Photosystem II

Advances in Photosynthesis and Respiration

VOLUME 22

The scope of our series, beginning with volume 11, reflects the concept that photosynthesis and respiration are intertwined with respect to both the protein complexes involved and to the entire bioenergetic machinery of all life. *Advances in Photosynthesis and Respiration* is a book series that provides a comprehensive and state-of-the-art account of research in photosynthesis and respiration. Photosynthesis is the process by which higher plants, algae, and certain species of bacteria transform and store solar energy in the form of energy-rich organic molecules. These compounds are in turn used as the energy source for all growth and reproduction in these and almost all other organisms. As such, virtually all life on the planet ultimately depends on photosynthetic energy conversion. Respiration, which occurs in mitochondrial and bacterial membranes, utilizes energy present in organic molecules to fuel a wide range of metabolic reactions critical for cell growth and development. In addition, many photosynthetic organisms engage in energetically wasteful photorespiration that begins in the chloroplast with an oxygenation reaction catalyzed by the same enzyme responsible for capturing carbon dioxide in photosynthesis. This series of books spans topics from physics to agronomy and medicine, from femtosecond processes to season long production, from the photophysics of reaction centers, through the electrochemistry of intermediate electron transfer, to the physiology of whole orgamisms, and from X-ray christallography of proteins to the morphology or organelles and intact organisms. The goal of the series is to offer beginning researchers, advanced undergraduate students, graduate students, and even research specialists, a comprehensive, up-to-date picture of the remarkable advances across the full scope of research on photosynthesis, respiration and related processes.

The titles published in this series are listed at the end of this volume and those of forthcoming volumes on the back cover.

Photosystem II

The Light-Driven Water:Plastoquinone Oxidoreductase

Edited by

Thomas J. Wydrzynski
The Australian National University,
Canberra, Australia

and

Kimiyuki Satoh
Okayama University,
Okayama, Japan

Assistant Editor

Joel A. Freeman

Springer

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Front Cover Image. An underwater scene of *Vallisneria* sp. from Ewans Ponds conservation area, V
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in Photosynthesis, Arizona State University, Tempe, Arizon 85287-1604, U.S.A.

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From the Series Editor

Advances in Photosynthesis and Respiration

Volume 22, Photosystem II: The Light-Driven Water:Plastoquinone Oxidoreductase

I am delighted to announce the publication, in *Advances in Photosynthesis and Respiration* (AIPH) Series, of *Photosystem II: The Light-Driven Water: Plastoquinone Oxidoreductase,* a book covering the central role of the oxygen-evolving system for life on earth; it deals with both the structure and the function of this unique process. Two distinguished authorities have edited this volume: Thomas J. Wydrzynski of Australia and Kimiyuki Satoh of Japan. Some of the earlier volumes have included descriptions of Photosystem II: Volume 4 (*Oxygenic Photosynthesis: The Light Reactions*, edited by Donald R. Ort and Charles F. Yocum); Volume 10 (*Photosynthesis: Photobiochemistry and Photobiophysics*, authored by Bacon Ke); and Volume 19 (*Chlorophyll a Fluorescence: A Signature of Photosynthesis*, edited by George C. Papageorgiou and Govindjee) . The current volume follows the 21 volumes listed below.

Published Volumes (1994–2005)

- *Volume 1*: *Molecular Biology of Cyanobacteria* (28 Chapters; 881 pages; 1994; edited by Donald A. Bryant, from USA; ISBN: 0-7923-3222-9);
- *Volume 2: Anoxygenic Photosynthetic Bacteria* (62 Chapters; 1331 pages; 1995; edited by Robert E. Blankenship, Michael T. Madigan and Carl E. Bauer, from USA; ISBN: 0-7923-3682-8);
- *Volume 3: Biophysical Techniques in Photosynthesis* (24 Chapters; 411 pages; 1996; edited by the late Jan Amesz and the late Arnold J. Hoff, from The Netherlands; ISBN: 0-7923-3642-9);
- *Volume 4: Oxygenic Photosynthesis: The Light Reactions* (34 Chapters; 682 pages; 1996; edited by Donald R. Ort and Charles F. Yocum, from USA; ISBN: 0-7923-3683-6);
- *Volume 5: Photosynthesis and the Environment* (20 Chapters; 491 pages; 1996; edited by Neil R. Baker, from UK; ISBN: 0-7923-4316-6);
- *Volume 6: Lipids in Photosynthesis: Structure, Function and Genetics* (15 Chapters; 321 pages; 1998; edited by Paul-André Siegenthaler and Norio Murata, from Switzerland and Japan; ISBN: 0-7923-5173-8);
- *Volume 7: The Molecular Biology of Chloroplasts and Mitochondria in Chlamydomonas* (36 Chapters; 733 pages; 1998; edited by Jean David Rochaix, Michel Goldschmidt-Clermont and Sabeeha Merchant, from Switzerland and USA; ISBN: 0-7923-5174-6);
- *Volume 8: The Photochemistry of Carotenoids* (20 Chapters; 399 pages; 1999; edited by Harry A. Frank, Andrew J. Young, George Britton and Richard J. Cogdell, from USA and UK; ISBN: 0-7923-5942-9);
- *Volume 9: Photosynthesis: Physiology and Metabolism* (24 Chapters; 624 pages; 2000; edited by Richard C. Leegood, Thomas D. Sharkey and Susanne von Caemmerer, from UK, USA and Australia; ISBN: 0-7923-6143-1);
- *Volume 10: Photosynthesis: Photobiochemistry and Photobiophysics* (36 Chapters; 763 pages; 2001; authored by Bacon Ke, from USA; ISBN: 0-7923-6334-5);
- *Volume 11: Regulation of Photosynthesis* (32 Chapters; 613 pages; 2001; edited by Eva-Mari Aro and Bertil Andersson, from Finland and Sweden; ISBN: 0-7923-6336-1);
- *Volume 12: Photosynthetic Nitrogen Assimilation and Associated Carbon and Respiratory Metabolism* (16 Chapters; 284 pages; 2002; edited by Christine Foyer and Graham Noctor, from UK and France);
- *Volume 13: Light Harvesting Antennas* (17 Chapters; 513 pages; 2003; edited by Beverley Green and William Parson, from Canada and USA; ISBN: 0-7923-6335-3);
- *Volume 14: Photosynthesis in Algae* (19 Chapters; 479 pages; 2003; edited by Anthony Larkum,

Susan Douglas and John Raven, from Australia, Canada and UK; ISBN: 0-7923-6333-7);

