Structure and Function of Photosystems I and II

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Abstract

Oxygenic photosynthesis, the principal converter of sunlight into chemical energy on earth, is catalyzed by four multi-subunit membrane-protein complexes: photosystem I (PSI), photosystem II (PSII), the cytochrome b_6f complex, and F-ATPase. PSI generates the most negative redox potential in nature and largely determines the global amount of enthalpy in living systems. PSII generates an oxidant whose redox potential is high enough to enable it to oxidize H_2O, a substrate so abundant that it assures a practically unlimited electron source for life on earth. During the last century, the sophisticated techniques of spectroscopy, molecular genetics, and biochemistry were used to reveal the structure and function of the two photosystems. The new structures of PSI and PSII from cyanobacteria, algae, and plants has shed light not only on the architecture and mechanism of action of these intricate membrane complexes, but also on the evolutionary forces that shaped oxygenic photosynthesis.

Contents

INTRODUCTION

Photosynthetic O_2 production and carbon dioxide assimilation established the composition of the biosphere and provide all life forms with essential food and fuel. Oxygenic photosynthesis in plants is accomplished by a series of reactions that occur mainly, but not exclusively, in the chloroplast. Early biochemical studies showed that chloroplast thylakoid membranes oxidize H_2O, reduce NADP, and synthesize ATP. These reactions are catalyzed by two photosystems [photosystem I (PSI) and photosystem II (PSII)], an ATP synthase (F-ATPase) that produces ATP at the expense of the protonmotive force (pmf) formed by light-driven electron-transfer reactions, and the cytochrome (cyt) b_6f complex, which mediates electron transport between PSII and PSI and converts the redox energy into part of the proton gradient used for ATP formation. The knowledge obtained from biophysical, biochemical, and physiological research during the twentieth century set the stage at the beginning of the twenty-first century for the determination at high resolution of the structures of most of the proteins involved in oxygenic photosynthesis (219). This review attempts to capture the excitement generated by the determination of the three-dimensional structures of the chlorophyll (Chl) containing complexes that catalyze oxygenic photosynthesis. Several reviews have been published that contain detailed discussions and list original references to earlier work (18, 44, 60, 62, 110, 121, 125, 137, 238, 246, 273). In this review, we focus on the photosystems of higher plants but also refer to the wealth of structural information that is available on the photosystems of the thermophilic cyanobacteria, especially in the case of PSII, for which a plant crystal structure is currently unavailable.

cyt: cytochrome
Chl: chlorophyll

Molecular Architecture of Thylakoid Membranes

In eukaryotes, most of the reactions of photosynthesis occur in the chloroplast. The four protein complexes required for the light-driven reactions of photosynthesis reside in a membrane continuum of flattened sacs called thylakoids (219). Thylakoids form a physically continuous three-dimensional network enclosing an aqueous space called the lumen and

are differentiated into two distinct physical domains: cylindrical stacked structures (called grana) and interconnecting single membrane regions (stroma lamellae). The protein complexes that catalyze electron transfer and energy transduction are unevenly distributed in thylakoids: PSI is located in the stroma lamellae, PSII is found almost exclusively in the grana (**Figure 1**), the F-ATPase is located mainly in the stroma lamellae, and the cyt b_6f complex is found in grana and grana margins (3, 13, 14, 154, 161).

Low-resolution models of thylakoid structure resulted from reconstituting serial thin sections, freeze etching, immuno-gold labeling, and biochemical and spectroscopic analyses (232). For example, fractionation of membrane fragments by aqueous polymer two-phase separation (3–5, 73) revealed five domains: grana surface, core, margins, stroma lamellae, and stroma lamellae Y-100 (**Figure 1**). A calculation of the total number of Chl associated with PSI and PSII suggested that more Chl (approximately 10%) are associated with PSI than with PSII, in agreement with results showing that PSI absorbs approximately 20% more photons than PSII (3, 5, 149, 150). Two distinct photosystem subtypes (PSIα, PSIβ and PSIIα, PSIIβ) were identified by biophysical experiments. Assuming an antenna size for PSIIβ in stroma lamellae of 100 Chl, the other antenna sizes are (*a*) PSIα (grana margins), 300 Chls; (*b*) PSIβ (stroma lamellae), 214 Chl; and (*c*) PSIIα (grana core), 280 Chl (73). These complexes were not characterized by biochemical methods, and the PSI results are inconsistent with those from an analysis of the recent structure of plant PSI (28). Moreover, the cyt b_6f complex and the F-ATPase were not quantified in these domains. Future studies of components of the thylakoid membrane must employ a concerted biochemical and structural approach, using current methods and available high-resolution structures. Used alone, any of the current methods runs the risk of producing artifacts. For example, treatment of thylakoid membranes with 0.5% dodecyl maltoside releases most of the F-ATPase, and surprisingly, PSII with very little contamination by PSI (9, 32). The current model for defined domains in the thylakoid membrane cannot explain this phenomenon.

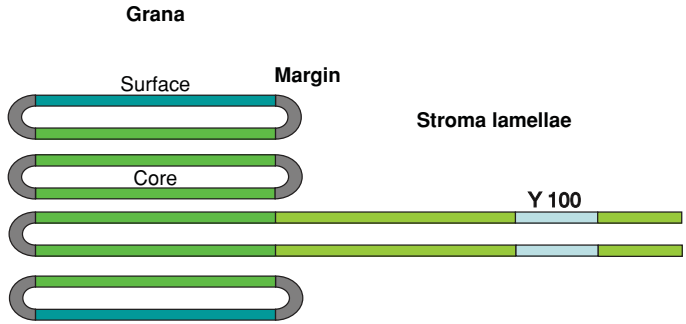

Figure 1
A schematic model of domains of the thylakoid membrane. Mechanically disrupted thylakoids were separated into various fractions by differential centrifugation and phase separation (3).

Thylakoid Membrane-Protein Complexes: Definitions and Limits

Resolution-reconstitution biochemistry and molecular genetics have identified the functions of individual proteins in many membrane complexes, which are defined as the minimal structures that catalyze specific biochemical reactions. Analysis by sodium dodecyl sulfate (SDS) gels of the first isolated thylakoid membrane complexes revealed a shocking number of subunits (12, 26, 27, 84, 165, 193, 214). By biochemical standards, these preparations were reasonably pure, but this criterion alone cannot establish a polypeptide as a genuine subunit (218). An authentic subunit must be present in stoichiometric amounts, be necessary for activity, and also be required for assembly and/or stability of the holoenzyme (305). Even purified preparations may contain irrelevant polypeptides or may lose genuine subunits during isolation without a detectable effect on activity. Because eukaryotic and prokaryotic PSI and PSII reaction centers (RCs) are almost identical in their subunit composition, *Synechocystis* genetics has been invaluable for determination of the subunit structure and function of both photosystems (62, 291) and has also identified special properties of individual subunits.

RC: reaction center

LHC: light-harvesting, chlorophyll-binding protein

CP: chlorophyll-binding protein

EM: electron microscopy

Sequencing of the *Synechocystis* genome ended the race for discovery of new genes in this cyanobacterium and opened up the post-genomic era (62, 146, 324).

The PSI subunit composition is now defined by the polypeptides identified in the detergent-isolated, highly active complex and by the subunits detected in the crystal structure of plant PSI (28, 142, 258). Thus, PsaA-PsaL and light-harvesting, Chl-binding protein (LHC) LHCa1, LHCa2, LHCa3, and LHCa4 were proven to be genuine subunits of plant PSI. The PsaN and O proteins that were not detected in the structure are likely to be genuine subunits, but this hypothesis is not certain at the present time (142, 143, 167). Several other proteins may function as assembly factors (211, 212, 278, 316).

The subunit composition of PSII is much more complex than that of PSI. Identification of polypeptides in the highly active detergent-isolated preparations from spinach (33, 179), coupled with stepwise removal of various subunits (48), defined the minimum protein complex capable of O_2 evolution activity. Intrinsic light-harvesting proteins, such as LHCII, LHCb4 [Chl-binding protein (CP) 29], LHCb5 (CP26), and LHCb6 (CP24)] are easily removed with minimal activity loss; the remaining subunits cannot be extracted from the plant enzyme without affecting activity. These biochemical results, combined with mutagenesis experiments carried out in *Synechocystis* 6803 (291), defined the major intrinsic proteins as Psb A (D1), B (CP47), C (CP43), D (D2), and E and F, the polypeptides that donate axial His ligands to the heme iron of cyt b_{559}. Nuclear-encoded extrinsic proteins (PsbO, P, and Q) are required for O_2 evolution activity under physiological conditions. Cyanobacterial PSII contains PsbO (53), but a cyt (c_{550}, PsbV) and a 12 kDa polypeptide (PsbU) replace the PsbP and Q subunits in eukaryotes (269). The other polypeptides found in PSII are authentic subunits that are not directly involved in light harvesting or electron transfer reaction. The PsbS subunit (162, 299) is unique to eukaryotes and is required for nonphotochemical quenching (185). A report that it binds Chl (112) has not been substantiated (91). Of the other polypeptides (Psb H-L, N, R, T, and W-Z) associated with PSII, the functions of PsbN (4.7 kDa) and R (10.2 kDa) are unclear at the present time. The other subunits are discussed below.

Formation of Supercomplexes

Photosystems interact with other membrane complexes such as light-harvesting proteins or soluble proteins that mediate electron transport. Whereas PSI and PSII form supercomplexes with light-harvesting proteins (LHCI, LHCII), PSI also forms complexes with soluble electron donors and acceptors (82). The plant PSI structure (28, 32) revealed two distinct complexes: the RC and LHCI (see below and **Figure 1**). Models of the interactions between PSI and its soluble electron donors and acceptors are discussed in detail below. Because PSII utilizes a bound inorganic ion cluster of four Mn, one Ca^{2+}, and one Cl^- to oxidize H_2O and produce the electrons for reduction of plastoquinone, it has no soluble proteinaceous electron donors or acceptors (48, 89, 90). Nevertheless, PSII exhibits extensive protein-protein interactions in thylakoids. The plant RC is a dimer surrounded by tightly bound trimeric primary LHCII complexes (18); this supercomplex can interact with different numbers of additional LHCII units depending on light intensity and quality (57, 82, 140, 250). Barber & Nield (19) constructed detailed models using data on individual subunits, subcomplexes, two-dimensional projection maps, and electron microscopy (EM) single particle analyses; the high-resolution structure of the cyanobacterial PSII dimer and single particle images of intact PSII were then used to model the interaction between plant PSII and LHCII (18, 36, 82, 126). These models contain useful details, but three-dimensional structures of the plant PSII RC, both alone and with as many attached LHCII units as possible, are still highly desirable goals.

Information about the evolution of PSII-LHCII interactions comes from recent studies on bacteria and algae (20, 59). The Chl d light-harvesting system of *Acaryochloris marina* is composed of Pcb proteins, which associate with the PSII RC to form a giant supercomplex (approximately 2300 kDa) (59) composed of two PSII-RC core dimers arranged end-to-end and flanked by eight symmetrically-related Pcb proteins on each side. The *pcb* genes encoding these antenna proteins are present in multiple copies in low-light strains but as a single copy in high-light strains (35). Therefore, it is possible that adaptation of *Acaryochloris* to low-light environments triggered a multiplication and specialization of Pcb proteins comparable to that found for Chl a- and Chl b-binding antenna proteins in eukaryotes (35). If so, then attempts to regulate light absorption by modulating light-harvesting complexes are ancient and are probably necessary for efficient light harvesting and protecting RCs.

Higher-Order Interactions: Fact and Fiction

The PSI and PSII supercomplexes that form with variable amounts of membrane-bound peripheral antenna complexes also associate into megacomplexes or even semicrystalline domains (82). Whether these associations are physiological or preparative artifacts is debatable. Biochemical methods for detecting complex association use mild detergent solubilization, followed by size analysis using sucrose-density gradient centrifugation or electrophoresis on blue native gels and analysis of the subunit composition or spectroscopic properties of an individual band. For example, biochemical experiments on digitonin-solubilized thylakoids subjected to 2D blue native polyacrylamide gel electrophoresis resolved two high-molecular-weight PSI complexes (approximately 1060 and 1600 kDa), which were assigned to dimers and trimers (130). Whereas the evidence for these supercomplexes is quite convincing, their origin and nature is unclear. A second method of analysis, using a combination of mild detergents and EM, identified similar aggregates: Dimers and larger aggregates of PSI were observed in spinach PSI preparations (40). However, a closer inspection of these particles revealed that they are composed of dimers and trimers that could not exist in native membranes, so it was concluded that these particles were formed during detergent treatment (173). It was also concluded that high-molecular weight bands detected on blue native gel electrophoresis, like the PSI dimers and trimers, do not constitute proof of the existence of native particles in the membrane.

