Photosystem II

Govindjee, *University of Illinois at Urbana-Champaign, Urbana, Illinois, USA*
Jan F Kern, *Lawrence Berkeley National Laboratory, Berkeley, California, USA*
Johannes Messinger, *Umeå University, Umeå, Sweden*
John Whitmarsh, *National Institutes of Health, Bethesda, Maryland, USA*

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Advanced article

Article Contents

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Photosystem II (PSII) is a specialized protein complex that uses light energy to drive the transfer of electrons from water to plastoquinone, resulting in the production of oxygen and the release of reduced plastoquinone into the photosynthetic membrane. The key components of the PSII complex include a peripheral antenna system that employs chlorophyll and other pigment molecules to absorb light, a reaction centre at the core of the complex that is the site of the initial electron transfer reactions, an Mn_4O_xCa cluster that catalyses water oxidation and a binding pocket for the reduction of plastoquinone. PSII is the sole source of oxygen production in all oxygenic photosynthetic organisms, which include plants, algae and cyanobacteria. In these organisms, PSII operates in series with other protein complexes, including the PSI reaction centre, to produce the reduced form of nicotenamide–adenine dinucleotide phosphate (NADPH) and adenosine triphosphate (ATP), which is used in the Calvin–Benson cycle to produce carbohydrates from carbon dioxide.

Introduction

Oxygenic photosynthesis is the physical-chemical process by which plants, algae and certain bacteria use light energy to build carbohydrates from carbon dioxide and water, resulting in the release of molecular oxygen into the atmosphere. The production of oxygen depends on photosystem II (PSII), a unique protein complex that removes electrons from water and transfers them to plastoquinone (PQ). An ancient form of photosynthesis occurs in certain types of bacteria that use light energy to oxidize molecules other than water (Hunter *et al.*, 2009). Fossil evidence indicates that PSII-containing organisms emerged more than three billion years ago, resulting in the conversion of the earth's atmosphere from a mildly reducing anaerobic state to the oxygen-rich air surrounding us today (Des Marais, 2000; Kasting and Siefert, 2002). The release of oxygen into the atmosphere by PSII enabled the evolution of oxidative respiration, which has had a profound impact on the diversity of life on our planet. **See also**: Earth: Changes Through Time; Evolution of Photosynthesis; Photosynthesis

Oxygenic photosynthesis depends on two reaction centre complexes, PSII and PSI, that are linked by the cytochrome *bf* complex and mobile electron carriers (Whitmarsh and Govindjee, 1999; **Figure 1**). PSII, the cytochrome *bf* complex and PSI are embedded in the photosynthetic membrane (**Figure 1a**; see legend for details) and operate in series to transfer electrons from water to nicotinamide–adenine dinucleotide phosphate ($NADP^+$) (see **Figure 1b** legend for details). The energy needed to transfer electrons from water to $NADP^+$ is provided by light, which is captured by the PSII and the PSI antenna systems. In plants and algae the photosynthetic membranes are located inside chloroplasts, which are subcellular organelles. In oxygenic cyanobacteria, the photosynthetic membranes are located inside the plasma membrane. **See also**: Chlorophyll: Structure and Function; Photosystem I; Plant Chloroplasts and Other Plastids

Chloroplasts originated from oxygenic bacteria that were engulfed by a eukaryotic nonphotosynthetic organism. In both chloroplasts and cyanobacteria, photosynthetic membranes form vesicles that define an inner and outer water space. Light-driven electron transfer through the PSII and PSI reaction centres provides energy for the creation of a proton electrochemical potential across the membrane. The energy stored in the proton electrochemical gradient is used by ATP synthase to produce ATP. In addition to oxygen, the products of the light-driven electron and proton transport reactions are NADPH and ATP, which provide the free energy needed

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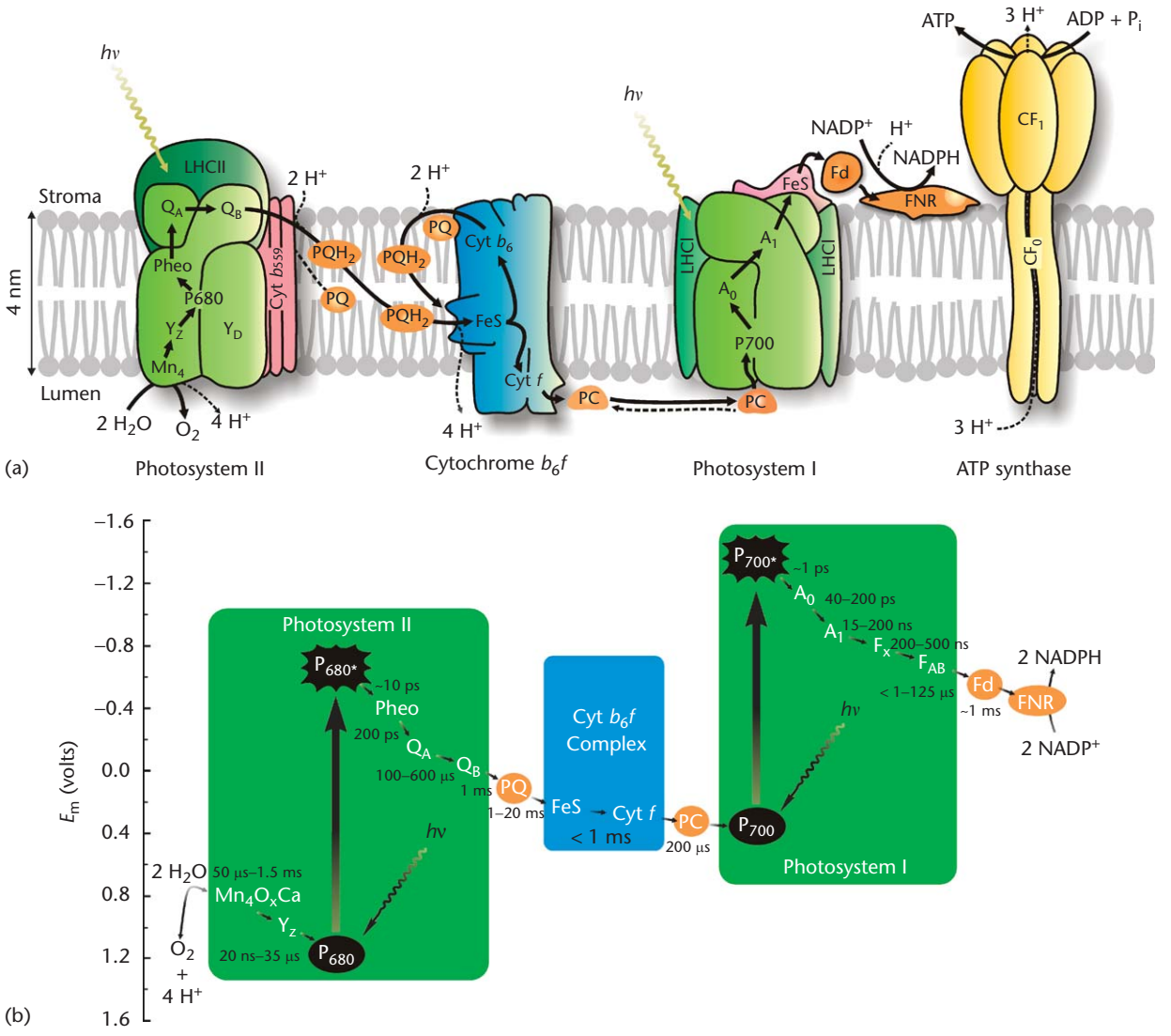


Figure 1 (a) Schematic representation of protein complexes and cofactors involved in the linear electron transport and the proton transport of photosynthesis in higher plants (for differences with other oxygenic organisms, see later discussion and the text). (b) The Z scheme showing the energetics of oxygenic photosynthetic electron transport. The vertical scale shows the equilibrium midpoint redox potential (E_m) of the electron transport components. Approximate electron transfer times are shown for several reactions. Looking at the components from the bottom left of the diagrams: Mn_4O_xCa (or Mn_4), tetranuclear manganese–oxygen–calcium cluster, where $x \geqslant 4$; Y_z, tyrosine-161 on the D1 protein; P680, primary electron donor of photosystem II; $P680^*$, excited electronic state of P680 (for details, see text and **Figure 3c**); Pheo, pheophytin; Q_A, a tightly bound plastoquinone; Q_B, a plastoquinone that binds and unbinds from photosystem II; PQ, a pool of mobile plastoquinone molecules; the middle box represents a protein complex containing two molecules of cytochrome b_6 (Cyt b_6; only one is shown), an iron–sulfur protein (FeS; known as Rieske FeS protein) and a cytochrome *f* (Cyt *f*); PC, plastocyanin (cyanobacteria often employ Cyt c_6); P700, reaction centre chlorophyll *a* of photosystem I; $P700^*$, excited electronic state of P700; A_0, a special chlorophyll *a* molecule; A_1, vitamin K; F_X, F_A, F_B, iron–sulfur centres; F_d, ferredoxin; FNR, ferredoxin–NADP reductase and $NADP^+$, nicotinamide–adenine dinucleotide phosphate. **Figure 1a** shows, in addition, LHC-I and LHC-II, light-harvesting complexes of photosystems I and II, respectively (see **Figure 2b** for cyanobacteria), and the ATP synthase with coupling factors (CF_0 and CF_1). This figure was drawn for the authors by Dmitriy Shevela (in the laboratory of JM).