- *Volume 15: Respiration in Archaea and Bacteria: Diversity of Prokaryotic Electron Transport Carriers* (13 Chapters; 326 pages; 2004; edited by Davide Zannoni, from Italy; ISBN: 1-4020-2001-5);
- *Volume 16: Respiration in Archaea and Bacteria 2: Diversity of Prokaryotic Respiratory Systems* (13 chapters; 310 pages; 2004; edited by Davide Zannoni, from Italy; ISBN: 1-4020-2002-3);
- *Volume 17: Plant Mitochondria: From Genome to Function* (14 Chapters; 325 pages; 2004; edited by David A. Day, A. Harvey Millar and James Whelan, from Australia; ISBN: 1-4020-2339-5);
- *Volume 18: Plant Respiration: From Cell to Ecosystem* (13 Chapters; 250 pages; 2005; edited by Hans Lambers, and Miquel Ribas-Carbo from Australia and Spain; ; ISBN: 1-4020-3588-8)
- *Volume 19: Chlorophyll a Fluorescence: A Signature of Photosynthesis* (31 Chapters; 817 pages; 2004; edited by George C. Papageorgiou and Govindjee, from Greece and USA; ISBN: 1-4020-3217-X);
- *Volume 20: Discoveries in Photosynthesis* (111 Chapters; 1262 + xxx pages; 2005; edited by Govindjee, J. Thomas Beatty, Howard Gest and John F. Allen, from USA, Canada and Sweden (& UK) ; ISBN: 1-4020-3323-0); and
- *Volume 21: Photoprotection, Photoinhibition, Gene Regulation, and Environment* (21 Chapters; ~500 pages; 2005; edited by Barbara Demmig-Adams, William W. Adams III and Autar K. Mattoo, all from USA; ISBN:1-4020-3564-0)

For a description of the scope of the AIPH Series, see the back cover of this book. Further information on these books and ordering instructions can be found at <http://www.springeronline.com> under the Book Series 'Advances in Photosynthesis and Respiration.' Special discounts are available for members of the International Society of Photosynthesis Research, ISPR (<http://www.photosynthesisresearch.org>). To ensure your discount, please order through Noeline.Gibson@springer-sbm.com.

Photosystem II: The Light-Driven Water:Plastoquinone Oxidoreductase

Photosystem II is truly an unprecedented discovery of evolution; one couldn't have modeled it 30–40 years ago despite all the advances in chemistry, physics and biology. It consists of a light-harvesting unit (antenna) and a reaction center unit that operates at an unusually high redox potential; it is this latter unique characteristic that allows it to oxidize water to oxygen at its 'oxygen-evolving complex.' A book on this unique system has been edited by two outstanding authorities in the area of the structure and the function of the oxygen-evolving Photosystem II: Thomas J. Wydrzynski (of the Research School of Biological Sciences, The Australian National University, Canberra, Australia) and Kimiyuki Satoh (of the Department of Biology, Okayama University, Okayama, Japan).

Respiring organisms, including humans, on this planet depend on the oxygen that green plants generate through Photosystem II. Thus, this book is a very important addition to the already published books in the AIPH Series. It essentially addresses water first as a source of the electrons that are necessary for the reductive syntheses of organic matter, and then as a source of molecular oxygen that is necessary for the energy producing catabolic oxidations, including respiration.

During the last decade, or so, dramatic advances have been made in elucidating the structure of Photosystem II to near atomic scale with the X-ray crystallography, and in relating it to its biophysical, biochemical and molecular biological properties. Thirty-four chapters, authored by 75 internationally acknowledged experts, summarize this extraordinary scientific progress, covering areas that range from the capture of fleeting photons, their conversion into chemical energy (oxidation-reduction), to the dynamic regulatory processes that sustain and optimize the photosynthetic oxidation of water. A discussion is also provided on the beginnings of Photosystem II and photosynthesis more than 3 billion years ago (in the Archaean Era) and on its eventful evolution to the present day diversity of microbial and higher plants. Lastly, the design of artificial (biomimetic) Photosystems II is also discussed. Who knows, one day these systems may serve the needs of humanity either on Earth, or on some distant outpost in space.

The book is designed to be used by graduate students, beginning researchers and advanced undergraduate students in the areas of plant sciences, microbiology, cell and molecular biology, biochemistry, biophysics, bioenergetics and chemistry, as well as those in agriculture and biotechnology.

This book is appropriately dedicated to a pioneer in the field Gerald T. Babcock (the dedication is authored by Charles F. Yocum, Robert Blankenship and Shelagh Ferguson-Miller, all of USA). Kimiyuki Satoh (Japan), Thomas J. Wydrzynski (Australia) and Govindjee (USA) provide an *Introduction* to Photosystem II and the chapters in this volume (*Chapter 1*). It is followed by five chapters that deal with the *Protein Constituents of Photosystem II*: Beverley Green (Canada) and Elisabeth Gantt (USA) discuss the distal and extrinsic antenna (*Chapter 2*); Julian Eaton-Rye (New Zealand) and Cindy Putnam-Evans (USA) summarize our understanding of the CP 47 and CP43 core antenna components (*Chapter 3*); Peter Nixon (UK), Mary Sarcina (UK) and Bruce Diner (USA) provide an account of the D1 and D2 core proteins (*Chapter 4*). This is followed by *Chapter 5*, by Terry Bricker (USA) and Robert Burnap (USA) on the oxygen enhancing extrinsic proteins, and *Chapter 6*, by Leeann Thornton (USA), Johnna Roose (USA), Himadri Pakrasi (USA) and Masahiko Ikeuchi (Japan) on the low molecular weight components.

The next nine chapters focus on the *Organization of the Functional Sites in Photosystem II*: Gernot Renger and Alfred Holzwarth (both of Germany) discuss the primary electron transfer (*Chapter 7*); Vasili Petrouleas (Greece) and Anthony Crofts (USA) summarize information on the quinone-iron acceptor complex (*Chapter* 8); Bruce Diner and David Britt (both of USA) discuss the redox active tyrosines Y_Z and Y_D (*Chapter* 9); Vittal Yachandra (USA) summarizes the current understanding about the organization of the manganese ions of the manganese cluster of the O_2-evolving complex (*Chapter* 10); Richard Debus (USA) summarizes what is known about protein ligands of the manganese cluster (*Chapter 11*); Karin Åhrling (Australia), Ronald Pace (Australia) and Michael Evans (UK) provide information on spectroscopic observations and their implications on structural and functional details of catalytic manganese cluster (*Chapter 12*); Hans van Gorkom (The Netherlands) and Charles Yocum (USA) discuss the roles of Calcium and Chloride ions (*Chapter 13*); Jack van Rensen (The Netherlands) and Vyacheslav Klimov (Russia) address the unique role of bicarbonate on the acceptor side and the donor side of Photosystem II reaction center (*Chapter 14*); and Peter Faller, Christian Fufezan and William Rutherford (all of France) examine the secondary electron transfer pathways around the Photosystem II reaction center (*Chapter 15*).

Subsequently, in the next six chapters, the focus shifts to the *Structural Basis for Photosystem II*: Takumi Noguchi (Japan) and Catherine Berthomieu (France) analyze the molecular structure of the intermediates of the system, using information obtained from vibrational spectroscopy (*Chapter 16*); Robert Bittl (Germany) and Asako Kawamori (Japan) summarize the configuration of the electron transport intermediates of Photosystem II, as obtained by electron paramagnetic resonance spectroscopy (*Chapter 17*); Ben Hankamer (Australia), James Barber (UK) and Jon Nield (UK) describe the structure of the core/antenna holocomplex as visualized by electron microscopy (*Chapter 18*); Horst Witt (Germany) discusses the first three-dimensional structure of Photosystem II obtained by X-ray crystallography and other biophysical methods (*Chapter 19*); Jian-Ren Shen and Nobuo Kamiya (both of Japan) discuss this structure, using also X-ray crystallography (*Chapter 20*); and James Barber and So Iwata (both of UK) discuss a somewhat refined structure, and its implications to the function of Photosystem II (*Chapter 21*).