EM investigations of the PSI–LHCI complex from spinach had already indicated that the LHCI subunits bind in one cluster at the side of the core complex occupied by PSI-F and PSI-J (38) when the plant PSI crystal structure revealed that it is a supercomplex containing an RC and a LHCI complex composed of four LHCa proteins (28). In contrast, *Chlamydomonas* is reported to contain considerably more LHCa polypeptides and is much larger than plant PSI (114, 156). One proteomics approach revealed up to 18 different LHCa proteins (134), but biochemical studies and a more recent proteomic analysis yielded 9 to10 different subunits (277). Single particle analysis of EM projections revealed two particles (21 and 18 nm), on which 18 and 11 LHCa proteins, respectively, were modeled (114, 156). Modeling of the pea PSI structure into that of *Chlamydomonas* suggested nine bound LHCa proteins, a result consistent with recent biochemical studies (282). Eight or nine LHCa polypeptides would occupy the PsaF side of the complex and one would be found between PsaL, A and K (82). However, recent observations suggest that only one row of four LHCa is bound on the PsaF side, and the extra density is attributed to a detergent layer (J. Neild, personal communication). Also, the number of Chl molecules per *Chlamydomonas* PSI was reduced to approximately 215 to agree with the LHCI structure of plant PSI, with the addition of two or three

PC: plastocyanin

Fd: ferredoxin

additional LHCa, bound proximal to PsaK and G. These results emphasize the facts that single particle analysis must be viewed with some caution if x-ray structural data are unavailable.

BIOCHEMISTRY OF PHOTOSYSTEM I AND II

Biochemical Preparations of P700 Containing Complexes

Although Bessel Kok discovered the PSI RC Chl, P700, in the 1950s (169, 170), isolation of a well-defined PSI complex required the advent of SDS-polyacrylamide gel electrophoresis (181, 298). This technique, which is probably as important to membrane biochemistry as the PCR reaction is to molecular biology, gave relatively precise identifications of proteins in membrane complexes. Initial studies with Chl-protein complexes separated from chloroplast thylakoids (26, 27) indicated that the photosystems are much more complex than bacterial RCs, which consist of three polypeptides, four bacteriochlorophylls, two bacteriopheophytins, and a nonheme iron (66, 228). Three well-defined biochemical preparations that catalyze light-induced oxidation of P700 have been isolated. As shown in **Figure 2**, the minimal structure that catalyzes this reaction, the P700 RC, contains two homologous polypeptides (PsaA and B) and approximately 80 Chl molecules (26, 27). The PSI RC, isolated from eukaryotes and cyanobacteria, catalyzes light-induced plastocyanin (PC)-ferredoxin (Fd) oxido-reduction and contains multiple protein subunits, approximately 100 Chl molecules and up to 14 different polypeptides (142, 143, 258). The largest complex, the PSI RC and LHCI, contains approximately 200 Chl molecules (17, 23, 210, 214, 218). The plant PSI structure identified 12 subunits in the RC and four different subunits in LHCI (28). Two subunits (PsaN and O) were not detected in the crystal structure. Future studies should determine whether they are genuine subunits or assembly factors.

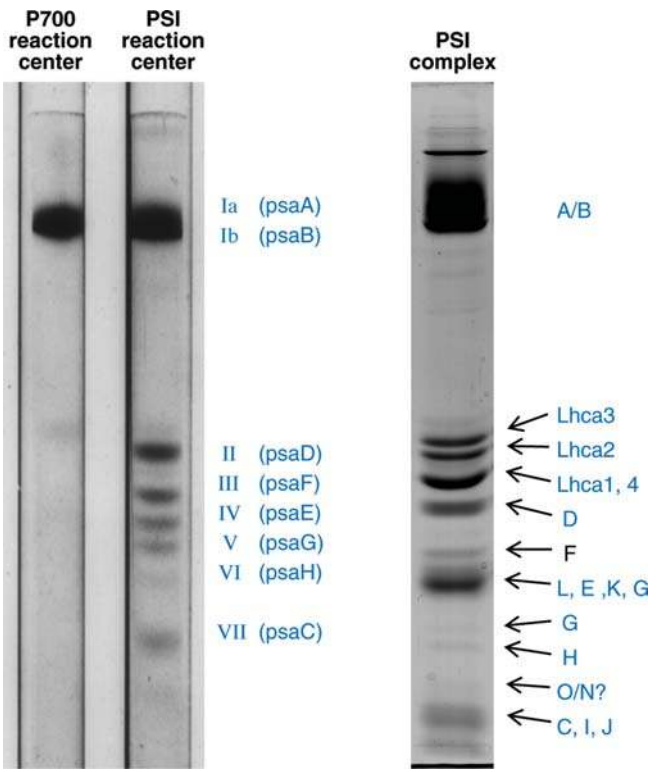

Figure 2

Subunit structure of photosystem I (PSI) preparations capable of light-induced P700 oxidation. Preparations of P700 RC and PSI RC were analyzed on cylinder SDS-gels (26). The PSI complex is the pea preparation used for crystallization. The probable subunit identities are indicated.

Biochemical Preparations of O_2-Evolving PSII

The pioneering efforts to isolate plant PSII used Triton X-100 (292) or digitonin (11); the resulting preparations retained some PSI and had low O_2-evolution activity. A surprising insight into the complexity of the biochemical composition of PSII was provided by Akerlund et al. (2), who showed that "inside-out" thylakoids contained an extrinsic polypeptide that was required for O_2-evolution activity. Lastly, Izawa et al. (254) discovered artificial electron acceptors (i.e., p-phenylenediamines and p-benzoquinones) that provided an unambiguous assay of PSII

activity. These discoveries facilitated the isolation of highly active PSII preparations (33, 179) and demolished the myth that the O_2-evolving reaction was an "Inner Sanctum" (171) that was impervious to biochemical manipulations. Isolation of cyanobacterial PSII from *Synechocystis* 6803 was much more challenging (226), and His tagging has been used to facilitate rapid isolation (49). Like PSI, analysis of the composition of spinach PSII required SDS polyacrylamide slab gels. Unlike PSI, the final subunit count exceeded 20 (125), excluding the major light-harvesting polypeptides mentioned earlier. Cyanobacteria contain a comparable number of subunits, several of which have been resolved in the cyanobacterial crystal structures discussed below. The largest intrinsic membrane proteins of PSII (PsbB, 56.3 kDa) and C (CP 43, 51.8 kDa) bind Chl a and function as antennas. Isolation of PsbA and D in a complex with cyt b_{559} settled the early debates about the identity and composition of the PSII RC (256); PsbA (38.8 kDa) and PsbD (38.4 kDa) provide the ligands for the cofactors [i.e., 6 Chl a, 2 pheophytin a (Pheo a) molecules], 2 plastoquinones, a nonheme iron, the redox active tyrosines (Y_Z, Y_D), and the inorganic ions that catalyze H_2O oxidation] that make up the PSII electron transfer chain. Roles of the small intrinsic subunits of PSII are reviewed in detail by Thornton et al. (284). These subunits of PSII are genuine components of the multisubunit membrane complex, although they do not ligate electron transfer cofactors. Instead, they are required for assembly and stability of the enzyme complex.

The extrinsic proteins of plant PSII are PsbO (the manganese stabilizing protein, 26.5 kDa), PsbP (called the 23 kDa subunit, which is actually 20 kDa) and PsbQ (the 17 kDa subunit) (261). Cyanobacterial PSII contains PsbO; PsbV (cyt c_{550}, 17 kDa) and PsbU (12 kDa) replace PsbP and Q (269). The PsbP and Q subunits, along with PsbO, form a structure that facilitates retention of inorganic cofactors (Ca^{2+}, Cl^-) of the O_2-evolving reaction (115, 187, 205, 261). As PsbP and Q can be removed without significant loss of Ca^{2+} (302), some reevaluation of their functions may be necessary. The plant subunits also protect the manganese atoms from damage from reductants such as plastohydroquinone (116). In cyanobacteria, the small extrinsic subunits also appear to play a role in cofactor retention (268, 270). In addition, Kashino et al. (157) identified a protein in PSII from *Synechocystis* 6803 with some sequence identity to PsbQ. Thornton et al. (283) described site-directed mutations that eliminate the putative PsbQ subunit and a polypeptide that bears a sequence similarity to the PsbP subunit. The phenotypes of both mutants display a defect in O_2-evolution activity when the cells are grown on medium deficient in Ca^{2+} and Cl^-. PsbQ is stoichiometric with other PSII polypeptides but the PsbP homolog is present at much lower levels. The authors conclude that these subunits have a regulatory role in cyanobacteria and are required during the assembly of cyanobacterial PSII to produce a fully active enzyme system.

All oxygenic photosynthetic organisms contain PsbO [the manganese stabilizing protein (MSP)]. Extraction of PsbO from PSII lowers the rate of O_2 evolution and the residual activity requires unphysiologically high concentrations of Cl^- (261); PsbO-depleted PSII slowly loses Mn atoms and activity upon dark incubation, phenomena that are reversed by high Cl^- concentrations (206). Deletion of PsbO by mutagenesis in *Synechocystis* produces a phenotype that assembles PSII and grows photoautotrophically (53). Eukaryotic PSII is quite different: A *Chlamydomonas* mutant lacking PsbO could not assemble PSII (194), and a recent study using RNAi to suppress MSP levels in *Arabidopsis* produced a very similar result (313). There are other differences between eukaryotic and bacterial PsbO. The crystal structures of *Thermosynechococcus elongatus* and *T. vulcanus* contain one copy of PsbO (95, 155, 322). Low resolution EM structures of plant PSII were interpreted to indicate a similar stoichiometry. However, reconstitution studies (184, 306) and the effects of site-directed

mutagenesis on the ability of PsbO to bind to PSII (34) support the hypothesis that two copies of PsbO are present, as does the absence from cyanobacterial PsbO of one of two N-terminal amino acid sequences in spinach PsbO that are necessary for binding of two copies of the protein to spinach PSII (239, 240). One PSII-PsbO interaction site is the latter's N terminus (92), which was localized by crosslinking to the large extrinsic domain of PsbB, between E364 and D440 (227). Specific N-terminal PsbO sequences required for binding have been identified (239, 240). In plant PSII, PsbO provides binding sites for attachment of PsbP and PsbQ, probably by electrostatic interactions or salt bridges (47, 285). The results of these experiments provide useful information on protein-protein interactions among the extrinsic and intrinsic subunits of PSII, but a complete understanding of such interactions requires high-resolution structural data that would be provided by crystals of plant PSII.

STRUCTURAL STUDIES ON PHOTOSYSTEM I AND II

The past two years have brought major additions to the steadily growing collection of molecular pictures of the components of the photosynthetic apparatus (**Figure 3**) (201, 218, 221). New structural work on PSII (37, 95, 160) and on LHCII (188, 276) has provided higher resolution structures than were previously available (155, 166, 175, 322). A portrait of the first membrane supercomplex of a plant PSI RC associated with its antenna LHCI also became available (**Figure 4**) (28). The similarity in composition and arrangement of cofactors in complexes that are separated by a billion years of evolution is striking (29, 220, 221), and the differences in protein-protein interactions and new features added during the long-term evolution of eukaryotic complexes emphasize the unique biological adaptations to ecological niches and environmental variation of these complex enzyme systems (220, 221). At the mechanistic level, the new structures place restrictions on theoretical speculations and suggest experiments to support or reject old and new hypotheses.

The Structure of Plant Photosystem I

PSI is a remarkable nano-photoelectric machine that operates with a quantum yield close to 1.0 (219, 222). Theoretical quantum-mechanics solutions for such a mechanism exist (87, 105, 251, 311, 312), but no synthetic systems have approached this efficiency. This efficiency is why structural biologists who like to solve intricate structures were attracted to RCs (8, 80). The complexity of plant PSI is one of these challenges (262); as it is composed of a RC and LHCI, the resulting supercomplex presents an even bigger challenge than the bacterial RC (139, 219). It is therefore not surprising that the first PSI structure to be solved was that of the thermophilic cyanobacterium *T. elongatus* (111, 152, 260). The 2.5 Å structure (152), which contains a model of 12 protein subunits and 127 cofactors (96 Chl, 22 carotenoids, 2 phylloquinones, 3 Fe_4S_4 clusters, and 4 lipids), is a landmark achievement that provided the first detailed insights into the molecular architecture of PSI. The cofactor orientations and their interactions with protein subunits and other cofactors were determined (152). In crystals and in vivo, *T. elongatus* PSI is a trimer with a diameter of 210 Å and a maximum height of 90 Å. In contrast, plant PSI is a monomer, which, at 4.4 Å resolution, contains the models of 16 protein subunits, 167 Chl, 2 phylloquinones, and 3 Fe_4S_4 clusters (28). The main features of cyanobacterial and plant PSI are summarized in **Table 1**.

