James Barber

“Achievements in science” with refs

James Barber is distinguished by his many contributions to photosynthesis research and particularly by his determination of the first complete atomic structure of the photosynthetic oxygen evolving machinery, an enormous advance in biology. The details of photosynthesis that he revealed not only represent a giant leap forward in our understanding of the biological energy cycle, but provides a molecular framework for the design of novel photo-chemically based green technologies capable of extracting chemical energy from solar radiation. His work therefore is a great intellectual achievement representing a major milestone in biology with implications for addressing the problem of energy/carbon dioxide/global climate change.

The oxygen evolving machinery of photosynthesis is located in a multisubunit membrane protein complex, known as photosystem II (PSII) found in plants, algae and cyanobacteria. The oxygen is generated by the light driven splitting of water which also provides ‘hydrogen’ in the form of reducing equivalents ultimately required for converting carbon dioxide to the organic molecules of life. All oxygen in the earth’s atmosphere is derived from this reaction and therefore revealing the details of the catalytic centre where the water splitting reaction occurs had long been the ‘holy grail’ of photosynthesis research.

Barber’s achievement, detailed in publications (1-5), is the culmination of many years of brilliant research. Initially he chose electron microscopy as a means to study the structure of well-defined biochemical preparations of PSII with varying numbers of protein subunits, for which he had developed several novel isolation procedures. At that time there was very little direct information on the structure of PSII. He adopted two strategies: (i) grow ordered 2D crystals for analysis by electron crystallography to obtain the highest possible resolution(6-11) and (ii) conduct single particle analyses on large supermolecular complexes (12-16) to give a framework for incorporation of higher resolution data to gain an understanding of how the light-harvesting antennae systems are structurally coupled to the reaction centre core. On both counts he was very successful and quickly became a world leader. However, the structures obtained were at intermediate resolutions and it was not possible to trace amino acid side chains and obtain critical information about the catalytic site of water splitting. In order to obtain this information, Barber turned to growing 3D crystals of PSII isolated from cyanobacteria and obtained a high resolution X-ray structure revealing details of PSII hitherto unknown (1-5) . The structure was refined at 3.5 Å and virtually all side chains were traced for the 19 different subunits that make up the monomeric PSII complex. Consequently not only were all the subunits assigned but also the structural detail of the protein environment of the cofactors revealed for the first time. In particular the work suggests that the catalytic centre for the water splitting reaction is composed of a cubane-like $Mn_3Ca^{2+}O_4$-cluster linked to a fourth Mn by a mono-oxo-bridge. Therefore for the first time a structural basis for elucidating the chemistry of the water splitting reaction had been provided. Indeed, the organization of the metal ions and the properties of the protein cavity in which they are contained, suggests a mechanism for the O-O bond formation. As emphasized by Barber in his publications, it seems highly likely that water splitting involves oxidation chemistry occurring on the Mn ion outside the cubane which is adjacent to the Ca^{2+}. Here a highly electrophilic oxo or oxyl radical could be formed at the final stage of the catalytic cycle which would then be poised for nucleophilic attack from the oxygen of the second substrate water located within the coordination sphere of the Ca^{2+}.

Many other important details of PSII have also been revealed by the crystal structure and Barber has undertaken a definitive analyses of these since its publication. For example: the structure of the PsbO protein (17), a novel subunit which stabilizes the functional state of the water splitting centre; the properties and implications of the chlorophyll molecules bound within the complex (18); the structural details of channels which facilitate the transfer of products (oxygen, protons and electrons) and reactants (water) from the water splitting site (19,20). He has also been able to grow and conduct analyses of crystals where the Ca^{2+} in the catalytic centre has been replaced by Sr^{2+} in order to take advantage of the X-ray absorption properties of Sr^{2+} and to investigate further the alkali metal binding site in the catalytic centre (21), work that has confirmed the original assignment. Following on from this , Barber had yet another “first” which involved in vitro and in vivo incorporation of bromide ions into the water splitting site in order to use X-ray crystallography to determine the halide binding sites (chloride is known to be required for the efficiency of the water splitting reaction) (22). These recent structural studies have played a pivotal role in further refinement of the molecular details of the catalytic site as emphasized in his latest papers (eg 23,24). Recently a Japanese research group improved the resolution of the cyanobacterial PSII structure to 1.9 Å resolution (25) confirming and refining the assignments made in Barber’s structure, including the cubic nature of the Mn_4Ca^{2+}-cluster. Moreover the detection of water molecules in the vicinity of the catalytic site are consistent with postulates presented by Barber and colleagues in their 2004 Science paper.

