The role of bicarbonate in limiting damage to Photosystem II

Jack Forsman

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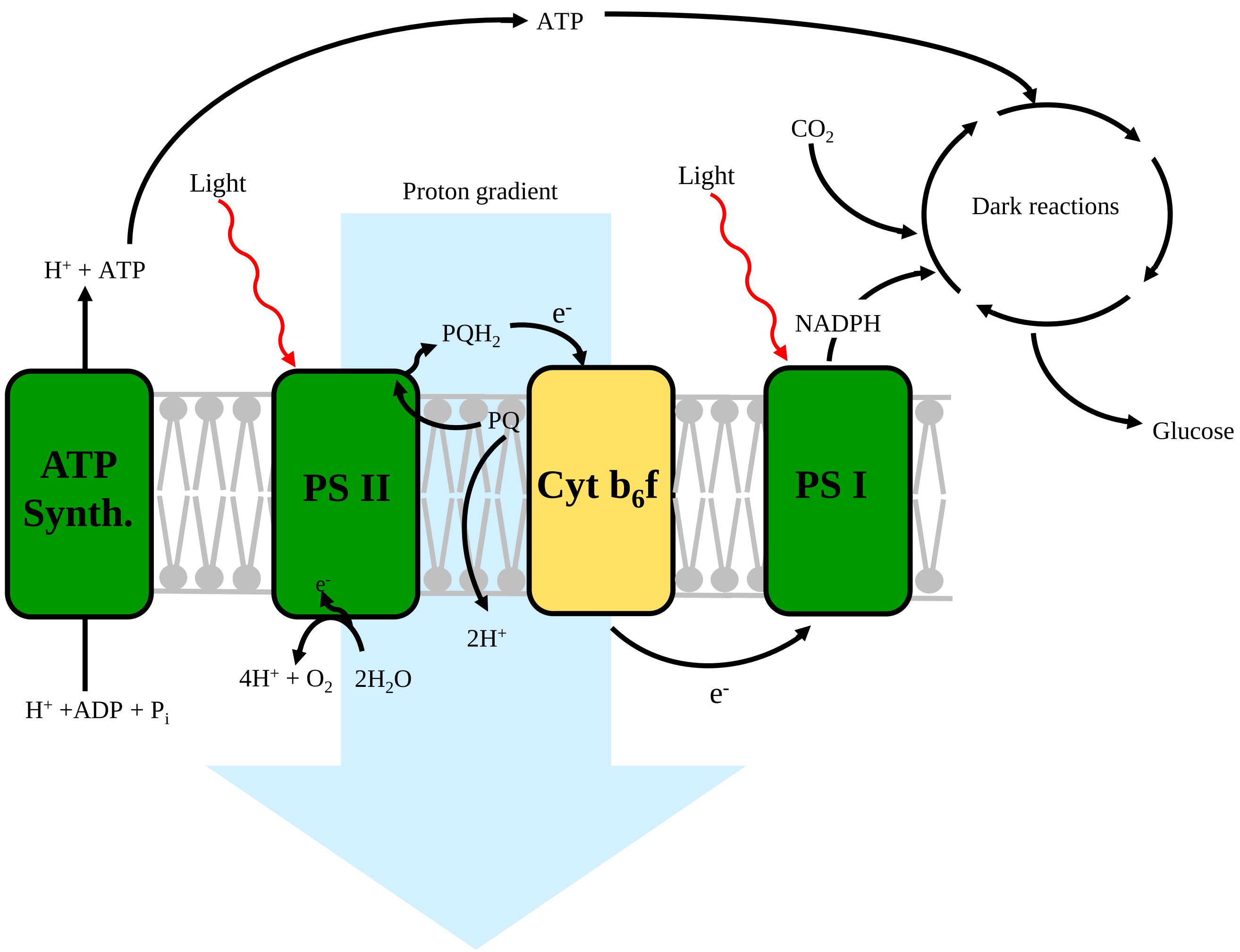
Photosynthesis

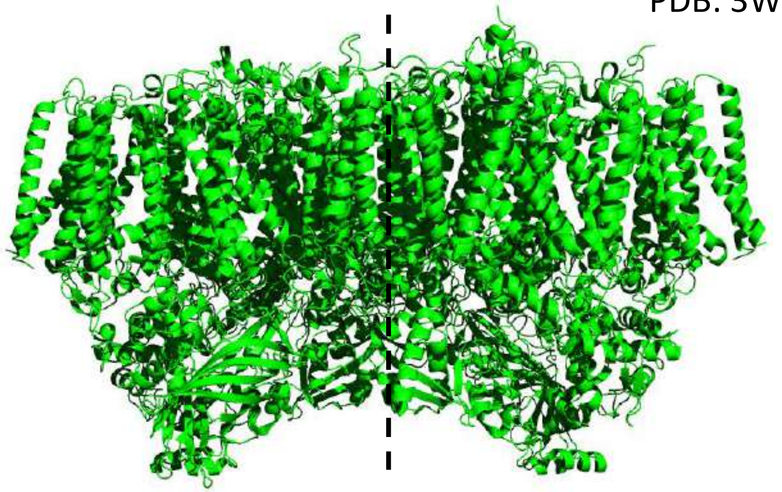


- Start of nearly every food chain on earth
- Produces oxygen for respiration and the ozone layer
- Photosystem II (PSII) is a vital component of photosynthesis