A stromal view of plant PSI (**Figure 4**) reveals two distinct, loosely-associated moieties: the RC and LHCI, which are separated by a deep cleft. The four LHCI subunits form two dimers arranged in series to create a half-moon-shaped belt docked on the F subunit side of the RC. This belt is the most prominent addition to the plant PSI structure. The RC retains the same location and

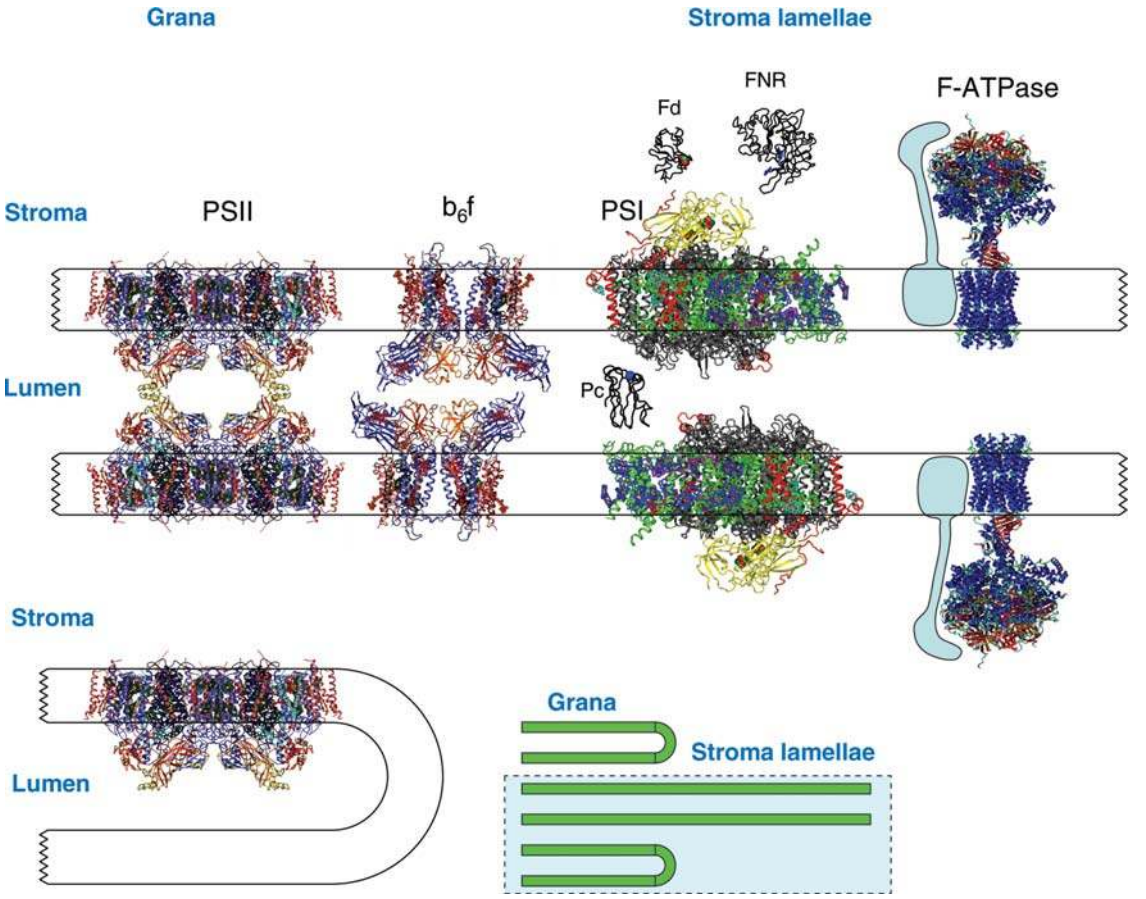

Figure 3

The architecture of thylakoid membrane complexes and soluble proteins based on high-resolution structures. Available structural data on membrane-protein complexes and soluble proteins have been adjusted to the relative size of plant photosystem I (PSI). The structural data were obtained from Protein Data Bank (PDB): PSI – 1QZV, 1YO9 (theoretical model); Fd – 1A70; PC – 1AG6; ferredoxin-NADP-reductase – 1QG0. The structure of chloroplast F-ATPase was constructed from data on mitochondrial and bacterial F-ATPase-PDB 1H8E (catalytic) and 1YCE (membranal) (O. Drory, unpublished communication). The insert presents a schematic depiction of the segment of the thylakoid that was modeled with the structures.

orientation of electron transfer components and transmembrane helices found in cyanobacterial PSI, except for those of subunits X and M, which were either lost during chloroplast evolution or added to cyanobacterial PSI after it diverged from eukaryotic PSI (29, 220). Two additional subunits (PsaG and H) are present in plant PSI (**Figure 4**). PsaH, located adjacent to PsaL, has a single transmembrane helix followed by a 20 Å long helix that lies on the stromal side of the membrane and coordinates one Chl molecule. PsaG is homologous to PsaK (230); it is situated on the opposite side of PsaK and contributes most of the contact surface area for association with LHCI (**Figure 4**). The two transmembrane helices of PsaG are connected by a relatively long loop that was assigned to the stromal side of the membrane (28), in agreement with recent biochemical data

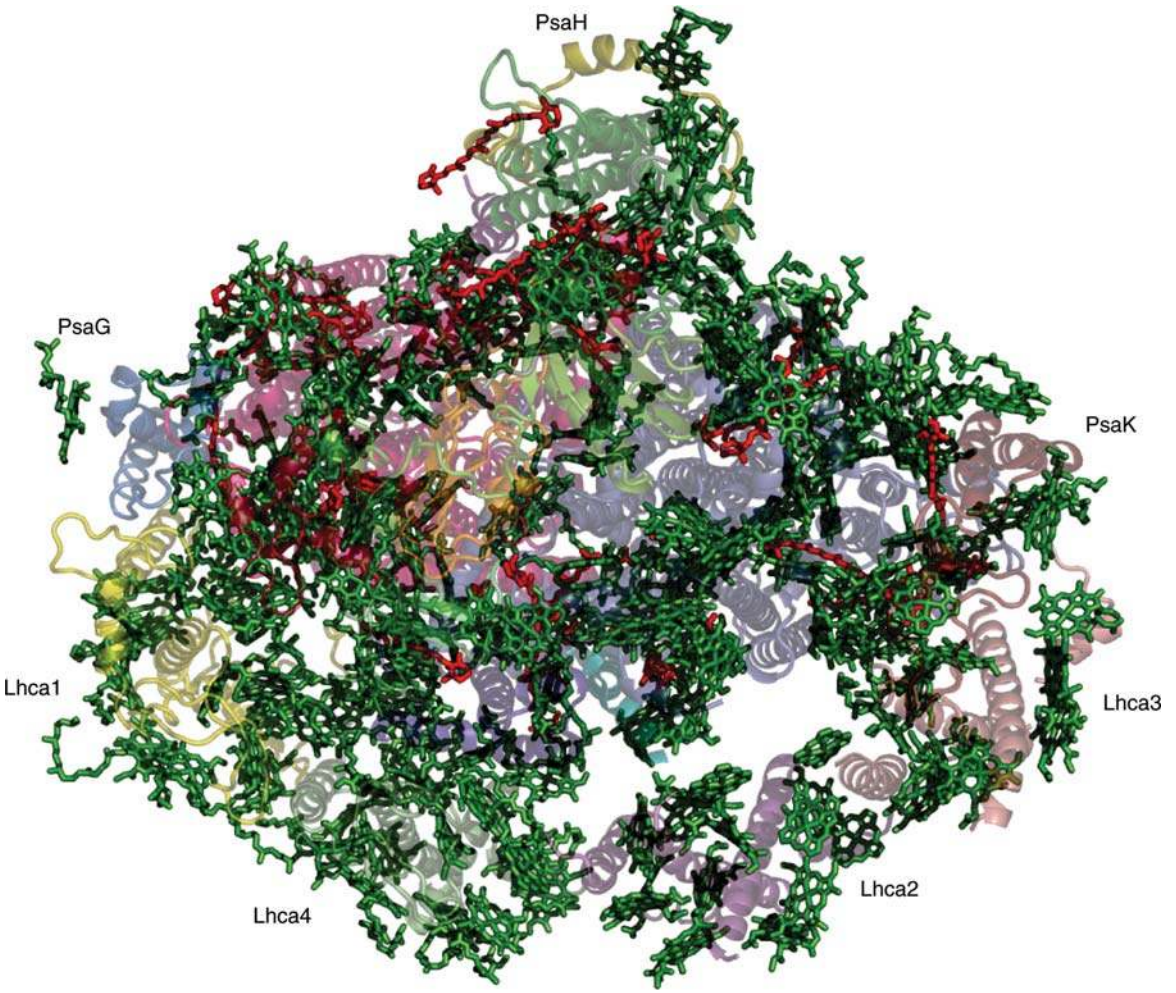

Figure 4

A view of the structure of plant photosystem I from the stromal side. The structural coordinates were taken from the theoretical refinement (PDB) of original structural data (PDB 1QZV) (26, 151). The Chl molecules (*green*) and the calculated positions of carotenoids and lipids (*red*) are shown. The protein backbone of the 16 subunits is in the background. The positions of PsaG, PsaH, PsaK, and LHCa1-4 subunits are shown.

(252). Although PsaK is so flexible in its position near PsaA that its loop was not apparent, even in the high-resolution structure of cyanobacterial PSI (152), PsaG is firmly bound to PsaB and also has helix-helix interactions with LHCa1 (**Figure 4**). Also on the stromal side, the general structure of the peripheral subunits PsaC, D, and E is almost identical to that of cyanobacterial PSI except for an N-terminal extension of PsaD that is unique to the eukaryotic subunit (**Figure 5**). We attribute the greater resistance of this domain of chloroplast PSI to chaotropic agents to this PsaD extension. On the lumenal side, the most noticeable distinction between plant and cyanobacterial RCs is the helix-loop-helix motif contributed by the longer N-terminal domain of plant PsaF (28), which facilitates more efficient PC binding. As a result, electron transfer from this copper protein to P_{700}

Table 1 Chlorophylls and transmembrane helices in PSI of cyanobacteria and higher plants*

	Transmembrane helices		Chlorophylls	
Subunits	Cyano	Plant	Cyano	Plant
A	11	11	40	40
B	11	11	39	39
F	1	1	—	—
I	1	1	—	—
J	1	1	3	2
K	2	2	2	2
L	3	3	3	3
M	1	—	1	—
X	1	—	1	—
G	—	2		1
H	—	1		1
Lhca1	—	3	—	13
Lhca2	—	3	—	13
Lhca3	—	3	—	12
Lhca4	—	3	—	13
RC			7	13
Linker (Chl)			—	5
Gap (Chl)			—	10
	32	45	96	167

*About eight additional densities in plant PSI are likely to be Chl molecules, giving a total of about 175 Chl molecules in plant PSI. The subunit-specific Chs coordinate the polypeptide chain. RC: Chls present in the reaction center with no apparent contact to specific subunit. Linker: Chls connecting the LHCa units. Gap: Chls situated between the reaction center and LHCI.

is two orders of magnitude faster than in cyanobacteria (135, 231).

In summary, the crystal structure of plant PSI reveals not only its architecture but also the possible mode of interaction with LHCI that causes supercomplex formation. The structure also provides new insights into the nature of the sites of interaction between PSI and PC, Fd, ferredoxin-NADP-reductase (FNR), and LHCII. As such, the structure provides a framework for investigating the mechanism of light harvesting and energy conversion, as well as the evolutionary forces that shaped the photosynthetic apparatus of terrestrial plants.

FNR: ferredoxin-NADP-oxidoreductase

Electron Donors

PC is the universal PSI electron donor, although a cytochrome can replace it in cyanobacteria and algae; under certain physiological conditions, cyt c_6 can alternate with PC as an electron carrier between cyt f and P700 (159, 245). Reports that plants contain an equivalent of cyt c_6 that can function as electron donor to PSI (123, 296) were called into question by results showing that *Arabidopsis* plants mutated in both PC genes but with a functional cyt c_6 could not grow photoautotrophically (208, 300, 301). The complete block in light-driven electron transport in these mutants, even in the presence of an increased dosage of the gene encoding the cyt c_6-like protein, makes it highly likely that PC is the only mobile electron donor to higher plant PSI.