for the reduction of carbon dioxide and the synthesis of carbohydrates, the final product of oxygenic photosynthesis. **See also**: Algal Chloroplasts; Photophosphorylation; Photosynthesis: The Calvin Cycle; Photosynthetic Carbon Metabolism; Rubisco

PSII uses light energy to drive two chemical reactions: the oxidation of water and the reduction of plastoquinone (Wydrzynski and Satoh, 2005; Lubitz *et al.*, 2008; Renger and Renger, 2008). These chemical reactions are driven by the primary photochemical reaction of PSII, which results in separating a positive and a negative charge within the reaction centre. The primary photochemical reaction is governed by Einstein's law of photochemistry – one absorbed photon drives the transfer of one electron. Four photochemical reactions are required to remove four electrons from two water molecules, which results in the

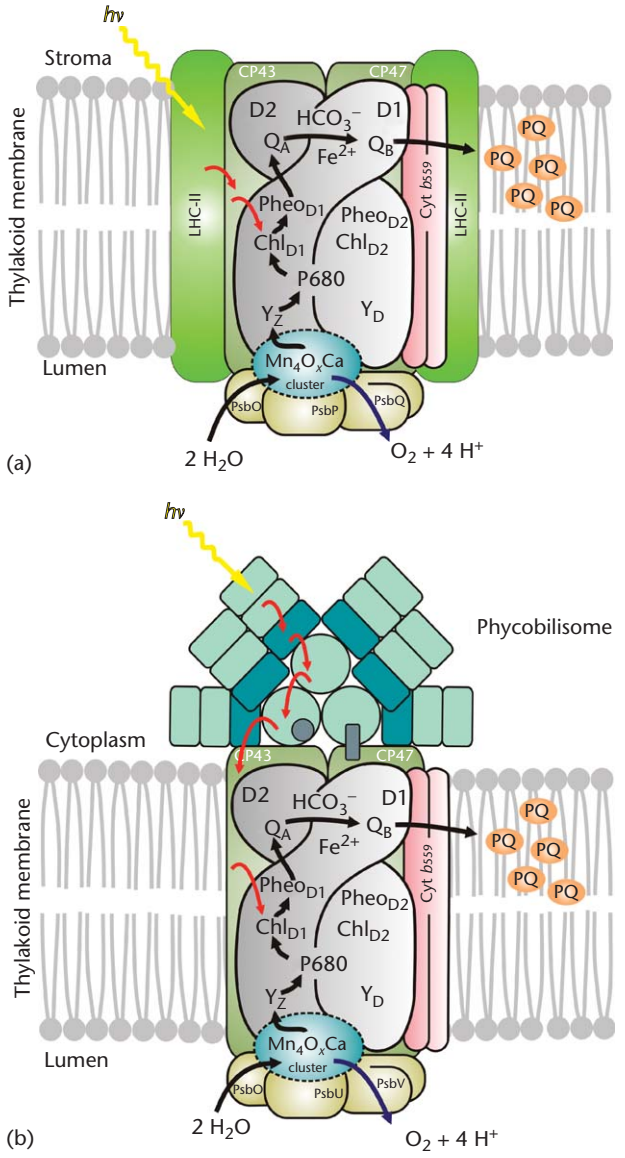


Figure 2 (a) Schematic representation of components of photosystem II in higher plants and green algae. (b) Schematic representation of components of photosystem II in cyanobacteria. D1 and D2 are the reaction centre proteins of photosystem II (PSII). PSII uses light energy to remove electrons from water, resulting in the release of oxygen and protons (see the Lumen side of the diagram). The electrons from water are transferred via redox cofactors in the protein complex to form reduced plastoquinone. Mn_4O_xCa is the manganese–oxygen–calcium cluster involved in removing electrons from water; P680 is a pair of chlorophylls (P_{D1} and P_{D2}) of PSII; Chl_{D1} is the primary electron donor and $Pheo_{D1}$, pheophytin on D1, is the primary electron acceptor; Q_A (on D2), bound plastoquinone; Q_B (on D1), plastoquinone that binds and unbinds from PSII; Y_z (on D1) and Y_D (on D2) are redox active tyrosine residues in PSII with different functions and PQ, mobile plastoquinone molecules in the membrane. CP43 and CP47 are chlorophyll–protein complexes of 43 and 47 kDa that form the inner (also called core) antenna system of PSII; LHC-II (light-harvesting complex II; **Figure 2a**) denotes all other PSII antenna in eukaryotes; PsbO (33 kDa), PsbQ (16 kDa) and PsbP (23 kDa) are extrinsic proteins that stabilize and optimize the water-splitting complex and its reactivity (**Figure 2a**); Cyt *b559* is a dimeric protein that contains the redox active cytochrome *b559* that maybe involved in photoprotection of PSII (this protein is also essential for the assembly of PSII). Bicarbonate (HCO_3^-; hydrogen carbonate) shown in the figure as bound to nonhaeme iron; it may be bound in the form of carbonate (CO_3^{2-}). In cyanobacteria (**Figure 2b**), the major antenna is the phycobilisome that is extrinsic to the membrane and connected to the CP47 protein of PSII via an anchor protein; also, instead of PsbP and PsbQ as extrinsic polypeptides on the luminal side, these organisms have PsbU (12 kDa) and PsbV (Cyt *c*550) proteins. This figure was drawn by Dmitriy Shevela (in the laboratory of JM).

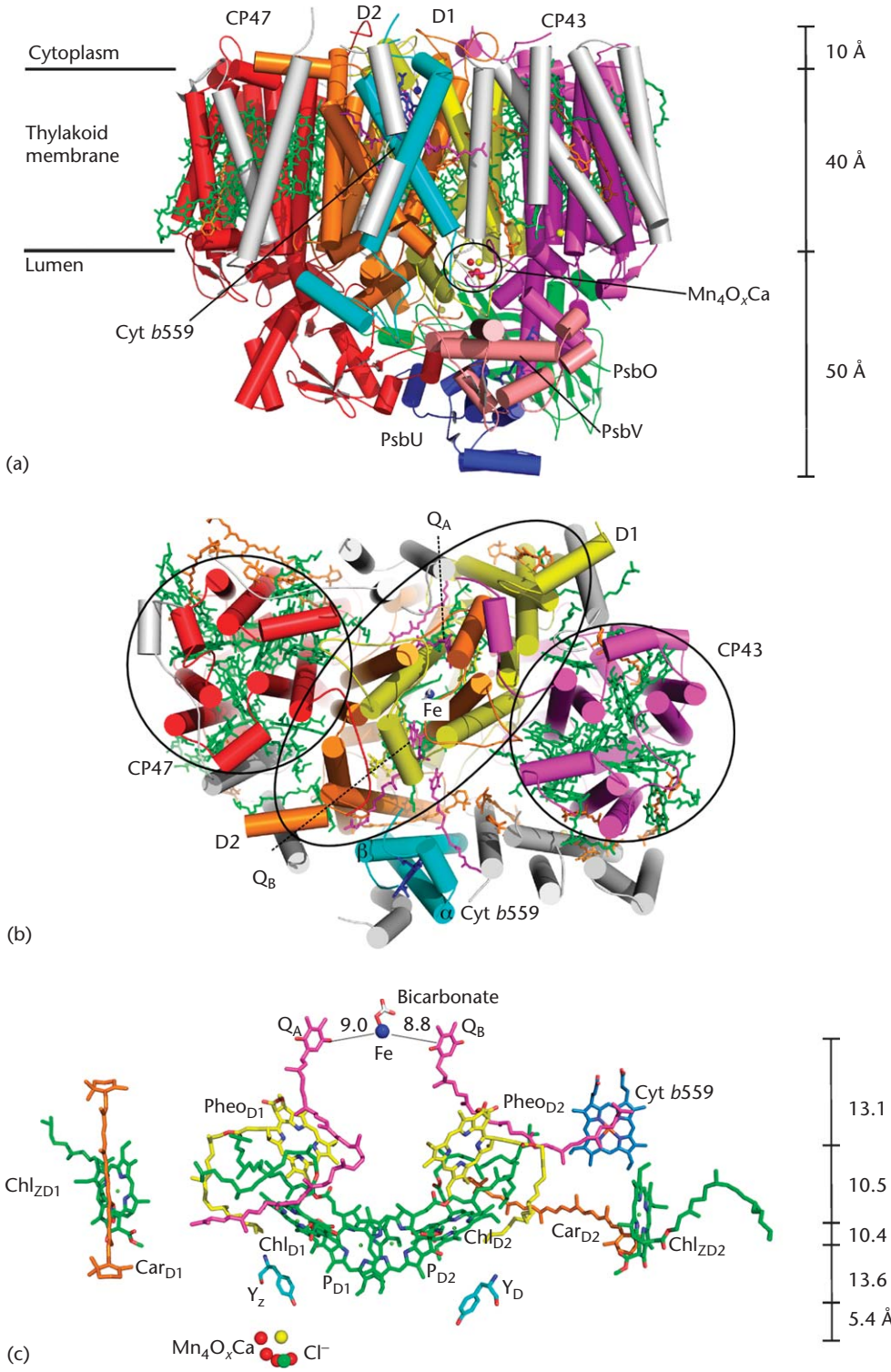
production of one molecule of oxygen and the release of four protons into the inner water phase (the lumen) of the photosynthetic membrane (**Figure 2**). The four electrons extracted from the water molecules are transferred to the plastoquinone-binding site where, in concert with four protons taken up from the outer water phase (the stroma/cytoplasm; see later discussion), two molecules of plastoquinone are reduced:

