exposed to H_2DCFDA solution for 1-2 h before starting the UV-A irradiation experiments. It can be seen that after irradiation with 360 nm UV-A light at an intensity of 250 W/m² for 10 minutes areas which contained microscopic damages exhibit strong DCF emission (Figure 5, left panel) while

the Chl a emission at 680 nm appears reduced in the same areas (middle panel) due to photobleaching. The simultaneous reduction of the Chl a fluorescence together with enhanced DCF fluorescence becomes evident in the overlay image (Figure 5, right panel) where Chl a emission is recolored in red and DCF in green. DCF studies together with observation of Chl a bleaching show the interaction of ROS and Chl a (Kreslavski et al., 2013b).

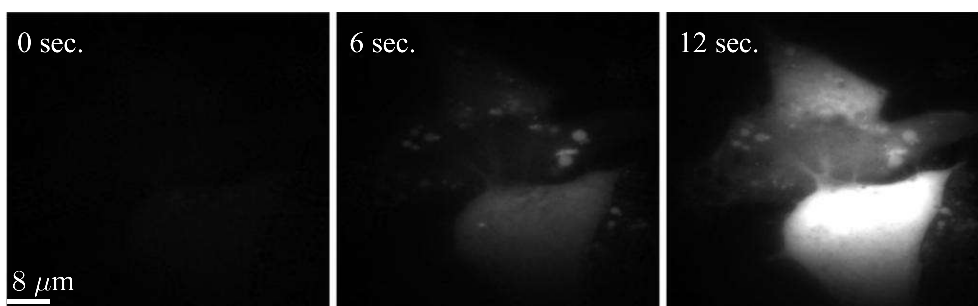


Figure 4. Increase of DCF fluorescence due to ROS production upon exposure of Chinese hamster ovary (CHO) cells to 440-480 nm light. The image shows the ROS content by intensity of the emission of DCF in three different cells

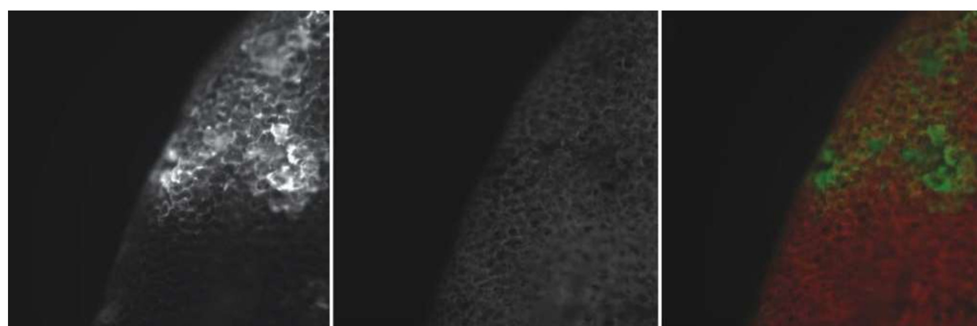


Figure 5. Fluorescence of a section of a 26-d-old *A. thaliana* leaf. The fluorescence was emitted from 2',7'-dichlorofluorescein (DCF) (excited at $\lambda_m = 470$ nm) after irradiation of the leaf with UV-A (360 nm; I – 250 Wm^{-2}) registered at 530 nm (left panel) in comparison to the Chl a fluorescence at 680 nm (middle panel). The overlay shows both (right panel) after recoloration

Incubation of *A. thaliana* leaves in a PBS buffer with a final apparent concentration of the polyaromatoic hydrocarbon (PAH) naphthalene (Naph) of 100 mg l^{-1} showed severe damage of the cell membrane upon illumination with UV-A as shown in Figure 6. Similar results were obtained for pea leaves (Kreslavski et al., 2014b). UV-radiation in combination with toxic compounds like PAHs lead to generation and accumulation of ROS as it can be nicely imaged with DCF.

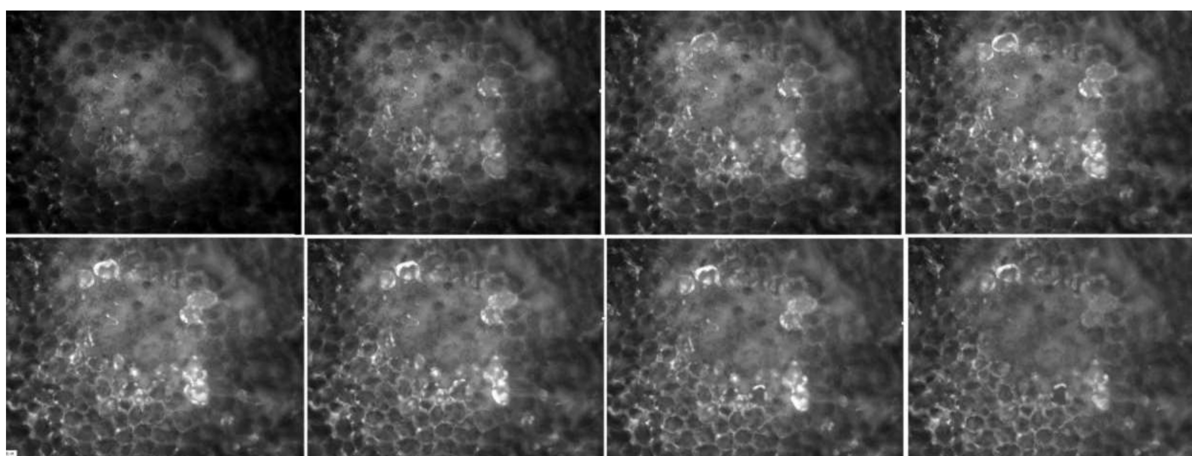


Figure 6. DCF fluorescence in leaves of *A. thaliana* incubated with Naph during illumination with UV-A

In leaves of *A. thaliana* treated with Naph, ROS waves with a temporal frequency of 20 minutes and a “wavelength” of several hundreds of micrometers were observed (Figure 7). Such a behavior is in line with wave-like closure and opening of stomata as observed in green plants under stress conditions.

In pea leaves the reduction of PSII activity at the presence of Naph is accompanied by transient generation of H_2O_2 as well as swelling of thylakoids and distortion of cell plasma membranes (Kreslavski et al., 2014b). It could be shown that Naph-treated leaves of *Arabidopsis thaliana* show enhanced DCF fluorescence in the cell membrane. The comparison of short term and long term exposure to different PAHs revealed that at short term exposure, the PAHs with high water solubility lead to the strongest reduction of PS II activity while after long term exposure the effect of PAHs with low water solubility is stronger.

While fluorescent ROS-sensing dyes respond to their target molecules without further spectroscopic signal structure, which impedes the selectivity of the otherwise highly sensitive fluorescence technique, the detection of the electron paramagnetic resonance (EPR) with spin traps enables a more selective technique for ROS monitoring. Since some ROS species are radicals, the application of spin traps appears sound to focus on spin-carrying ROS. Therefore, spin traps are widely applied to EPR-detectable ROS species like superoxide and hydroxyl radicals (Hideg et al., 1994; Hideg et al., 1998; Hideg et al., 2000; Zulfugarov et al., 2011). Fluorescent spin traps for ROS detection like DanePy which is quenched in presence of $^1\Delta_gO_2$ are suitable for an optical measurement of the interaction between ROS and spin trap molecules (Hideg et al. 1998, Hideg et al., 2000; Hideg et al., 2001).

The detection of ROS in cyanobacteria faces additional difficulties because their accessibility to EPR and fluorescent spin traps is limited. An alternative technique is chemical trapping by ROS scavengers like histidine. Recently, it was shown that chemical trapping by

histidine is suitable to monitor singlet oxygen generation in *Synechocystis* sp. PCC 6803 (Rehman et al., 2013).

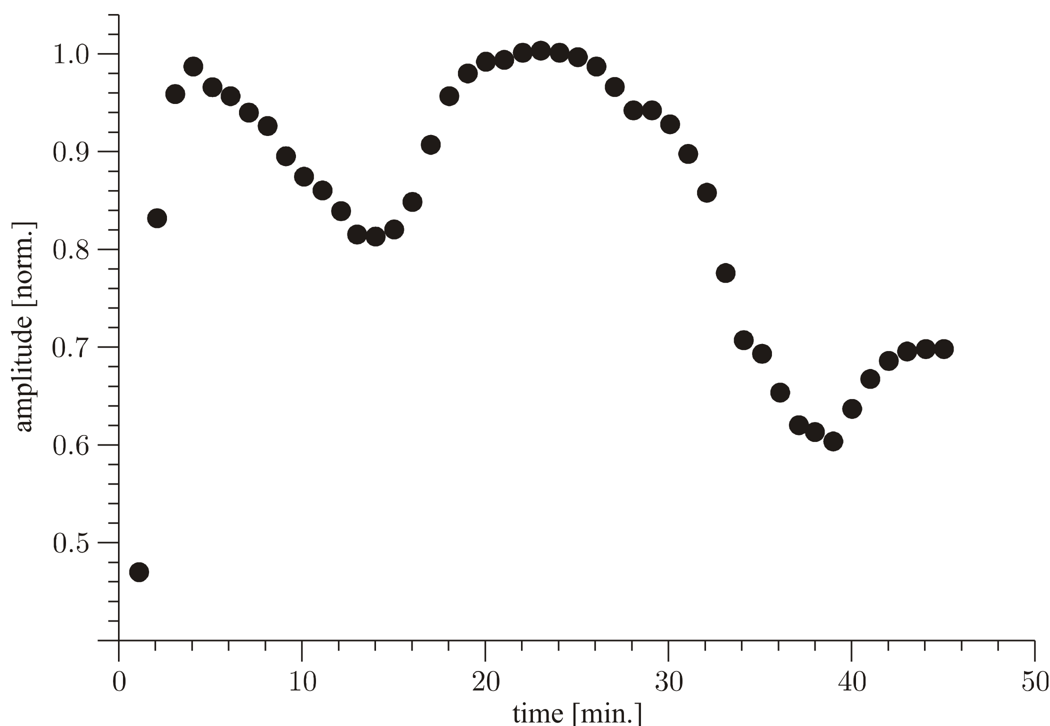


Figure 7. Temporal intensity variation of the DCF fluorescence emitted from a single cell of A.thaliana after incubating the leaves with Naph and illuminating with UV-A over 45 minutes

4.2. Genetically Encoded ROS Sensors

Fluorescence proteins, in particular the green fluorescent protein (GFP) and its variants are widely used tools to study a large variety of cellular processes (Tsien, 2008). They are used as novel biosensors for the local chemical environment in cells and cell organelles. Highly resolved fluorescence nanoscopy (Klar et al., 2000; Westphal et al., 2005) was boosted by the development of photo-switchable derivatives of GFP (Andresen et al., 2005; Andresen et al., 2007; Hofmann et al., 2005; Dedecker et al., 2007, Eggeling et al., 2007; Brakemann et al., 2011).

To exploit the potential of GFP for sensing the local chemical matrix, extensive studies have been undertaken to develop GFP-based *in vivo* sensors by targeted mutations and generalized approaches like directed evolution. The optical properties of these biosensors depend on selective binding of protons, oxygen atoms, water molecules and/or cofactors or are induced by electron transfer (Heim et al., 1995; Yang et al., 1996; Brakemann et al., 2011; Kremers et al., 2011).