Photosystem II structure

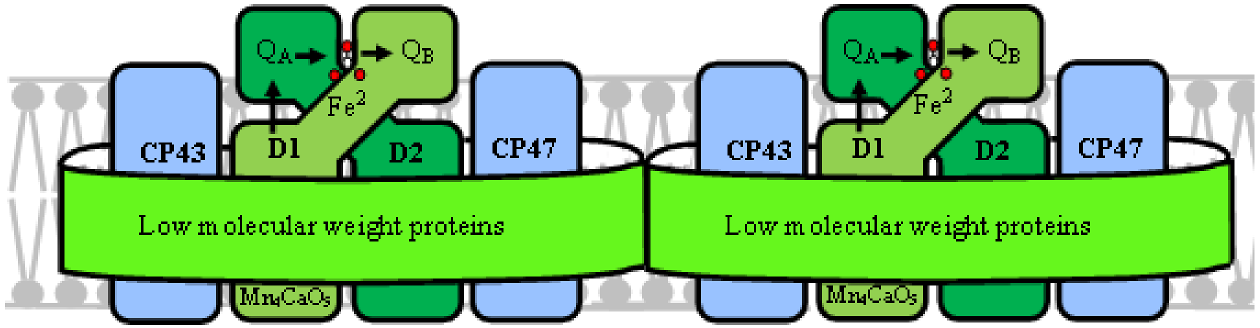
A

PDB: 3WU2



Monomer 1 Monomer 2

B



- Photosystem II is bound in the thylakoid membranes of photosynthetic organisms
- Exists as a dimer
- Made up of 4 core protein subunits, and a suite of low molecular weight peripheral proteins
- The core is made up of the D1 and D2 proteins which hold all of the redox active cofactors and 2 antenna proteins CP43 and CP47

Photosystem II structure

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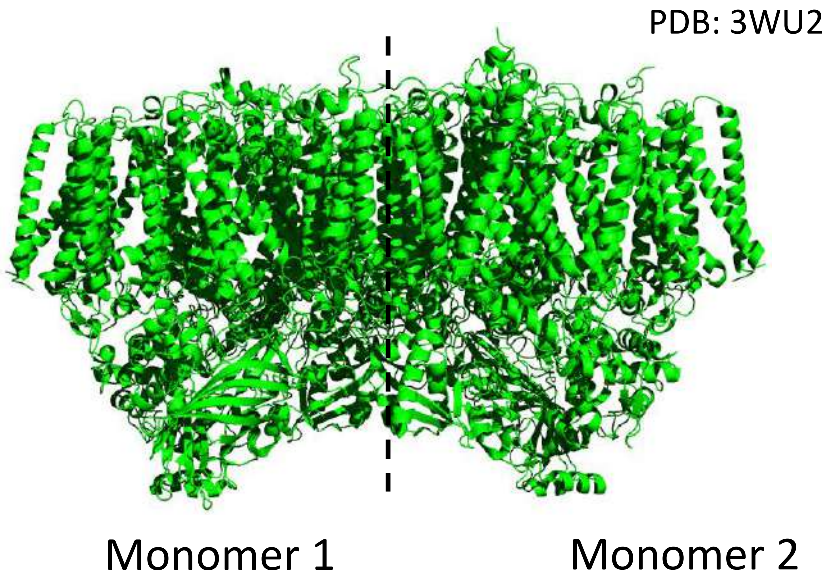
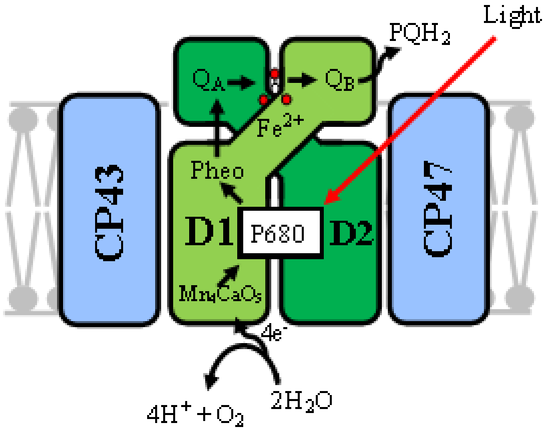