$$2H_2O + 2\,PQ + 4\,H^+_{out} + 4\,h\nu \rightarrow O_2 + 2\,PQH_2 + 4\,H^+_{in}$$

Here we describe the structure and function of PSII without discussing the experimental results that underlie our knowledge. The references at the end of the article provide an entry to the literature describing progress over the past half century in understanding this ubiquitous enzyme, whose emergence three billion years ago can be viewed as a seminal event in the evolution.

Organization, Composition and Structure

PSII is located in the photosynthetic membrane, with the oxygen-evolving site near the inner water phase (lumen), and the plastoquinone-binding site near the outer water phase (stroma in eukaryotes and cytoplasm in cyanobacteria; **Figure 2a** and **b**), an orientation that enables the oxidation–reduction chemistry of the reaction centre to contribute to the proton electrochemical difference across the thylakoid membrane (see the legend of **Figure 2**). In chloroplasts, the architecture of the photosynthetic membrane is complicated, with regions of stacked membranes (grana membranes) and regions of nonstacked membrane (stromal membranes). PSII and PSI are unevenly distributed between the two regions, with most of the PSII complexes located in the stacked membranes, and virtually all of the PSI complexes located in the nonstacked membranes. It is not clear why PSII and PSI are spatially separated in chloroplasts, but location of PSII in the stacked membranes allows for very close packing of the membranes because of the relatively limited extension of PSII into the outer water phase (the stroma) compared to PSI. In chloroplasts, the PSII complex is densely packed in the photosynthetic membrane, with average centre-to-centre distances of 150–250 Å. One square centimeter of a typical leaf contains approximately 30 trillion PSII complexes. In prokaryotes, the photosynthetic membranes do not form



stacked membranes and the PSII and PSI complexes appear to be intermixed.

There is a remarkable similarity in the structure and function of PSII in higher plants, algae and bacteria. Furthermore, the PSII, PSI and (anoxygenic) bacterial reaction centres share several structural features, indicating ancient evolutionary links (Sadekar *et al.*, 2006). In contrast, the structures of the light-capturing antenna systems in various photosynthetic systems are quite different, indicating multiple origins. **See also**: Evolution of Photosynthesis

PSII is composed of a central reaction centre core surrounded by a light-harvesting antenna system (**Figure 2a** and **b**). The reaction centre core includes D1 and D2 polypeptides that bind the cofactors of the photochemical charge separation and electron transfer carriers that oxidize water and reduce plastoquinone (**Figure 1**, **Figure 2** and **Figure 3**). The antenna system consists of protein complexes that contain light-absorbing molecules (chlorophyll or phycobilins and other accessory pigments; see later discussion) which operate in concert to capture photons and transfer the excitation energy to reaction centres where primary charge separation occurs. In most eukaryotic organisms (e.g. higher plants and green algae), the light-harvesting complexes are organized as an inner antenna system located close to the reaction centre, and a peripheral antenna system composed of pigment proteins known as light-harvesting complex II (LHC-II; Lhcb 1–6) (**Figure 2a**). In other eukaryotic organisms (e.g. red algae) and in many prokaryotic organisms (e.g. most cyanobacteria), the light-harvesting complexes, which are known as phycobilisomes, are extrinsic to the photosynthetic membrane and use phycobilins rather than chlorophylls to capture light (**Figure 2b**). The PSII reaction centre complex, excluding the peripheral light-harvesting complexes, is composed of more than 20 different polypeptides, most of which are integral membrane polypeptides (**Figure 3a** and **b**). The only known membrane peripheral proteins are located in the lumen. In addition to the differences between the antenna, the photosystems II of higher plants and cyanobacteria differ with respect to the composition of these membrane peripheral proteins (see **Figure 2a** and **b**) as plant PSII have PsbO (33 kDa), PsbP (23 kDa) and PsbQ (16 kDa) and cyanobacterial PSII PsbO (33 kDa), PsbU (12 kDa) and PsbV (Cyt *c*550) (see later discussion). **Table 1** lists the genes encoding the PSII polypeptides, together with the polypeptide molecular weights and their putative functions. **See also**: Chloroplast Genome

PSII contains at least eight different types of redox components that have been observed to undergo light-induced electron transfer. These components include chlorophyll, pheophytin, plastoquinone, tyrosine, manganese, iron, cytochrome *b*559 and carotenoid (**Figure 3**). However, only the following redox components are known to be involved in the electron transfer from water to the plastoquinone: the water-oxidizing manganese–oxygen–calcium cluster (Mn_4O_xCa, where $x \geq 4$ is the number of bridging oxygens), a tyrosine (Y_z), a chlorophyll dimer (P_{D1} and P_{D2}), which is also referred to as P680, historically thought to be the primary electron donor, but see the discussion on the primary charge separation event below), a monomeric chlorophyll (Chl_{D1}), a pheophytin ($Pheo_{D1}$) and two plastoquinone molecules (Q_A and Q_B) (**Figure 2**). The primary electron donor molecule involved in the first charge separation reaction is Chl_{D1} (**Figure 3c**; see the section on Primary photochemistry: The reaction centre).

After decades of effort by many researchers, the three-dimensional structure of the PSII inner core from a thermophilic cyanobacterium was determined to 3.8 Å resolution by HT Witt, W Saenger and coworkers (Zouni *et al.*, 2001). Following the work of Witt and coworkers, more highly resolved PSII structures (3.7–2.9 Å resolution) have been determined (Kamiya and Shen, 2003; Ferreira *et al.*, 2004; Loll *et al.*, 2005; Guskov *et al.*, 2009). The PSII reaction centre core is 100 Å across (in the plane of the membrane) and extends approximately 10 Å into the stromal aqueous phase and approximately 55 Å into the lumen (**Figure 3a**). At the centre of PSII are the D1 and D2 polypeptides, which form two branches that provide the primary scaffolding for the electron carriers (**Figure 3a** and **c**). The Mn_4O_xCa cluster is ligated by amino acids from the D1 polypeptide and the inner antenna (also called core antenna) protein CP43 (**Figure 4**; **Table 1**). In addition to these components, the PSII reaction centre core and the two inner (or core) antenna proteins (CP43 and CP47) bind 29 molecules of chlorophyll *a*, 12 carotenoids, one non-haeme iron, one or more chloride ions and one carbonate (CO_3^{2-}) or hydrogen carbonate (HCO_3^-) ion (**Figure 3b** and **c**). All PSII complexes contain cytochrome *b*559, a haeme protein composed of two polypeptides located at the periphery of the complex, as well as at least 12 small membrane intrinsic proteins (**Figure 3**; **Table 1**). In plants, the

Figure 3 Structure of the photosystem II (PSII) complex from the thermophilic cyanobacterium *Thermosynechocuus elongatus* (Guskov *et al.*, 2009). (a) A view of one monomer of the complex; the view direction is along the membrane plane. Dimensions, in angstroms, are indicated on the right side. Protein subunits are shown as cartoon and coloured in yellow (D1), orange (D2), red (CP47), magenta (CP43), cyan (Cyt *b*559), green (PsbO), blue (PsbU), salmon (PsbV) and grey (remaining small subunits). Cofactors are shown as sticks in green (chlorophylls), orange (carotenoids) and blue (haeme). The location of the catalytic site of water oxidation, the Mn_4O_xCa cluster ($x > 4$), is highlighted at the luminal side. (b) The membrane intrinsic part of PSII; this view is onto the membrane plane from the cytoplasmic side; the colouring is as in panel (a). The reaction centre domain D1 and D2 and the antenna subunits CP43 and CP47 are highlighted by ellipses, and the position of the Cyt *b*559, the nonhaeme iron (blue sphere) and of Q_A and Q_B are labelled. (c) Redox active cofactors in the reaction centre. At the right side, the centre-to-centre distances, in angstroms, between the cofactors are indicated starting (from bottom to top) from Ca (yellow sphere) of the Mn_4O_xCa cluster, to the OH of the tyrosine, labelled as Y_z, chlorophyll P_{D1} (of P680), Chl_{D1} (green), pheophytin $Pheo_{D1}$ (yellow) and plastoquinone Q_A (magenta) and the distances between Q_A, Fe (blue sphere) and Q_B are given directly in the figure in angstroms. Bicarbonate (more appropriately called hydrogen carbonate) is shown to be bound to the nonhaeme iron. (We do not exclude the possibility that the bound species may also be carbonate). The figure was generated by using the coordinates (pdb code: 3BZ1, 3BZ2) of the 2.9 Å resolution crystal structure. This figure was drawn by one of us (JFK).