Table 2. Spin traps suitable for imaging ROS

Compound	Specificity Further information / localizability
DMPO (Davies, 2002)	Spin trapping of $^1O_2$, superoxide and hydroxyl radicals, Transient EPR spectra specific for trapped radicals but spontaneous decay of DMPO-superoxide adduct with 45 sec. half lifetime
alpha-phenyl N-tertiary-butyl nitrone (PBN) (Davies, 2002)	EPR spectra rather unspecific for trapped radicals.
3,5-Dibromo-4-nitrosobenzenesulfonic acid (DBNBS) (Davies, 2002)	Used for H_2O_2 sensing, specific EPR spectra
5-Diisopropoxyphosphoryl-5-methyl-1-pyrroline-N-oxide (DIPPMPO) (Zoia and Argyropoulosm, 2010)	Used in mitochondria, strongly applied for detecting superoxide
TEMPO-9-AC (Cohn et al., 2008)	Fluorogenic spin trap specific for hydroxyl radicals and superoxide
BODIPY® 665/676 (Pap et al., 1999)	sensitive fluorescent reporter for lipid peroxidation
DanePy (Hideg et al., 1998, Hideg et al., 2000)	Specific to $^1O_2$ Fluorescent spin trap - Fluorescence is quenched in presence of $^1O_2$

Fluorescent proteins which are sensitive to the microenvironment like pH (Hanson et al., 2002; Miesenböck et al., 1998; Bizzarri et al., 2009; Campbell et al., 2001), ROS (Ostergaard et al., 2001; Schwarzländer et al., 2009; Belousov et al., 2006) or NADH (Hung et al., 2011) are used as standard tools for the selective imaging of physiological parameters and their dynamics. GFP can directly be targeted or fused to specific target proteins for precise sub-cellular localization and analysis *in vivo*. Genetically encoded ROS sensors are one approach to overcome problems regarding the specificity of localization of the applied dyes, Often the GFP-based ROS sensor variants contain pairs of redox-active cysteines forming a disulfide bridge as

redox switch. These proteins can be selectively expressed as fluorescence markers, fused to specific target proteins or to organelle-specific targeting sequences, thus enabling a specific and localized monitoring (and manipulation) of ROS at a molecular level (for a review, see Swanson et al., 2011).

Progress in engineering of ROS-sensitive fluorescence proteins led to the development of several derivatives of GFP containing the mentioned redox-active cysteins forming a disulfide bridge as redox switch (Jimenez-Banzo et al, 2001). One example is roGFP (Hanson et al., 2004; Schwarzländer et al., 2008). Derivatives of the yellow fluorescent protein (YFP) have also been described, which are modified by introduction of redox-active cysteins in constructs termed $rxYFP^{149}{}_{202}$ (Ostergaard et al., 2001) or HyPer (Belousov, 2006). Chromophore transformations in red-fluorescent proteins offer tools for designing suitable red-shifted probes, which are advantageous for imaging studies due to the strong absorption in the green spectral range, in which chlorophylls exhibit only very low absorption. Excitation with longer wavelengths also leads to reduced autofluorescence (for a review, see (Subach and Verkusha, 2012)).

The disulfide bridge in the oxidized rxYFP leads to a distortion of the typical beta-barrel structure of GFP derivatives, thus changing the fluorescence properties of rxYFP (Ostergaard, 2012). The mitochondrially-targeted redox sensitive GFP termed roGFP-mito does not specifically react in response to a certain species of ROS, but it is used to selectively label mitochondria in plants (Schwarzländer et al., 2009).

In an alternative approach, the H_2O_2-sensitive probe HyPer was constructed by fusing the regulatory domain of the H_2O_2-sensitive transcription factor OxyR from E. coli to a cyclically permuted YFP (Belousov, 2006). For applications of the genetically encoded ROS sensors in studies on ROS effects, see (Maulucci et al., 2008; Meyer and Dick, 2010; Mullineaux and Lawson, 2008).

Table 3 gives an overview on genetically encoded fluorescence proteins and their basic properties of selectivity and applicability in plants.

The application of fluorescence markers for ROS sensing is generally complicated by photobleaching. In addition, fluorophores often act as $^1\Delta_gO_2$ sensitizers themselves (see chapter 4.3). This problem is especially important for GFP derivates as ROS sensors. However, the generation of new GFP mutants that produce reduced amounts of ROS is a promising approach to overcome this problem, which again votes for the importance of developing improved genetically encoded fluorescence proteins for ROS sensing for future studies.

4.3 Chromophore-Assisted Laser Inactivation (CALI)

For investigations on ROS production and the effects of ROS species on cells or their constituents, a technique is desirable that enables controlled species-specific ROS production with high spatial precision and - ultimately - confined to distinct protein targets within a living cell.

Table 3. Genetically encoded fluorescence proteins applicable for ROS monitoring

Compound / reference	Specificity Further information / localizability
rxYFP (Ostergaard et al., 2001)	Unspecific
roGFP (Schwarzländer et al., 2008; Schwarzländer et al., 2009)	Unspecific, applied to label plant mitochondria
HyPer (Belousov et al., 2006)	H_2O_2 sensitive by fusing the regulatory domain of the H_2O_2-sensitive transcription factor OxyR to YFP, not yet expressed in plant cells
GFP redox sensor (Niethammer et al., 2009)	Specific to H_2O_2, successfully applied in Zebrafish larvae to detect H_2O_2 patterns after wounding

A novel approach that applies targeted production of ROS for selective inactivation of certain proteins by spatially-confined ROS generation is chromophore-activated laser inactivation (CALI).

CALI utilizes the general feature of fluorescent dyes to serve as ROS sensitizers, albeit they do so with variable species specificity and efficiency. As examples, two applications for CALI are listed. In the first, malachite-green-conjugated antibodies directed against purified proteins in solution or in cell membranes were used, and the protein-inactivating effect was initially thought to be due to localized heat generation in the vicinity of the chromophore (Jay, 1988). However, later reports showed that inactivation was due to the production of hydroxyl radicals with a radius for half-maximal damage of about 15 Å (Liao et al., 1994). Unfortunately, this approach is not suited to specifically attack protein targets in living cells. Cellular applications of CALI have greatly benefited from the availability of genetically-encoded chromophores such as the GFP and its spectral variants, which can act as ROS sensitizers (Jimenez-Banzo et al., 2008). $^1\Delta_gO_2$ production has been shown to occur from eGFP (Jimenez-Banzo et al., 2008) and TagRFP (Ragas et al., 2011), albeit with a low quantum yield of about 0.004. In contrast, KillerRed, which was developed from a non-fluorescent jellyfish red

chromoprotein (Bulina et al., 2006), was shown to exhibit a more than 1,000-fold enhanced phototoxicity compared to eGFP, and has successfully been used in CALI applications (Baumgart et al., 2012). Furthermore, chemical conjugation schemes were developed that allow for site-specific fluorescence labeling at cysteins by sulfhydryl coupling chemistry. A different labeling scheme utilizes short peptide motifs like the tetra-Cys motif CCxxCC that allows for the coupling of fluorescein (or resorufin) biarsenical hairpin reagents (FlAsH-EDT2 and ReAsH-EDT2, respectively) (Griffin et al., 1998; Griffin et al., 2000). Whereas unbound FlAsH-EDT2 or ReAsH-EDT2 are only very weakly fluorescent (Griffin et al., 2000; Madani et al., 2009), binding of the compounds to tetra-Cys motif-containing proteins results in the generation of fluorescent dithioarsolan-protein complexes. Since the biarsenical reagents are membrane-permeant, they can even be employed for intracellular protein labeling. In addition to their wide-spread use as labeling reagents for in vivo fluorescence imaging microscopy, biarsenical hairpin reagents have also been successfully used for CALI applications.

It has been shown that ReAsH is a better ROS sensitizer than FlAsH, produces $^1\Delta_gO_2$ within 3 nm precision (Tour et al., 2003), and thus efficiently inactivates proteins within an action radius of a few nm. This has been utilized to inactivate heterologously expressed connexin43, a constituent of gap junctions, and L-type Ca^{2+} channels, each endowed with a tetra-Cys-motif, with high spatial precision and efficiency in living cells (Tour et al., 2003). Also in this case, the CALI effect has been traced to $^1\Delta_gO_2$. Thus, the application of CALI, either with fluorescent proteins as ROS sensitizers or with the help of cell-permeant biarsenical hairpin reagents, will provide excellent means for the species- and target-specific monitoring of ROS and of ROS-induced signaling or protein repair pathways in photosynthetic organisms. Successful visualization of FlAsH-EDT_2- and ReAsH-EDT_2-labeled peptides in higher plants has been reported (Estevez and Somerville, 2006), but the potential of the CALI technique for plant cell research has not been exploited so far.

The elucidation of mechanistic details of ROS regulation pathways in plants will provide a framework for the elaboration of new strategies and methods for achieving the goal of improved stress tolerance of agricultural and industrial crops.

5. Signaling Role of ROS

During evolution ROS was steadily forming a constraint for the development of stable systems as living plants that had to adapt to the environment in an ideal fashion. Therefore in billions of years of evolutionary acclimation not only the damaging effects of ROS were

defeated but ROS developed a strong signaling role as the trigger mechanism for the processes that help to acclimatize to high ROS levels or even need ROS as cofactors. ROS have not only damaging but also a signaling role (Hung et al., 2005; Mubarakshina et al., 2010; Zorina et al., 2011; Kreslavski et al., 2012b, Kreslavski et al., 2013a). Figure 8 gives a general overview on the molecular generation and signaling of ROS and the acclimation of the photosynthetic aparatus (PA) (Zorina et al., 2011). The response of cells starts with the perception of stress by sensors or the response of sensors to ROS that are formed under stress conditions (Kanesaki et al., 2010).

Typically, cascades of mitogen-activated protein kinases (MAPK), other transcription factors (TFs), Ca^{2+}, phytohormones and other compounds function as sensors and/or transducers (Kaur and Gupta, 2005; Jung et al., 2009). In the following, characteristic examples will be described for the signaling action of $^1\Delta_gO_2$, H_2O_2 and $O_2^{-\bullet}$ in cells, seperatly discussed for cyanobacteria (chap. 5.1) and plants (chap. 5.2).

Detailed studies of such systems have been conducted in cyanobacteria. Especially, the important aspects of superoxide and hydrogen peroxide signaling in cyanobacteria is treated separately (chap. 5.1). As mentioned above, cyanobacteria serve as efficient models for studying the molecular mechanisms of stress responses. The genes of these cells can be easily knocked out or overexpressed which permit strightforward approaches to investigate the genetic aspects of signaling. This enabled the intensive studies of the potential stress sensors and signal transducers in cyanobacteria (Los et al. 2010; Kanesaki et al., 2010; Zorina et al., 2011, Kreslavski et al., 2013a).

Resulting from a long evolutionary adaption process, systems of perception and transduction of stress signals as well as the hormonal regulation system (see Figure 8) work in close coordination. Their interaction was fine-tuned during billions of years of evolution.

In the cytoplasm of plant cells, low temperature, drought and salinity cause an increased concentration of Ca^{2+}. In this case, calcium channels may serve as multifunctional sensors that perceive stress-induced changes in the physical properties of cell membranes (see Figure 8). The discovery of such multifunctional sensory systems is important to understand perception and transmission of stress signals. Apparently, changes in membrane fluidity, regardless of the nature of the stress effect are a signal that is perceived by sensory histidine kinases or ion channels localized in the membranes (Zorina et al., 2011; Kreslavski et al., 2013a).