B



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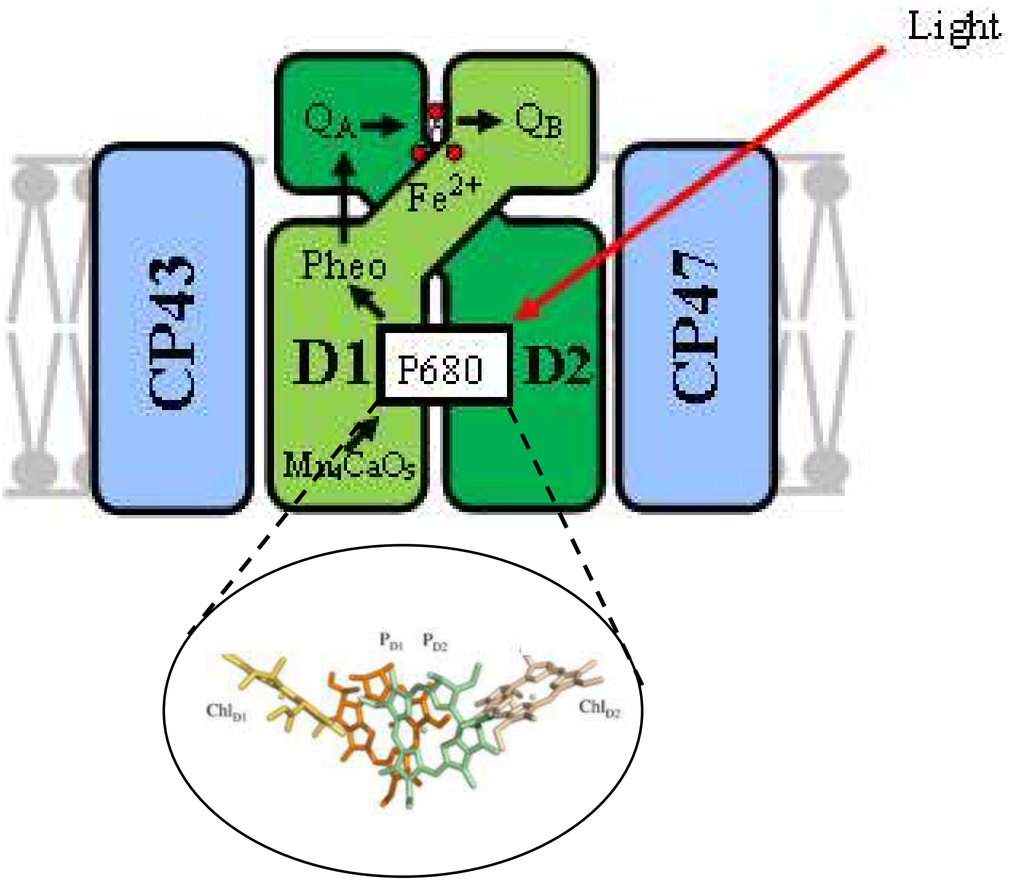
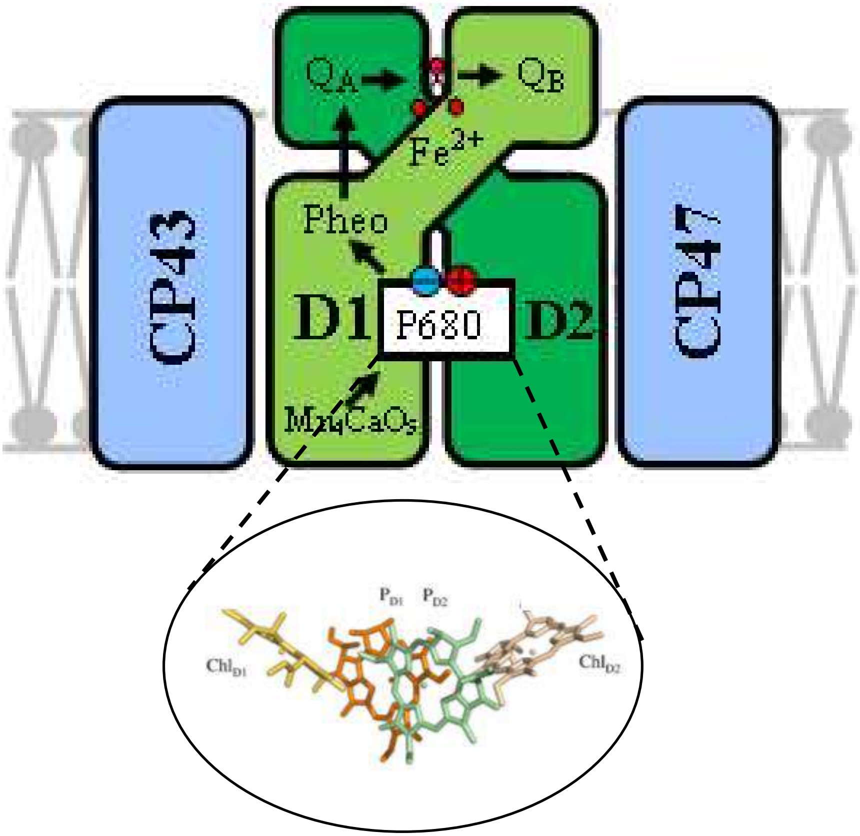
Photosystem II function



- Light excites the P680 pigment cluster leading to charge separation
- The electron is passed to pheophytin before reaching the bound quinone (Q_A) and finally the reversibly bound quinone (Q_B)
- The positive charge is shifted onto a redox active tyrosine (Y_z) before being passed onto the Manganese cluster (Mn-cluster)

Photosystem II function



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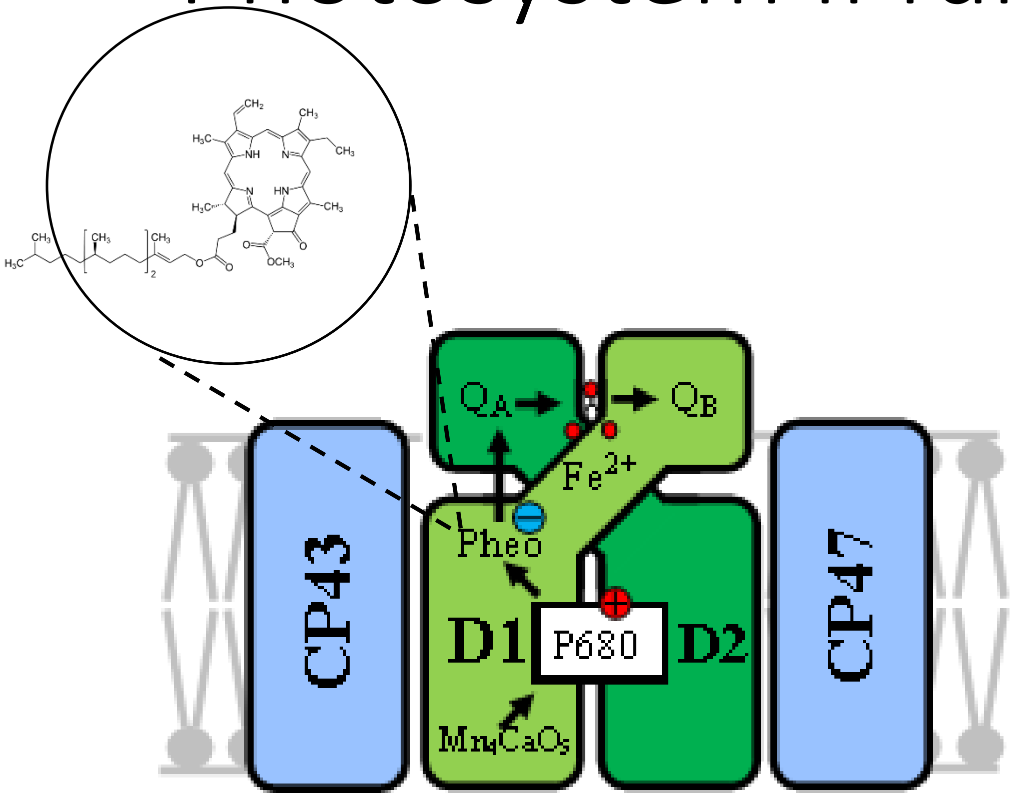