These chapters on the structure are followed by four chapters on *Molecular Dynamics of Photosystem II*: Laura Barter (UK), David Klug (UK) and Rienk van Grondelle (The Netherlands) summarize our understanding about excitation energy trapping and its equilibration (*Chapter 22*); Barry Pogson (Australia), Heather Rissler (Australia) and Harry Frank (USA) elaborate the role of carotenoids in energy quenching (*Chapter 23*); Vladimir Shinkarev (USA) discusses the pattern and the analyses of the O_2 evolution in a train of light flashes (*Chapter 24*); and Warwick Hillier (Australia) and Johannes Messinger (Germany) present an overview on the mechanism of water oxidation (*Chapter 25*).

This is followed by a discussion of *Assembly and Biodynamics of Photosystem II* in four chapters: Charles Dismukes, Gennady Ananyev and Richard Watt (all of USA) discuss the photoassembly of the catalytic manganese cluster (*Chapter 26*); Wah Soon Chow (Australia) and Eva-Mari Aro (Finland) summarize our understanding of photoinactivation and mechanisms of recovery (*Chapter 27*); Kenichi Yamaguchi (USA), Stephen Mayfield (USA) and Mamoru Sugita (Japan) present a current picture of transcriptional and translational regulation of gene expression (*Chapter 28*); and Steven Theg and Lan-Xin Shi (both of USA) discuss transport and post-translational processing in biosynthesis and homeostatis (*Chapter 29*).

This is followed by a discussion of the *Comparison of Photosystem II with Other Natural/Artificial Systems* in four chapters: Charles Dismukes and Robert Blankenship (both of USA) describe the origins and the evolution of oxygenic photosynthesis (*Chapter 30*); Gary Brudvig (USA) and Mårten Wikström present mechanistic comparisons between Photosystem II and Cytochrome *c* oxidase (*Chapter 31*); Lázló Kálmán (Hungary), JoAnn Williams (USA) and James Allen (USA) summarize research on mimicking the properties of Photosystem II in purple bacterial reaction centers (*Chapter 32*); Brian Gibney (USA) and Cecilia Tommos (Sweden) discuss de novo protein design in respiration and photosynthesis (*Chapter 33*); and Ann Magnuson, Stenbjörn Styring and Leif Hammarström (all of Sweden) end this book with an understanding of Photosystem II through artificial photosynthesis.

A Bit of History: First Clear Evidence of the Series Scheme, and the Naming of System 2 (Now Photosystem II) by Louis N.M. Duysens, Jan Amesz and B. M. Kamp in 1961

A recently published time-line on oxygenic photosynthesis covers many aspects of the history of 'Photosystem II' (see Govindjee and D. Krogmann (2004) Discoveries in oxygenic photosynthesis (1727–2003): A perspective. Photosynth Res 80: 15–57). Chapter 1 of this book by K. Satoh, T.J. Wydrzynski and Govindjee includes a historical account of Photosystem II (for references, see this chapter). In a paper, published on May 6, 1961, Louis N.M. Duysens, Jan Amesz and B.M. Kamp (Two photochemical systems in photosynthesis. Nature 190: 510-511) used for the first time the name 'System 2' for the photosystem responsible for the action spectrum of chlorophyll *a* fluorescence; it was the system that was suggested to oxidize water to oxygen, and reduce cytochrome. 'System 1', on the other hand, oxidized cytochrome, and reduced pyridine nucleotide. Duysens and colleagues added first red light (680 nm light; absorbed mainly by chlorophyll) and observed oxidation of a cytochrome in a red alga *Porphyridium cruentum*, and then they added green light (562 nm; absorbed mainly in phycoerythrin) and observed reduction of this oxidized cytochrome. Addition of the herbicide DCMU eliminated the reduction of cytochrome by green light, but not its oxidation by red light. This antagonistic effect of light 1 and 2 on cytochrome provided not only the evidence for the series scheme of photosynthesis, but was the first paper to call the system that oxidized water and reduced cytochrome as 'System 2' (currently, Photosystem II), whereas the other system that oxidized cytochrome as 'System 1' (currently, Photosystem I). In this seminal paper, Duysens and colleagues had recognized not only their own work, but that of Robert Emerson (with Marcia Brody), Eugene Rabinowitch (with Emerson, and with Rajni Govindjee and Jan B. Thomas), C. Stacy French (with V.K. Young, and with Jack Myers), Norman Bishop, and Leo Vernon (with L.P. Zaugg). Since in sunlight both systems are excited simultaneously and begin to function almost simultaneously, it is not a question of which starts first. The naming of the system is thus arbitrary.

Future AIPH Books

The readers of the current series are encouraged to watch for the publication of the forthcoming books (not necessarily arranged in the order of future appearance):

- *The Structure and Function of Plastids* (Editors: Robert Wise and J. Kenneth Hoober; expected to contain 27 Chapters and ~775 pages; ISBN: 1-4020-4060-1);
- *Biochemistry, Biophysics and Biological Functions of Chlorophylls* (Editors: Bernhard Grimm, Robert J. Porra, Wolfhart Rüdiger and Hugo Scheer);
- *Photosystem I: The Light-Driven Plastocyanin: Ferredoxin Oxidoreductase* (Editor: John Golbeck);
- *Biophysical Techniques II* (Editors : Thijs J. Aartsma and Jörg Matysik);
- *Photosynthesis: A Comprehensive Treatise; Biochemistry, Biophysics Physiology and Molecular Biology, Part 1* (Editors: Julian Eaton-Rye and Baishnab Tripathy); and
- *Photosynthesis: A Comprehensive Treatise; Biochemistry, Biophysics Physiology and Molecular Biology, Part 2* (Editors: Baishnab Tripathy and Julian Eaton-Rye).

In addition to these contracted books, we are already in touch with prospective Editors for the following books:

- Molecular Biology of Cyanobacteria II
- Protonation and ATP Synthases
- Genomics and Proteomics

- Protein Complexes of Respiration and Photosynthesis
- Sulfur Metabolism in Photosynthetic Systems
- Molecular Biology of Stress in Plants
- Global Aspects of Photosynthesis and Respiration (2 volumes)
- Artificial Photosynthesis.

Readers are encouraged to send their suggestions for future volumes (topics, names of future editors, and of future authors) to me by E-mail (gov@uiuc.edu) or fax (1-217-244-7246).

In view of the interdisciplinary character of research in photosynthesis and respiration, it is my earnest hope that this series of books will be used in educating students and researchers not only in Plant Sciences, Molecular and Cell Biology, Integrative Biology, Biotechnology, Agricultural Sciences, Microbiology, Biochemistry, and Biophysics, but also in Bioengineering, Chemistry, and Physics.