It is known that ROS are produced in all cell compartments and their formation is necessary for the functioning of photosynthetic organisms (Suzuki and Mittler 2006). Certain ROS are considered as signaling molecules and regulators of expression of some chloroplast and

nuclear genes (Schmitt et al., 2014a; Kreslavski et al., 2013a; Minibayeva et al. 1998; Minibayeva and Gordon, 2003; Desikan et al., 2001, 2003; Hung et al., 2005; Galvez-Valdivieso and Mullineaux, 2010; Mubarakshina et al., 2010; Dickinson and Chang, 2011). A new view on the effects of ROS as signaling molecules first appeared in the study of hormone signaling and the regulation of expression of genes involved in plant protection from pathogen infections (Chen et al., 1993; Pei et al., 2000), conditions under which interactions of ROS with salicylic acid and nitric oxide play a crucial role in regulation of the response to infection (Wilson I.D. et al., 2008; Kreslavski, 2013a; Vallad and Goodman, 2004).

One of the key points in understanding of the effect of ROS on photosynthesis was the discovery of the formation of the superoxide anion and hydrogen peroxide in the pseudo-cyclic electron transport (See Figure 3), which does not lead to the reduction of $NADP^+$, but to the absorption of O_2 (Asada, 1999). In addition, it was shown that the activation of plasma membrane redox-systems and the increased formation of ROS in the apoplast is one of the universal reactions of plant cells to stress (Kreslavski et al., 2013a; Minibayeva et al., 1998, 2009; Minibayeva and Gordon, 2003; Dickinson and Chang, 2011).

It was found that the main generators of ROS in the apoplast of root cells are the cell wall peroxidases (Minibayeva et al., 2009; Minibayeva and Gordon, 2003). Apparently, the release of ROS from cells followed by a switch of peroxidase/oxidase modes of extracellular peroxidases form the basis for the fast response of plant cells to stress.

In addition to ROS, the stress signaling functions may be attributed to some metabolites, whose formation is initiated by ROS, for example, the products of lipid peroxidation (LP) (see Figure 8). The primary subjects for peroxidation in living cells are unsaturated fatty acids that constitute major components of phospho- and glycolipids of biological membranes.

ROS regulate the processes of polar growth, the activity of stomata, light-induced movement of chloroplasts and plant responses to the action of biotic and abiotic environmental actors (Pitzschke and Hirt, 2006; Miller et al., 2007; Swanson and Gilroy, 2010).

Signaling by ROS may be realized through changes in potential of the redox-sensitive cell systems and through phosphorylation/dephosphorylation cycles of signaling proteins (transcription factors, etc). The accumulation of redox-active compounds such as ROS within the chloroplast is associated with the rate of photosynthetic electron transport. Redox-sensitive thioredoxin or PQ may act as sensors of changes in redox properties under stress conditions (Figure 3). Signals generated from modulation in the activity of ETC may also lead to changes in gene expression (Vallad and Goodman, 2004).

Although many things have been ruled out form the mechanisms of action of ROS as signal molecules, there are still many gaps in understanding the complete network of these regulatory

events. The sensor(s) of H_2O_2 in higher plants remain largely unknown (Galvez-Valdivieso and Mullineaux, 2010; Mubarakshina et al., 2010; Kreslavski et al., 2012b). There is no information about specific proteins that convert a signal about an increase in the intracellular ROS levels to a biochemical response in the cells. It is not known exactly which particular ROS play a signaling role in the chloroplast and other cellular compartments and how different signaling pathways respond to an increase in the level of different types of ROS. Knowledge of the mechanisms of regulation of these signaling pathways may help to construct biochemical pathways and to produce genetically engineered plants with enhanced stress resistance.

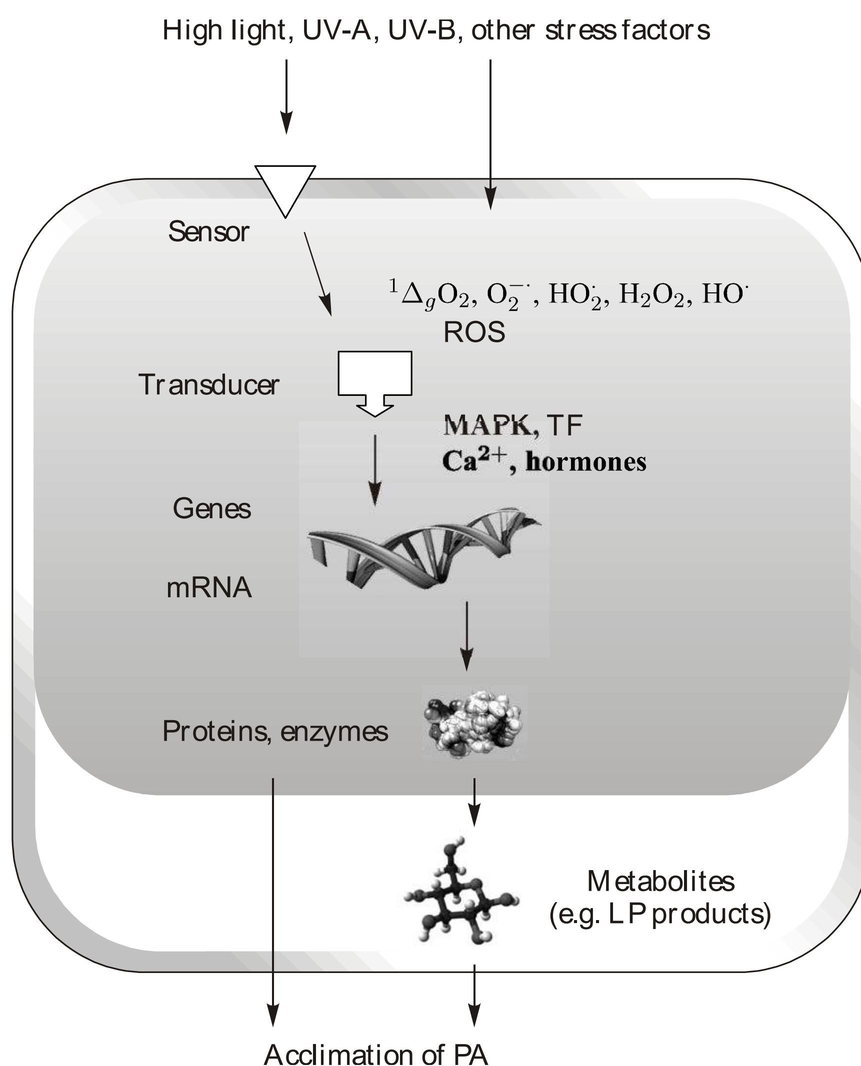


Figure 8. Scheme for perception and transduction of stress signals and formation of ROS as signal molecules for genetic signaling supporting the acclimation of cells to stress conditions (adapted from Zorina et al., 2011)

High light, especially high doses of UV-A or UV-B lead to the damage of the PA. Plastoquinones (the primary and secondary plastoquinone, Q_A and Q_B, respectively) as well as the D1 and D2 proteins are amongst the primary targets of UV radiation (Strid et al., 1994; Babu

et al., 1999; Asada, 2006; Carvalho et al., 2011). The Mn_4CaO_5 cluster of PSII is also vulnerable to damage by UV irradiation (Najafpour et al., 2013). However, UV light-induced damage can also depend on the additional interaction with light in the visible region. Or – more generally spoken – the light induced signaling after interaction of visible light with certain sensors leads to the activation of protection mechanisms agains UV-A and UV-B.

Red light (RL) of low intensity can alleviate the negative effect of UV radiation on plants and their PA (Lingakumar and Kulandaivelu, 1993; Qi et al., 2000, 2002; Biswal et al., 2003; Sicora et al., 2003; Kreslavski et al., 2012a,b; Kreslavski et al., 2013a,b,c; Kreslavski et al., 2014a,b). Recent studies have shown that low intensity RL pulses activate the phytochrome system, which triggers protective mechanisms against UV-radiation (Kreslavski et al., 2013a,b). However, many details of this protective action of RL acting via the phytochrome system on PA have not been clarified so far.

The phytochrome system plays an important role in plant growth and PA development. This concept is in agreement with recent studies on mutant *Arabidopsis* strains with deficiencies in different types of phytochromes, which demonstrated that deletion of phytochromes is critical for plant development (Strasser et al., 2010; Zhao et al., 2013). Even if light capable of driving photosynthesis is available, normal seedling greening and plant development is impossible if phytochromes are absent (Strasser et al., 2010; Zhao et al., 2013). The effects of phytochrome deficiency on photosynthetic parameters have been investigated in previous studies, including the impact on PSII activity (Kreslavski et al., 2013b) and Chl (*a*+*b*) content (Strasser et al., 2010; Zhao et al., 2013).

Protective effects against UV are caused by the RL-induced formation of the far-red-absorbing active form of phytochrome and/or enhancement of phytochrome biosynthesis as a result of RL illumination (Kreslavski et al., 2012a, 2013b, c). It was suggested that this protective effect is due to decreased Chl degradation and higher stability of the PSII, as well as higher photochemical activity and a reduced damage of thylakoid membranes (Lingakumar and Kulandaivelu, 1993; Biswal et al., 2003; Kreslavski et al., 2004). On the other hand, a decreased phytochrome level can reduce the resistance of the PA. For example, *hy2* mutants of *Arabidopsis* show a decreased level of PhyB and other pytochromes due to reduced biosynthesis of the phytochrome chromophore, phytochromobilin (Parks and Quail, 1991). This *hy2* mutant also showed decreased UV-A resistance of PSII, as determined from delayed luminescence emission (Kreslavski et al., 2013b). It was also shown that the resistance of PA in *Arabidopsis* WT increased after preillumination with RL, whereas in the *hy2* mutant the PSII resistance to UV-A did not change upon the same treatment. It was suggested that the PA resistance to UV radiation depends on the ratio of pro- and antioxidant compounds, which can be affected by PhyB and

other phytochromes (Kreslavski et al., 2013b). The role of different phytochromes for the UV resistance of PSII has not been studied so far.

PhyB, one of the key phytochromes in green plants, is involved in the synthesis of photosynthetic pigments, chloroplast development (Zhao et al., 2013), as well as in the synthesis of some photosynthetic proteins and stomatal activity (Boccalandro et al., 2009). It is also known that an increased PhyB content can enhance the resistance of the photosynthetic machinery to environmental stress (Thiele et al., 1999; Boccalandro et al., 2009; Carvalho et al., 2011; Kreslavskii et al., 2012a,c; Kreslavski et al. 2004, 2013b,c). In particular, transgenic cotton plants, in which the phytochrome B (PhyB) gene of Arabidopsis thaliana was introduced, showed more than a two-fold increase in the photosynthetic rate and more than a four-fold increase in transpiration rate and stomatal conductance (Rao et al. 2011). In addition, the increase of PhyB content in transgenic potato plants (Dara-5 and Dara-12), which are superproducers of PhyB, led to enhanced resistance of the PA to high irradiance (Thiele et al., 1999). It can be suggested that the increased resistance results from higher Chl content or enhanced stomatal conductance.

Today it is well established that ROS exert important functions in signaling pathways within the cells of both plants and animals. The mode of signaling under the participation of ROS depends on the nature of stress. In response to different types of stress, ROS can act in a dual manner: a) by functioning as signal molecules which induce molecular, biochemical, and physiological responses leading to development of adaptive mechanisms and improving the tolerance of the organisms to stress (acclimation) or b) by inducing reaction sequences that eventually cause programmed cell death (Galvez-Valdivieso and Mullineaux, 2010; Mittler et al., 2011; Vranova et al., 2002; Kreslavski et al., 2007; Jaspers and Kangasjärvi , 2010; Los et al., 2010; Kreslavski et al., 2011).