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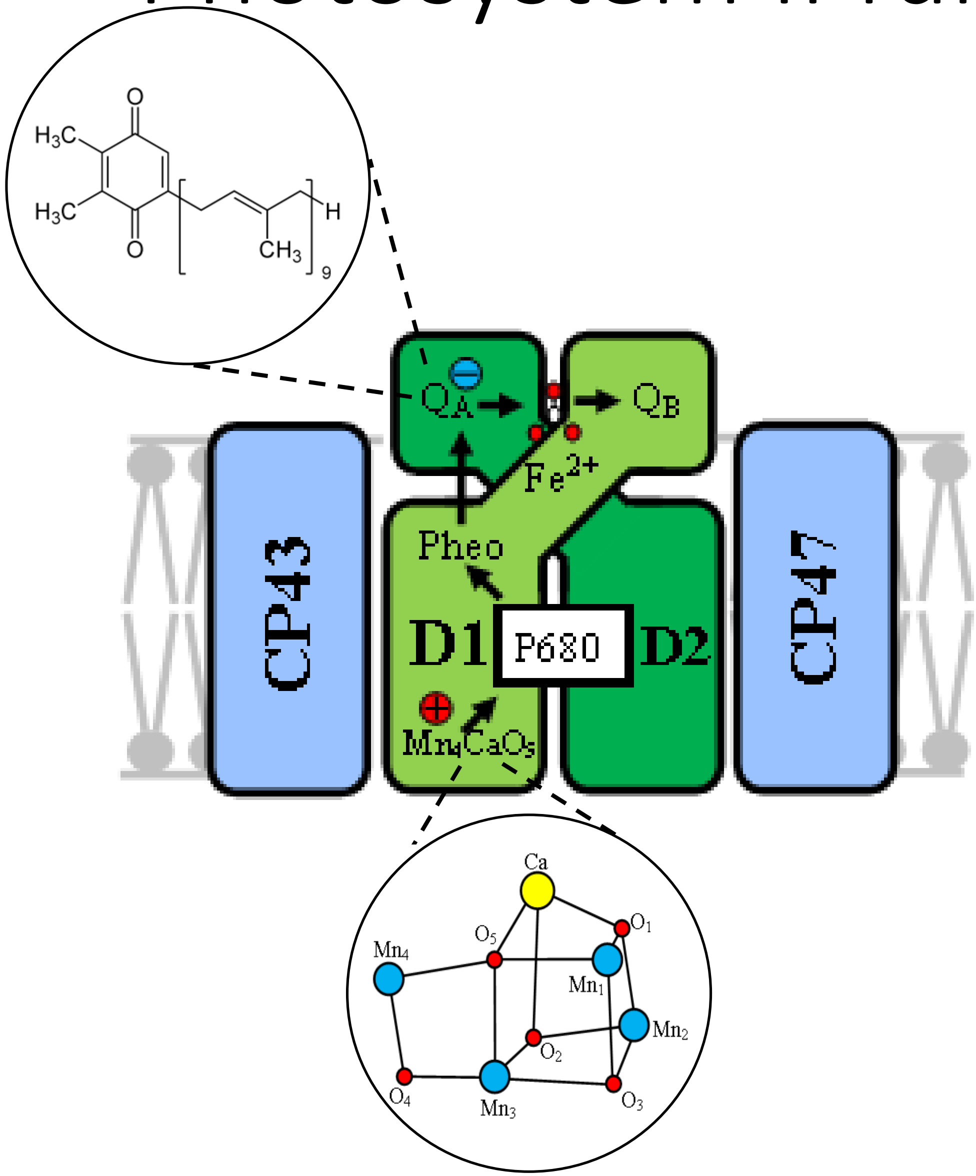