Acknowledgments

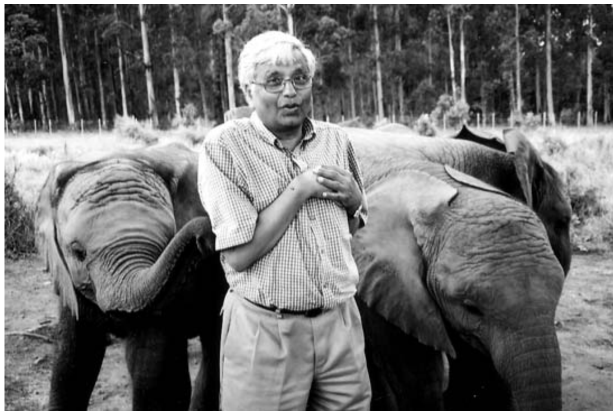
I take this opportunity to thank Thomas J. Wydrzynski and Kimiyuki Satoh for their outstanding and painstaking editorial work. We are grateful to them for (personally) subsidizing 8 of the 16 color plates in this volume. I thank all the 75 authors of volume 22: without their authoritative chapters, there would be no such volume. I thank Jacco Flipsen and Noeline Gibson (both of Springer) for their friendly working relationship with us that led to the production of this book. I thank Jeff Haas (Director of Information Technology, Life Sciences, University of Illinois at Urbana-Champaign, UIUC) and Evan DeLucia (Head, Department of Plant Biology, UIUC) for their support. My family (my wife Rajni Govindjee; our daughter Anita, her husband Morten Christiansen, and our grand-daughter Sunita; our son Sanjay, his wife Marilyn, and our grandsons Arjun and Rajiv) has been very supportive during the preparation of this book.

I am grateful to George Papageorgiou for his suggestions to improve this Editorial.

Special thanks go to Larry Orr for his wonderful work in typesetting this book. His constant advise to the editors and his outstanding interactions with all those involved in in this book are a source of inspiration to all of us.

August 1, 2005

Govindjee
Series Editor, *Advances in Photosynthesis and Respiration*
University of Illinois at Urbana-Champaign,
Department of Plant Biology
Urbana, IL 61801-3707, USA
E-mail: gov@uiuc.edu
URL: http://www.life.uiuc.edu/govindjee



Govindjee in South Africa, 2005

Govindjee**,** born in 1932, has been Professor Emeritus of Biochemistry, Biophysics and Plant Biology at the University of Illinois at Urbana-Champaign (UIUC), Illinois, USA, since 1999. He received his B.Sc. (Chemistry and Biology) and M.Sc. (Botany: Plant Physiology) from the University of Allahabad, India, in 1952 and 1954, respectively. He earned his Ph.D. in Biophysics from the UIUC in 1960, working first with Robert Emerson and then with Eugene Rabinowitch. He served on the faculty of the University of Allahabad from 1954–1956; and the UIUC from 1961–1999. His honors include: Fellow of the American Association of Advancement of Science (AAAS); Fellow of the National Academy of Sciences (India); Distinguished Lecturer of the School of Life Sciences at UIUC (1976) ; President of the American Society for Photobiology (1980–1981); Fulbright Senior Lecturer (1996–1997); and Honorary President of the 2004 International Photosynthesis Congress (Montreal, Canada). Govindjee's research interests have been, since 1960, on the function of Photosystem (PS) II even before it was called as such. Most of his work has been collaborative, but due to lack of space, the names of his collaborators are not mentioned here; they are available on his web page (http://www.life.uiuc.edu/govindjee). He discovered that, in addition to auxiliary pigments, a short-wavelength form of Chlorophyll (Chl) *a* is present in what is now called PS II (1960); discovery of the two-light two-pigment system effect in Chl *a* fluorescence (1960); Emerson Enhancement Effect in NADP reduction in chloroplasts (1963,1964). Together with his graduate students, he discovered a 693–696 nm emission band when photosynthesis was saturated or blocked; made the first measurements on the temperature dependence, down to 4K, of Chl *a* fluorescence; provided explanation for the fluorescence transient curve in terms of a traffic jam of electrons on the acceptor side of PS I, as well as in terms of non-Q_A-related changes. Again, with several graduate students, he focused on the role and the site of bicarbonate ions on PS II, particularly on its acceptor side: a role of bicarbonate on the protonation at the Q_B site was suggested. His other major contributions have been the first picosecond measurements on the primary charge separation in PS II, and the theory of 'thermoluminescence from PS II'. It is worth mentioning that George C. Papageorgiou, and Thomas J. Wydrzynski, editor of volume 19 and this volume, respectively, had worked with Govindjee for their doctorate degrees at the UIUC. His current interests are: (1) Imaging and regulation of lifetime of Chl *a* fluorescence in single algal or cyanobacterial cells; (2) History of photosynthesis research; and (3) Photosynthesis education. He is a member of the American Society of Plant Biology, American Society for Photobiology, Biophysical Society of America, and the International Society of Photosynthesis Research (ISPR). For further information, see his web page at: (http://www.life.uiuc.edu/govindjee). He can be reached by e-mail at gov@life.uiuc.edu.

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Part VII: Comparison of Photosystem II with Other Natural/Artificial Systems

Preface

Photosystem II: The Light-Driven Water:Plastoquinone Oxidoreductase is the 22nd volume in the *Advances in Photosynthesis and Respiration* (AIPH) series (Series Editor, Govindjee) published by Springer (formerly Kluwer Academic Publishers). Photosystem II (PS II) is the heart of oxygenic photosynthesis, catalyzing the oxidation of water to molecular oxygen. Many volumes in the AIPH series have dealt with the biophysics, biochemistry and molecular biology of PS II but always within the framework of a much broader picture. In Volume 4, *Oxygenic Photosynthesis: The Light Reactions*, PS II was discussed along with Photosystem I and thylakoid structure while in Volume 10, *Photosynthesis: Photobiochemistry and Photobiophysics*, PS II was included with discussions on bacterial photosynthesis. In other volumes such as Volume 5, *Photosynthesis and the Environment*, the role of PS II in stress response and photo-inhibition was discussed; in Volume 13, *Light Harvesting Antennas*, the various light harvesting pigment-proteins of PS II are documented; and in Volume 19, *Chlorophyll a Fluorescence: A Signature of Photosynthesis*, the use of PS II chlorophyll fluorescence as a molecular probe was taken to a global scale. The present volume is unique in the AIPH series in that it covers all aspects of the biophysics, biochemistry and molecular biology of PS II, making it the most comprehensive text to be published on this subject to date. A companion volume on *Photosystem I* is currently being edited by John Golbeck.

All aerobic organisms on earth, whether plant, animal or microbial, depend on the function of PS II to maintain the atmospheric O_2 that sustains life. The strongest oxidant known in biology is created within PS II by visible light and is used to oxidize water as the ultimate source of electrons for the carbon-fixing reactions (i.e., the Calvin-Benson-Bassham cycle). The carbon-fixing reactions store chemical energy in the form of organic food stuff and as consequence, molecular oxygen is released as a by-product. Several other books (Volumes 15, 16, 17, 18) in the AIPH series cover the equally important, reverse process of photosynthesis, i.e., respiration, in which molecular oxygen is reduced to water by metabolically burning the organic food stuff releasing the stored chemical energy to power all other life processes.

PS II is an extremely complex enzyme that catalyzes a series of reaction events, from the capture and transfer of light energy (occurring on the femtosecond or the 10^{-15} s time scale) to the efficient conversion of excitation energy into the chemical energy of a stabilized charge separation and the transfer of electrons from water to plastoquinone (occurring on a millisecond or the 10^{-3} s time scale). In recent years there has been a dramatic surge in our knowledge of the molecular organization, dynamics, and reaction paths of PS II. In particular, the overall atomic structure of PS II has been successfully elucidated by X-ray crystallographic analysis, down to a 3.2–3.5 Å resolution. This last accomplishment is no trivial feat considering the subunit complexity and molecular size of the PS II core complex (molecular mass ~260,000 kDa). Simultaneously, the biophysics and molecular biology of PS II has also been greatly advanced. Thus, the time was ripe for a comprehensive book dedicated to PS II to appear in the literature and to summarize our current knowledge as a basis for future research and for the application of the unique PS II chemistry in biotechnology and renewable energy schemes.