In general, significant differences exist in the response to abiotic (light, draught, cold, heat etc.) and biotic (infection by viruses and bacteria) stress. This includes also the type of ROS molecules involved. In case of abiotic stress, $^1\Delta_gO_2$ is often formed in addition to $O_2^{-\bullet}$ and H_2O_2, while biotic stress mainly leads to enzymatic generation of $O_2^{-\bullet}$ and H_2O_2 which are used as a defense mechanism against biotic stress (Laloi et al., 2004). Different types of ROS give rise to specific signaling, as has been shown in animal cells (Klotz et al., 2003).

ROS have several advantages in acting as signal molecules (Miller et al., 2009; Mittler et al., 2011): i) Cells are able to rapidly generate and scavenge different forms of ROS in a simultaneous manner, thereby permitting rapid response to stress. ii) The subcellular localization of ROS signals can be strongly controlled within cells, i.e. a spatial control of ROS accumulation

exists in a highly specific manner. iii) ROS can be used as rapid long-distance auto-propagating signals to be transferred throughout the plant, as recently reported for *Arabidopsis thaliana*, in which ROS signals propagate at rates of up to 8.4 cm/min (Miller et al., 2009, Schmitt at al., 2014a). iv) ROS are tightly linked to cellular homeostasis and metabolism.

Most probably, the mechanism of stromatal closure and it spatiotemporal patterns result from an underlaying ROS signaling mechanism. Therefore, it is proposed that ROS are implemented in very general signaling schemes that influence the expression of genes and consequently the molecular biology of green plants. Additionally, ROS are responsible for macroscopic long range effects that are directly observable on the cellular level like stromatal closure. It is a trigger for adaption of the whole cell metabolism and, in case of biotic stress, actively produced with respect to long range interaction as found for $O_2^{-\bullet}$ and H_2O_2 (in contrast to singlet oxygen which has a much shorter lifetime) to be used as oxidizing defense molecules against the biotic stressors.

A comparison with ROS signaling in animal cells revealed that the communication of mitochondria in heart cells occurs via ROS-induced waves. An abrupt collapse or oscillation of the mitochondrial energy state is assumed to be synchronized across the mitochondrial network by local ROS-mediated interactions (Zhou et al., 2010; Zhou and O'Rourke, 2012). This model is based on the idea that a depolarization of the electrical potential difference across the coupling membrane is specifically mediated by $O_2^{-\bullet}$ via its diffusion and the $O_2^{-\bullet}$-dependent activation of an inner membrane anion channel, in agreement with experimental data. This mode of a ROS-induced ROS release mechanism in animal cells can also be used in plants for propagation of cell-to-cell ROS signaling over long distances (Miller et al., 2009; Mittler et al., 2011).

The concept of a transient ROS burst occurring in selected cells can be further extended to the more general concept of a ROS wave propagating in time and space as response to different types of stress (Schmitt et al., 2014a).

5.1. Signaling by Superoxide and Hydrogen Peroxide in Cyanobacteria

Various mechanisms are involved in the signal function of ROS. At first, ROS-induced modifications of proteins can lead to changes of either structure or activity or both, in particular via oxidation of thiol groups.

Illustrative examples are the suppression of CO_2 fixation and the blockage of the elongation factor EF-G in cyanobacteria and iron-containing clusters in enzymes (Spadaro et al., 2010). The oxidation of EF-G represents a rather general signaling scheme. Such a reaction chain as

represented by the EF-G oxidation can be understood as a chemical inactivation process that is switched on and off by the oxidative potential. High oxidative potential in cyanobacteria leads to the oxidation of the two residues 105Cys and 242Cys in EF-G, and subsequent formation of a disulfide bridge between the two cysteine residues blocks the elongation of translation (Kojima et al., 2007). Replacement of these conserved cysteine residues by serine makes EF-G insensitive to ROS (Kojima et al., 2009). The mechanism of translation blockage under the influence of oxidative stress via post-translational redox regulation of the elongation factor state is a universal way of cell protection against ROS. Thus, EF-G is a primary target for ROS action and a key regulator of the translation efficiency (Nishiyama and Allakhverdiev, 2011; Murata et al., 2012).

This H_2O_2-induced blockage of the translation machinery interrupts the repair of photodamaged PS II, thus eventually leading to the disappearance of PS II and, consequently, the interruption of the linear electron transport chain. Studies on the effect of other stress factors (heat, drought, salinity) on photoinhibition have shown that the suppression of PS II repair determines the PS II sensitivity of cyanobacteria to environmental conditions (Allakhverdiev and Murata, 2004; Murata et al., 2007; Nishiyama and Allakhverdiev, 2011; Murata et al., 2012).

The two Cys residues oxidatively linked to an S-S bridge by H_2O_2 are highly conserved in EF-G of cyanobacteria and of chloroplasts in algae and higher plants. Therefore, it seems very likely that ROS induces similar effects in the chloroplasts of plant cells. The translation of the D1 protein in chloroplasts is also regulated by redox components at both initiation and elongation steps (Zhang et al., 2000). A marked difference to cyanobacterial D1 is the possibility to phosphorylate D1 in plants. This property permits a regulation process of the circadian rhythm of degradation and metabolism. In this context, it is important to know the extent of how ROS affect the phosphorylation pattern of D1 in plants. This question remains to be answered in future studies.

Depending on the lifetime, different types of ROS molecules can either directly act as signal molecules or generate signal chains by formation of oxidation products (e.g. LP, see Figure 8).

It must be emphasized that fundamental differences exist between prokaryotic cyanobacteria and eukaryotic plants. In cyanobacteria, the photosynthetic and respiratory electron transport reactions take place in the intracytoplasmic (thylakoids) and cytoplasmic membrane, respectively, and close interactions exist between both photosynthesis and respiration (Peschek, 2008). On the other hand, eukaryotic plant cells contain semi-autonomous organelles (chloroplasts, mitochondria, peroxisomes, nucleus) with specific functional activities. This differentiation requires a more complex signaling system for "cross-talk" between these organelles. As a consequence, the mechanisms of "handling" stress-induced ROS and the modes

of protection are markedly different between cyanobacteria and plants, and even within the plant kingdom. Therefore, a generalized and unified scheme cannot be presented ate the moment and only selected characteristic examples of signaling are presented.

In cyanobacteria and plants, the $O_2^{-\bullet}$ radical is predominantly produced at the acceptor side of PS I (Asada, 1999). The lifetime of $O_2^{-\bullet}$ is mainly determined by the presence of SOD and does not exceed a few microseconds in cells (Gechev et al., 2006). The signaling function of $O_2^{-\bullet}$ has been investigated by analyses of gene expression using DNA microarrays (Scarpeci et al., 2008) and studies on $O_2^{-\bullet}$ accumulation in plants deficient in Cu/Zn-SOD (Rizhsky et al., 2003). The results are in favor of a signaling role of this radical but details of the pathway(s) are not well known today.

$O_2^{-\bullet}$ can react with NO under formation of peroxinitrite. This species is likely to be synthesized in chloroplasts, where it can fulfill signaling functions (Foyer and Shigeoka, 2011). Under normal pH conditions, $O_2^{-\bullet}$ is deprotonated in animal cells (pH = 7.4 in blood cells) due to its pK_a value of 4.8. However, at sufficiently low pH values (e.g. sometimes existing in the thylakoid lumen, see Joliot and Joliot, 2005), $O_2^{-\bullet}$ anion radicals become protonated and the neutral hydroperoxyl radical ($HO_2^{\bullet}$) can cross membranes (Sagi and Fluhr, 2006) (see chapter 2).

The formation of H_2O_2 occurs mainly via the formation of $O_2^{-\bullet}$ followed by SOD-catalyzed dismutation (Asada, 1999; Asada, 2006) and in the process of photorespiration (Foyer and Noctor, 2009) (see Figure 2). H_2O_2 is markedly less reactive than $^1\Delta_gO_2$ (Halliwell and Gutteridge, 1985) (see chap. 2) and characterized by a much longer lifetime in the order of 1 ms (Henzler and Steudle, 2000; Gechev and Hille, 2005). Therefore, H_2O_2 is a most promising candidate to function as an intra- and intercellular messenger (Vranova et al., 2002; Hung et al., 2005; Bienert et al., 2007; Foyer and Shigeoka, 2011; Mittler et al., 2011). Numerous results on H_2O_2 signaling were reported for both, prokaryotic cyanobacteria and eukaryotic plants.

Eubacteria, including cyanobacteria, actively use characteristic two-component systems of signal perception and transduction (Kreslavski et al., 2013a).

Such two-component regulatory systems are typically composed of a sensory histidine kinase (Hik) and a response regulator form the central core of the phosphate signaling system in cyanobacteria (Los et al., 2010; Kreslavski et al., 2013a). The sensory histidine kinase perceives changes in the environment with its sensory domain. A subsequent change of its conformation often leads to autophosphorylation of the conservative histidine residue in a Hik from a donor ATP molecule from which a phosphate group is then transferred to the conserved aspartate in a

receiver domain of the response regulator protein (RRP). After phosphorylation, the RRP also changes its conformation and gains (positive regulation) or looses (negative regulation) the ability to bind to DNA. The RRP usually binds the promoter region(s) of genes for proteins that are involved in the stress signal network or are linked to stress protection pathways (Kreslavski et al., 2013 a).

Hik33 of *Synechocystis* is the multisensory protein, which perceives cold, salt, and oxidative stresses. The mechanisms by which Hik33 recognizes the stresses are still not fully clear. It is assumed that changes in the physical mobility of membrane lipids and changes in the surface charge on the membrane, associated with changing mobility, are activators for Hik33. Activation may be also caused by depolarization of the cytoplasmic membrane upon cold stress or due to changes in charge density of the membrane surface under stress (Nazarenko et al., 2003; Kreslavski et al., 2013a).

Sensory histidine kinases are also important for the functioning of genes involved in photosynthesis and/or regulated by high light intensity. Experiments with the *Synechocystis* mutant deficient in Hik33 (this mutant is also named DspA, see Hsiao et al., 2004) revealed that low or moderate light intensity causes retardation in growth and decrease in photosynthetic oxygen evolution in mutant cells, compared to wild-type cells, under photoautotrophic conditions. The addition of glucose neutralized these differences. However, mutant cells were more sensitive to light intensity and quickly died under strong light (Hsiao et al., 2004; Kreslavski et al., 2013a).

The defense of bacteria against oxidative stress and adaptive regulation mechanisms have been thoroughly analyzed in *Escherichia* (*E.*) *coli* and *Bacillus* (*B.*) *subtilis*. In eubacteria (heterotrophic, autotrophic, and chemotrophic), two global regulators, OxyR and PerR, are involved in the control of gene transcription induced by H_2O_2 addition (Zheng et al., 1998) (see Figure 10). Both these regulators have active thiol groups and can directly recognize changes in the redox state of the cytoplasm. The ferric uptake repressor (Fur) type protein PerR was found to be the central regulator of inducible stress response (Herbig and Helmann, 2001; Mongkolsuk and Helmann, 2002). In the cyanobacterium *Synechocystis* sp. PCC 6803, a gene (*srl*1738) encoding a protein similar to PerR was identified as being induced by H_2O_2 (Li et al., 2004) in methylviologen treated cells upon illumination (Kobayashi et al., 2004). It was concluded that the Fur-type protein Slr 1738 functions as a regulator in inducing the potent antioxidant gene *sll*1621, which encodes for a peroxiredoxin.