Table 1 Photosystem II genes, proteins and putative roles (excluding antenna light-harvesting complex II)

Gene[a]	Protein	Mass (kDa)[b]	Integral or peripheral[c]	Comments
psb A (c)	D1	39	I (5)	D1 (and D2) form the reaction centre core that binds most of the PSII electron transport components; Q_B binds to D1
psb B (c)	CP47	56	I (6)	Binds antenna chlorophyll *a*
psb C (c)	CP43	47	I (6)	Binds antenna chlorophyll *a*, provides a ligand to the Mn_4O_xCa complex
psb D (c)	D2	39	I (5)	D2 (and D1) form the reaction centre core that binds most of the PSII electron transport components; Q_A binds to D2
psb E (c)	α Subunit Cyt *b*559	9.3	I (1)	Binds *b*-haeme; may be involved in photoprotection
psb F (c)	β Subunit Cyt *b*559	4.5	I (1)	Binds *b*-haeme; may be involved in photoprotection
psb H (c)	PsbH	7.8	I (1)	Can be phosphorylated in plants, involved in repair of D1, optimizes electron flow in prokaryotes
psb I (c)	PsbI	4.2	I (1)	Stabilization and assembly of the complex
psb J (c)	PsbJ	4.2	I (1)	Influences plastoquinone exchange and electron flow on acceptor side
psb K (c)	PsbK	4.3	I (1)	Stabilization of the complex
psb L (c)	PsbL	4.5	I (1)	Influences plastoquinone binding and electron flow on acceptor side, stabilizes dimerization
psb M (c)	PsbM	4	I (1)	Mediates interaction between the monomers in the dimeric complex
psb O (n)	PsbO (MSP)	27	P (0)	Involved in optimizing oxygen evolution, binds possible regulatory calcium
psb P (n)	PsbP	20	P (0)	Involved in oxygen evolution; eukaryote specific (in prokaryotes a PsbP-like protein is found in substoichiometric amounts)
psb Q (n)	PsbQ	17	P (0)	Involved in oxygen evolution; eukaryote specific, a slightly different form of PsbQ' is also present in prokaryotes, optimizing oxygen evolution activity
psb R (n)	PsbR	10	I (1)	Needed for stable assembly of PsbP in the complex, influences donor and acceptor side electron transfer; eukaryote specific
psb S (n)	PsbS	21	I (4)	Involved in nonphotochemical quenching
psb T (c)	PsbT	3.8	P (1)	Stabilizes Q_A-binding site, supports dimerization
psb T_n (n)	$PsbT_n$	3.2	P (0)	Unknown function; eukaryote specific
psb U	PsbU	10	P (0)	Maybe involved in calcium and chlorine delivery to the OEC; prokaryote specific; but also found in brown and red algae
psb V	Cyt *c*550	12	P (0)	Binds *c*-haeme, optimizes oxygen evolution activity; prokaryote specific; but also found in brown and red algae
psb W (n)	PsbW	6	I (1)	Involved in PSII dimerization; eukaryote specific
psb X (c)	PsbX	4	I (1)	Unknown function
psb Y (c)	PsbY	4.7	I (1)	Unknown function
psb Z (c)	PsbZ	11	I (2)	Connection to external antenna subunits in plants
ycf12 (c)	Ycf12 (Psb30)	5	I (1)	Unknown function

Notes: Cyt, cytochrome; I, integral; MSP, manganese-stabilizing protein; OEC, oxygen evolving complex; P, peripheral and PS, photosystem. We acknowledge the help of Kimberly Wegner, Johanna Roose, Himadri Pakrasi and Julian Eaton-Rye in the preparation of this table.
[a]For eukaryotic organisms, the letter in parentheses indicates whether nuclear (n) or chloroplast (c) gene is encoded.
[b]Mass calculated from amino acid sequence.
[c]Number of α helices is given in parentheses.

luminal side of the complex is shielded by three membrane-extrinsic proteins known as the 33 kDa or PsbO protein, the 16 kDa or PsbQ protein and the 23 kDa or PsbP protein. In cyanobacteria, two additional extrinsic proteins, PsbU and PsbV, are present at the luminal side, as are two less tightly (or transiently) bound proteins, PsbP' and PsbQ', which are analogous to the 16 kDa and 23 kDa proteins found in eukaryotic cells. A notable difference between cyanobacteria and plants is the presence of cytochrome *c*550 (PsbV) in cyanobacteria. Although the cytochrome undergoes light-activated redox reactions, its role in PSII is unknown.

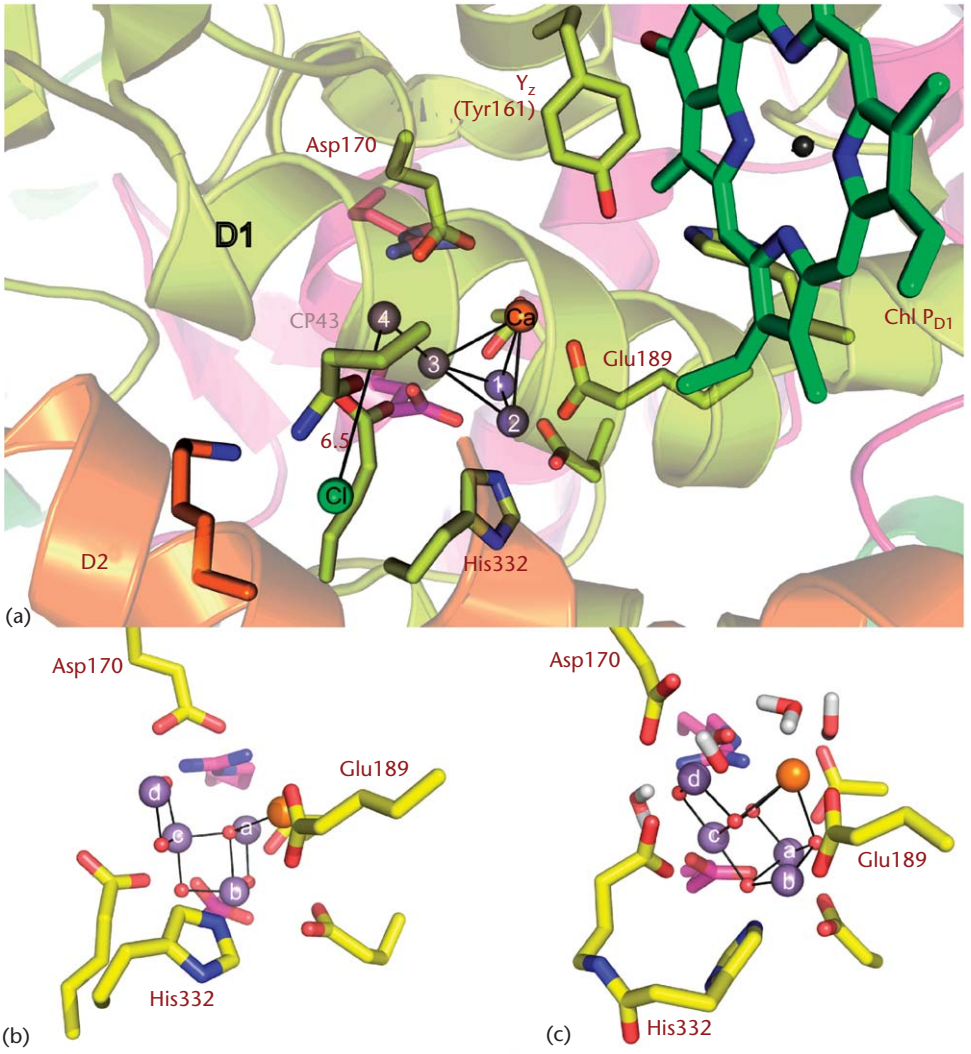


Figure 4 The catalytic site of water oxidation in photosystem II (PSII); amino acids are shown with their 3-letter codes. (a) Structural model for the metal ions and amino acid ligands of the Mn_4O_xCa cluster, the redox active tyrosine Y_z (Tyr161) and the chlorophyll P_{D1}, as derived from the 2.9 Å resolution crystal structure (Guskov *et al.*, 2009); the view is along the membrane with lumen at the bottom and cytoplasm at the top. The protein surrounding is shown in cartoon mode in light yellow (D1), orange (D2) and magenta (CP43). Mn (purple), Ca^{2+} (orange) and Cl^- (green) ions are shown as spheres, ligating amino acids as sticks. The nitrogen and oxygen atoms of the amino acid ligands are coloured in blue and red, respectively; the carbon atoms are coloured depending on the subunit the amino acid belongs to: yellow for D1, orange for D2 and magenta for CP43. (b) Model for the Mn_4O_xCa cluster in the dark stable S_1 state of the water oxidizing complex, obtained from orientation dependent X-ray spectroscopy on PSII single crystals (Yano *et al.*, 2006) embedded in the ligand environment derived from the crystal structure. The colouring and the view direction is as in panel (a), bridging oxygens are shown as small red spheres. (c) Theoretical model for the Mn_4O_xCa cluster and its first ligand sphere in the S_1 state derived from density functional calculations (Siegbahn, 2008); the colouring and the view direction is as in panel (a); the bridging oxygens are shown as small red spheres. This model also includes some water/hydroxide groups (hydrogens shown in grey) as ligands to the manganese and calcium ions. This figure was drawn by one of us (JFK).