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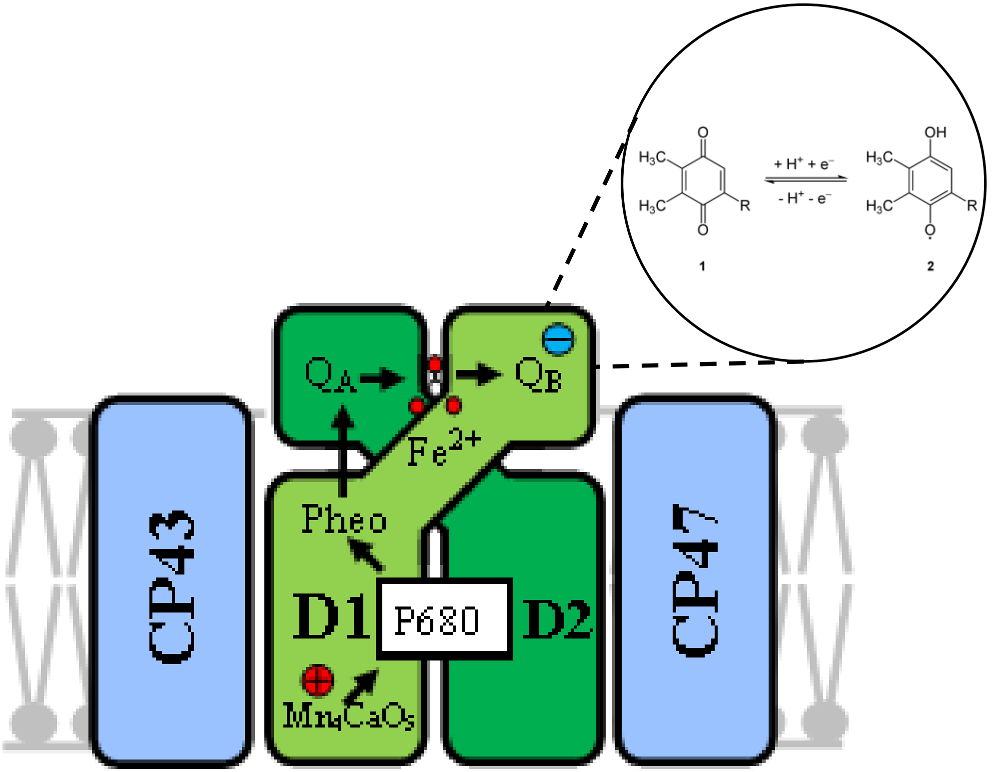
Photosystem II function



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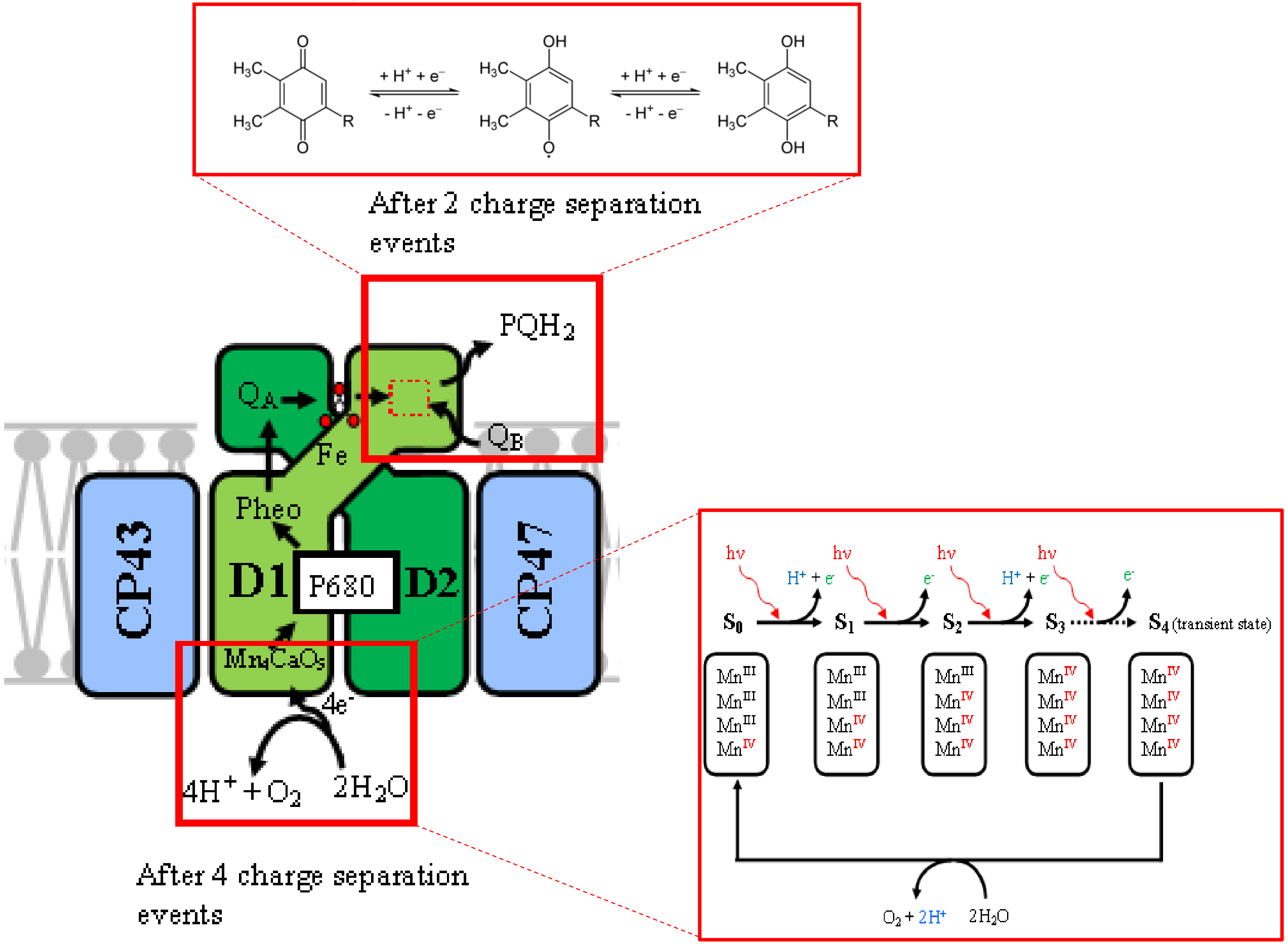
Photosystem II function