The regulator OxyR is absent in *Synechocystis* sp. PCC 6803. Studies on *Synechocystis* sp. PCC 6803 incubated for 20 min with 0.25 mM H_2O_2 proved how several histidine kinases can serve as H_2O_2 sensors (Kreslavski et al., 2013a). Mutations of genes Hik34, Hik16, Hik41,

and Hik33 encoding histidine kinases led to blockage of the H_2O_2-induced gene expression (Zheng et al., 1998). Peroxidases were found to control 26 of 77 genes induced by H_2O_2. The histidine kinase Hik34 was shown to regulate the expression of the gene htpG under oxidative stress. This kinase was characterized as regulator of gene expression due to heat (Suzuki et al., 2005), salt, and hyperosmotic stress (Shoumskaya et al., 2005). In addition, Hik34 is subjected to autoregulation in the presence of H_2O_2. The pair of histidine kinases Hik16-Hik41 regulates the genes sll0967 and sll0939 with unknown functions not only in response to H_2O_2 but also under salinity and hyperosmotic stress. Hik33 controls 22 genes; among them are ndhD2 encoding NADH dehydrogenase, three hli (high-light-inducible) genes, pgr5 encoding ferredoxin-plastoquinone reductase, the genes nblA1 and nblA2 involved in phycobilisome degradation, and others.

It should be noted that ROS induce also the expression of the genes hspA, dnaJ, dnaK2, clpB1, ctpA and sigB. These genes were activated by mechanisms without the involvement of histidine kinases, although Hik34 is acting as repressor of genes encoding heat shock proteins (Zheng et al., 1998; Kanesaki et al., 2002; Suzuki et al., 2005; Los et al., 2010).

In addition to histidine kinases, the transcription factor PerR participates in the response of Synechocystis sp. PCC 6803 to ROS. PerR is involved in the regulation of only six genes, of which four encode proteins with unknown function. Based on evidence for both PerR and Hik33 being components in the control of the induction of nbl gene expression due to oxidative stress, it seems possible that PerR interacts with a two-component regulatory system (Zheng et al., 1998; Kanesaki et al., 2002; Suzuki et al., 2005; Los et al., 2010).

5.2. Signaling by $^1\Delta_gO_2$ and Hydrogen Peroxide in Eucaryotic Cells and Plants

In plants cells, $^1\Delta_gO_2$ is known to function predominantly as a plastid ROS signal which activates nuclear gene expression (Li et al., 2012). Because of its high reactivity, $^1\Delta_gO_2$ has a very short lifetime in cells (about 200 ns (Gorman and Rodgers, 1992) and, consequently, a rather limited diffusion radius (for a report on markedly longer lifetime in cells, see (Skovsen et al., 2005)). Therefore, the involvement of additional components is required for signal transfer from the site of formation within the chloroplast through the cytosol to the nucleus, which is termed chloroplast-to-nucleus signaling (Kreslavski et al., 2012b, Schmitt et al., 2014a).

Generally like in canobacteria, so also in plants, two types of fundamentally different responses to $^1\Delta_gO_2$ stress are known: i) development of increased tolerance and ii) induction of programmed cell death.

A $^1\Delta_gO_2$ signaling pathway in *C. reinhardtii* was shown to give rise to gene expression that leads to increased tolerance to ROS (acclimation). This phenomenon comprises enhanced expression of genes for ROS protection and detoxification, e.g. of a glutathione peroxidase-homologous gene (*gpxh/gpsx*), and also the expression of a σ-class glutathione-S-transferase gene (*gsts*) greatly increases (Fischer et al., 2012). The effect on components participating in signaling was analyzed in a $^1\Delta_gO_2$-resistant mutant (SOR 1). The results obtained revealed the involvement of reactive electrophilic species that are formed by $^1\Delta_gO_2$-induced lipid peroxidation (Fischer et al., 2012). It was found that the *SOR1* gene encodes a leucine zipper transcription factor, which controls the expression of numerous genes of stress response and detoxification. It was inferred from these results that reactive electrophilic species play a key signaling role in acclimation of *C. reinhardtii* cells to $^1\Delta_gO_2$ stress (Kreslavski et al., 2012b).

In many cases, $^1\Delta_gO_2$ signaling induces programmed cell death, in particular under biotic stress. Much information on the genetic control of this phenomenon has been gathered from investigations on the *A. thaliana* mutant *flu1* which is defective in the feedback control of the Chl biosynthesis pathway. This mutant, which accumulates the photosensitizer protochlorophyllide in the dark, generates $^1\Delta_gO_2$ within the first minute of illumination after a dark-to-light shift (op den Camp et al., 2003). The $^1\Delta_gO_2$ formation taking place in the vicinity of the thylakoid membrane (Przybyla et al., 2008) can be manipulated by altering the degree of light exposure and the preceding dark period. In contrast to wild-type plants, the $^1\Delta_gO_2$ production in *flu1* is not associated with excess excitation of PSII (Mullineaux and Baker, 2010). The studies on the *flu1* mutant revealed that $^1\Delta_gO_2$ can trigger the activation of programmed cell death and that two chloroplast-located proteins, EXECUTER1 and 2 (EXE1 and EXE2), control this process (Przybyla et al., 2008; Wagner et al., 2004; Lee et al., 2007) (see Figure 12). EXE1 and EXE2 act as suppressors (Wagner et al., 2004; Lee et al., 2007), but their mode of function in signaling of the $^1\Delta_gO_2$-induced programmed cell death is not yet resolved.

As a consequence of the special mode of $^1\Delta_gO_2$ formation in the *flu1* mutant, a cell death in their leaves can be induced either due to direct oxidative destruction (necrosis) under a large excess of ROS or at a slower rate of $^1\Delta_gO_2$ formation via signaling the activation of a programmed cell death pathway.

On the basis of data obtained on *C. reinhardtii* cells, $^1\Delta_gO_2$ was inferred to be able to leave chloroplasts directly into the cytosol and even to reach the nucleus, thereby inducing the expression of nuclear gene *gpxh*, which encodes glutathione peroxidase (Fischer et al., 2007). Since the fraction of “mobile” $^1\Delta_gO_2$ is extremely small, a direct effect of $^1\Delta_gO_2$ was manifested only under high light and so far observed only in cells of this microalga (Fischer et al., 2007). It

appears much more likely that oxidation products of special molecules are formed, which act as second signal messengers and are transferred via the cytosol and to the nucleus. This idea is confirmed by experimental data obtained on both, cells of the unicellular green alga *C. reinhardtii* and multicellular leaves of the higher plant *A. thaliana*. In the latter, plant ß-cyclocitral was shown to be formed by the oxidation of ß-carotene under ROS stress and identified as a stress signal that acts as a second messenger in $^1\Delta_gO_2$ signaling (Ramel et al., 2012). Likewise, oxidation of polyunsaturated fatty acids due to interaction with $^1\Delta_gO_2$ in the lipid fraction of thylakoid membranes leads to formation of reactive electrophilic species, which are able to exit into the cytosol (Galvez-Valdivieso and Mullineaux, 2010). Via autocatalytic cascades, lipoperoxide radicals can result in generation of $^1\Delta_gO_2$ in the cytosol (Flors et al., 2006) and trigger the EXE1/EXE2-mediated pathway of programmed cell death (Wagner et al., 2004).

The enzymatic peroxidation of lipids is catalyzed by lipoxygenases. These enzymes play an essential role in response to pathogen infection and wounding (Feussner and Wasternack, 2002; Overmyer and Brosché, 2003; Hoeberichts and Woltering, 2003). Specific lipoxygenase pathways lead to formation of lipoxide species which are likely to be different when induced by chemically different ROS like $^1\Delta_gO_2$ versus $O_2^{-\bullet}/H_2O_2$. Studies on the *flu1* mutant of *A. thaliana* revealed that 70 genes are up-regulated by $^1\Delta_gO_2$ but not by $O_2^{-\bullet}/H_2O_2$, the latter being formed at PS I via the methylviologen mediation reaction (op den Camp et al., 2003).

The signaling pathway(s) of $^1\Delta_gO_2$ leading to cell apoptosis tightly interact(s) with other signaling pathways involving hormones and other ROS. The $^1\Delta_gO_2$ species activates the signaling pathways controlled by salicylic and jasmonic acid resulting in changes of the expression of numerous genes which are related to anti-stress defense systems. An example of regulatory interaction is the decrease in cell injury and death induced by $^1\Delta_gO_2$ due to its conversion into H_2O_2 (Laloi et al. 2007).

This effect is possible because the cell is able to scavenge $^1\Delta_gO_2$ via the increase of the amount of lipid-soluble antioxidants and also the acceleration of reduction of photodamaged D1 protein in the PS II reaction center. This pathway counteracts cell apoptosis along the EXE1 and EXE2 pathways (Mullineaux and Baker 2010).

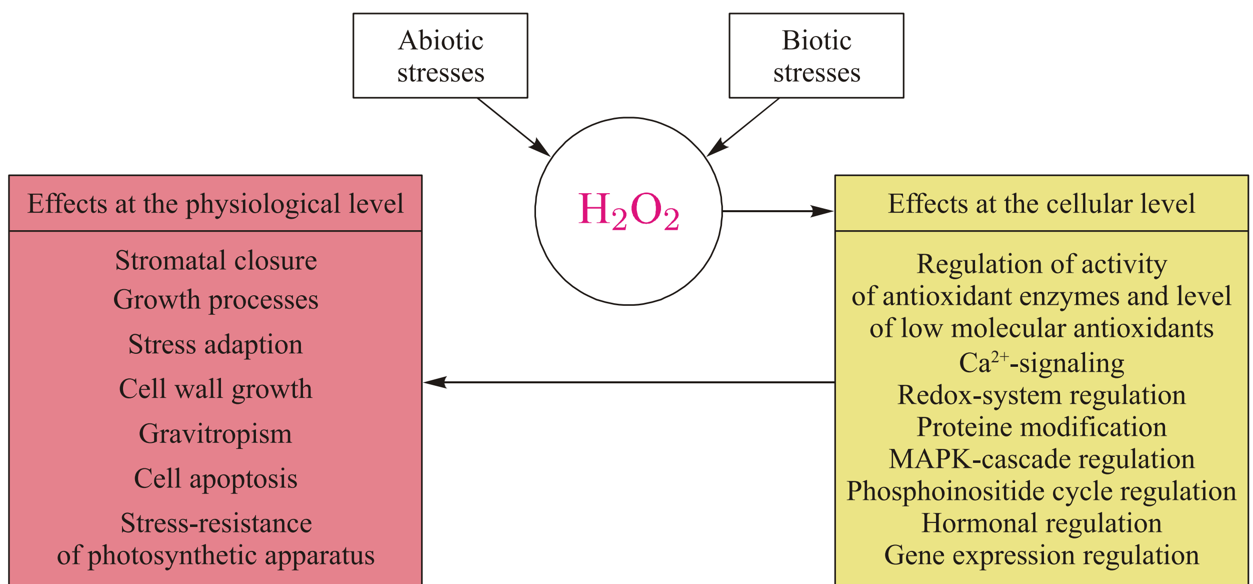


Figure 9. Cellular and physiological processes regulated by H_2O_2

H_2O_2 stress in plants induces the expression of many chloroplast and nuclear genes (Figure 9) (Foyer and Noctor, 2009; Bechtold et al., 2008). It was found that several genes are down-regulated, while others are up-regulated (Vandenabeele et al., 2004). In particular, H_2O_2 was shown to activate several genes encoding antioxidant and signaling proteins: ascorbate peroxidase (APX), glutathione reductase, catalase, mitogen-activated protein kinase (MAPK), and phosphatases (see Figure 3, Figure 8 and Figure 12) (Mullineaux et al., 2000; Vranova et al., 2002). H_2O_2 of chloroplast origin can serve as a redox signal which triggers the expression of the gene encoding cytoplasmic APX2 (Davletova et al., 2005). Likewise H_2O_2 of extracellular/plasmamembrane origin has been shown to be important for APX2 expression (Bechtold et al., 2008; Galvez-Valdivieso et al., 2009). Furthermore, H_2O_2 is also involved in inducing the expression of some light-responsive genes.