Information on the PSI-PC interaction came from PsaF-depleted PSI RCs that exhibited impaired $P700^+$ reduction by PC and slowed photo-oxidation of cyt c_{552} (a PC analog from green algae) (27). Although this result suggested that PsaF provided the PC binding site (27, 135, 231), a null mutation in PsaF in *Synechocystis* grew photoautotrophically at nearly wild-type rates (61). This enigma was resolved by the cyanobacterial PSI structure and by studies in *Chlamydomonas* that demonstrated the presence of a hydrophobic binding site shared by PsaA and B that exposes a conserved tryptophan residue to the lumen surface (152, 275). A *Chlamydomonas* PsaA mutation (W651F) abolished formation of a first-order electron transfer complex between PC and PSI (274). Thus, the PC binding site comprises mainly a hydrophobic interaction with PsaA and B and is facilitated and controlled by charge-charge interactions with PsaF. As a result, electron transfer from PC to PSI is two orders of magnitude faster in plants than in cyanobacteria, and the release of

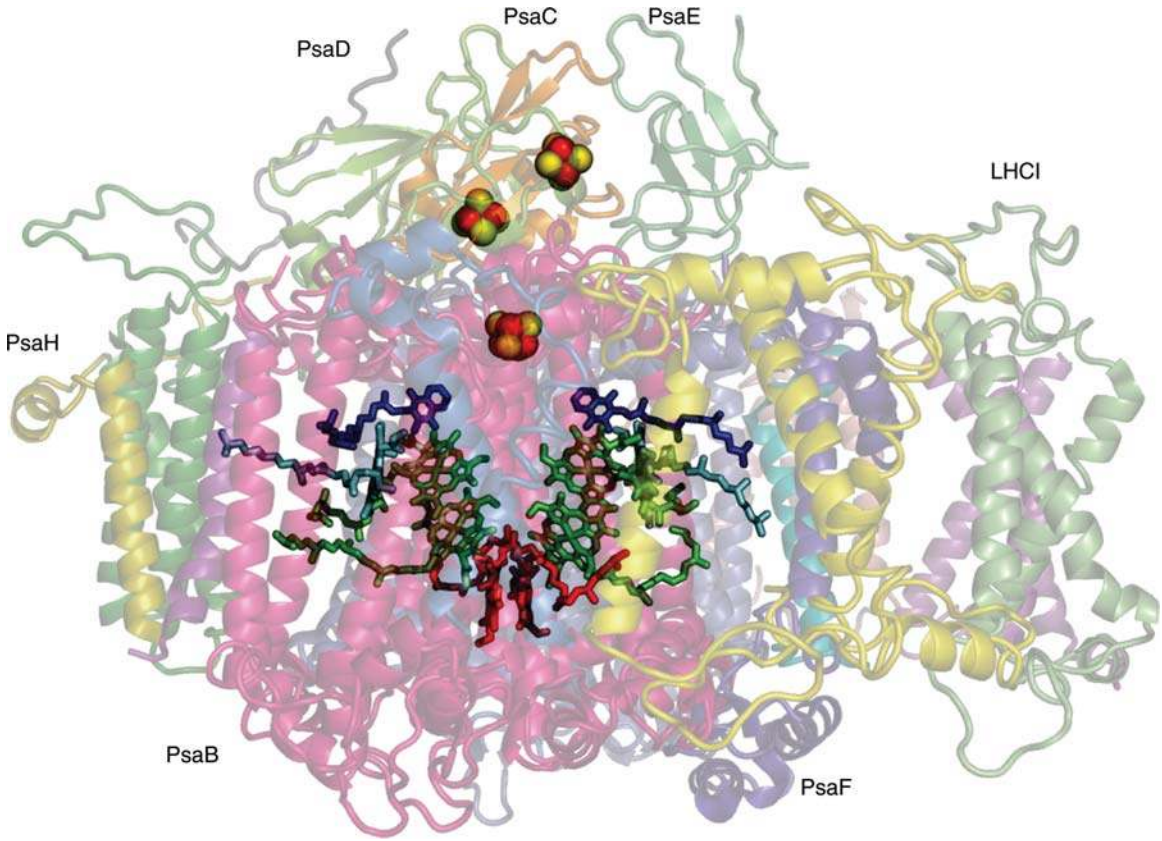

Figure 5

A side view of the structure of plant photosystem I. This figure was constructed as in **Figure 4**. The Chl, carotenoids, and lipids were eliminated. The cofactors involved in light-induced electron transport, i.e., P700, A_0, A_1, F_X, F_A, and F_B, are shown along with the backbones of the 16 subunits. The positions of PsaB, PsaC, PsaD, PsaE, and PsaF are shown. In the electron transport chain, the P700 Chl (*red*) and the other Chl (*green*) are indicated. The quinones (*blue*) and, in the iron-sulfur clusters, the iron (*red*) and the sulfur (*yellow*) are also indicated.

oxidized PC limits the electron-transfer rates (99, 119, 132, 133, 135). This effect was attributed to more efficient PC binding in plants that was mediated by the extra 18 amino acid residues in the plant PsaF N terminus. In the plant PSI structure, this extra N-terminal domain forms an amphipathic helix-loop-helix motif on the lumenal side of the thylakoid membrane (28), which, in comparison to the cyanobacterial structure (152), is the only alteration in the PC binding pocket. A model for the interaction of plant PC and PSI positions PC so that it interacts with the hydrophobic surface on PsaA and B and a positively charged site on PsaF (28). Superfluous degrees of freedom have been resolved by bringing a cluster of negatively charged conserved residues (i.e., Asp42, Glu43, Asp44, and Glu45) of PC into contact with the positively charged N-terminal domain of PsaF, which contains a few lysine residues that are missing in cyanobacteria (61, 135, 231, 246). The model in **Figure 6** suggests that the additional charges are responsible for more efficient PC binding in chloroplasts. One wonders whether this new interaction might generate

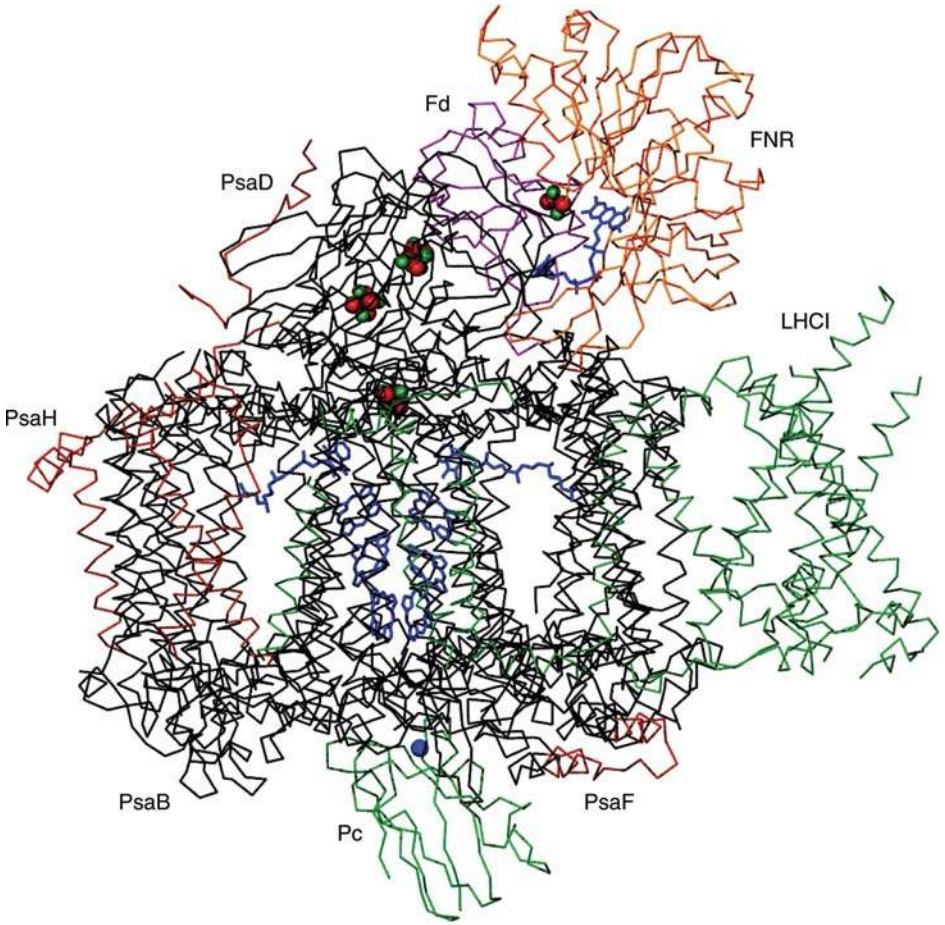

Figure 6

A side view model of putative interactions between plant photosystem I (PSI), plastocyanin, and the ferredoxin-ferredoxin-NADP-reductase complex. The four light-harvesting proteins (LHCa1-4) are shown (*green*). Novel structural elements within the RC (core) absent from cyanobacterial PSI (*red*) and the conserved features of both RC (*black*) are indicated. The Fe (*red balls*) and S (*green balls*) of the Fe-S clusters are shown. PC (*green*), its copper atom (*blue*), Fd (*magenta*), FNR (*orange*), and its FAD (*blue*), as well as the positions of the PsaB, PsaD, PsaF, and PsaH subunits, are also shown. The cofactors involved in light-induced electron transport from P700 to F_X are indicated (*blue*). The crystallographic data were from PDB: PSI – 1QZV, PC – 1AG6, and Fd-FNR complex – 1GAQ.

a constraint that restricts donor flexibility and therefore evolutionary loss of functional cyt c_6 in vascular plants (201).

Electron Transport Chain

The components of the PSI electron transport chain (ETC), P700, A_0, A_1, F_X, F_A, and F_B, were first identified spectroscopically during the last half-century (44). Light-induced charge separation oxidizes the primary electron donor P700 (Redox potential E'_m + 430 mV), a Chl a/a′ heterodimer, and reduces the primary electron acceptor A_0 ($E'_m \sim$ –1000 mV), a Chl a monomer. The electron is transferred to A_1 ($E'_m \sim$ –800 mV), a phylloquinone in most organisms; to F_X (E'_m –705 mV), an interpolypeptide (4Fe-4S)

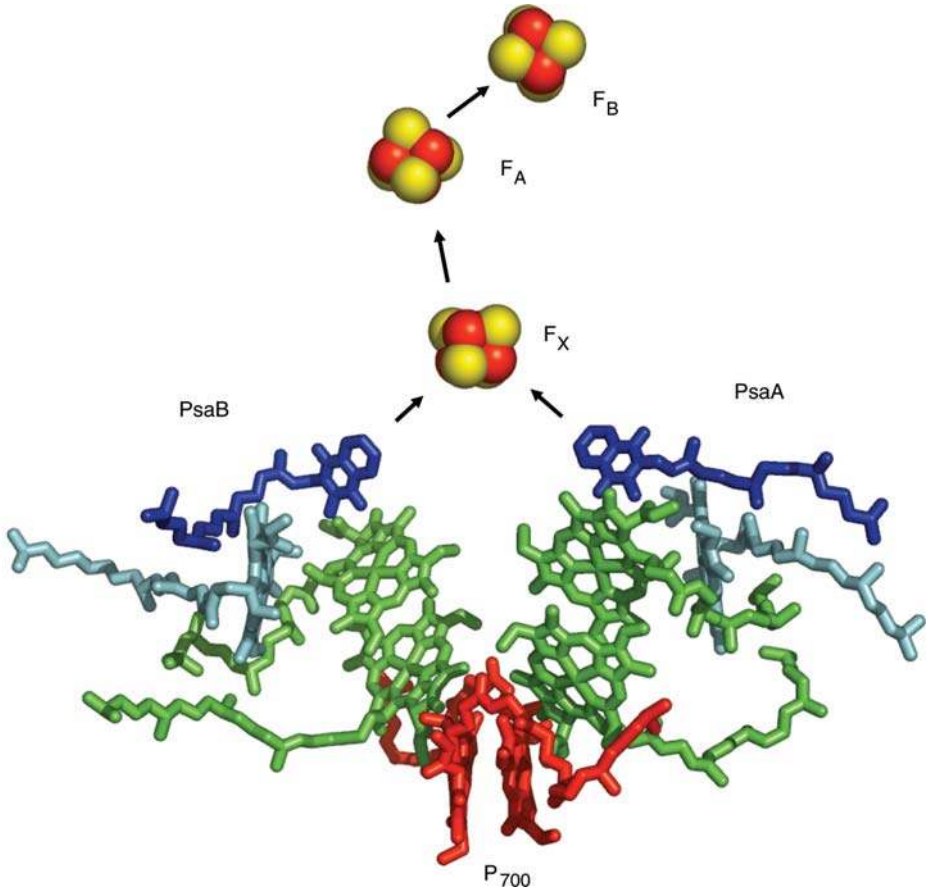

Figure 7

Structural model of the pathway for light-induced electron transport from P700 to F_B in photosystem I (PSI). The cofactors involved in light-induced electron transport in PSI are presented using the same color scheme as in **Figure 5**. PsaA and PsaB indicate the sidedness of the model.

cluster; and finally to F_A (E'_m – 520 mV) and F_B (E'_m – 580 mV), which are 4Fe-4S clusters bound to the extrinsic subunit PsaC (**Figures 7** and **8**). The high-resolution structure of PSI established the spatial arrangement among these cofactors but also raised questions about their mode of action and the possible involvement of neighboring molecules in their activity (120, 152, 317). The ETC is arranged in two quasi-symmetrical branches consisting of six Chl, two phylloquinones (A_1), and three Fe_4S_4 clusters (F_X, F_A, and F_B). P700 is composed of a Chl pair, Chl a and Chl a′, that are not identical and therefore deviate from perfect symmetry. A pair of Chl a molecules situated symmetrically approximately 16 Å from P700 were assigned to the spectroscopically-characterized primary acceptor A_0. To complicate matters, another pair of Chl a monomers is located approximately halfway between P700 and A_0 (**Figures 7** and **8**) that are assigned as accessory Chl that may participate in excitation and/or electron transfer (see below). From A_0, the electron is transferred to one of two clearly resolved quinones and from there to F_X. The quinones are placed on a pseudo-twofold-symmetry axis, but their angles and interactions with the protein are clearly not identical.