To begin the book, we provide a special perspective dedicated to the late Gerald (Jerry) T. Babcock as one of the truly outstanding pioneers in PS II research. His untimely death in 2000 occurred just as he was advocating a new proposal for the mechanism of water oxidation. As the readers of this book will soon realize, many of Jerry's ideas continue to provide the underlying basis of current thinking. The following 34 chapters in the book were written by authors who were invited as leading experts in their respective fields of PS II research. Many chapters are jointly authored by experts from different parts of the world so as to provide the reader with the most in depth perspective on each topic. A total of 75 authors from 13 countries have contributed to the book, representing major centers of PS II research in Europe, North America, Asia and Australia and making this book a truly international effort. The book is divided into six distinct parts which are summarized as follows:

Part I, *A Perspective of Photosystem II Research*, provides an introduction to PS II, correlating our current knowledge of PS II with important historical developments in photosynthesis research. The structural and functional properties of PS II that are discussed in detail in the following chapters are outlined and put into the perspective of PS II as a functional unit in the broader framework of oxygenic photosynthesis. The future of PS II research and its role in biotechnological applications are also summarized.

Part II, *Protein Constituents of Photosystem II*, is devoted to a comprehensive description of the protein subunit composition of PS II, focusing on the known function(s) of each component. Emphasis is placed on the diverse distal and extrinsic antenna pigment-proteins involved in the light-harvesting function of PS II found across the many different classes of photosynthetic organisms; the CP43 and CP47 proximal antenna pigment-proteins, which are universal components of PSII that channel the excitation energy in the light-harvesting array to the photochemical reaction center; the intrinsic D1 and D2 subunits, which form the reaction core and harbor the primary photo-reactants and the electron carriers that catalyze the oxidation of water and the reduction of plastoquinone; the O_2-enhancing extrinsic proteins of the thylakoid membrane, which are important for optimizing molecular oxygen production by PS II; and the identification and proposed structure and function of minor protein components contained in the PS II complexes from cyanobacteria, algae and higher plants.

Part III, *Organization of the Functional Sites in Photosystem II*, discusses in depth the arrangement and properties of the electron transfer components in PS II. These functional components include the reaction center P680, chlorophyll-pheophytin complex that forms the site of primary charge separation in the PS II; the Q_A and Q_B iron-quinone acceptor complex that links the one-electron reactions at the reaction center with the two-electron reduction of plastoquinone; the Y_Z redox-active tyrosine that mediates a proton-coupled electron transfer from the manganese-calcium (Mn_4Ca) cluster to the reaction center and the symmetrical Y_D redox-active tyrosine that interacts with the PS II donor side; the catalytic Mn_4Ca cluster that sequentially accumulates oxidizing equivalents from the reaction center and catalyzes the production of molecular O_2 from water; and the side-path electron donors chlorophyll Z, cytochrome b_{559} and β-carotene, which provide alternate electron transfer routes for the dissipation of excess energy in PS II. Emphasis is also given in this section to the function of the calcium and chloride in the O_2-producing reactions and the role of bicarbonate in electron transfer on both the donor and acceptor sides of the PS II reaction center.

Part IV, *Structural Basis for Photosystem II*, provides the latest information on the atomic and molecular structure of PS II in both prokaryotic and eukaryotic photosynthetic organisms. A range of biophysical techniques are employed in the structural studies, which include the molecular analysis of the PS II functional sites by vibrational spectroscopy (e.g. Fourier transform infrared or FTIR spectroscopy) and electron paramagnetic resonance (EPR) spectroscopy; the determination of the subunit organization in PS II core and antenna holocomplexes by electron cryomicroscopy; and the resolution of atomic structure of the PS II core complex from thermophilic species of cyanobacteria by X-ray crystallography down to 3.5–3.8 Å.

Part V, *Molecular Dynamics of Photosystem II*, provides detailed accounts of the molecular events that define the role of PS II function in oxygenic photosynthesis. These include an analysis of the energy trapping and equilibration with the PS II reaction center; the special role of carotenoid pigments in the quenching of the excess energy absorbed by PS II; the unique flash-induced oscillatory processes in PS II that are characteristic in promoting electron transfer from water to plastoquinone; and the ultimate question of how the oxidation of water takes place to produce molecular oxygen without the formation of highly reactive oxygen radical intermediates.

Part VI, *Assembly and Biodynamics of Photosystem II*, is devoted to discussions of the unique biodynamic processes that sustain PS II function in vivo. Topics include the special process for the light-induced assembly of the catalytic Mn_4Ca cluster; the mechanisms of recovery from the light-induced inactivation of PS II, in particular, the special damage and repair cycle of the D1 protein; transcriptional and translational regulation during PS II gene expression; and the transport and post-translational processing in PS II protein biosynthesis.

Part VII, *Comparison of Photosystem II with Other Natural/Artificial Systems*, addresses the role of PS II with respect to life on earth in general and more specifically to applications in biotechnology. The peculiar lack of diversity in the structural/functional organization of the catalytic site for water oxidation in PSII of present-day photosynthetic organisms is central to the role PS II has had in the evolution of life. Similarly, a comparison between PS II and the cytochrome *c* oxidase enzyme, which catalyzes the reverse reaction by reducing O_2 to water, reveals very little mechanistic commonality, implying that the appearance of PS II was a unique, one-time event in the history of the earth. Finally, attempts to mimic PS II reactions in natural bacterial reaction centers, synthetic proteins, and bioinorganic complexes stand unique in the construction and application of artificial photosynthesis.

Throughout the conceptualization, refinement and final realization of this book, we have many people to thank. First of all we wish to sincerely thank all of the authors. Their patience, fortitude and willingness to provide in depth accounts covering all aspects of PS II structure and function have made this book a truly outstanding addition to the scientific literature.

Likewise, without the expert advice of the many outside reviewers, a book of this scope would not have been possible. In this capacity, we sincerely thank: Jan M. Anderson, The Australian National University; Lars Eric Andreasson, University of Gothenburg; Terry M. Bricker, Louisiana State University; Gary W. Brudvig, Yale University; Wah-Soon (Fred) Chow, The Australian National University; Richard Debus, University of California at Riverside; Bruce Diner, E.I. du Pont de Nemours & Company; Julian Eaton-Rye, University of Otago; Graham Flemming, University of California at Berkeley; Govindjee, University of Illinois at Urbana-Champaign; Sam Hay, The Australian National University; Warwick Hillier, The Australian National University; Vaughan Hurry, University of Umeå; Wolfgang Junge; University of Osnabrück; Hiroyuki Koike, University of Hyogo; Johannes Messinger, Max Planck Institute for Bioinorganic Chemistry; Mamoru Mimuro, Kyoto University; Melvin Y. Okamura, University of California at San Diego; Takaaki Ono, Institute of Physical and Chemical Research; Ronald J. Pace, The Australian National University; Jean-David Rochaix, University of Geneva; Michael Seibert; National Renewable Energy Laboratory; Jian-Ren Shen, Okayama University; Michael R. Wasilewski, Northwestern University; Vittal K. Yachandra, Lawrence Berkeley National Laboratory.