Plant treatment with H_2O_2 stimulates the expression of the gene APX2 and of genes ZAT10 and ZAT12, which encode transcription factors (Davletova et al., 2005; Rossel et al., 2007). Both factors ZAT10 and ZAT12 mediate different subsets of the high light-inducible or -repressible gene set, including genes coding for APX2 and APX1, respectively.

It has been suggested that H_2O_2 molecules produced in the chloroplasts can exit the organelles by diffusion, likely via water channels (aquaporins), and induce signaling processes in the cytoplasm (Mubarakshina et al., 2010), i.e. triggering the MAPK cascade (Pfannschmidt et al., 2009), by which nuclear genes are activated in the cell, in particular the gene encoding cytoplasmic APX (Apel and Hirt, 2004; Yabuta et al., 2004; Vranova et al., 2012). H_2O_2, produced on the cytoplasmic membrane or in the apoplast, can also play a signaling role, possibly by functioning together with abscisic acid (Bechtold et al., 2008; Yabuta et al., 2004).

A new genetic approach for analyzing the signaling effect of H_2O_2 in plants has been reported (Maruta et al., 2012). This method is based on chemically inducible RNAi. It has been shown that silencing the expression of ascorbate peroxidase bound to the thylakoid membrane (t-APX) in *A. thaliana* leaves leads to both, an increase of the fraction of oxidized proteins in chloroplasts and to effects on the expression of a large set of genes. Among these, the transcription levels of a central regulator of cold acclimation are suppressed and the levels of salicylic acid (SA) increase together with the response to SA. The results reveal synergistic and antagonistic effects of H_2O_2, when chloroplasts are exposed to high light.

Another striking feature is the finding that growth of *A. thaliana* plants under short-day illumination gives rise to a diminished expression of several genes which are involved in sensing and hormone synthesis (Thimm et al., 2004). It was found that the level of ROS production is higher by a factor of about two in leaves from short-day (8 h light) tobacco than in leaves from long-day (16 h light) plants. Based on these results, an unknown regulatory protein was proposed to exist which changes the relative extent of cyclic and pseudo-cyclic photosynthetic electron transport, thereby affecting the ROS content in chloroplasts (Michelet and Krieger-Liszkay, 2012). These findings suggest that light sensor(s) participate in this phenomenon.

The expression of ROS sensitive genes was shown to depend on diurnal and circadian conditions, thus illustrating a role of the biological clock in transcriptional regulation of these genes. Likewise, H_2O_2 generation and scavenging exhibit a diurnal rhythm. These findings indicate that an important functional relation exists between ROS signaling and circadian output, which provides a mechanistic link for plant response to oxidative stress (Lai et al., 2012). The components involved and the underlying mechanism(s) of these mutual interactions of signal networks are not yet resolved and represent challenging topics for future research.

6. Light Induced ROS and Cell Redox Control and Interaction with the Nuclear Gene Expression

The discovery of multisensory systems is important for understanding the basic question how perception and transmission of stress signals operate in large cell cultures and tissue. Generally, this becomes more complicated in plants than in cyanobacteria. Apparently, changes in membrane fluidity, regardless of the nature of the stress effects, are a signal that is perceived by sensory histidine kinases or ion channels localized in the membranes. The ROS signals are transducued by rather macroscopic structures like membranes that regulate single molecules like Hik signaling directly to the molecular fundament of each cell, the genome. Therefore ROS

signaling covers a large hierarchy from top down and bottom up mechanisms involving the genome, the proteom, cell tissues and the whole organism.

Structural modifications give rise to detachment of weakly bound enzymes from the cell wall, as shown for the isoforms of peroxidases (Minibayeva and Gordon, 2003). Concomitantly, ROS modulate the activity of antioxidant enzymes, e.g. in case of catalase and ascorbate peroxidases (Shao et al., 2008). Likewise, also the redox state of cell components acting as antioxidants or being involved in signaling (glutathione system, ascorbate system, plastoquinone pool, thioredoxin, etc.) is prone to changes by ROS (see Figure 3 and chap. 6). Furthermore, the activity of ion channels can be affected, goin along with variations in the concentration of relevant ions like Ca^{2+} in the cytosol (see chap. 5).

The by far most important regulatory control in acclimation of organisms to different stress factors is the modulation of gene expression. ROS in general and H_2O_2 in particular play an important role in cell signaling pathways and are involved in the regulation of gene expression (Apel and Hirt, 2004; Laloi et al., 2007). Studies using DNA microarrays (Gadjev et al., 2006; Scarpeci et al., 2008) revealed that an increase of the ROS concentration affects the expression of a rather large number of genes. This response can sometimes comprise up to one third of the entire genome. Experiments performed with the unicellular green alga *Chlamydomonas* (*C.*) *reinhardtii* showed that H_2O_2 and $^1\Delta_gO_2$ interact with different targets leading to activation of specific promoters (Shao et al., 2007).

With respect to regulatory and signaling effects of ROS including the function of second messengers, the general control of cellular processes by the ambient redox conditions should be pointed out clearly as a generalized working framework of the cell chemistry rather than ROS taking the role of “isolated” signal molecules (Foyer and Noctor, 2005; Pfannschmidt et al., 2009; Shao et al., 2008; Buchanan and Luan, 2005). Several models have been proposed for this redox control which includes oxidation/reduction of thiol groups, iron-sulfur centers, hemes, and flavin (Foyer and Noctor, 2005; Vranova et al., 2002). The redox homeostasis in cells is mainly controlled by the presence of large pools of the thiol buffer glutathione and of $NADPH/NADP^+$ and also by high concentrations of ascorbic acid (Foyer and Noctor, 2005). The fraction of reduced glutathione is normally higher than 90% (Noctor et al., 2002). Concomitant with these hydrophilic compounds, tocopherols can function as a lipophilic redox buffer system (for the antioxidant efficiency of different tocopherol species, see (Krumova et al., 2012)). These systems protect lipids and other membrane components of chloroplasts by physical scavenging and chemical interaction with ROS (Krumova et al., 2012).

Redox-sensitive enzymes serve as a molecular “switch” by undergoing reversible oxidation and reduction reactions in response to redox changes within the cells. ROS can oxidize the

redox-sensitive enzymes directly or indirectly under the participation of low-molecular redox-sensitive molecules like glutathione or thioredoxin, from which the latter interacts with ferredoxin (Foyer and Noctor, 2005; Shao et al., 2008). In this way, the whole cell metabolism can be tuned. On the other hand, redox-sensitive signaling proteins function in combination with other components of signaling pathways, including MAPKs, phosphatases, transcription factors, etc. (Foyer and Noctor, 2005; Shao et al., 2008, Pfannschmidt et al., 2009). Redox regulators available in the apoplast have been suggested to be among the key ROS sources during stress (Minibayeva et al., 1998, Minibayeva and Gordon, 2003; Minibayeva et al., 2009a).

It has to be mentioned that the molecular mechanisms that transfer ROS by dedicated oxidation of covalent bonds producing chemical oxidation products are maybe just a minor example of the general regulation that occurs from the overall redox state of the cell. Fundamental concepts may also arise from physical principles like the membrane potential or the decoupling or coupling of photosynthetic subunits by electrostatic interaction, which has been suggested to be the driving mechanism for the coupling state of cyanobacterial light harvesting complexes and the cell membrane in A. marina (see Schmitt et al., 2006; 2007) or in artificial systems consisting of cyanobacterial antenna complexes and semiconductor quantum dots (Schmitt et al., 2010; 2011; Schmitt, 2011).

However, the main sources of ROS in plant cells are still the chloroplasts, where ROS are produced as the so called "waste product" during photosynthesis. Within the chloroplasts primarily the components of the photosynthetic ETC produce ROS (Shao et al., 2007). Several possible sources are known for chloroplast signals, which can affect gene expression in the nucleus of the plant cells (Galvez-Valdivieso and Mullineaux, 2010; Buchanan and Luan, 2005). These sources include the biosynthetic pathway of tetrapyrrole compounds, changes in the redox state of photosynthetic ETC components (e.g. the PQ pool) and ROS generation. All these pathways induced by different signals are interconnected and therefore often considered as tightly coupled. At present, only rather limited information is available on the exact mechanisms of the transduction of signals from the chloroplast to the nucleus due to the accumulation of redox-sensitive compounds and ROS in the chloroplasts (Fey at al., 2005a,b; Pogson et al., 2008; Shao et al., 2008, Pfannschmidt et al., 2009; Kreslavski et al., 2011; Schmitt et al., 2014a).

Light is the most important signal in regulating a vast majority of processes in living organisms, as reflected by numerous light sensors and biological clocks. However, light is at first the unique Gibbs free energy source for the existence of living matter though the process of photosynthesis. On the other hand, light at high intensities also leads to stress giving rise to the deleterious process of photoinhibition in photosynthetic organisms (Adir et al., 2003; Allakhverdiev and Murata, 2004; Nishiyama et al., 2006; Murata et al., 2007; Vass and Aro,

2008; Li et al., 2009; Goh et al., 2012; Allahverdiyeva and Aro, 2012). Imbalances in the redox state of components of the ETC lead to dangerous ROS production. Therefore, suitable sensors are required to permit efficient adaptation to illumination conditions which vary in time (diurnal, seasonal rhythm) and space (e.g. plants in different altitudes of a tropical rain forest or bacteria in different water depth and living environment).

One of the key sensors in adaptation of the ETC to light is the redox state of the PQ pool which regulates the phosphorylation of light harvesting complexes II (LHC II) (Vener et al., 1998) and also acts as a signal for regulation of the expression of a set of plastid and nuclear genes (Pfannschmidt et al., 2003), such as *Lhcb*, *petE*, *APX2*, and *ELIP2* encoding light harvesting complex proteins, plastocyanin, ascorbate peroxidase 2 and early light inducible protein, respectively. Likewise, the expression of SOD is affected (Shaikhali et al., 2008). It should be noted that the expression of *Lhcb* genes is only partially controlled by the redox state of PQ, because additional factors are involved like ATP synthesis and the electric potential difference across the thylakoid membrane (Yang et al., 2001).

The redox state of PQ is proposed to induce two signaling pathways, which are initiated under the influence of high and low light and subsequently activate the expression of plastid and nuclear genes (Fey et al., 2005a,b; Pfannschmidt et al., 2009). ROS arising from reactions at the acceptor side of PSII could be one type of signals which trigger the regulation of these pathways (Ivanov et al., 2007). Under high light stress of *A. thaliana*, the PQ pool was shown to be oxidized by both $^1\Delta_gO_2$ and less electron input from PS II due to the effect of NPQ with implications on redox signaling (Kruk and Szymańska, 2012). Furthermore, a plastid terminal oxidase (PTOX) leading to slow PQH_2 oxidation is probably involved in a ROS-triggered signal transduction cascade (Troillard et al., 2012). The underlying mechanism of the specific role of PTOX in acclimation of plants to high light remains to be clarified.

The expression of genes encoding PSI proteins (psaD and psaF) is also affected (Pogson et al., 2008). Changes in the redox state of components on the PSI acceptor side contribute to the regulation of nuclear and chloroplast genes (Shaikhali et al., 2008). This effect is primarily related to the redox state of thioredoxin, which depends on the rate of electron transport from ferredoxin (Scheibe et al., 2005). The redox states of thioredoxin, glutathione and glutaredoxin act as signals for regulation of stress-responsive genes (Mullineaux and Rausch, 2005; Schürmann and Buchanan, 2008).