The presence of two symmetrical cofactor branches in PSI (**Figures 7** and **8**) raised the question of whether one or both are active in electron transport under physiologically relevant conditions (43, 45, 74). By analogy to the RC in purple bacteria, it was proposed that electron transfer in PSI occurs preferentially along one branch. Alternatively, the fact that

PSI is related to the green bacterial type I RC, which is a homodimer (29, 54, 55, 93, 108, 128, 129, 186, 220), and the nearly perfect symmetry of the PSI ETC suggested that electron transfer should occur along either branch (243). Electron-nuclear double resonance (ENDOR) studies of PSI mutations in the residues binding P700 showed that the Chl on the PsaB side carries most of the electron spin density of $P700^+$ (174, 297); this observation indicates that there are differences in the electronic characteristics of the two branches. Low-temperature Electron Paramagnetic Resonance (EPR) experiments on the accumulation or reoxidation of the quinone acceptor A_1 detected a single quinone, but the identity of the active branch was unclear (213, 247).

In cyanobacterial PSI, site-directed mutations on the PsbA branch markedly alter the kinetics of the first steps of electron transfer and the spectral properties of the primary electron acceptor A_0, whereas mutations on the PsaB-branch yield kinetics and spectral properties that are essentially undistinguishable from the wild-type (68, 308, 309). It was therefore concluded that most of the electron transfer takes place on the PsaA branch in prokaryotes. Studies on eukaryotes, however, find evidence of significant PsaB-branch activity (41, 94, 122, 148, 213, 241, 242). Picosecond optical spectroscopy showed that the replacement of the Met axial ligand to Chl a (either eC-A3 or eC-B3) (152) by His in *C. reinhardtii* PSI partially blocked electron transfer; this observation indicates that both branches are active in electron transfer (243). However, these data were challenged by a low-temperature transient EPR study (197). This result raises the point that, although site-directed mutants are useful tools for mechanistic research, studies of the mutants have to be complemented by high-resolution structures; small changes due to a slight movement in one of the polypeptides that bind cofactors could lead to erroneous conclusions.

At the present time, the most convincing studies on the sidedness of electron transport in PSI come from optical spectroscopy in wild-type organisms (148); these studies suggest that fast absorption changes are associated with PsaB quinone reoxidation. This hypothesis was based on the observation that mutations in the PsaA quinone-binding site have substantial effects only on the ~200 ns

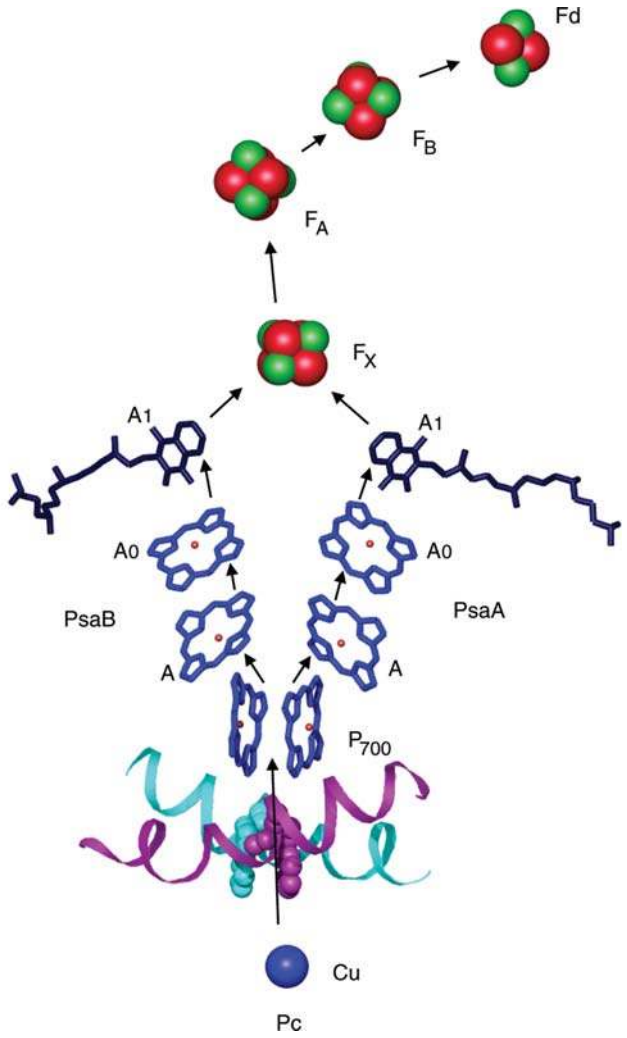

Figure 8

Structural model of the pathway for light-induced electron transport from plastocyanin to ferredoxin in photosystem I. Chls (*blue*), quinines (*black*), the copper atom of PC (*blue*), and Fe (*red balls*) and S (*green balls*) of the three Fe4-S4 clusters and the Fd Fe2-S2 are depicted. Two tryptophan residues (*light-blue and light-pink space-filling structures*) that might be involved in electron transport from PC to P700 are also shown in the context of their secondary structural environment.

reoxidation rate, whereas symmetrical mutations in the PsaB quinone-binding site affect only the ~20 ns reoxidation rate (122). In a very recent discussion of the sidedness in PSI electron transfer with the phylloquinones bound to either the PsaA or the PsaB subunits (255), the partial reaction in the electron transfer chain that could not be simulated is the phylloquinone (A_1) reoxidation reaction. In order to simulate measured rates of the biphasic decay (approximately 20 and 200 ns), a novel model was presented that suggests that the redox potentials of the quinones are almost isoenergetic with that of the iron sulfur center, F_X. Therefore, the only substantially irreversible electron-transfer reactions would be the reoxidation of A_0 on both electron transfer branches and the reduction of F_A by F_X. This hypothesis, along with future ultrafast measurements and high resolution studies of wild-type and mutated PSI, are likely to elucidate the mechanism of electron transfer in PSI.

Electron Acceptors

Fd's function as the principle PSI electron-acceptor plays a significant role in determining the enthalpy on earth. Fd reduces $NADP^+$ via FNR for various reductive biosynthetic pathways, thioredoxin via Fd-thioredoxin reductase for redox regulation, and also enzymes such as acyl carrier protein (ACP) desaturase, nitrite reductase, and glutamic acid synthase. Fd also reduces the cyt b_6f complex or plastoquinone in a cyclic electron transfer pathway around PSI that generates a proton gradient and, hence, ATP synthesis (52, 141, 153, 195, 196) (see below). Fd is a soluble protein with one 2Fe-2S cluster that accepts electrons from the F_B cluster on the stromal side of the PSI complex. In certain organisms, this reaction takes place under extreme conditions such as high temperature (103, 217). The Fd-PSI interaction involves the PsaC, D, and E subunits (10, 190, 204). The reduction of Fd by F_B involves three first-order components with $t_{1/2}$ values of 500 ns, 13–20 μs, and 100–123 μs (266, 267). The 500 ns phase corresponds to electron transfer from F_A/F_B to Fd. Based on kinetic arguments, it has been proposed that a PsaE-dependent, transient tertiary complex containing PSI, Fd, and FNR forms during linear electron transport (288). **Figure 6** depicts a model of such a tertiary complex that is based on the structures of plant PSI (28), the Fd-FNR complex (177), and cross-linking data (101, 102, 183, 265). The Fd-FNR structure was fitted to the most likely contact sites that (*a*) obey the structural constraints and (*b*) place the electron carrier at distances that allow for the observed kinetics of electron transport (**Figure 6**). Although the two structures could not be fitted in a way that places Fd close enough to F_B to obtain the necessary rate of electron transfer between them, the model allows oxidized Fd to toggle towards F_B and close the gap between them. Upon reduction, Fd returns to its initial position, close enough to the FNR flavin for efficient electron transfer. Obviously, the actual structures of PSI-Fd and PSI-Fd-FNR supercomplexes are needed to better understand the mechanism of electron transport between F_B and $NADP^+$. The recent report of a cyanobacterial crystal of a 1:1 PSI:Fd complex (109) that diffracts to 7–8 Å may be the first step in this direction. Fd-mediated electron transport is not the only reaction that can occur on the reducing side of PSI. Cyanobacteria grown under iron-depleted conditions synthesize a flavoprotein (flavodoxin) that replaces Fd functionally in most, but not all, reactions (199, 225).

Light-Harvesting and Excitation Migration in Plant Photosystem I

PSI maintains a quantum yield of approximately one in all its forms in various organisms (219, 220). This efficiency persisted for 3.5 billion years of evolution and survived an enormous number of potential mutations. Not surprisingly, the sequences of genes encoding PsaA and B exhibit very high amino acid sequence conservation, in particular for the amino acids that are likely to coordinate

Chl (29, 30, 151, 262). Other factors are also important for Chl binding, however. The plant PSI structure revealed that only 3 of the 96 Chl molecules reported in the model of the cyanobacterial PSI RC are missing: two bound to PsaM and PsaX, and one bound to PsaJ (**Table 1**). Of the remaining 93 Chl, 92 are found at the same position in the plant RC; these Chls include 15 that have their Mg^{2+} coordinated by H_2O (28). Only one of these (B33) had a significantly changed position; this change was due to the insertion in plant PSI of a three-amino-acid loop that coordinates this Chl, whose novel position resulted in loss of the long wavelength (730 nm) "red trap" of cyanobacterial PSI. A few other minor alterations, mainly in chromophore orientation, were also observed (28). Thus, to adapt the plant RC to utilize energy from the LHCI antenna required the addition of only 10 Chl molecules at three contact regions (17, 210). It is not clear whether the exact position and coordination of each Chl molecule contributes to the almost perfect quantum yield of the system, and, if so, how a deleterious mutation in the system would be detected and corrected (220).

Structural information on the geometry of the Chl molecules in PSI permits the construction of microscopic models for an excitation-transfer network of PSI (56, 72, 118, 158, 200, 263, 264, 310). Once the location and orientation of pigments are determined, excitation-transfer rates between pigments are described by Forster theory (105, 251), or, for strong couplings and fast timescales, by Redfield theory (310). Thus, excitation-transfer pathways among the pigments of cyanobacterial and plant PSI can be defined as an excitation-transfer network (262). This approach yielded computations of kinetic parameters (average excitation lifetimes, overall quantum efficiency) to a reasonable accuracy, as well as the construction of stochastic models whose robustness (error tolerance) and optimality (high relative fitness) allow probing of the network by comparing the pigment network geometry with alternative geometries (289). These models must ultimately be verified experimentally.

Structure of Photosystem II

In the case of plant PSII, a three-dimensional model of the plant PSII supercomplex obtained by cryoelectron microscopy and single particle analysis is available (223), but the only available crystal structures are of the PsbP and PsbQ extrinsic subunits, at 1.6 and 1.95 Å resolution, respectively (58, 138) These structures are presented in **Figure 9**. The larger subunit is composed mainly of β-sheets, and does not appear to have any structural features in common with its cyanobacterial counterpart (PsbV). The structure of PsbQ likewise has no counterpart among cyanobacterial subunits. The core of this protein is a four-helix bundle, but the N-terminal 45 residues are mobile and are not resolved in the structure shown in the figure. This flexible domain of PsbQ is believed to be involved in binding to PSII (261). Attempts to crystallize PsbO failed, possibly because it is intrinsically disordered (191). Attempts to produce diffraction quality crystals of intact plant PSII were difficult (107) due to proteolysis of samples during crystallization (D.F. Ghanotakis, personal communication). This problem was not encountered in attempts to crystallize PSII from thermophilic cyanobacteria (i.e., *T. elongatus*, *T. vulcanus*) (95, 155, 322). The protein complex forms dimers in the crystals, and the resolution of the structures ranges from 3.8 to 3.5 Å; a more recent report gave a resolution of 3.2 Å (37), and further improvements may appear before this review is published.