We also wish to thank those who were critical for finalizing the book for publication. In this regard we sincerely thank Joel Freeman for his expert assistance in the editing of the book. Without his help the final stages would have taken a lot longer to come to fruition. And we offer a very special thanks to the person who was most crucial in bringing this book to the publication stage, Larry Orr. Through our many mistakes we caused many problems for Larry, and we wish to express our sincere appreciation of his perseverance, expert assistance and unlimited guidance in bringing this book to print. In terms of the practical aspects in publishing the book we thank the staff at Springer, in particular Jacco Flipsen and Noeline Gibson.

Last but not least we give our very special thanks to Govindjee. He has provided generous advice and encouragement to us and to the authors over the several years from the inception of this project to its final outcome. As the AIPH Series Editor, Govindjee has promoted the most comprehensive set of books on photosynthesis yet to appear, covering subjects from the historical perspectives of photosynthesis to its relationship with respiration and the functioning of the biosphere. Govindjee has provided a treatise for our time comparable to the Eugene I. Rabinowich treatise on Photosynthesis of 50 years ago.

Finally, TW thanks all those in the Photobioenergetics Group for their understanding and support during this project, in particular to Sam Hay, Brett Wallace, Adele Williamson, Iain McConnell and Brendon Conlan. A special thanks from TW goes to Warwick Hillier, for being an outstanding scientific colleague and a good mate over the years. KS thanks his wife (Tamiko Satoh) for her support.

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Thomas J. Wydrzynski
The Australian National University,
Canberra,Australia
Email: tom.wydrzynski@anu.edu.au

Kimiyuki Satoh
Okayama University, Okayama, Japan
Email: kimiyuki@cc.okayama-u.ac.jp

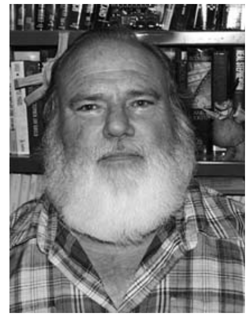
Thomas John Wydrzynski

Thomas J. Wydrzynski was born in 1947 in Saint Louis, Missouri, and is currently a Senior Fellow in the Research School of Biological Sciences (RSBS) at the Australian National University (ANU), Canberra, Australia. He completed his PhD (Plant Physiology) in 1977 at the University of Illinois at Urbana-Champaign (UIUC) under the supervision of Govindjee. For his PhD thesis research he was the first to apply solvent water proton nuclear magnetic resonance (NMR) relaxation measurements as a dynamic probe of the functional manganese in Photosystem II in situ. Also, while he was a PhD student, he provided the first clear experimental evidence, in 1975, for a site of bicarbonate action on the electron acceptor site in Photosystem II. He was awarded a National Science Foundation (NSF) Energy-Related Postdoctoral Research Fellowship in 1976 and worked with Kenneth Sauer at the Lawrence Berkeley National Laboratory from 1977 to 1979, where he obtained some of the first experimental evidence to indicate that the functional manganese changes oxidation state during O_2 production. He then joined industry and worked from 1980 to 1984 in the Biotechnology Division, Corporate Research, Standard Oil Company Indiana in Chicago (now a part of the British Petroleum (BP) Corporation). Subsequently, he re-joined academia and received research fellowships from the Alexander von Humboldt Foundation, Germany (1985), the Science and Technology Agency, Japan (1985), the Wennergren Foundation, Sweden (1986), the Nordiska Forseningsradet (NFR), Sweden (1987), and the Deutscheforschungsgemeinschaft (DFG), Germany (1989). Over this period in his career he worked with Gernot Renger at the Max-Volmer Institute for Physical and Biophysical Chemistry, Technical University Berlin, Germany; Tore Vänngård in the Department of Biochemistry and Biophysics, Chalmers University, Göteborg, Sweden; and Yorinao Inoue in the Solar Energy Research Group, the RIKEN Institute of Physical and Chemical Research, Saitama, Japan. During this time he pursued the idea that the controlled access of solvent water through the protein superstructure to the catalytic site was critical not only for maintaining the stability of the functional manganese but also in O-O bond formation during O_2 production. In 1991 he joined the Research School of Biological Science (RSBS) at The Australian National University in Canberra and during 1998-2001 became the first Head of the newly created Photobioenergetics Group. At the RSBS he embarked on some of his most significant work by developing with his PhD students the first rapid (millisecond time range) mass spectrometric methods of oxygen isotopic exchange for monitoring the substrate water directly at the catalytic site in Photosystem II. The binding properties of the substrate water as determined by these measurements are critical for the chemical mechanism of O_2 formation. In 2000, he set up a research program on the design and synthesis of photo-active proteins in which the first artificial, quinone-based photosynthetic reaction center was engineered from a natural cytochrome protein. The overall goal of these studies is to establish the practical experimental principles for the future development of artificial systems for light energy conversion processes. In 2002, he set up another research program under a Human Frontier Scientific Program grant to study the evolutionary chemistry of oxygenic photosynthesis in present-day organisms from extreme and unusual environments and the possible role of bicarbonate as an alternative substrate for O_2 production. With respect to other professional activities, he was chair of the organizing committees for the *Robertson Symposium on Chlorophyll Fluorescence* in 1994 and the *22nd Annual Meeting of the Australian Society for Biophysics* in 1998, co-chair for two symposia at the *12th International Photosynthesis Congress* in 2001, and was on the organizing committee and co-editor for the special symposium *From Biophysics to Molecular Biology: A Path in the Research of Photosystem II* in 2004.

Kimiyuki Satoh

Kimiyuki Satoh is an Emeritus Professor at the Okayama University in Japan. He received his undergraduate degree from Okayama University and obtained his Ph.D. (Doctor of Science) from the University of Tokyo in 1972 in Biochemistry and Biophysics. He started his work on photosynthesis under the guidance of Professor Hirosi Huzisige of Okayama University. At that time, he contributed to the identification of ferredoxin-dependent nitrite reductase in chloroplasts, and was involved in the analysis of photoinactivation of photochemical activities in chloroplasts. From 1975 to 1977, he was a postdoctoral fellow in the laboratory of Professor Warren Butler at the University of California at San Diego, La Jolla, California. Here, he initiated work on the biochemical separation of chlorophyll protein complexes aiming to identify the pigment-protein complexes responsible for each one of the three fluorescence emission bands (F685; F696 and F735), observed at 77 K. Through this study, he became deeply involved in the biochemical study of Photosystem II (PS II) and succeeded in purifying the PS II core complex from spinach by introducing isoelectric focusing. He then worked in the laboratories of J. Philip Thornber at the University of California at Los Angeles, and of Charles Arntzen at the Plant Research Laboratory at Michigan Sate University, East Lansing, Michigan. There, he identified the polypeptide composition of the purified PS II core complex. In collaboration with Arntzen's research group, he demonstrated that the PS II core complex contains two polypeptides of apparent molecular masses of about 30 kDa, which eventually were identified as the D1 and D2 proteins. In 1982, he became Professor of Plant Physiology at the Okayama University, where he continued his work on the PS II core complex. One of the successes in his laboratory was the isolation of an O_2-evolving PS II core complex, which was the first demonstration that O_2 evolution could take place in the isolated protein-pigment complex. A major achievement from his laboratory at the Okayama University was the isolation of the D1-D2-cytochrome b_{559} complex. This study established that the site of primary charge separation in the PS II is located in the complex that contains D1 and D2 proteins, the proteins that are homologous to the L and M subunits of the purple bacterial reaction center. He then purified the carboxy-terminal processing protease for the D1 precursor protein from spinach and extensively analyzed the enzymatic process. From 1992 to 1997, he served as an Adjunct Professor in the National Institute for Basic Biology at Okazaki. Since then, he has been engaged in the random mutagenesis of the D1 protein from the cyanobacterium *Synechocystis* sp. PCC 6803 with the goal of obtaining photo-tolerant mutants and mutants deficient in autotrophy for use in detailed structure/function analyses of the PS II reaction center. Kimiyuki Satoh has served as the President of the Japanese Society of Plant Physiologists (2002–2003) and as the Secretary of the International Society of Photosynthesis Research (2001–2004).