- Reduction of Q_B to Q_B^- is accompanied by a proton binding to Q_B^-
- After 2 reductions $Q_B(H)_2$ (PQ) is released into the membrane
- A new fully oxidised Q_B replaces PQ from the Q_B pool in the membrane
- After 4 electrons are removed from the Mn-cluster, $2H_2O$ is broken down to O_2, restoring the oxidised Mn-cluster

Why study Photosystem II

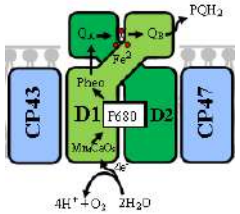
Solar panel

Light energy

Electrical energy

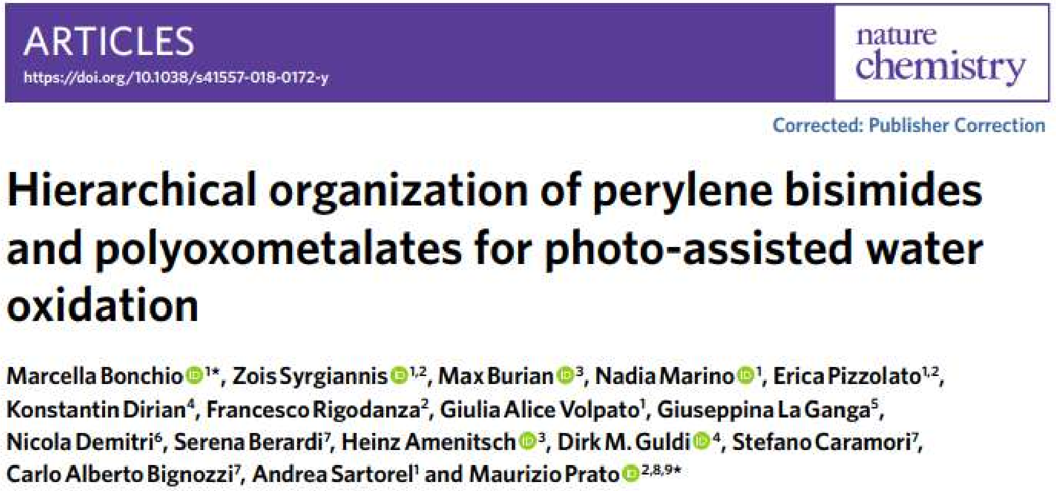
Photosystem II

Light energy



Chemical energy

- Studying the natural system of solar energy capture can lead to innovation in the field of solar energy research



ARTICLES

https://doi.org/10.1038/s41557-018-0172-y

nature chemistry

Corrected: Publisher Correction

Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation

Marcella Bonchio[1*], Zois Syrgiannis[1,2], Max Burian[3], Nadia Marino[1], Erica Pizzolato[1,2], Konstantin Dirian[4], Francesco Rigodanza[2], Giulia Alice Volpato[1], Giuseppina La Ganga[5], Nicola Demitri[6], Serena Berardi[7], Heinz Amenitsch[3], Dirk M. Guldi[4], Stefano Caramori[7], Carlo Alberto Bignozzi[7], Andrea Sartorel[1] and Maurizio Prato[2,8,9*]

Bonchio, M *et al.*, (2018). Hierarchical organization of perylene bisimides and polyoxometalates for photo-assisted water oxidation. *Nature Chemistry*, **11(2)**, 146-153.

Why study Photosystem II

Solar panel

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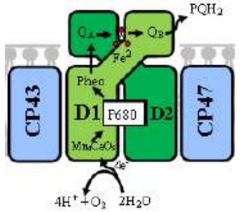


Chemical energy

- Study of ‘artificial’ solar energy capture can help genetically enegineer plants with improved quantum yields


PNAS

CrossMark

PERSPECTIVE

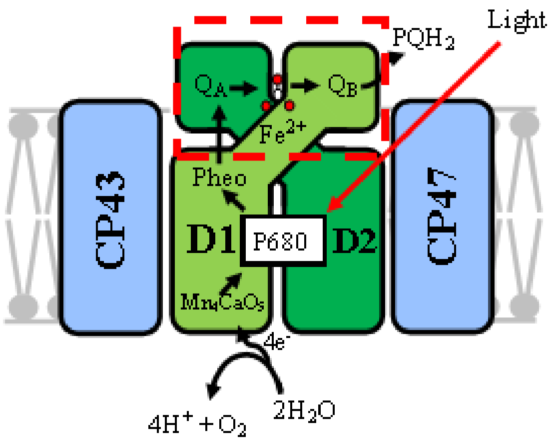
PERSPECTIVE

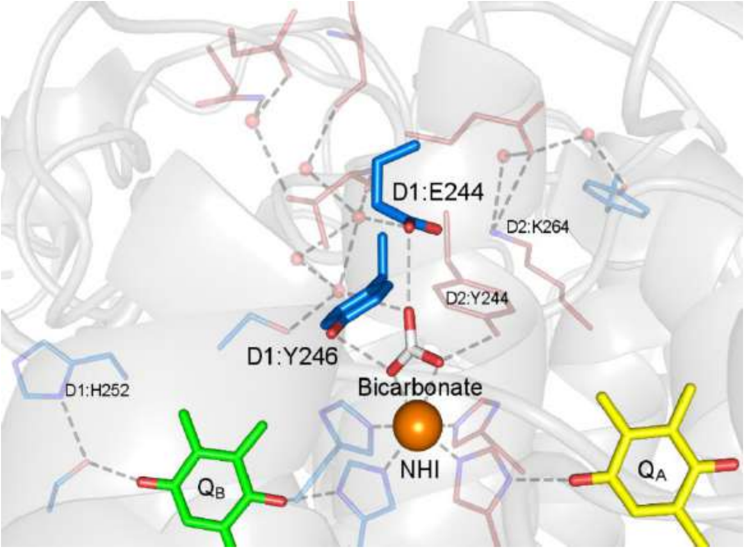
Redesigning photosynthesis to sustainably meet global food and bioenergy demand