Stromal and sideview models of PSII structure based on the data presented by Ferriera et al. (95) are shown in **Figures 10** and **11**. Such models are satisfying because many of their features coincide with predictions derived from biochemical and spectroscopic probing experiments; however, they also provide enhanced structural details regarding placement of the individual subunits and the orientations of pigments associated

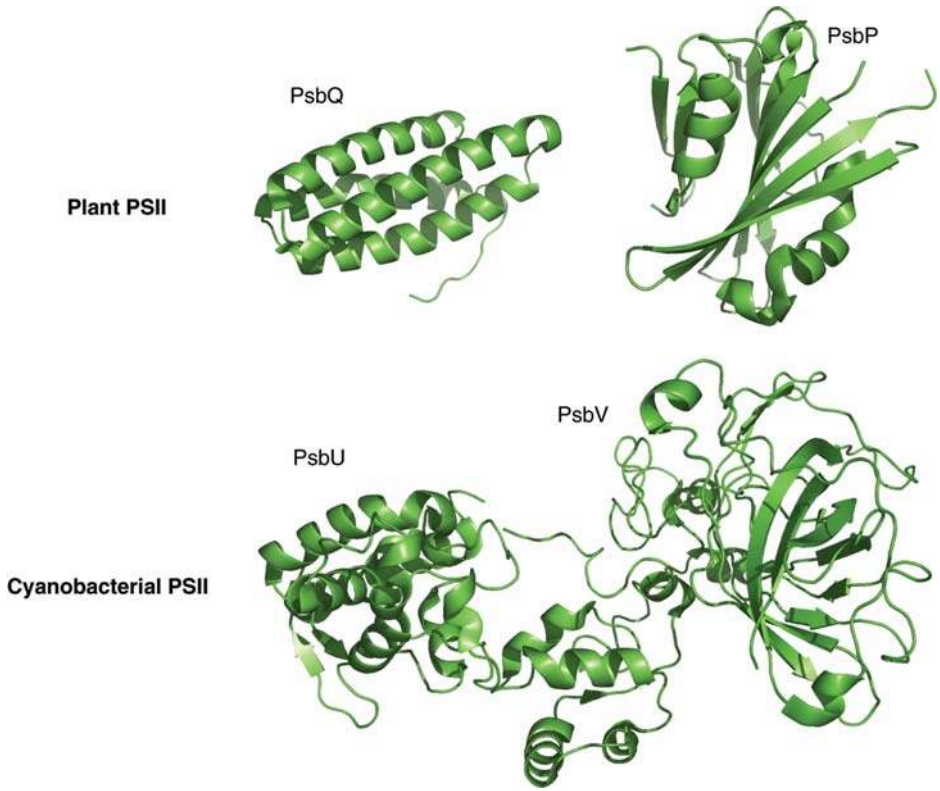

Figure 9

Structures of the smaller extrinsic polypeptides of photosystem II (PSII). The plant PSII subunit structures are taken from crystals of the isolated proteins (58, 138). Structural data are from PDB: PsbQ-1NZE and PsbP - 1V2B. The cyanobacterial structure shows the interaction between PsbU and PsbV, taken from the *T. elongatus* structure (PDB: PSII-1S5L) (95).

with the RC and its antenna system. In all of the structures now available, it can be seen that membrane-spanning helices of the PsbA and PsbD RC subunits are in close proximity to one another. RC chromophores (comprising six Chl, two $Pheo_a$, the plastoquinones Q_A and Q_B, and the redox-active tyrosines Y_Z and Y_D) are bound to these subunits, as expected. The PsbC subunit is close to PsbA, and PsbD is in close proximity to PsbB. The disposition of Chl molecules in PsbB and C are now better resolved; 14 Chl a are bound to PsbB, and 16 are bound to PsbC. For 23 Chl, the ligand to the central Mg^{2+} atom of the chlorin ring is a His-imidazole nitrogen. Seven β-carotenes are resolved in the structure; one of these connects cyt b_{559}, Chl_{zD1}, and P680, the RC Chl of photosystem II (37). The large extrinsic loops of PsbB and C are readily visible as significant protrusions into the lumenal space above the membrane-spanning α-helices of these large subunits. Accessory subunits (i.e., PsbH, I, J, K, L, M, N, T, X, and Z) are modeled into the structure; L, M, and T are suggested to be involved in formation of PSII dimers, whereas I and X are proposed to stabilize binding of the fifth and sixth Chl molecules, Chl_{ZD1} and Chl_{ZD2}, that are bound to PsbA and D, respectively. The PsbJ, K, N, and Z subunits are clustered near PsbC, and are hypothesized to be involved in carotenoid binding (95). On the stromal side of the structure, the Q_A binding site is composed of amino acid residues contributed by PsaD; for the Q_B site, the ligands are donated by PsbA. A nonheme iron ligated between these sites completes a structure that is quite similar, but not identical, to the quinone sites in photosynthetic bacteria (160). A summary of this information, including the proposed subunit-cofactor interactions, is presented in **Table 2**.

As predicted from biochemical and mutagenesis experiments (46), the large extrinsic loops of PsbB and C provide binding sites for

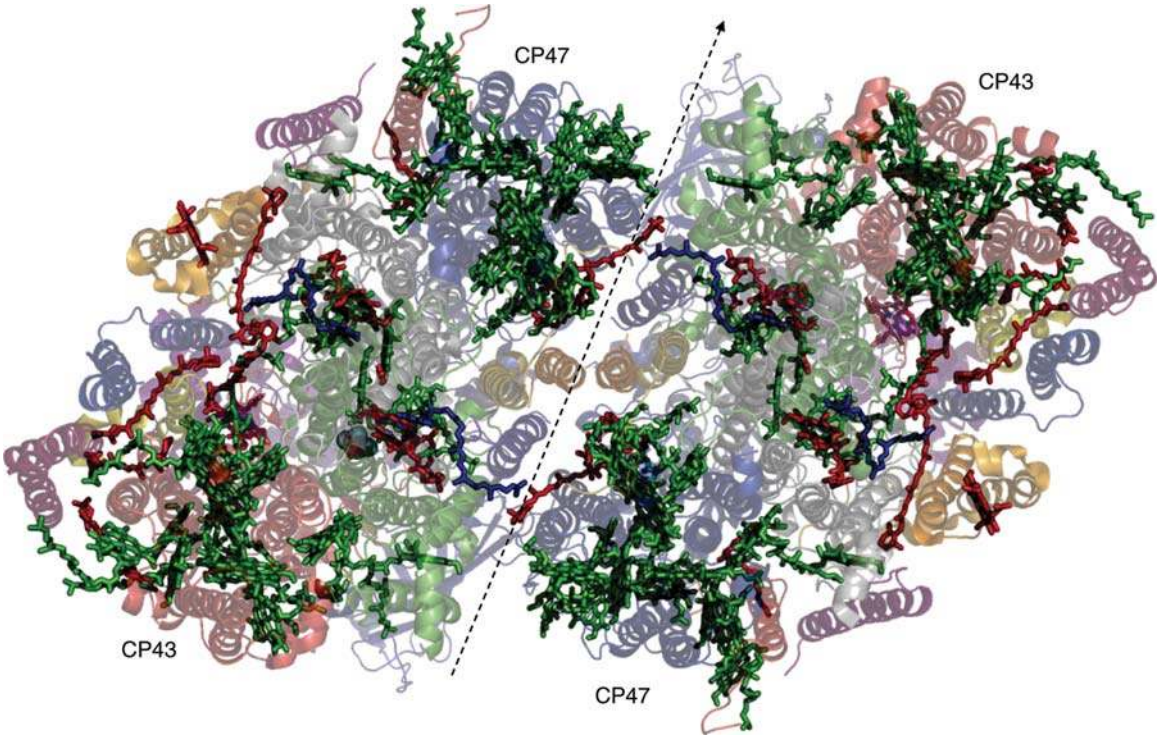

Figure 10

A stromal side view of the structure of the cyanobacterial photosystem II (PSII) dimer. The polypeptide chains are shown at lower contrast to reveal the chromophores; PsbB (*PsbB*) and PsbC (*PsbC*) are labeled, and the boundary between the monomeric RCs is indicated (*dashed arrow*). Chl a (*green*), carotenoids (*red*), and plastoquinones (*blue*) are also shown. The structure is based on PSII PDB-1S5L.

attachment of PsbO, which is visible on the lumenal side of the complex as an elongated structure containing β-sheets, consistent with predictions from physical characterizations of the soluble protein (34, 191, 192, 272, 307, 323). In the structural model, the N terminus of the protein is bound to the extrinsic loop of PsbC, whereas a loop in the PSbO structure makes contact with the extrinsic domain of PsbB. The structure gives no evidence for the interaction detected in plant PSII between the PsbO N terminus and the extrinsic loop of PsbB (227). The presence of two copies of PsbO in plants (306) may be responsible for the extra PsbO-PsbB interaction in spinach. Although PsbO stabilizes the inorganic ion cluster, the 3.5 Å model predicts that no PsbO ligands bind to the Mn atoms. However, a loop in PsbO extends in the direction of the Mn cluster, and this loop is proposed to function as a hydrophilic pathway between the lumen and the inorganic ion cluster (95). The smaller extrinsic subunits of cyanobacterial PSII appear to bind through interactions with PsbO and with one another; a model of the PsbU-PsbV subunits is given in **Figure 9**. A comparison of this structure with that of the two plant subunits, as shown in **Figure 9**, points to the substantial differences between these pairs of proteins. The plant subunits either contain a four-helix bundle (PsbQ) or are rich in β-sheets (PsbP), features that are absent from the structures of PsbU and V. The presence of a heme in PsbV gives further evidence for the marked differences between the prokaryotic and eukaryotic subunits.

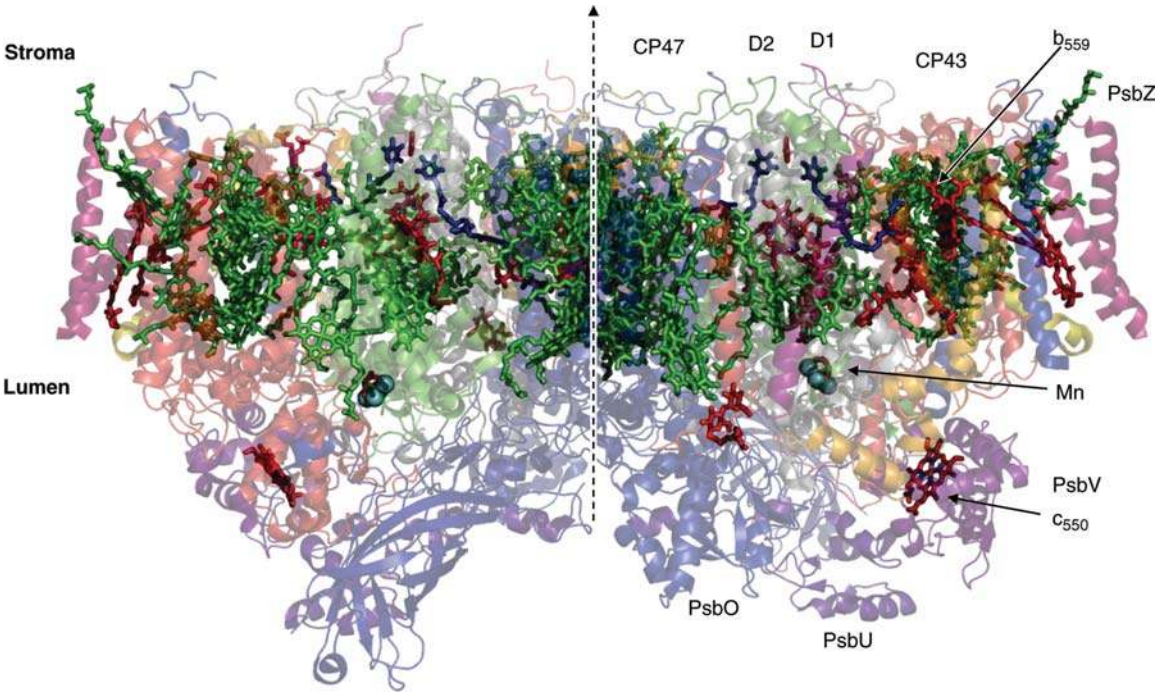

Figure 11

Side view of the structure of cyanobacterial photosystem II. Positions of the extrinsic polypeptides are indicated, along with the intrinsic subunits PsbA-D and the small intrinsic accessory subunit, PsbZ. The chromophore colors are as given in **Figure 10**; the c_{550} and b_{559} hemes (*red*) and the Mn cluster (*blue*) are highlighted. The pseudo-C_2-symmetry axis between the monomeric subunits of the homodimer is also indicated (*vertical dashed arrow*).