The pathway and rate of electron transfer within the PSII complex must be rigorously controlled for efficient operation in the electron transport chain. One of the key factors controlling electron transfer from one redox site to another is the distance between the components (Moser *et al.*, 1992), which is determined by the orientation and position of the redox components established by the protein scaffolding of the complex. The importance of distance in controlling electron transfer is demonstrated by the remarkable homology between (anoxygenic) bacterial reaction centres and plant, algal and cyanobacterial PSII reaction centres (Sadekar *et al.*, 2006). Another factor in controlling electron transfer is protein dynamics, which appears to play an important role in the stabilization of the primary charge separation and many other reactions within PSII. Note that the central core formed by the D1 and D2 polypeptides forms a symmetrical structure, which provides two potential electron transport pathways through the reaction centre. However, only one pathway is active (**Figure 2**). Although the electron transfer pathways in

the reaction centre are tightly controlled, there appear to be multiple pathways for proton transfer from the outer water phase to the Q_B site, and for the release of protons from the Mn_4O_xCa cluster into the inner water phase (the lumen).

Light Capture: The Antenna System

Oxygenic photosynthesis is driven by visible light that is absorbed by chlorophyll/phycobilins and other pigments (e.g. carotenoids) bound to the light-harvesting proteins that surround the PSII and PSI reaction centres in the photosynthetic membrane. The major light-absorbing pigment in plants and many algae is chlorophyll, which is a cyclic tetrapyrrole in which the nitrogens of the pyrroles are coordinated to a central magnesium ion. Chlorophyll is a green pigment that strongly absorbs blue and red light. Plants and many types of algae contain two types of chlorophyll, *a* and *b*, which differ by a single group on one of the pyrrole rings. In contrast to plants, cyanobacteria and red algae employ phycobilins (that are open-chain tetrapyrroles bound covalently to proteins) as the major light-absorbing pigments, which transfer excitation energy to chlorophyll *a*. In many plants and algae, the antenna system serving a single PSII reaction centre contains 200–250 chlorophyll and 60–70 carotenoid molecules (**Table 2**). Carotenoids, which are linear polyenes that absorb blue and green light, serve a dual role in photosynthesis. They are important light-harvesting pigments, significantly enhancing the spectrum of visible light absorbed by the antenna system. In addition, carotenoids serve a critical role in protecting the photosynthetic apparatus from damage associated with light capture. These protective processes include downregulation, which protects membrane components under conditions of excess light, and quenching of excited triplet states of chlorophyll that can induce oxidative damage (Demmig-Adams *et al*., 2006; Frank *et al*., 1999).

The structure of one of the light-harvesting protein complexes (LHC-II) associated with eukaryotic PSII has been determined by electron crystallography (Kühlbrandt *et al*., 1994) and by X-ray crystallography (see review by Barros and Kühlbrandt, 2009). The LHC-II complex forms a trimer, with each subunit binding eight molecules of chlorophyll *a*, six molecules of chlorophyll *b* and four molecules of carotenoids. **See also**: Chlorophyll-binding Proteins

Photosynthesis is initiated by absorption of a photon by an antenna molecule, which induces a rapid (10^{-15} s) transition from the electronic ground state to an excited electronic state. The excited state decays rapidly (10^{-13} s) by vibrational relaxation to the first excited singlet state. The fate of these short-lived excited states is guided by the structure and composition of the light-harvesting protein–pigment complexes. Because of the proximity of other antenna molecules with the same or similar electronic energy levels, the excited singlet state energy has a high probability of being transferred to a neighbouring molecule by a process known as Förster Resonance Energy Transfer (FRET) (Lakowicz, 1999). Transfer of excitation energy between antenna molecules depends on the interaction between the transition dipole moments of the donor and acceptor molecules. The probability of transfer falls off quickly as the distance between the pigments increases (in many cases, the rate is proportional to R^{-6}, where R is the distance between the transition dipoles), and depends strongly on the overlap of the emission spectrum of the donor molecule and the absorption spectrum of the acceptor molecule, as well as the relative orientation of the donor and acceptor pigments. A schematic representation of excitation energy migration over the antenna system is shown in **Figure 5**. Because the first excited singlet state of chlorophyll *a* is energetically lower than that of chlorophyll *b* or the carotenoids, excitation energy is rapidly localized on the chlorophyll *a* molecules. As a consequence, excitation energy that escapes the antenna system as fluorescence comes almost entirely from chlorophyll *a*.

Photosynthetic antenna systems have evolved to be highly efficient at guiding excited state energy to a reaction centre to promote primary photochemistry, rather than allowing the energy to be lost as heat or fluorescence. However, if a reaction centre is unable

Table 2 Distribution of chlorophylls and carotenoids in photosystem II from higher plants

Protein	Number of chlorophyll molecules	Number of carotenoid molecules
Reaction centre proteins (D1/D2)	6 Chl *a*	2
Inner antenna proteins		
CP47	16 Chl *a*	5
CP43	13 Chl *a*	3 (+2 bound by small subunits)
CP24 + CP26 + CP29	18 Chl *a* + 9 Chl *b*	6
Outer antenna proteins		
One tightly bound + one medium-bound LHC-IIb trimer	48 Chl *a* + 36 Chl *b*	24
Loosely bound LHC-IIb + other LHCs	Approximately 100 Chl (*a* + *b*)	Approximately 30 Car
Photosystem II (reaction centre + antenna system)	Approximately 250 Chl (*a* + *b*)	Approximately 70 Car

Notes: Car, carotenoid; Chl, chlorophyll; CP, chlorophyll-binding protein; LHC, light-harvesting complex.

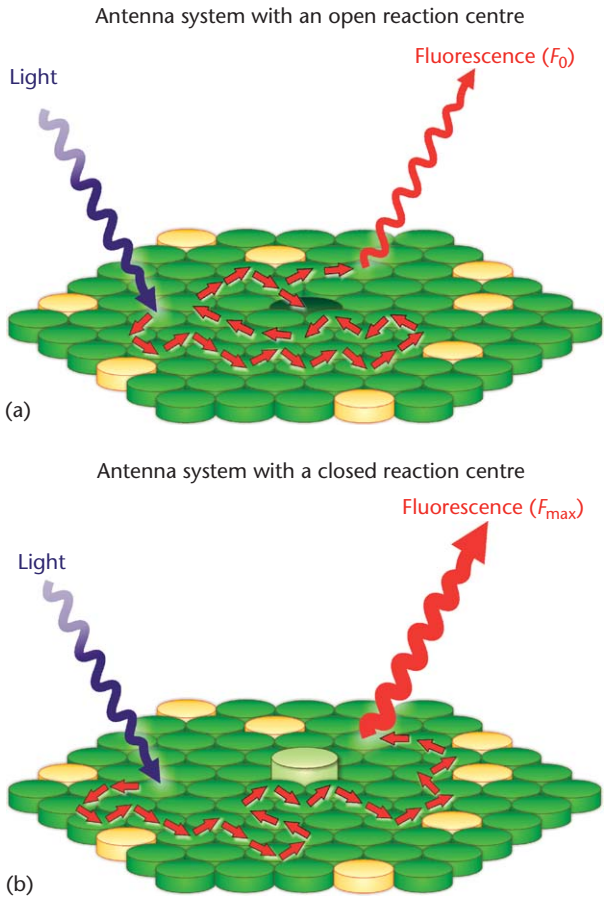


Figure 5 Schematic representation showing excitation energy transfer (small red arrows) from one chlorophyll molecule to another in a 'generic' LHC-type antenna system of higher plants. Green discs represent chlorophylls *a* and *b*, and yellow discs represent carotenoids; the darker green disc in the middle of panel (a) represents an open reaction centre and the lighter green disc in the middle of panel (b) represents a closed reaction centre. When the reaction centre is open (a), most energy is used for charge separation, and the system emits minimal chlorophyll *a* fluorescence (labelled as F_0); when the reaction centre is closed (b), chlorophyll *a* fluorescence is maximal (F_{max}). This figure was drawn by Dmitriy Shevela (in the laboratory of one of us, JM).

to undergo primary charge separation (closed), then the probability of the excitation energy going into fluorescence or heat is higher (cf. **Figure 5a** and **b**). Measurements of photosynthesis under optimal conditions show that over 90% of absorbed photons can be trapped by a reaction centre and promote charge separation. However, environmental conditions may impose limitations on photosynthesis that significantly limit the rate of electron transport, which significantly increases the fraction of absorbed light energy that goes into fluorescence and heat. Measurements of chlorophyll fluorescence provide an effective and noninvasive method for monitoring photosynthetic performance under remarkably wide range of conditions and environments (Papageorgiou and Govindjee, 2004).