Donald R. Ort[a,b,c,1], Sabeeha S. Merchant[d,e], Jean Alric[f], Alice Barkan[g], Robert E. Blankenship[h,i], Ralph Bock[j], Roberta Croce[k], Maureen R. Hanson[l], Julian M. Hibberd[m], Stephen P. Long[b,c,n], Thomas A. Moore[o,p], James Moroney[q], Krishna K. Niyogi[r,s,t], Martin A. J. Parry[u], Pamela P. Peralta-Yahya[v], Roger C. Prince[w], Kevin E. Redding[o,p], Martin H. Spalding[x], Klaas J. van Wijk[y], Wim F. J. Vermaas[p,z], Susanne von Caemmerer[aa], Andreas P. M. Weber[bb,cc], Todd O. Yeates[d,e], Joshua S. Yuan[dd], and Xin Guang Zhu[ee]

Ort, M *et al.*, (2015). Redesigning photosynthesis to sustainably meet global food and bioenergy demand. *PNAS*, **112(28)**, 8529-8536.

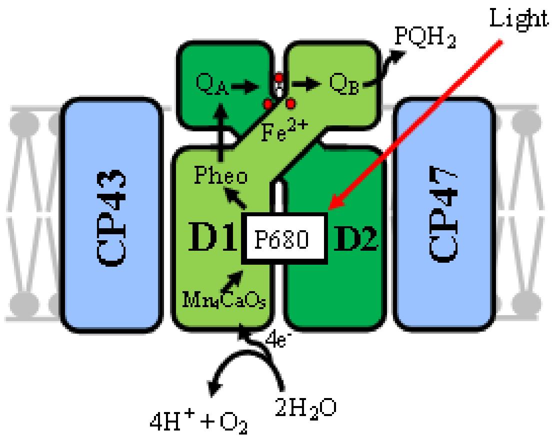
My area of research

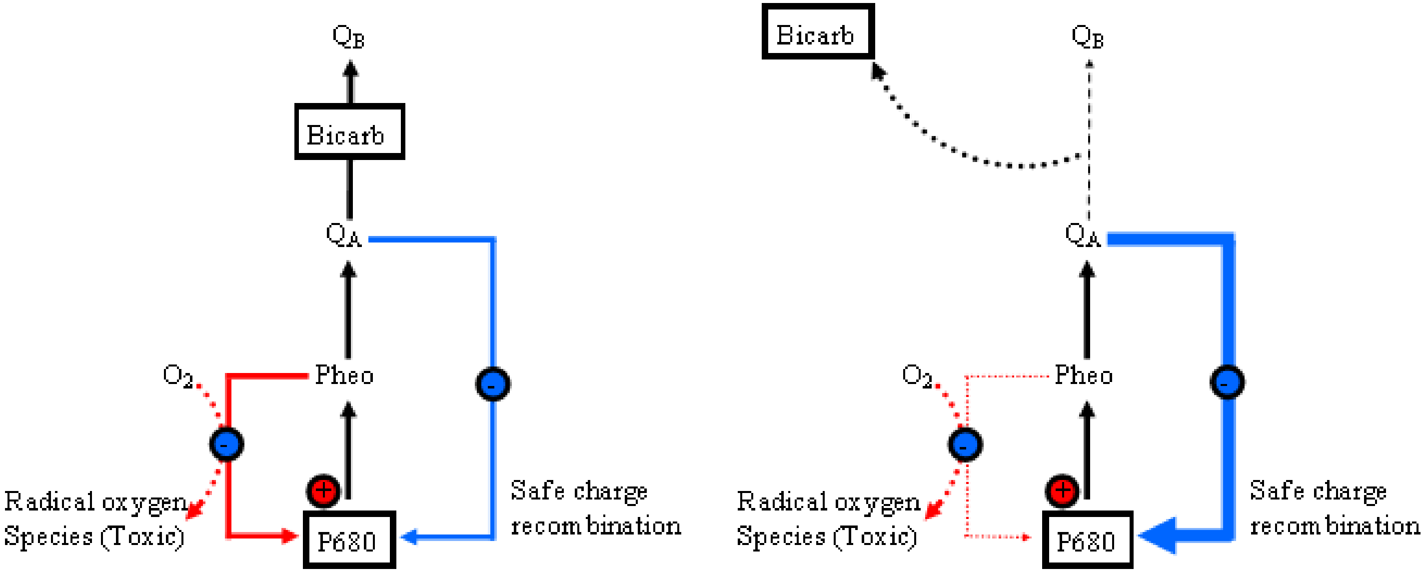




- My research was centred on the 'acceptor side' of PS II
- Specifically I was interested in the bicarbonate ligand to the non-heme iron located between Q_A and Q_B
- To investigate the bicarbonate I generated point mutants on the acceptor side of PS II, then characterized the mutants