Caution is advisable in drawing firm conclusions about the structure of PSII from the available structures. Limited resolution (3.8–3.2 Å) requires some interpretive modeling to build structures as, for example, with the amino acid side chains (37). A major issue concerns the structure of the inorganic ion cluster itself. All models to date propose a monomer-trimer arrangement of the Mn atoms in the cluster, in agreement with spectroscopic experiments (236). In the detailed model of Ferreira et al. (95), three Mn atoms and an atom of Ca^{2+} form a distorted cube-like structure; an isolated Mn atom may be positioned to play a role in H_2O oxidation, which we discuss below. Unfortunately, high X-ray energies and exposure times used to obtain diffraction data resulted in radiation damage that reduced the Mn atoms, probably to all Mn^{2+}, in contrast to the native Mn^{3+} and Mn^{4+} oxidation states (164, 248). It is likely that Mn^{2+} has dissociated from native ligands, causing some rearrangement of the amino acid residues in the binding site (76). This possibility is also suggested by Fourier Transfer Infra Red spectoscopy (FTIR) experiments on *Synechocystis* 6803 PSII that showed that the carboxyl terminus of PsbA (Ala344) is a ligand to the Mn cluster (63, 207, 279). The most detailed model based on the crystal structure places this residue near the Ca^{2+} atom but not as a Mn ligand. These reservations should not detract from the enormous achievement of obtaining a crystal structure of PSII; however, more data, obtained at shorter exposure times, are required to validate current models of the inorganic ion cluster.

Electron Transport in Photosystem II

Characterizations of PSII by a variety of methods summarized in References 78, 89, 90, 117, and 203 identified the electron transport cofactors in PSII, including Mn, Ca^{2+}, and Cl^- in H_2O oxidation and their stoichiometries (i.e., four Mn, one Ca^{2+}, and one Cl^- per RC) (1, 179, 187, 271, 315). The identification of redox-active tyrosines, one of which (Y_Z) mediates electron transfer from the inorganic ion cluster to P680 in the RC, was a significant advance in understanding PSII electron transfer (21). A functional analogy between PSII and the bacterial RC formed the basis for the current model of electron transfer (89). Therefore, the pathway of electron transfer in PSII is generally agreed to be as follows: $H_2O \rightarrow [Mn_4CaCl] \rightarrow Yz/Y_Z^{\bullet} \rightarrow P680/P680^+ \rightarrow Pheo_a/Pheo_a^- \rightarrow Q_A/Q_A^- \rightarrow Q_B/Q_B^-$. Double reduction and protonation of Q_B^- releases Q_BH_2 from its PSII binding site in exchange for an oxidized quinone (89). It is now clear from mutagenesis of the heme-binding pocket of cyt b_{559} that it is not required for O_2-evolution activity (209), although cyt b_{559} is necessary for assembly of stable PSII complexes and may function in a cyclic reaction around PSII (290).

The estimated redox potentials of intermediates in the PSII electron transfer pathway depend on the potential (E'_m) of the primary oxidant, $P680^+/P680$, which was set at +1.12 V based on a potential of −0.64 V for the Pheo a/Pheo a- couple (90). Other potentials are as follows: (*a*) O_2/H_2O, +0.93V; (*b*) $Y_Z^{\bullet}/Y_Z$, +0.97 V; (*c*) Q_A^-/Q_A, −0.03 V; and (*d*) Q_B/Q_B^-, +0.030V (89, 287). A reevaluation of the P680 and $Pheo_a$ reduction potentials are in order (71, 244), based on new results that suggest a more positive potential (+1.27 V) for $P680^+/P680$ and therefore for Pheo a/a- and for intermediate redox states in the H_2O-oxidizing reaction as well. The kinetics of electron-transfer reactions have been worked out in detail. The rate-limiting step in H_2O-oxidation is approximately 1.4 ms;

Table 2 Chlorophylls, transmembrane helices, and cofactors of O_2-evolving PSII RCs from cyanobacteria and plants[1]

Subunits	Transmembrane helices		Chlorophylls		Other cofactors
	Cyano	Plant	Cyano	Plant	
A	5	5	3	3	Y_Z, 4Mn, Pheo a, Q_B
B	6	6	16	16 (?)	
C	6	6	14	14 (?)	
D	5	5	3	3	Y_D, Q_A
E	1	1			Cyt b_{559} heme
F	1	1			Cyt b_{559} heme
H	1	1			
I	1	1			
J	1	1			
K	1	1			
L	1	1			
M	1	1			
O	0	0			
P[2]	—	0			
Q[2]	—	0			
S	—	4			
T	1				
U[3]	0	—			
V[3]	0	—			Cyt c_{550} heme
X	1	1			
Y	1	1			
Z	2	2		—	
	…	…	…	….	
	35	38 (?)	36	36 (?)	

[1]The number given for transmembrane helices in cyanobacteria is taken from the models constructed from crystallographic data (95, 155, 160, 322), but should be viewed as provisional until higher-resolution data become available (37). For higher plants, hydropathy plotting was used to predict the number of transmembrane helices.
[2]An extrinsic subunit unique to plant PSII.
[3]Extrinsic subunits unique to cyanobacteria.

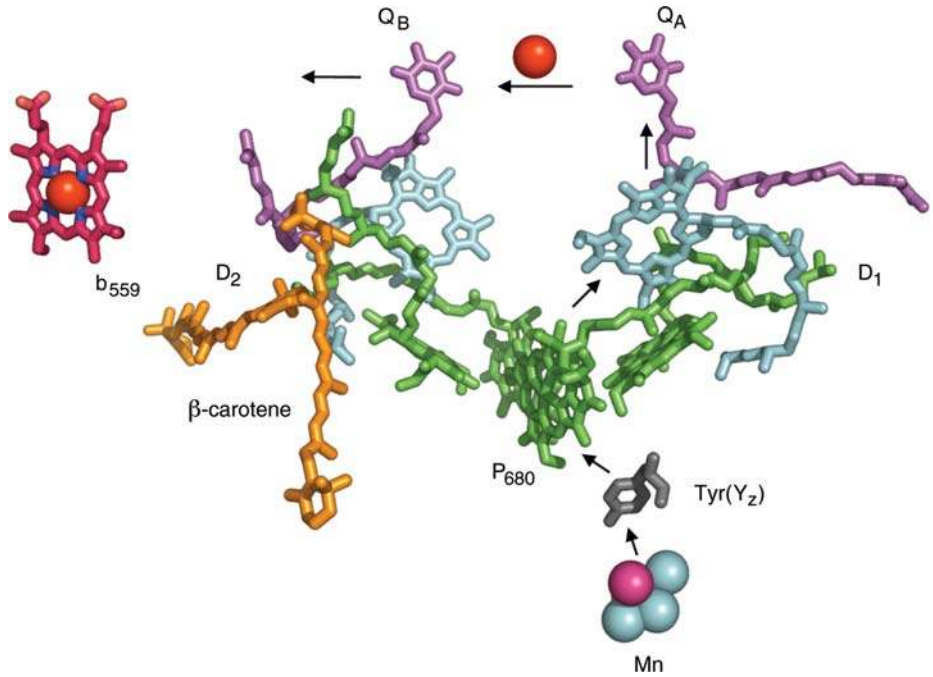

Figure 12

Structure of the photosystem II (PSII) electron transfer chain. The direction of electron transfer down the right (D1 or PsbA) side from P690 to Q_A is indicated (*arrows*). The following cofactors are shown: Chl a (*green*), Pheo a (*light blue*), plastoquinones (*purple*), cyt b_{559} heme and reducing-side nonheme iron (*red*), carotenoids (*orange*), Ca^{2+} (*magenta*), and Mn atoms (*blue*); one Mn atom is obscured in the structure. The structure is based on PDB: PSII-1S5L.

electron transfer from Y_Z to $P680^+$ occurs in the ns to μs time domain, and electron transfer from P680 to $Pheo_a$ occurs in approximately 3 ps. Reduction of Q_A by Pheo a- occurs in 250–300 ps, and the $Q_A^- \rightarrow Q_B$ reaction has a half-time of approximately 100 μs (89, 90).

The crystal structures of PSII have revealed more exact details of the organization of electron transfer cofactors (95, 155, 322); a model is presented in **Figure 12** in which the accessory Chls (Chl_{ZD1} and Chl_{ZD2}) are omitted for clarity. The bifurcated electron transfer pathway comprised of Chl a, Pheo a, and plastoquinones is similar to the arrangement of cofactors of the RC of purple photosynthetic bacteria (80). A notable difference is the spacing of the two Chl molecules that are presumed to make up P680. In PSII this distance is estimated to be 8.3 Å (95) rather than the 7.6 Å in bacteria. The longer distance is in accord with the proposal that, in PSII, the entire array of RC pigments might be able to function as a multimeric RC (83), even though a localized Chl cation radical is present in the charge-separated state (90). The structural model shows that the cofactors are separated by relatively short distances: 10.6 Å for P680-Chl a [PsbA(D1)] and for Chl a [PsbA (D1)]-Pheo a, and 14 Å for Pheo a -Q_A (160). These distances are consistent with the rapid rates of electron transfer that have been measured. The two carotenoids shown in the model presented in **Figure 12** include the pigment that, along with the accessory Chl molecule (Chl_{ZD1}) and cyt b_{559}, may be involved in a cyclic electron-transfer pathway from b_{559} on the reducing side of PSII back to the oxidizing side (90, 290). The Y_Z-Mn cluster complex is shown at the bottom of the figure.

The model, a monomer-trimer arrangement of Mn atoms, is similar to the structure derived from magnetic resonance experiments (236, 281). The distance between the tyrosine and the metal center is approximately 7 Å; this observation is in agreement with the distance derived from magnetic resonance experiments (50, 182). Mn ligands proposed in the model (D170, E189, E333, E354, H337, H332, and D342) (95) are all donated by PsbA. These ligands include residues identified as possible ligands by either site-directed mutagenesis (79, 88) or pulsed-magnetic-resonance spectroscopy (51). All models based on either crystal structures or on spectroscopic measurements (64, 163) predict a close interaction (3.5–4.5 Å) between Mn atoms and the Ca^{2+} in the metal cluster.

Mechanism of O_2 Evolution

The model for O_2 evolution invokes a set of oxidation states ("S" states) (172) to explain the period-four release of O_2 from thylakoids exposed to short (<10 μs) flashes of light. The reaction is a linear sequence of photocatalyzed oxidations, beginning in dark-adapted material from the S_1 state; the S_4 state decomposes spontaneously to release O_2 and form the S_0 state. The entire sequence may be written as: $2H_2O + S_0 \rightarrow S_1 \rightarrow S_2 \rightarrow S_3 \rightarrow S_4 \rightarrow S_0 + O_2 + 4\ H^+$. Because Mn is the only redox-active metal in the site of H_2O oxidation, considerable effort has gone into probing its behavior. Spectroscopic experiments (164, 236, 248) as well as reductive titrations (176) give Mn oxidation states for S_1 of 2 Mn^{3+}/2 Mn^{4+}. Results of several spectroscopic experiments (75, 81, 233, 236) point to Mn oxidation on each S-state advancement up to S_3. The rapid decay of the S_4 state ($t_{1/2} = \sim 1.4$ ms) prohibits characterization of the step in which O_2 is formed and released from PSII. Speculations about the identity of the terminal oxidant in the mechanism include $Y_Z^{\bullet}$ and a Mn^{5+} species as possible candidates (136, 235, 294, 295). The identity of the terminal oxidant is a critical issue that must be resolved for a full understanding of the chemistry of H_2O oxidation.

The roles of Cl^- and Ca^{2+} in H_2O oxidation are also topics of great interest. Removal of either ion from PSII blocks S-state advancement at S_2 (42, 187, 234). In the case of Cl^-, it has been shown that the anion is required for the $S_4 \rightarrow S_0$ transition and that its binding to the oxygen-evolving complex (OEC) is weaker in the higher S-states (302, 303). Evidence for a close proximity of Cl^- to the Mn cluster has also been presented (67, 182), and some models of the OEC show it as a ligand to Mn (286, 295), although this status has not been definitively confirmed by spectroscopic methods (127). Calcium has been shown to stabilize the ligand environment of the Mn cluster (198, 249); however, the requirement for Ca^{2+} to advance the S-states beyond S_2 suggests that it may play a more direct role in the mechanism of H_2O oxidation as well.