Primary Photochemistry: The Reaction Centre

There is convincing evidence that the primary photochemical reaction in PSII results in charge separation between P_{D1} and $Pheo_{D1}$ within 8 ps (Greenfield *et al.*, 1997), creating $P_{D1}^{+}/Pheo_{D1}^{-}$ (also denoted as $P_{680}^{+}/Pheo^{-}$). However, there is uncertainty concerning how this charge-separated state is formed, which is due in part to the proximity of the four chlorophyll (Chl_{D1}, P_{D1}, P_{D2} and Chl_{D2}) and two pheophytin ($Pheo_{D1}$ and $Pheo_{D2}$) molecules (**Figure 3c**). Because the electronic energy levels of core chromophore molecules are nearly similar, excitation energy within the reaction centre equilibrates rapidly (within 1 ps) between the core chlorophyll and pheophytin molecules before charge separation occurs. It appears that this ensemble of molecules forms the excited state of the primary donor and that charge separation can occur between different chromophores in the reaction centre (Groot *et al.*, 2005). (Thus, several authors (see, e.g. Renger and Renger, 2008) have adopted an alternate definition for P680 for the entire ensemble of pigment molecules; however, we prefer to keep the original definition of P680.) A few picoseconds after the formation of the excited state, the primary photochemical reaction of PSII begins, most likely by electron transfer from the monomeric Chl_{D1} to the $Pheo_{D1}$, which is followed by a second electron transfer leading to the formation of $P_{D1}^{+}/Pheo_{D1}^{-}$ (Diner *et al.*, 2001; Holzwarth *et al.*, 2006; Di Donato *et al.*, 2008).

The high efficiency of reaction centre photochemistry depends on preventing recombination of the primary charge separation, which is accomplished by the rapid (in the range of 200 ps) transfer of the electron from $Pheo_{D1}^{-}$ to Q_A (**Figure 1b**, **Figure 2a** and **b** and **Figure 3c**). From Q_A^{-}, the electron is transferred to another plastoquinone molecule bound at the Q_B site. After two photochemical turnovers, Q_B becomes fully reduced and protonated, forming PQH_2, which debinds from PSII and enters the hydrophobic core of the photosynthetic membrane. Concurrent with electron transfer to plastoquinone, the tyrosine residue (Y_Z) on the D1 polypeptide transfers an electron to $(P_{D1}P_{D2})^{+}$. Electrons for the reduction of oxidized Y_Z ($Y_Z^{\bullet}$) are extracted from the Mn_4O_xCa cluster, which is the core of the water-oxidizing complex. (The notation $Y_Z^{\bullet}$ denotes a neutral radical due to proton transfer to the nearby histidine residue.) The rate of electron transfer from Y_Z to $P680^{+}$ ranges from 20 ns to 35 µs, depending on the redox states of the components involved in water oxidation (**Figure 1b** and **Figure 3c**).

Oxidation of Water: The Source of Atmospheric Oxygen

In 1969, Pierre Joliot and coworkers measured oxygen release during successive single-turnover light flashes in dark-adapted algae (Joliot *et al.*, 1969). They found that the

yield of oxygen plotted as a function of the flash number exhibited a periodicity of four (**Figure 6a**). This classic experiment demonstrated that each PSII complex operates independently and that four photochemical reactions are required for the release of one oxygen molecule (Joliot and Kok, 1975). The periodicity of four was readily explained by the chemistry of water oxidation, but the observation that the maximum oxygen yield occurred on the third rather than fourth flash, and that the periodicity disappeared after several cycles indicated an unexpected level of complexity in the mechanism of water oxidation.

On the basis of Joliot's observations and their own experiments, Kok *et al.* (1970) showed that the period four oscillation is independent of the number of active PSII centres and developed an elegant model of water oxidation in which the oxygen-evolving complex can exist in one of the five oxidation states, labelled S_0, S_1, S_2, S_3 and S_4 (**Figure 6b**). In Kok's model, each photochemical reaction removes a single electron from the water-oxidizing complex, which advances PSII to the next higher S state until there are four oxidizing equivalents in the complex, leading to the oxidation of two molecules of water. Identifying the chemical steps leading to water oxidation has proven to be a challenging problem. It appears that no stable O–O intermediate is formed up to the S_3 state (Messinger *et al.*, 1995; Hillier and Wydrzynski, 2000; Hillier and Messinger, 2005), and that the formation of molecular oxygen occurs during the $S_3 \rightarrow S_4 \rightarrow S_0$ transition, either through two sequential two-electron steps, or through one concerted four-electron oxidation event (see later discussion and Hillier and Messinger, 2005; McEvoy and Brudvig, 2006; Brudvig, 2008; Messinger and Renger, 2008). The complete water-oxidation cycle results in the production of one oxygen molecule, the release of four protons into the inner water phase (the luminal phase) and the sequential transfer of four electrons through the reaction centre to the plastoquinone pool. **See also**: Oxygen Production