Barber's determination of the first complete atomic structure of PSII and his follow up studies casts a bright light on his parallel, pioneering work on the isolation and structural analyses of large PSII supercomplexes from higher plants and green algae. In many of these structures, common throughout the world, the light harvesting antenna proteins remain attached to the reaction center core (10,12,14,16). The electron microscopy conducted on these supercomplexes has led to the discovery of novel types of light harvesting systems (26-33) that are of global and environmental significance. He continues with the challenge of obtaining improved structural information of higher plant PSII supercomplexes as emphasised in his most recent publication directed at this challenge (34)

It is hard to understate the importance of Barber's contributions. His work sits comfortably in the pantheon of the greatest advances in biology. The structural chemistry of photosynthesis that he has revealed and described will have impact for future generations. In particular it is providing both inspiration and momentum towards the development of new technologies able to exploit the enormous amounts of solar energy available (on a global basis, about one hour of sunlight equals the total energy used by mankind in a year) while at the same time provide the foundations of efforts to address the environmental and political problems associated with the release of carbon dioxide and other greenhouse gases derived from oxidation of fossil fuel. This has been emphasised in several of his recent commentaries (35-37) and via numerous key note lectures at international gatherings. The impact is already leading to the development of new and exciting photochemical and electrochemical catalysts which split water making hydrogen available as an energy source as emphasised by the recent work of Nocera at MIT (38,39) and by Barber's own work. Through visiting professorships he has established the Solar Fuels Laboratory within the School of Material Sciences at Nanyang Technological University (NTU) Singapore and the Biosolar Laboratory within the Applied Science and Technology Department at the Politecnico di Torino. In this way he is collaborating with chemists, electrochemists and material scientists to develop artificial photosynthesis technology for solar fuel production. The impact of his own work is already leading to the development of new and exciting photochemical and electrochemical catalysts which split water making hydrogen available as an energy source. During 2012 alone he, together with colleagues, published 14 papers/reviews in this area. One study reports the discovery of a novel Cu-Mo bimetal sulphide catalyst for efficient hydrogen production (39,40) while another described haematite nanorods showing remarkable water splitting activity (41). His successes call on his interdisciplinary approach; merging principles of biology, chemistry and material sciences.

(1) Ferreira KN, Iverson TM, Maghlaoui K, **Barber J**, Iwata S (2004) Architecture of the photosynthetic oxygen-evolving center. Science. 303, 1831-8

(2) **Barber J**, Ferreira K, Maghlaoui K, Iwata S (2004) Structure of the oxygen evolving centre of photosystem II with mechanistic implications. PhotoChem. Chem. Phys. 6, 4737-4742

(3) Iwata S, **Barber J** (2004) Structure of photosystem II and molecular architecture of the oxygen-evolving centre. Curr Opin Struct Biol. 14, 447-453

(4) **Barber J** (2006) Photosystem II; The Engine of Life. The Biochemist 28, 7-11

(5) **Barber J** (2006) Photosystem II; An Enzyme of Global Significance. Biochem. Soc. Trans.34, 619-631

(6) Morris, E.P., Hankamer, B., Zheleva, D., Friso, G, **Barber, J.** (1997) The 3-D structure of a photosystem II core complex determined by electron crystallography. Structure 5, 837-849

(7) Rhee, K-H., Morris, E.P, Zheleva, D., Hankamer, B., Kühlbrandt, W, **Barber, J**. (1997) Two-dimensional structure of plant photosystem II at 8Å resolution. Nature 389, 522-526