Critical questions about the mechanism of H_2O oxidation focus on (*a*) the steps at which substrate oxidation occurs and (*b*) the roles of Mn, Ca^{2+}, and Cl^- in this process. Experiments employing time-resolved mass spectrometry and isotopically-labeled H_2O indicate that the substrate binds in S_0 and S_3 (131). Advancements of the S-states are accompanied by H^+ release; the prevailing notion is that H^+ release follows a 1:0:1:2 pattern starting from S_0 (259). The origin of the protons released into the medium continues to be a subject of debate (see Reference 90); H_2O is the ultimate source, but the phenolic H^+ of Y_Z may form part of a H^+-transfer network. Another question concerns the pathway(s) by which H^+ exits the site of H_2O oxidation. Evidence that His190 of the PsbA subunit is involved, perhaps by hydrogen-bonding to the phenolic proton of Y_Z as a first step in H^+ transfer network, has been presented, but this observation has not been confirmed by spectroscopic methods (79). A proposal, based on the 3.5 Å structure, suggesting that some lumenal residues of PsbA participate in a proton transfer pathway (95), has not been tested

experimentally. Regardless of the pathway, proton transfer coupled to electron transfer from the Mn cluster to $Y_Z^{\bullet}$ is an essential component of H_2O-oxidation chemistry. An uncompensated positive charge increase on the Mn cluster would generate an energetic barrier to subsequent oxidation reactions; this would be avoided by coupling of electron and H^+ transfer, or by the transfer of H-atoms. The latter mechanism is the basis of the proposal that the mechanism of H_2O oxidation proceeds by H-atom transfer (136, 286). This hypothesis provided the impetus for renewed interest in electron-transfer mechanisms on the oxidizing side of PSII. The Y_Z-Mn distance (~7 Å) measured in PSII crystals is too long for H-atom transfer (95), but this observation needs to be reevaluated in light of the evidence that the Mn cluster in these crystals is damaged.

The complexity of the H_2O-oxidation site in PSII has presented an enormous challenge to the development of hypothetical mechanisms for the reaction. A real chemical intermediate in S_3 has been detected at high O_2 pressures (20 bar) (65). Three substrate binding sites for such an intermediate are the two redox-active Mn atoms and Ca^{2+}, which has been proposed to be a H_2O-binding site because it generally accommodates two or more bound H_2O molecules as ligands in other protein systems (253, 314). This aspect of Ca^{2+} chemistry forms the basis for including the metal in proposed mechanisms for H_2O oxidation (235, 295). These mechanisms utilize Ca^{2+} as a Lewis acid to deprotonate a bound H_2O; the resulting Ca^{2+}-bound OH^- is used as a nucleophile to attack an $O{=}Mn^{+5}$ to form the O-O bond that leads to O_2 formation and reduction of the cluster to S_0. Of all of the metals that can occupy the PSII Ca^{2+} site, only Sr^{2+} can restore O_2-evolution activity in place of Ca^{2+}, but at much lower rates (314). This observation correlates with the Lewis acidity of both $Sr^{2+}$and Ca^{2+}, both of which have higher acidities than other metals that bind to PSII but are ineffective in restoration of activity (295).

Although many questions remain, substantial progress has been made towards a better understanding of the mechanism of H_2O oxidation. The role of Mn as a redox-active catalyst has been established in all but the final step of the mechanism, and there are rational proposals for the function of Ca^{2+} in the mechanism. What is now required is a structure of the undamaged inorganic ion cluster at higher resolution, as well as additional experiments to characterize both possible reaction intermediates and the oxidation states of Mn in S_4.

Light Harvesting and Excitation Transfer in Photosystem II

Isolated plant PSII supercomplexes retain the light harvesting apparatus, which comprises trimeric LHCII complexes (82); the number of LHC per RC is reported to vary between two and four trimers (38, 39), whereas core dimers of PSII contain approximately eight LHC trimers (237). Monomeric LHCII contains 8 Chl a and 6 Chl b, so approximately 170 Chl per monomeric PSII RC are associated with this protein (188, 276). Less abundant Chl a-binding proteins such as LHCb4, LHCb5, and LHCb6 are also present as monomers in PSII. A summary of the structural evidence to date indicates that LHCb4 is located close to PsbB, LHCb5 is near PsbC, and LHCb6 makes contact with LHCb4. Strongly bound LHCII trimers are in close contact with the RC polypeptides of PSII whereas a second population of these complexes makes contact with LHCb4 and LHCb6 (82). Based on structural models, the pathway of energy transfer in PSII can be formulated as follows: Direct energy transfer from strongly-bound LHCII and from LHCb5 to PsbC is to be expected from the proximity of these subunits to one another and to the RC. Energy transfer to PsbB is believed to occur by a pathway from a less-tightly-bound population of LHCII to LHCb6, and then through LHCb4, which is in close contact with PsbB. The exact size of the pool

of LHCII associated with each PSII supercomplex is fluid due to state transitions (304), which we discuss in the next section.

Exciton transfer from the Chl a bound to PsbB and PsbC to the RC itself constitutes the final step in energy transfer. In this case, the recent crystal structures have been useful in providing estimates of the distance (approximately 20 Å) between the RC Chl and the nearest antenna pigments in PsbB and PsbC. This placement has the advantage of protecting the antennae Chl from oxidation by $P680^+$, but also has little effect on fast-excitation transfer to the RC, which in the case of PsbB has been estimated to occur in approximately 20 ps (15). Competing models for the kinetics of energy transfer propose that either (*a*) exciton transfer is rapid, and formation of the charge separated state is rate limiting, or (*b*) energy transfer between antennae and the RC is slow and constitutes the rate-limiting step (77, 202). There is evidence to support either model at the present time (90).

MOLECULAR BIOLOGY AND PHYSIOLOGY OF PHOTOSYSTEMS I AND II

Cyclic Electron Transport and State Transitions

Cyclic electron transport around PSI, first described 50 years ago by Arnon et al. (16), required relatively high Fd concentrations. The early evidence for cyclic activity was demonstrated first under nonphysiological conditions in isolated chloroplasts and then in vivo (106). It was later shown that cyclic electron flow might be induced by CO_2 depletion, drought, and other stress conditions (for review, see Reference 25). Cyclic electron flow was also observed in dark-adapted leaves at the onset of illumination (147, 149, 150) and also on the basis of measurements of PSI-dependent energy storage by photoacoustic methods (144). Two parallel paths of cyclic electron transport have been identified by differences in antimycin sensitivity, saturation characteristics, and substrate specificity (257). A mutation in the PGR5 protein causes decreased PSI cyclic activity (216); PGR5 is membrane bound, but has no extensive hydrophobic sequence. PGR5 is therefore unlikely to be intrinsic to the thylakoid or to fulfill the function of a Fd-cyt b_6f or Fd-plastoquinone oxidoreductase. Nevertheless, PGR5 is thought to have a role in electron transport from FNR to the cyt b_6f complex (216) [FNR was proposed to be a genuine subunit of the complex (320), but this proposal is not supported by the cyt b_6f structure (280)]. It was shown that Fd reduction of plastoquinone is PGR5 dependent (216); this reduction could be direct (through an unknown Fd- plastoquinone oxidoreductase), or indirect (through the cyt b_6f complex). An *Arabidopsis* mutant with a conditional defect in Q-cycle activity, *pgr1*, showed no difference in PGR5-dependent plastoquinone reduction by Fd; this observation suggests direct reduction of plastoquinone (229). This result forces one to reconsider direct reduction by Fd of the cyt b_6f complex. The recent structures of cyt b_6f revealed a unique heme, termed heme x, that is high-spin five-coordinate with no strong field ligand. It is positioned close to the intramembrane heme b(n) that is occupied by the n-side bound quinone in the cyt bc_1 complex of the mitochondrial respiratory chain. Thus, heme x could function in Fd-dependent cyclic electron transport (70, 178, 280). Tight binding of FNR to the cyt b_6f complex would provide a possible Fd-binding site for F_D and would provide a pathway for electron flow from the acceptor side of PSI to plastoquinone via Fd, FNR, and heme x in the cyt b_6f complex. From plastoquinone, electrons would follow the normal pathway (i.e., via cyt f and PC) to P700. At the present time there is no experimental evidence for such a pathway, so the structural basis for cyclic electron transport remains unknown.

Cyclic photophosphorylation is an essential component of state transitions, which are used by photosynthetic organisms to adapt to

changes in light quality by redistributing excitation energy between the two photosystems to enhance photosynthetic yield (24). At high light intensities, LHCII migrates from PSII to PSI (7). This movement is correlated with protein phosphorylation and an increase in the 77 K fluorescence signal from PSI at 735 nm relative to that at 685 nm from PSII (180). It was concluded that phosphorylation of a population of granal LHCII caused migration of these pigment proteins from the PSII-rich appressed membranes into the PSI-enriched unstacked regions. Numerous experiments, including single particle analysis (69), conducted in higher plants supported this model, but the detailed mechanism of state transitions was unclear (113, 318, 319). The existence of LHCII migration at high light intensity was challenged by experiments using pea plants (168), but isolation of photoautotrophic *Chlamydomonas* mutants that were deficient in state transitions moved the debate to firmer grounds (96, 104). The *stt7* mutant cannot undergo state transitions and is blocked in state I. This mutant displays the same deficiency in LHCII phosphorylation as cyt b_6f mutants that cannot undergo state transitions (100). A thylakoid-associated serine-threonine protein kinase, Stt7, has been identified (86) and was shown to be required for phosphorylation of the major light-harvesting protein (LHCII) and for state transitions (293). *Arabidopsis* state transitions and light adaptation require a thylakoid protein kinase STN7 (24), so a protein kinase governs state transitions in both algae and higher plants.

Crosslinking experiments to analyze PSI-LHCII interactions showed that LHCII is situated in close proximity to the PsaI, L, and H subunits (189, 321). However, attempts to fit LHCII monomer or trimer structures into PSI in a way that satisfied the crosslinking data were only partially successful (31). None of the configurations tested would fit LHCII into the supercomplex so that it would be in simultaneous contact with the three subunits and also provide efficient energy transfer to the RC. A model for the binding of a LHCII trimer on the PsaA side of plant PSI was proposed (31), but it is not clear whether trimeric, rather than monomeric LHCII, actually binds to PSI, or if phosphorylated LHCII is even needed for binding (124, 321). It is nevertheless clear that supercomplexes of PSI-LHCII form under stress, and a high-resolution structure of such a supercomplex will clarify the nature of PSI-LCHII interactions.

State transitions in higher plants are limited. In state II, additional light harvesting by PSI does not exceed 20% (6). In contrast, PSI light harvesting in *Chlamydomonas* almost doubles; approximately 80% of the LHCII associates with PSI (85), and, as a result, PSI of *Chlamydomonas* has to accommodate a greater number of LHCII complexes in state II. Whereas addition of a single LHCII trimer could explain the 20% increase in state II light harvesting of plant PSI, a much larger number is required for the state II capacity in *Chlamydomonas.* The model proposed for binding of a LHCII trimer on the PsaA side of plant PSI (31) was supported by a single particle analysis of state II-enriched PSI (173). In addition, several observations using single particle analysis of PSI in *Chlamydomonas* demonstrated the presence of additional LHCII trimers, and probably monomers as well, attached to PSI (114, 156, 282, 224).

State transitions and cyclic phosphorylation activity are mutually regulated in ways that are unique to organisms inhabiting different ecological niches (6, 24, 145). For example, under state II conditions, a large fraction of ATP synthesis is coupled to cyclic electron transport, whereas, under state I conditions, no evidence for cyclic flow has been obtained (97). In *Chlamydomonas*, the State I-State II transition induces a switch from linear to cyclic electron flow; this switch reveals a strict cause-and-effect relationship between the redistribution of antenna complexes and the onset of cyclic electron flow (98). In C4 plants, in which PSII is largely absent from bundle sheath cells, cyclic electron transport is dominant (22). In C3 plants, the existence of

simultaneous cyclic and linear electron transport reactions was questioned, even after one component of the cyclic electron flow pathway was characterized (216). Now it has been shown that cyclic electron transport not only occurs in C3 plants, but is essential for growth (215). A mutant that lacks both the principal pathways of cyclic electron transport is grossly impaired in growth and development. Thus, cyclic electron transport in conjunction with state transitions constitutes a vital mechanism for adaptations to a changing environment.

CONCLUDING REMARKS

At an earlier point in our careers, we were privileged to work at the same time in the laboratory of Ephraim Racker at Cornell University. Ef was justifiably famous for his groundbreaking work on membrane-protein complexes of the mitochondrial inner membrane, among many other significant accomplishments. This research had given him a world-wise view of this branch of science. Ef was also famous for his brief aphorisms, which were liberally applied to his research team, particularly complaining postdocs. One of the most famous of these was "Troubles are good for you," which was handed out when a preparative procedure went bad or a tricky reconstitution experiment failed to yield the expected result. Indeed, troubles lie in the path of anyone who takes on the challenges of working with the intricate membrane-protein complexes that catalyze the reactions of oxygenic photosynthesis. Isolation of active enzymes, the discovery of double-digit polypeptide contents, and crystals that grow slowly, if at all, are at the head of a long list of difficulties. And yet, here we are, at the start of a new century with the structures of all the membrane complexes laid out before us. This scenario would have delighted Ef, who spent his career cleaning up enzymes. Perhaps his most famous aphorism was "Don't waste clean thoughts on dirty enzymes." Now, with structures, techniques, and models proliferating at an incredible rate, we think that it is time for a revised aphorism: *Don't use your dirty thoughts on clean enzymes!*

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