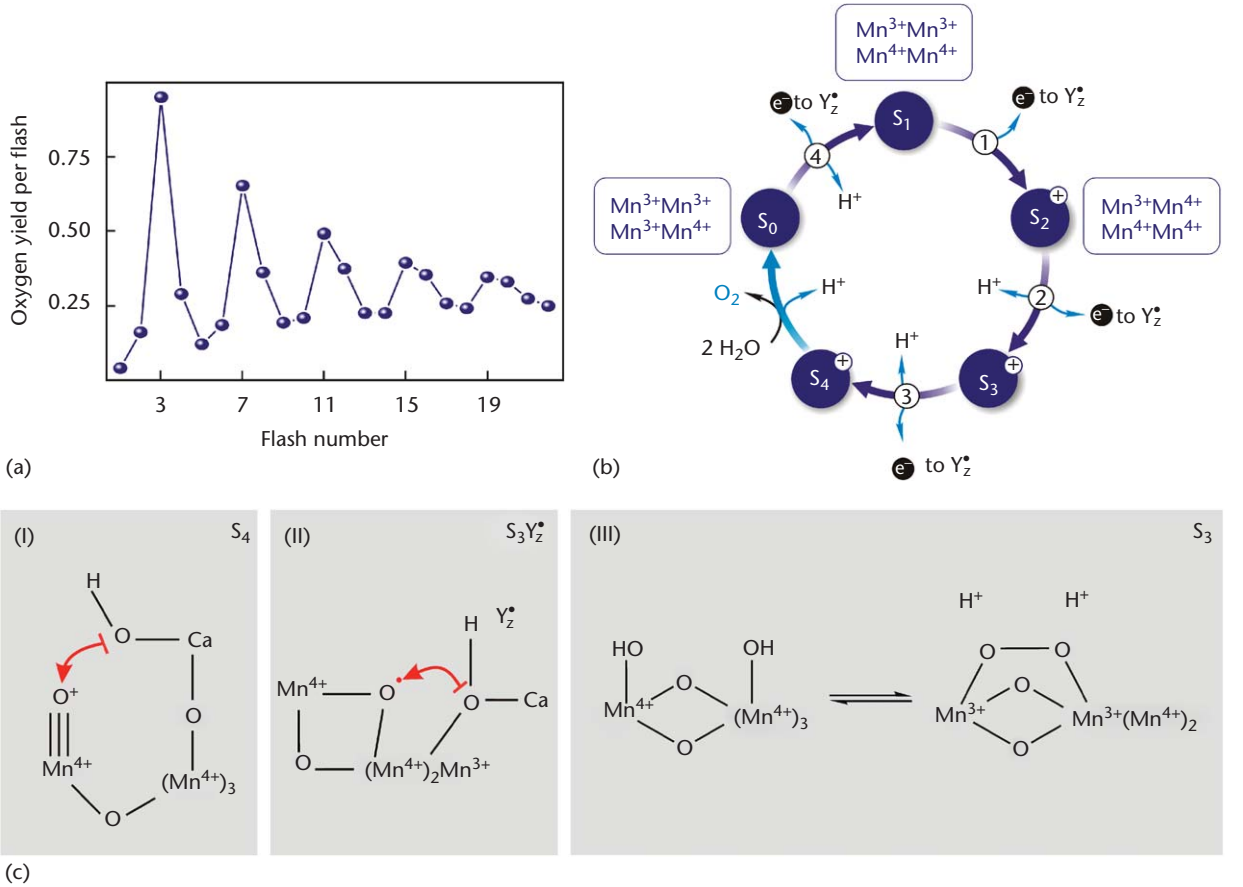


Figure 6 The oxygen cycle (also called the 'oxygen clock') of photosystem II (PSII). (a) Oxygen yield from PSII as a function of flash number (oxygen cycle) (see Joliot and Kok, 1975). (b) One of the current models of the steps in oxygen evolution in PSII. See text and Joliot and Kok (1975) for details. (c) Simplified schemes for three currently discussed pathways for the O–O bond formation at the Mn_4O_xCa cluster in photosystem II. The three displayed mechanisms differ in the way how the substrate 'water' molecules (term 'water' includes here all deprotonated and partially oxidized water-derived ligands) are bound, and the O–O bond formation is initiated: (I) via a nucleophilic attack mechanism (S_4 is shown); (II) a radical mechanism ($S_3Y_Z^{\bullet}$ is shown) or (III) an oxidative coupling of two hydroxo groups within an equilibrium in the S_3 state. In the latter example the complexed oxo would represent a minor fraction of the centres, but only this fraction would be oxidized by $Y_Z^{\bullet}$. For further details see text and the references stated therein. This figure was drawn by Dmitriy Shevela (in the laboratory of one of us, JM).

To account for the observation that the maximum oxygen yield occurs on the third, rather than the fourth flash (**Figure 6a**), Kok *et al*. (1970) proposed that most of the water-oxidizing complexes are in the S_1 state in dark-adapted PSII reaction centres. As a consequence, the S_4 state is reached after three flashes resulting in the release of oxygen. To account for the small yield of oxygen on the second and fourth flash, and the loss of periodicity as the flash number increased, Kok *et al*. (1970) assumed that in some PSII complexes a short saturating light flash may fail to advance the S-state (misses), whereas in other complexes the flash may promote a two-state advance (double hits). The Kok model successfully explained the flash dependence of oxygen evolution and continues to guide research into the mechanism of water oxidation and oxygen release by PSII (Messinger and Renger, 2008).

The core of the oxygen-evolving complex is an inorganic cluster of four manganese ions and one calcium ion held together by several μ-oxo bridges. The Mn_4O_xCa cluster ($x \geq 4$) is located on the luminal side of the D1 protein and has one ligand from the CP43 protein (**Figure 4**). The Mn_4O_xCa cluster is surrounded by a protein microenvironment that includes D1 and D2 proteins, the luminal extensions of the CP43 and CP47 proteins and several extrinsic polypeptides (**Figure 2** and **Figure 3**). Although the protein sphere serves to shield the water-oxidizing complex from the inner aqueous phase, channels exist for the entry of substrate water and the release of molecular oxygen and protons. Recently a chloride-binding site has been identified approximately 6–7 Å from the Mn_4O_xCa cluster (**Figure 4**; Guskov *et al*., 2009). Although chloride has been shown to influence water-oxidation, the relatively distant location from the cluster makes it difficult to propose a mechanism. One possibility is that chloride plays a role in stabilizing the proton network surrounding the Mn_4O_xCa cluster (Oleson and Andreasson, 2003).

As aforementioned, the structure of the PSII reaction centre is now available at 3.5–2.9 Å resolution (Ferreira *et al*., 2004; Loll *et al*., 2005; Guskov *et al*., 2009), and reasonably detailed models for the Mn_4O_xCa cluster have been proposed based on these structures and on polarized Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy (Yano *et al*., 2006). In combination with experimental data that includes Fourier-Transform Infra Red (FTIR) and Electron Paramagnetic Resonance (EPR) spectroscopy, as well as mass spectrometry and detailed theoretical calculations, the goal of understanding the molecular mechanism of water oxidation appears to be within reach (Siegbahn, 2008; Sproviero *et al*., 2008; Zein *et al*., 2008). **Figure 4b** and **c** show two of the proposed geometric arrangements of the manganese and calcium ions. The binding sites for substrate water are speculative, with at least one water molecule bound in the S_0 and S_1 states, and two water molecules bound in the S_2 and S_3 states. There is evidence that calcium is involved in binding one substrate water molecule and that manganese is involved in binding at least one of the two water molecules.

One of the challenges in modelling water oxidation is accounting for the pattern of proton release into the lumen during the $S_0 \rightarrow S_1$, $S_1 \rightarrow S_2$, $S_2 \rightarrow S_3$ and $S_3 \rightarrow (S_4) \rightarrow S_0$ transitions (**Figure 6b**). The problem is that the protons appearing in the lumen could come from amino acids near the water oxidation site rather than directly from the catalytic steps involved in water oxidation (see Suzuki *et al*., 2009 and references therein).

As the Mn_4O_xCa cluster transitions from one S-state to another, the early oxidation states must be stabilized long enough to enable the relatively slow water-oxidation chemistry ($\sim$ 1 ms) to occur during the $S_3 \rightarrow S_4 \rightarrow S_0$ transition. The formal oxidation state of S_0 includes 3 Mn^{3+} and 1 Mn^{4+} (Kulik *et al*., 2007; **Figure 6b**). (In the literature, an alternative notation $Mn(III)_3Mn(IV)$ is also used to describe the formal oxidation state of Mn in the OEC.) Assignment of these oxidation states to specific manganese ions within the cluster has proven difficult. Furthermore, charge delocalization over the manganese ions and the oxygen bridges and ligands of the cluster resulting in partial charges has been proposed for some S-states.

During the $S_0 \rightarrow S_1$ transition, an Mn^{3+} to Mn^{4+} oxidation occurs that is coupled to a structural change of the Mn_4O_xCa cluster. The structural change appears to include a decrease in one of the Mn–Mn distances from 2.85 to 2.75 Å due to deprotonation of one μ-OH bridge (Kulik *et al*., 2007). In the $S_1 \rightarrow S_2$ transition, another Mn^{3+} to Mn^{4+} oxidation occurs, but without any significant structural change and no significant proton release is observed. Thus, in the S_2 state the Mn_4O_xCa cluster has an additional positive charge. The $S_2 \rightarrow S_3$ transition involves the release of a proton, which is followed by the oxidation of the Mn_4O_xCa cluster by tyrosine $Y_Z^{\bullet}$. The nature of this oxidation is controversial – it has been proposed to be Mn^{3+} to Mn^{4+} oxidation, or an oxidation of a μ-oxo bridge. The $S_2 \rightarrow S_3$ transition involves a significant structural change that has yet to be fully characterized.

During the $S_3 \rightarrow S_4 \rightarrow S_0$ transition, the O–O bond is formed and two protons are released. The formation of the O–O bond, a critical step in water oxidation, requires activation of the two substrate water molecules. Three possibilities have been proposed (**Figure 6c**): (I) One of the substrate water molecules (bound to Mn) is deprotonated and becomes electrophilic during the S-state cycle by successive oxidation of the ligating Mn ion. This species is described in the S_4 state as $Mn^{4+}=O^{\bullet}$, $Mn^{5+}=O$ or $Mn^{4+} \equiv O^{+}$ and is thought to be attacked by the second (nucleophilic) substrate water molecule, which is activated and positioned by binding to a lower valent manganese and/or calcium and may be partially deprotonated. (II) During oxidation of the Mn_4O_xCa cluster, one of the oxygen bridges or an oxygen ligand (originating from substrate water) becomes partially oxidized forming an oxygen radical, which can form the O–O bond in a radical-like mechanism with a second oxygen species that maybe coordinated to manganese and/or calcium. (III) In the S_3 state, a small fraction of the Mn_4O_xCa clusters may contain the O–O bond in the form of a complexed peroxide, which

is postulated to be the species that is oxidized by $Y_Z^{\bullet}$ in the next transition. In this model the rate of the $S_3 \rightarrow S_4$ transition depends on the equilibrium constant between the open and closed forms of the $S_3Y_Z^{\bullet}$ state (for reviews see Hillier and Messinger, 2005; McEvoy and Brudvig, 2006; Brudvig, 2008; Messinger and Renger, 2008; Lubitz *et al*., 2008). **See also**: Oxygen Production

Reduction of Plastoquinone: The Two-electron Gate

Plastoquinone plays a key role in photosynthesis by linking electron transport to proton transfer across the photosynthetic membrane. In the PSII complex, two plastoquinone molecules work in tandem, with one molecule permanently bound at the Q_A site, and another molecule bound at the Q_B site. Once plastoquinone at the Q_B site has been fully reduced by the addition of two electrons and two protons, the reduced form (PQH_2) is released into the photosynthetic membrane. The reduction of plastoquinone at the Q_B site is known as the two-electron gate, because two electrons, and therefore two photochemical reactions are required for the formation and release of PQH_2 (Bouges-Bocquet, 1973; Velthuys and Amesz, 1974; **Figure 7**). The Q_B site of PSII is of particular interest because some herbicides used in agriculture (e.g. Atrazine) inhibit photosynthesis by binding at or near the Q_B site (Oettmeier, 1999).