Joel Freeman



Larry Orr

Joel Freeman, born in 1978, was the technical officer for the Photobioenergetics Group in the Research School of Biological Sciences at the Australian National University (2002–2005). He completed his Bachelor of Aquaculture with honours in 2001 from The University of Tasmania. During this period, he was granted membership in the Golden Key National Honour Society (1998) and placed on the Dean's Roll of Excellence (1998-2000). He then joined the Photobioenergetics Group where he has developed a protocol for the extraction of the functional manganese and calcium from Photosystem II and has since worked on projects including spectroscopic studies of Photosystem II in chlorophyll *d*-containing *Acaryochloris marina*, hydrogen production mechanism in microalgae and its industrial potential and the evolutionary biology of oxygenic photosynthesis, in particular, the role of bicarbonate in Photosystem II steady-state electron transport in *Spirulina maxima*. Joel now works as a policy and technical officer with Plant Programs at the Australian Quarantine and Inspection Service. He assists in the development and implementation of operational standards and procedures for the importation of grains, seeds and nursery stock into Australia.

Larry Orr was born in 1947 and raised in a traveling carnival until his family settled down in northern Wisconsin. Years later he graduated from Arizona State University (ASU) with a BA in English (literature, not grammar). Like most Liberal Arts majors, he worked at a variety of odd jobs until he landed a position in 1983 as Administrative Coordinator for the NSF office in McMurdo, Antarctica. There he became very interested in working with the scientists that came to 'The Ice' from all over the world and, using one of his odd skills learned as a pizza parlor manager, produced the most famous pizza parties on the continent. After leaving the Antarctic program, he was hired for a similar position with the ASU Center for the Study of Early Events in Photosynthesis in 1988. No pizzas were needed there, but other past job skills proved useful: writing, photography, purchasing, proof-reading, office administration, editing, word processing and typesetting. Still at the Photosynthesis Center, he is interested in science education, especially photosynthesis, for the general public. Larry has played a key role in the success of the AIPH (Advances in Photosynthesis and Respiration) Series since its inception in 1994. He has guided, with humor, the Editors as well as the authors in 'staying on track.' Together with Govindjee, Larry has produced one of the most used web articles on 'Photosynthesis and the Web.' It is available at http://photoscience.la.asu.edu/photosyn/photoweb/; as well as at http://www.life.uiuc.edu/govindjee/photoweb/. It is currently undergoing revision; thus, readers are welcome to send suggestions to larry.orr@asu.edu and gov@life.uiuc.edu.

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Color Plates

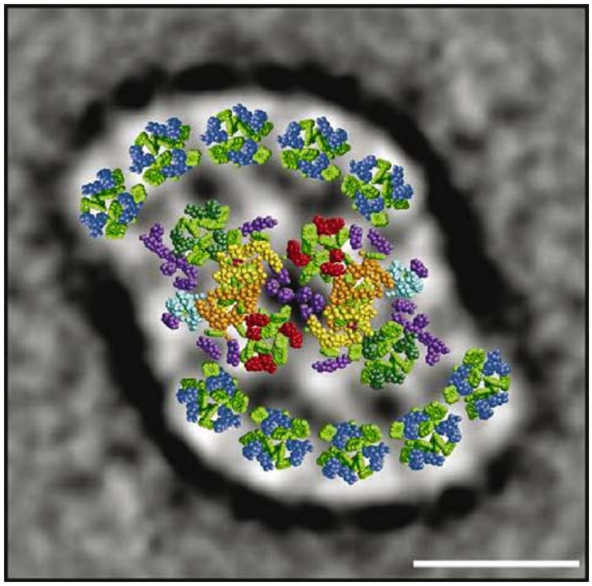

Fig. 1. Prochloron PS II dimer surrounded by 10 prochlorophyte Chl *a/b* (Pcb) monomers. Color code: green, Chl *a* or Chl *b*; blue, transmembrane helices; yellow, D1; orange, D2; dark green, CP43; red, CP47; purple, low molecular weight subunits; cyan, cytochrome b_{559}. Scale bar, 100 Å. Courtesy of J. Barber. See Chapter 2, p. 31.

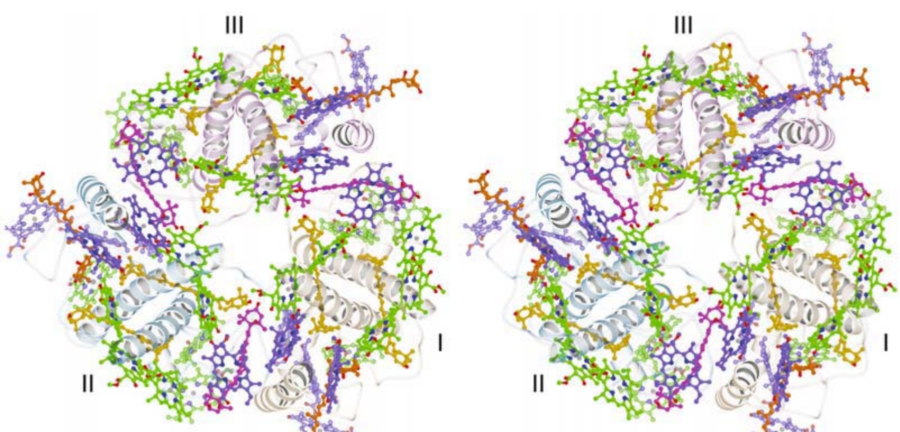

Fig. 2. Stereogram of LHCII trimer (individual monomers indicated by I, II and III) viewed from the stromal side, showing positions of Chls and carotenoids. Color code green, Chl *a*; blue, Chl *b*; orange, neoxanthin; magenta, xanthophyll-cycle carotenoids;grey ribbons, helices. Courtesy of W. Chang. See Chapter 2, p. 35.