Several examples of regulation by thiols, in particular chloroplast gene translation and transcription have been described in recent reviews (Oelze et al., 2008).

In addition to signaling modes where ROS generated in response to different types of stress act either directly as signal molecules, or, via generation of second messengers (e.g.

oxidation products of Cars and lipids, *vide supra*), also pathways operating in the opposite direction are established in plants. This does not only account for producing ROS as defensive molecules but it also accounts for the active production of ROS as messanger molecules.

In these both cases ROS are produced as second messengers or as reactive species in response to stress, e.g. in the defense to biotic infection.

Special proteins are involved in the development of cell response to changes of the redox state. These proteins are encoded by so-called reporter genes. Investigations on redox signaling between chloroplasts and nucleus have been focused on the induction of genes of cytosolic ascorbate peroxidases APX1 and APX2, genes *ZAT10* and *ZAT12* encoding zinc-finger transcription factors, and also gene *ELIP2* encoding the early light-induced chlorophyll-binding protein ELIP2. Both transcription factors, ZAT10 and ZAT12, favor the induction of gene clusters related to activation of the photosynthetic ETC under high light by switching on the expression of genes *APX1* and *APX2* (Davletova et al., 2005; Pogson et al., 2008).

The expression of genes *APX2*, *ZAT10*, and *ZAT12* is stimulated by treatment with H_2O_2 (Karpinski et al., 1999; Davletova et al., 2005; Pogson et al., 2008) (see chapter 5.2). It seems reasonable to assume that H_2O_2 regulates the expression of these genes, thus acting via direct or indirect effects of the redox state in ignaling from chloroplast through cytosol to the nucleus. Kinetic experiments revealed that the redox signal arising from the response to a change in light quality (spectral composition) is transmitted within about 30 min from the chloroplast to the nucleus (Zhang et al., 2000). Studies on high-light effects in *A. thaliana* plants showed that the nuclear genes encoding cytosolic peroxidases APX1 and APX2 were activated in 15-20 min. It was also found that the activation of these genes is part of the systemic response to superfluous light exposure (Karpinski et al., 1999). The induction of chloroplast gene expression occurred also in the range of 15-20 min in response to changes of the redox state in the organelles induced by changes in light quality (Pfannschmidt et al., 2009). These kinetic results on signal transduction suggest that some components of the signal cascade triggered by stress-induced changes of ROS concentration are present in the cells already under optimum conditions and do not need to be synthesized in response to stress. This idea explains the correspondence of the kinetics of signal transduction in response to ROS appearance and of the transduction of other intracellular stimuli (Pfannschmidt et al., 2009).

7. Second Messengers and Signaling Molecules in H_2O_2 Signaling Chains and (Nonlinear) Networking

A genetic screen aimed at identifying $^1\Delta_gO_2$-responsive genes (Baruah et al., 2009) led to the proposal of the gene named “pleiotropic response locus 1” (PRL1) acting as a point of convergence of several different signaling pathways, thus integrating various intra- and extracellular signals. Under pathogen-induced stress, the gene “enhanced disease susceptibility 1” (EDS1) plays a role in development of the hypersensitive reaction and in mediating EXE1/EXE2-regulated cell death induced by $^1\Delta_gO_2$ (Ochsenbein et al., 2006). The EDS1 protein has been shown to be required for the resistance to biotrophic pathogens and the accumulation of SA. SA likely enhances the plant defenses by inducing the synthesis of pathogen-related proteins (Mullineaux and Baker, 2010). EDS1 seems to play a pivotal role in a mutually antagonistic system, integrating ROS signals from chloroplasts in cells suffering from photooxidative stress (Straus et al., 2010).

A general problem in identifying different $^1\Delta_gO_2$-induced signal pathways and their (synergistic) interplay has to be mentioned. The effect on the gene expression pattern is expected to depend on the nature of the nearest neighborhood of $^1\Delta_gO_2$ formation, if one accepts that signaling directly by $^1\Delta_gO_2$ can take place only at a site very close to its generation. This would also imply that the signal pathway comprises the participation of oxidation products of Cars, lipids and other molecules acting as second messengers which can induce different genetic responses. The $^1\Delta_gO_2$ site differs in WT plants and in mutants like flu1 and, also, if $^1\Delta gO_2$ is generated by using exogenous sensitizers (Hideg et al., 1994; Krieger-Liszkay, 2005). Therefore, different types of second messenger species are likely to be formed in mutant studies in contrast to wild type studies. Thus, it is difficult to gather straightforward conclusions on the mechanism of $^1\Delta_gO_2$ signaling from studies performed under different assay conditions and using different sample material including single gene mutants. This important problem needs to be further addressed in forthcoming studies.

ROS can be involved in several signaling pathways by modulating the activity of different components like MAPKs and phosphatases, transcription factors, and calcium channels (Pei et al., 2000; Mori and Schroeder, 2004; Pfannschmidt et al., 2009; Kreslavski et al., 2011; Pogson et al., 2008; Kovtun et al., 2000; Gupta and Luan, 2003). Heterotrimeric G-proteins may also participate in the signaling pathways initiated by ROS (Joo et al., 2005). An effect of ROS on the activity of Ca^{2+} channels was shown to arise for both abiotic stress and plant-pathogene interaction (Demidchik et al., 2003).

Very few details have been resolved so far on the nature of steps which link various pathways in coordinating ROS signaling. One piece of the puzzle is the finding that MAPKs are

involved in transducing signals derived from ROS generated by sources in chloroplasts (Liu et al., 2007).

One mode of ROS-induced signaling is given by the activation of transcription factors containing SH groups like OxyR in eubacteria and/or iron-sulfur clusters (Zheng et al., 1998). Formation of S-S bridge(s) by H_2O_2 is expected to change the structure of OxyR, therby inducing the transition from the inactive into the active form, as is schematically illustrated in Figure 10.

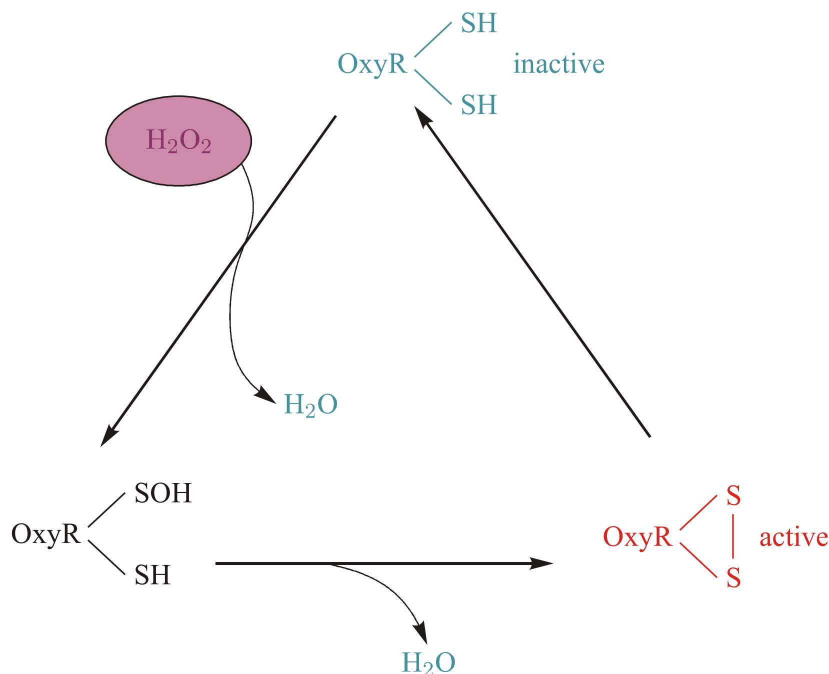


Figure 10. Hypothetical scheme of regulation of bacterial transcription factor OxyR activity. The inactive form contains thiol groups (SH). Under the influence of H_2O_2, the thiol group is oxidized with the formation of an SOH group and then rapid formation of a disulfide bond occurs and OxyR transits into its active form

Another possibility of ROS signaling is changes of the subcellular distribution of these factors as in the case of yeast. Yeast cells express the protein Yap1, which is functionally homologous to the transcription factor OxyR in eubacteria. Yap1 can regulate the transcription of specific genes in response to changes of the redox state of the cell (Liu et al., 2005). The inactive form of Yap1 is localized in the cytoplasm. H_2O_2 oxidizes Yap1 via the peroxidase Gpx3 (Delaunay et al., 2000) under formation of disulfide bonds between neighboring cysteines, thus leading to conformational changes, which enables the transport of this Yap1 form to the nucleus, where it induces the expression of genes encoding for components of antioxidant defense system(s). Mutants lacking Yap1 were shown not to be able to induce antioxidant defense upon treatment with H_2O_2 (Liu et al., 2005).

In analogy to the thiol-based sensor OxyR of bacteria, Yap1 is part of a relatively simple regulatory loop, where ROS induce the expression of certain antioxidative enzymes. Although a gene homologous to OxyR is absent in higher plants, attempts to complement mutations of the gene OxyR in E. coli by using the expression gene library of A. thaliana identified the AnnAt1 gene encoding annexin as to be capable of restoring a functional defect in the OxyR bacterial mutant (Gidrol et al., 1996). Recently identified signaling proteins undergoing thiol modulation (modification) in plants include a protein tyrosine phosphatase (Dixon et al., 2005) and a histidine kinase ETR1, which is involved in ethylene signaling (Desikan et al., 2005).

Based on these findings, it seems reasonable to assume that analogous mechanisms also exist in plant cells, but they are likely to be more complex. Figure 11 presents a proposed simplified scheme for redox-sensitive sensors (RsS) acting as primary sensors of H_2O_2 signal transduction.

The signal can be transmitted directly from H_2O_2 or via RsSs to the MAPK cascade and/or to transcription factors (Neill et al., 2002; Pogson et al., 2008; Pfannschmidt et al., 2009). The conformation and activity caused by reversible oxidation of cysteine residues of regulatory proteins, which are involved in gene expression at different developmental stages, offer a simple and elegant mechanism for regulation of transcription and translation systems under oxidative stress. As a result, transcription of nuclear genes required for ROS scavenging is activated. By oxidation of the translation elongation factor G (EF-G) in chloroplasts and by blocking translation of new proteins, H_2O_2 can also regulate gene expression on the level of translation, in particular (see chap. 5) (Nishiyama et al., 2011; Murata et al., 2012).

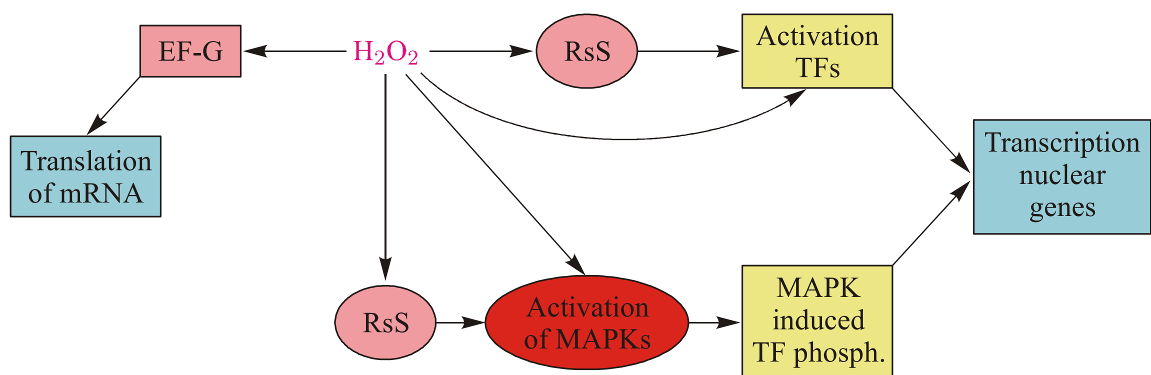


Figure 11. Effects of H_2O_2 on processes of transcription and translation. RsS, MAPK and TF are redox-sensitive sensor(s), MAP-kinase and transcription factor(s), respectively. For details, see text

Figure 12 presents a hypothetical scheme of pathways of photosynthetic redox signal transduction in plants. It summarizes selected mechanisms described in the chap. 5, 6 and 7 in a

general picture that aims to denote the complex networking of different species to establish ROS-iniated and ROS-mediated signaling pathways between cell organelles.