The pathway of electrons from the primary electron donor (Chl_{D1}) to Q_B is shown in **Figure 2**. In the first reaction, an electron is transferred from Q_A^- to Q_B within 100–200 µs, producing the state Q_A/Q_B^- (**Figure 7b**). In the second reaction an electron is transferred from Q_A^- to Q_B^- within 400–600 µs, producing the state Q_A/Q_B^{2-}, which takes up protons from the outer water phase, producing PQH_2. Although the pathway of protons through PSII involves specific amino acids, **Figure 7b** shows a proton (H^+) near Q_B without specifying its source. There is evidence that bicarbonate/carbonate ions play a role in protonation by binding near the Q_B site (Van Rensen *et al*., 1999; cf. Rose *et al*., 2008), which is supported by structural data (Ferreira *et al*., 2004; Loll *et al*., 2005) showing that a bicarbonate/carbonate is bound to the nonhaeme iron and is within 3.2 Å of Lysine 264 (on protein D2; see Cox *et al*., 2009 for evidence). On full reduction, PQH_2 debinds from the Q_B site, migrates through a hydrophobic quinone exchange cavity within the protein complex, and enters the hydrophobic core of the photosynthetic membrane (Guskov *et al*., 2009). The reduction cycle is repeated by binding of a PQ molecule from the quinone exchange cavity.

Photosystem II contributes to the transmembrane proton electrochemical potential difference that drives ATP synthesis

The production of ATP in photosynthesis depends on the conversion of redox-free energy into a 'transmembrane proton electrochemical potential difference', which is made up of a pH difference (ΔpH) and an electrical potential difference (ΔΨ) across the photosynthetic membrane (Mitchell, 1961; reviewed in Renger, 2008). PSII contributes to the proton potential energy by the release of protons into the inner water phase associated with oxidation of water, and by the uptake of protons from the outer water phase associated with the reduction of PQ. Reduction of plastoquinone at the Q_B site by PSII is followed by uptake of protons from the outer water phase. This reaction is the first step in a proton-transporting mechanism that is completed by the oxidation of PQH_2 by the cytochrome b_6f complex. As PQH_2 is oxidized, two electrons from it are passed on to the cytochrome b_6f complex and the protons are released into the lumen. In addition to the ΔpH that is built up in this way, an electrical potential difference (ΔΨ) is also created across the thylakoid membrane due to the directional electron transfer through the PSII reaction centre from water (luminal side) to plastoquinone (stromal/cytoplasmic side). **See also**: Photophosphorylation; Photosynthesis: Light Reactions

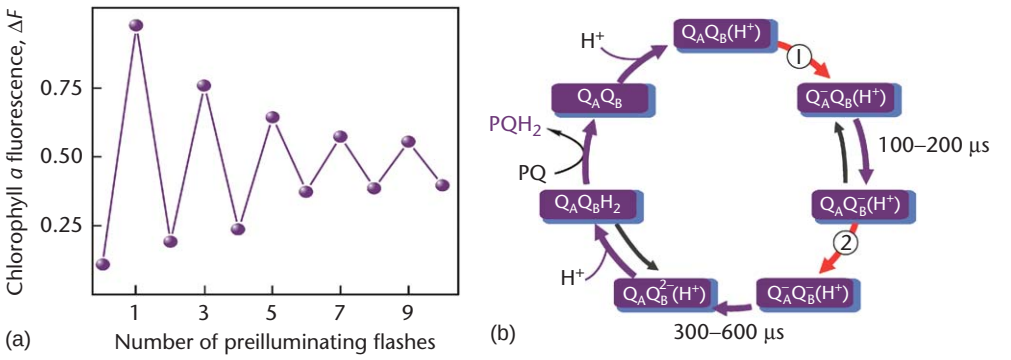


Figure 7 The two-electron gate on the electron acceptor side of photosystem II (PSII). (a) Chlorophyll *a* fluorescence from PSII, as a function of flash number, after the 'oxygen cycle' is inhibited and water is replaced by an artificial electron donor (Velthuys and Amesz, 1974); data show clearly the two-flash dependence. (b) Steps in the two-electron reduction of plastoquinone at the Q_B site of PSII (see **Figure 2** and text for details). This figure was drawn by Dmitriy Shevela (in the laboratory of one of us, JM).

Downregulation: Energy can be diverted away from the photosystem II reaction centre in excess light

Environmental conditions often impose severe limitations on both the rate and efficiency of photosynthesis. A common stress situation for a photosynthetic organism is the absorption of more light than it can use for carbon reduction. The excess light can drive inopportune electron transfer reactions, which can cause both long- and short-term damage to PSII, impairing photosynthetic productivity. Photosynthetic organisms have evolved different strategies to avoid injury due to excess light. One of the dominant protective mechanisms in plants and algae is known as downregulation or 'nonphotochemical' quenching, which is a dynamic regulation of excitation energy transfer pathways within the antenna system that diverts excitation energy into heat before it reaches the reaction centre (Demmig-Adams *et al*., 2006). This process involves xanthophylls, a special class of carotenoids. Under excess light it is not unusual for half of the absorbed quanta to be converted into heat.

Secondary electron transfer reactions in photosystem II protect against photodamage

Despite the protection provided by downregulation, PSII is susceptible to damage by inopportune redox reactions associated with the powerful oxidants required for the oxidation of water, and reductants required for the reduction of plastoquinone. To avoid such damage, PSII contains redox components that protect by accepting or donating electrons at opportune times. For example, cytochrome *b*559 appears to deactivate a rarely formed, but highly damaging, redox state of PSII (Whitmarsh and Pakrasi, 1996; Kaminskaya *et al*., 2007). In addition, some carotenoid and chlorophyll molecules on the D1/D2 reaction centre have been shown to act as alternative electron donors to $P680^+$ [$(P_{D1}, P_{D2})^+$] in cases when the water-oxidizing complex is inactive.

Some photosystem II centres are inactive

Although most PSII reaction centre complexes work efficiently to oxidize water and reduce plastoquinone, a number of *in vivo* assays have shown that a significant proportion of these centres are unable to transfer electrons to the plastoquinone pool at physiologically significant rates. Experiments using higher plants, algae and cyanobacteria indicate that inactive PSII complexes are a common feature of oxygenic organisms. It has been estimated that inactive centres may reduce the quantum efficiency of photosynthesis by as much as 10%. These inactive centres may be a consequence of the significant turn-over of damaged PSII centres which requires partial disassembly of the complex, replacement of the subunit D1 and reassembly of an active complex. The D1 subunit of PSII is prone to light-induced damage, exhibiting a half-life time in plants as short as 30 min (see Vass and Aro, 2008 for review on assembly). Many of the intermediate states occurring during the disassembly and reassembly process have impaired oxygen-evolving activity, which may necessitate control processes to avoid the production of deleterious products such as hydrogen peroxide.

Concluding Remarks

As the source of atmospheric oxygen, PSII has played a seminal role in the evolution of life on our planet. PSII is a chlorophyll–protein complex found in all oxygenic photosynthetic organisms, which include cyanobacteria, algae and plants. It is composed of an antenna system for capturing light, and a reaction centre core that uses the light energy to drive electron and proton transfer reactions. The antenna system consists of protein complexes that bind chlorophyll and other molecules that convert light energy into excitation energy. At the centre of PSII is a reaction centre that contains electron carriers that transfer electrons from water to plastoquinone. These carriers include an oxygen bridged cluster of four manganese ions and one calcium ion (Mn_4O_xCa cluster) that is the site of water oxidation, a tyrosine (Y_z), an array of four chlorophyll molecules (Chl_{D1}, P_{D1} (we can also call it $ChlP_{D1}$) P_{D2} (we can also call it $ChlP_{D2}$), Chl_{D2}), two pheophytin molecules ($Pheo_{D1}$ and $Pheo_{D2}$), a permanently bound plastoquinone (Q_A) and a plastoquinone that binds reversibly to PSII at the Q_B site. Within a PSII complex, four consecutive photochemical reactions lead to the oxidation of two water molecules, which results in the release of one oxygen molecule, four protons and the release of two reduced plastoquinone molecules. Now that we have well-resolved PSII structures, detailed spectroscopic information on the structure and function of the Mn_4O_xCa cluster, and powerful theoretical methods, the goal of understanding the molecular mechanism of water oxidation appears to be within reach. A deep understanding of this fundamental biological process can accelerate the development of artificial catalysts for solar hydrogen and oxygen production from water (Lubitz *et al*., 2008).

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