T. Wydrzynski and K. Satoh (eds): Photosystem II: The Light-Driven Water:Plastoquinone Oxidoreductase, pp. CP1–CP16.

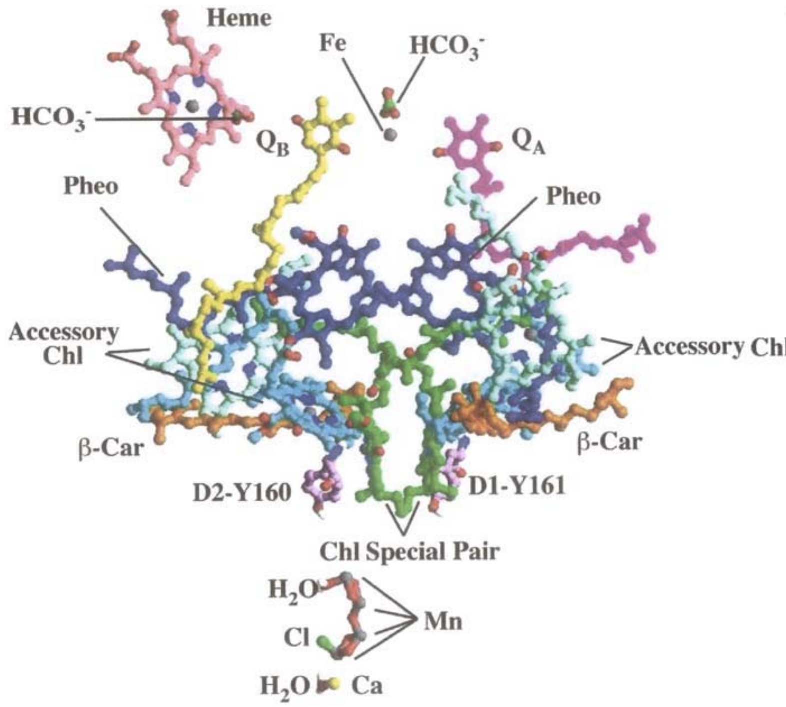

Fig. 1. The modeled cofactors in the PS II reaction center. Adapted from Van Rensen (2002) and originally from Xiong et al. (1998a). See Chapter 14, p. 334.

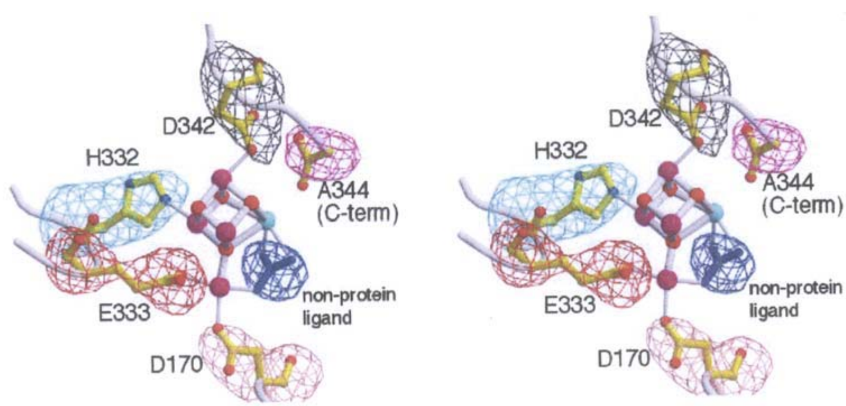

Fig. 2. Stereoviews of electron density maps for part of the water-oxidizing complex; a putative non-protein ligand (modeled as bicarbonate) is shown in blue. Reproduced with permission from Ferreira et al. (2004). See Chapter 14, p 342.

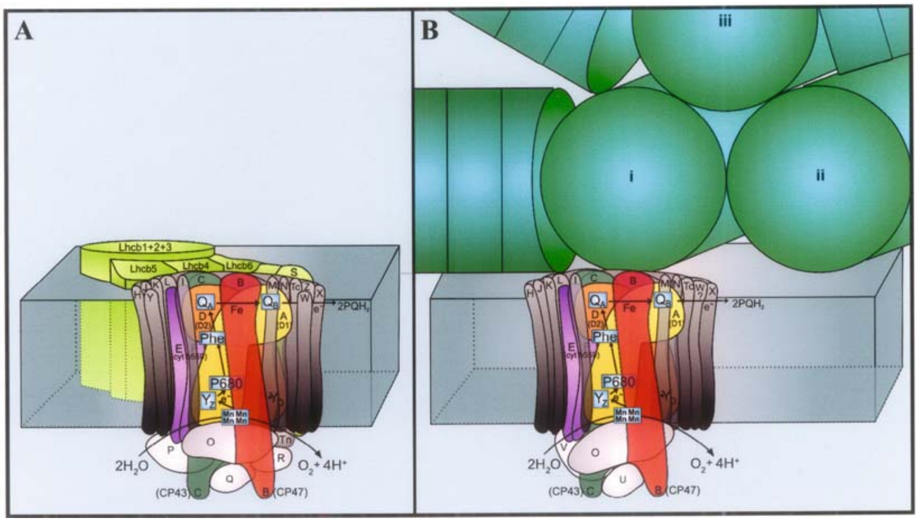

Fig. 1. Cartoons of PS II and its associated light-harvesting components (A) of higher plants and green algae and (B) of cyanobacteria, emphasizing subunit composition and primary and secondary electron transfer steps that occur in the reaction center D1 and D2 proteins. In the case of the higher plants and green algae (A) note that the secondary antenna is made up of Chl *a/b* binding Lhcb proteins, intrinsic to the membrane, while in (B), the cyanobacterial PS II is serviced by a large extrinsic, soluble phycobiliprotein mass on its stromal side. Also note, when comparing the two systems, the compositional differences present for the lumenally bound extrinsic subunits of the OEC. See Chapter 18, p 412.

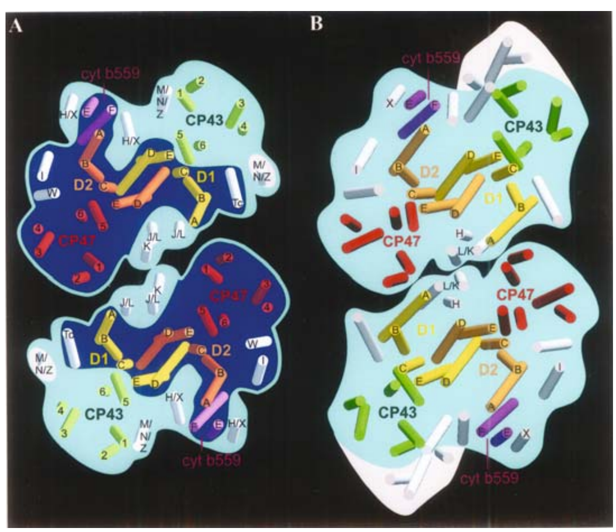

Fig. 2. Comparison of the PS II core dimer of (A) spinach (Hankamer et al., 2001b) and (B) S. elongatus (Zouni et al., 2001), and respective assignments of the low molecular weight (LMW) single transmembrane helical subunits. The dark blue region in (A) shows the helix organization of the spinach CP47-RC subcomplex (Rhee et al., 1998), which had to be modified, two transmembrane helices adjacent to helix B of the D1 and D2 proteins being removed. The remaining cyan regions contain the additional transmembrane helices of CP43 and other LMW core dimer subunits. Color code: red, CP47; green, CP43; yellow, D1; orange, D2; purple, Cyt b_{559}; white, LMW subunits. See Chapter 18, p. 415.