Although our current knowledge is still rather fragmentary, the general conclusion on signal networks is clearly illustrated by different lines of evidence for the interference between various pathways (see Figure 12). Some further description intends to pint out the difference between (nonlinear) networking and a single ROS signalling pathway.

It was found that H_2O_2 stimulates a rapid increase of intracellular Ca^{2+} concentration (Kim et al., 2009). The development of oxidative stress controls the activity of several isoforms of calmodulin. In plant cells, on the other hand, the ROS generation in mitochondria is activated by an increase of the Ca^{2+} concentration. Likewise, under certain conditions, the Ca^{2+} concentration depends on the actual ROS level and additionally Ca^{2+} stimulates the formation of ROS in plant cells (Bolwer and Fluhr, 2000). These findings indicate that ROS/redox state and calcium-dependent signaling pathways are closely interconnected in a strongly nonlinear way (Yin et al., 2000). Heat hardening, at least a short-term treatment, can also be accompanied by an increase of the ROS content in cells (Dat et al., 1998), i.e. ROS might function in transduction of a temperature signal (Suzuki and Mittler, 2006; Yu et al., 2008). It is also suggested that ROS participate in acclimation of the photosynthetic apparatus to high light under conditions similar to heat hardening (Kuznetsov and Shevyakova, 1999; Allakhverdiev et al., 2007; Kreslavski et al., 2009; 2012a).

Common intermediates were found to participate in mechanism(s) of ROS and phytohormone action (Jung et al., 2009), as is shown by the involvement of the species $O_2^{-\bullet}$ and O_3 in programmed cell death together with ethylene- and jasmonate-dependent metabolic pathways. On the other hand, ROS can function as second messengers in the transduction of hormonal signals, as was shown for the auxin affect on gene expression, where ROS are used as second messengers, which simultaneously regulate activity and expression of glutathione transferase in antioxidant function (Tognetti et al., 2012).

H_2O_2 induces the phosphoinositide cycle that leads to switching on signaling pathways associated with the secondary messengers, IP_3 and diacylglycerol (DAG) (Munnik et al., 1998), whereas phospholipase D was reported to stimulate H_2O_2 production in *A. thaliana* leaves via generation of phosphatidic acid acting as lipid messenger (Sang et al., 2001).

It is well known that exogenous salicylic acid and pathogens induce a burst of ROS generation in plant tissues (Dmitriev, 2003). However, it remains unclear how and to what extent ROS are involved in the improvement of plant stress resistance. Exogenous salicylic acid was

found to give rise to enhanced plant cold tolerance (Horváth et al., 2002). This effect is attributed to the inhibition of catalase and related to oxidative stress leading to accumulation of H_2O_2.

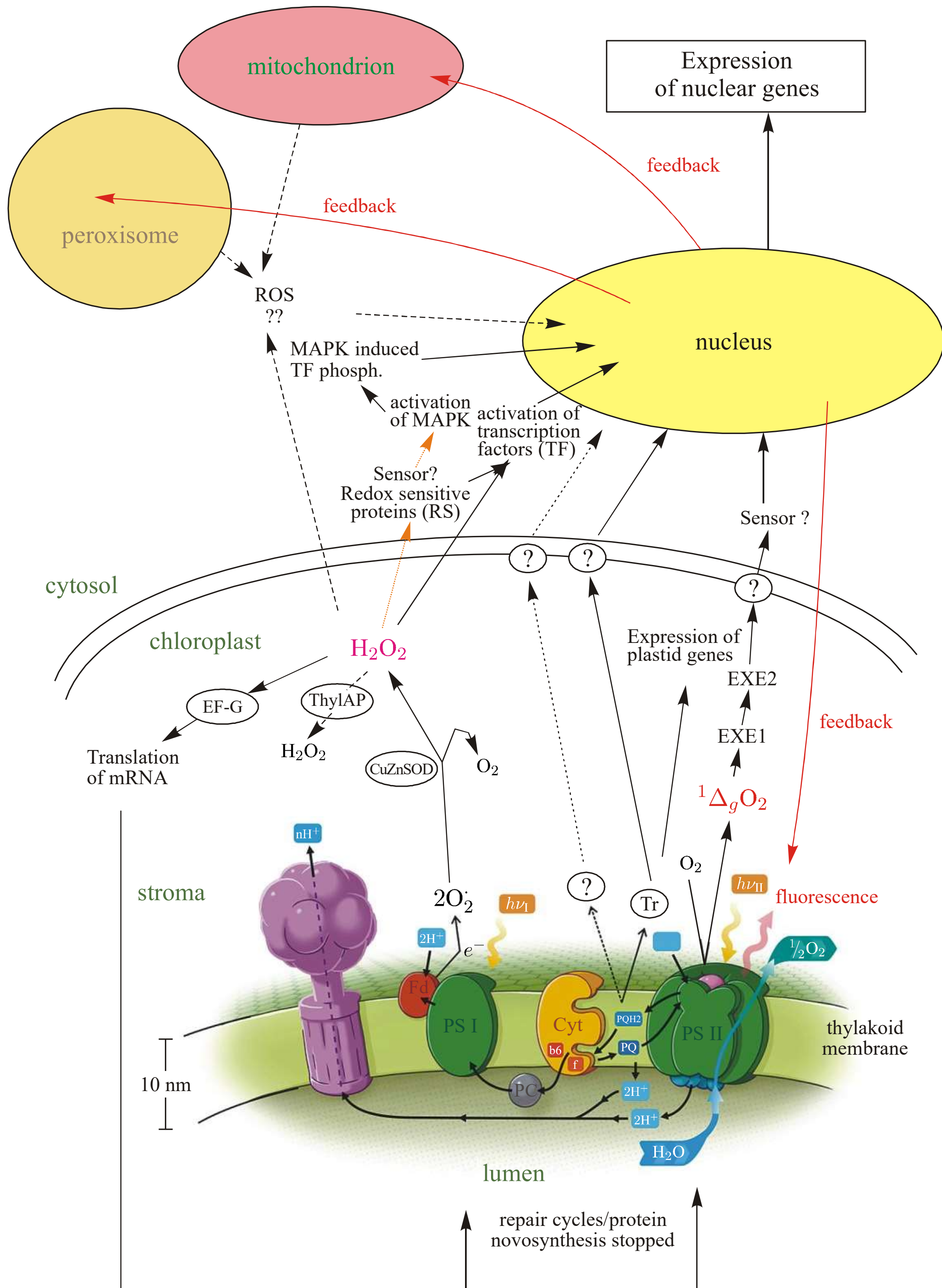


Figure 12. Hypothetical scheme of pathways of photosynthetic redox signal transduction in plants initiated at the thylakoid membrane. For the sake of simplicity, other cell organells (nucleus, mitochondrion, peroxisome) are symbolized by colored ovals. Interrupted arrows designate hypothetic pathways of signal transduction. The question marks designate unknown components of signal transduction pathways. Solid lines designate signal transduction pathways

with some experimental confirmation. Dotted lines designate experimentally established signal transduction pathways in chloroplast ETC and in the stroma. The abbreviations RS, MAPK and TF denote redox-sensitive protein(s), MAP-kinase and transcription factor(s), respectively. See text for details

Studies on two maize genotypes revealed that the cold-resistant line had a molecular form of catalase, which was more severely inhibited by salicylic acid than the catalase of the sensitive line (Horváth et al., 2002). Oxidative stress caused by exogenous salicylic acid depends on the calcium status of the cells and is not manifested in the presence of calcium channel blockers.

When considering the existence of signaling networks, it must be emphasized that different hierarchies of complexity exist in ROS-induced signaling depending primarily on the evolutionary level of the organism. Networking is evidently simpler in prokaryotic than in eukaryotic cells, which contain various cell organelles (chloroplasts, mitochondria, peroxisomes, nucleus, endoplasmatic reticulum) and loci of genomic information (e.g. plastids and nucleus in plants). An even more complex signal network exists in multi-cellular organisms, e.g. in leavess of higher plants with different cell types (mesophyll, bundle sheath, guard cells). The deciphering of the latter type of networks requires detailed analyses, and this topic is just at the beginning to reach a level of deeper understanding.

8. Concluding remarks and future perspectives

The enormous work perfomed during the last decades has clarified the deleterious effects of ROS on photosynthetic organisms. However, this is only one side of ROS functions. The other side is the very important signaling role of ROS in the response of cyanobacteria, alga and higher plants to different forms and conditions of stress. In spite of significant progress achieved during the last decade, our current state of knowledge on this topic is still rather fragmentary.

There are several questions that need to be answered:

1. How do ROS generated in chloroplasts affect the transcription of the chloroplast genome?
2. How can ROS leave the chloroplasts and directly induce a significant expression of genes of the nuclear genome?
3. What is the nature and the mechanistic function of second messengers formed by reaction of ROS with specific molecules like lipids and Cars?
4. What determines the mechanism of ROS wave propagation in plant cells ?

5. What is the identity of the primary sensor(s) of ROS (transcription factors and/or protein kinases) and the primary genes responding to oxidative stress?

6. Do ROS induce new signaling pathways by acting as second messengers?

Significant progress in answering these questions is expected from the development of new spectroscopic methods for monitoring ROS, in particular with high spatial resolution, and their application in combination with directed genetic engineering of plants. Among the methods for manipulations at molecular level the targeted ROS production within specific cell compartments and organelles is of high interest.

One important approach towards exploitation of photosynthetic organisms as sustainable sources of biomass is the improvement of the resistance of the cells against environmental stress conditions. This problem targets world food and world energy supply. On the other side plants function as sensitive indicators for the environmental conditions and photosynthetic activity changes in contact to diverse dust pollutants leading to dynamic changes of chlorophyll fluorescence. The full understanding and technical explotation of these mechanisms has implications on food production. It additionally opens the way to develop rapid alert systems for dust pollutants or, more generally, as reporters for the environmental quality, by monitoring the fluorescence properties of plants like for example lichens (e.g. *Peltigera aphtosa*) which are sensitive to pollutants (Maksimov et al., 2014b).

As the world health organization (WHO) just recently pointed out air pollution as the worst environmental threat for human and environmental health, the need for techniques to quantify the air contamination and its impact on plants is pressing. The World Health Organization (WHO) estimates that seven million people worldwide died due to illnesses linked to air pollution in 2012 alone, according to new data released onm March 25th 2014. These shocking developments urgently require new techniques and initatives that are able to quantify the air pollution and might help to decontaminate air especially in the big cities. Plants with selected and specialised properties might be a solution for these problems.

The genetic transformation of plants according to a deep molecular biological knowledge of all processes that interact with ROS delivers a tool to produce enhanced plants as ROS sensors, ROS scavengers or crop plants with improved resistance to ROS. The analyzes of the capability of cyanobacteria and algae for the decontamination of water and air give rise to genetically enhanced ROS scavengers.

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