(8) Rhee, K.-H., Morris, E.P., **Barber, J**, Kühlbrandt, W. (1998) Three-dimensional structure of the photosystem II reaction centre at 8Å resolution. Nature 396, 283-286

(9) Hankamer, B., Morris, E.P, **Barber, J**. (1999) Cryoelectron microscopy of photosystem two shows that CP43 and CP47 are located on opposite sides of the D1/D2 reaction centre proteins. Nature Structural Biology 6, 560-564

(10) **Barber, J**., Nield, J., Morris, E.P,Hankamer, B. (1999) Subunit positioning in PSII revisited. Trends Biochem. Sci. 278, 43-45

(11) Hankamer, B., Morris, E.P., Nield, J., Gerle, C, **Barber, J**. (2001) Three-dimensional structure of photosystem II core dimer of higher plants determined by electron microscopy. J. Struct. Biol. 135, 262-269

(12) Nield, J., Orlova, E., Morris, E., Gowen, B., van Heel, M, **Barber, J**. (2000) 3D map of the plant photosystem two supercomplex obtained by cryoelectron microscopy and single particle analysis. Nature Structural Biology 7, 44-47

(13) Nield, J., Kruse, O., Ruprecht, J., Da Fonseca, P, Büchel, C, **Barber, J**. (2000) 3D structure of *Chlamydomonas reinhardtii* and *Synechococcus elongatus* photosystem II complexes allow for comparison of their OEC organisation. J. Biol. Chem. 275, 27940-27946

(14) Nield, J., Funk, C, **Barber, J.**.(2000) Supermolecular structure of photosystem two and location of the PsbS protein. Phil. Trans. R. Soc. Lond. B 355, 1337-1344

(15) Nield, J., Balsera, M., De Las Rivas, J.,**Barber, J**. (2002) 3D cryo-EM study of the extrinsic domains of the oxygen evolving complex of spinach. Assignment of the PsbO protein. J. Biol. Chem. 277, 15006-15012

(16) Neild, J., **Barber, J.** (2006) Refinement of the structural model of the Photosystem II supercomplex of higher plants. Biochim.Biophys.Acta 1757, 353-361.

(17) De Las Rivas, J, **Barber, J**. (2004) Analyses of the structure of the PsbO protein and its implications. Photosyn. Res. 81, 329-343

(18) Murray, J.W., Duncan, J., **Barber, J**. (2006) CP43-like chlorophyll binding proteins: structural and evolutionary implications. Trends Plant Sci. 11, 152-158

(19) Murray J.W., **Barber, J.** (2006) Identification of a calcium-binding site in the PsbO protein of photosystem II. Biochemistry 45, 4128-4130.

(20) Murray, J.W. and **Barber, J.** (2007) Structural characteristics of channels in Photosystem II. J. Struct. Biol. 159, 228-237.

(21) Kargul, J., Maghlaoui, K., Murray, J.W., Deak, Z., Boussac, A., Rutherford, A.W., Vass, I, **Barber, J**. (2006) Purification, crystallization and X-ray diffraction analyses of the *T. elongatus* PSII core dimer with strontium replacing calcium in the oxygen-evolving complex. Biochim.Biophys. 1767, 404-413

(22) Murray, J.W., Maghlaoui, K., Kargul, J., Ishida, N., Lai, T-L, Rutherford, A.W., Sugiura, M., Boussac, A.and **Barber, J**. (2008) X-ray crystallography identifies two chloride binding sites in the oxygen evolving centre of Photosystem II. Energy Environ. Sci., 1, 161-166

(23) **Barber, J.** (2008) Photosynthetic Generation of Oxygen. Phil. Trans. R. Soc. B. 363, 2665-2674

(24) **Barber, J.** (2008) Crystal structure of the oxygen-evolving complex of photosystem II. Inorgan. Chem. 47, 1700 – 1710.

(25) Umena Y, Kawakami K, Shen JR, Kamiya N 2011 Crystal structure of oxygen evolving photosystem II at a resolution of 1.9 angstrom. Nature **473:** 55-65.

(26) Bibby, T.S., Nield, J, **Barber, J**. (2001) Iron deficiency induces the formation of an antenna ring around trimeric photosystem I in cyanobacteria. Nature 412, 743-745

(27) Bibby, T.S., Nield, J, **Barber, J**. (2001) 3D model and characterisation of the iron stress induced CP43-PSI supercomplex isolated from the cyanobacteria *Synechocystis* PCC 6803. J. Biol. Chem. 276, 43246-43252

(28) Nield, J., Morris, E.P., Bibby, T.S., **Barber, J**. (2003) Structural analysis of the photosystem one supercomplex of cyanobacteria induced by iron deficiency. Biochemistry 42, 3180-3188

(29) Bibby, T.S., Nield, J., Chen, M., Larkum, A.W.S., **Barber, J.** (2003) Structure of a photosystem II supercomplex isolated from *Prochloron didemni* retaining its chlorophyll *a/b* light-harvesting system. Proc. Natl. Acad. Sci. USA 100, 9050-9054

(30) Chen, M., Bibby, T.S., Nield, J., Larkum, A.W.S., **Barber, J.** (2005) Iron deficiency induces a chlorophyll *d*-binding Pcb antenna around photosystem II in *Acaryochloris marina*. Biochim. Biophys. Acta Bioenerg. 1708, 367-374

(31) Chen, M., Bibby, T.S., Nield, J., Larkum, A.W., **Barber, J**. (2005) Structure of a large photosystem II supercomplex from *Acaryochloris marina*. FEBS Lett. 579, 1306-1310

(32) Bibby, T.S., Nield, J., Partensky, F, **Barber, J**. (2001) Oxyphotobacteria: Antenna ring around PSI. Nature 413, 590

(33) Bibby, T.S., Mary, I., Nield, J., Partensky, F., **Barber, J.** (2003) Low light-adapted *Prochlorococcus* spp. possess specific antenna for each photosystem. Nature 424, 1051-1954

(34) Barera, S, Pagliano, C, Tillmann, P, Saracco,G and Barber, J. (2012) Characterization of PSII-LHCII supercomplexes isolated from pea thylakoid membranes by one-step treatment with α-and β- dodecyl-D-maltoside. Phil. Trans. R. Soc. B. 367, 3389-3399

(35) **Barber J.** (2007) Biological solar energy. Philos Transact A Math Phys Eng Sci. 365:1007-1023.
(36) **Barber, J.** (2008) Photosynthesic Energy Conversion: Natural and Artificial Chem. Soc. 38, 185-196
(37) Kanan, M.W. Nocera D.G. (2008) Science 321, 1072-1075
(38) Reece SY, Hamel JA, Sung K, Jarvi TD, Esswein AJ, Pijpers JJH, Nocera DG. 2011
Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts. Science **334:** 645–648
(39) Tran, P.D. Nguyen, M., Pramana, S., Chiam, S.Y., Bhattacharjee, A., Fize, J.,Field, M.J., Artero, V., Wong, L.H., Loo, J. and **Barber, J.** (2012) Copper Molybdenum Sulfide: A New Efficient Electrocatalyst for Hydrogen Production from Water. Energy and Envir. Sci. 5, 8912-8916
(40) Tran, P.D., Chiam, S.Y., Pramana, S.S, Ren, Y., Fize, J., Artero, V., and **Barber, J**. (2013). Novel Ternary Metal Sulfide Catalysts for Electrocatalytic Hydrogen Generation in Water. Energy and Environmental Sciences. 6, 2452-2459
(41) Xi, L. Chiam, S.Y., Mak, W.F., **Barber, J.,** Loo, S.C.J., Wong, L.H.(2012). A novel strategy for doping and passivating surface defects on hematite photoanode for efficient water oxidation. Chemical Sciences, 4, 164–169