The bicarbonate

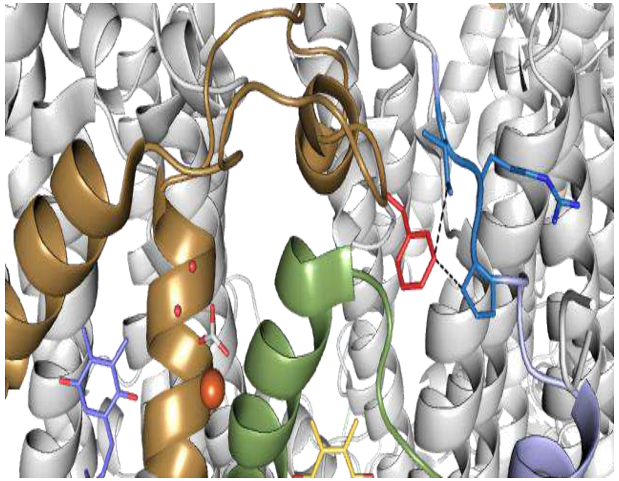




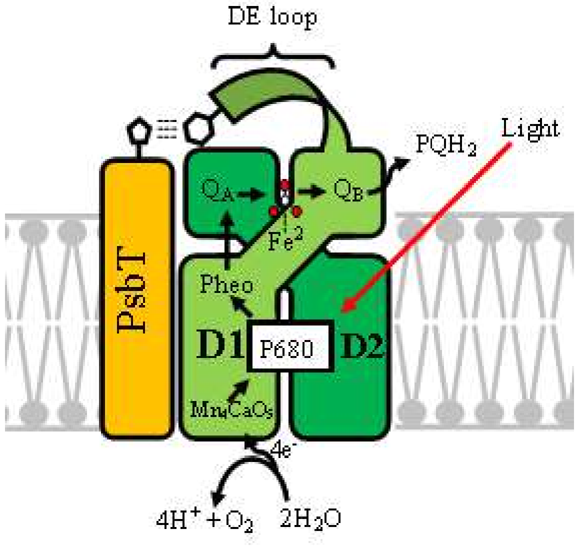
- Removing the bicarbonate slows electron transfer from Q_A to Q_B
- This slows down PS II activity
- The removal of the bicarbonate also 'encourages' charge recombination via the 'safe' route

DE loop mutants

- The DE loop of the D1 subunit is the most frequently damage region of PS II
- The DE loop lies directly above the bicarbonate with many DE loop residues appearing to interact with the bicarbonate
- The DE loop appears to be stabilised by an interaction between the Phe-239 residue of D1 and the PsbT subunit
- Point mutants were made at the D1-239 position to disrupt the interaction between the DE loop and PsbT



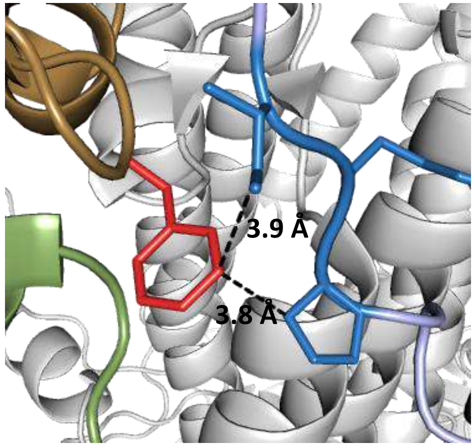
PDB: 3ARC



DE loop mutants

- The Phe-239 residue in D1 was changed to an alanine to disrupt the putative hydrophobic interaction (F239A)

- The Phe-239 residue in D1 was also changed to a Leucine to weaken the putative hydrophobic interaction (F239L)



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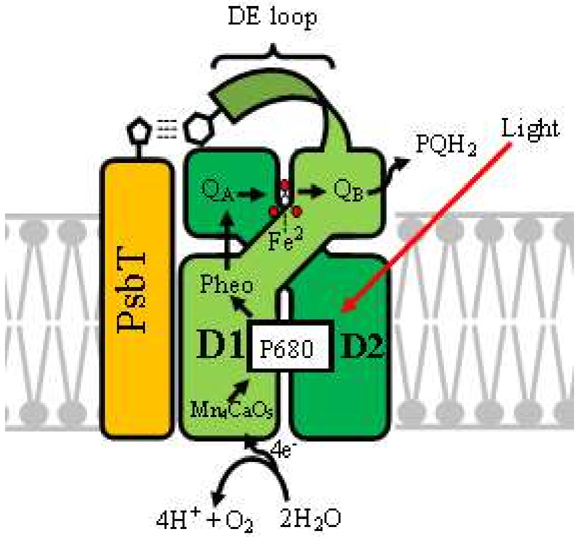
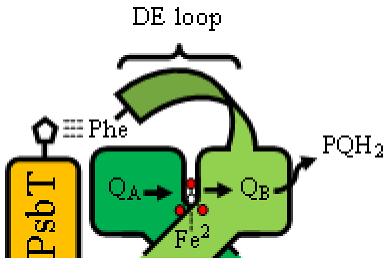
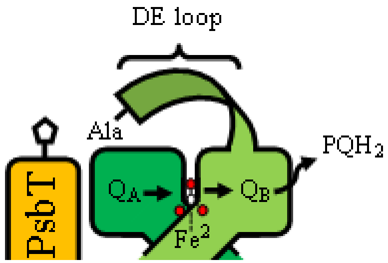
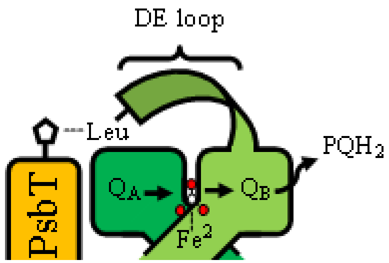




Wild type



F239A

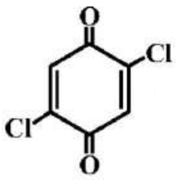


F239L

Mobility of the DE loop

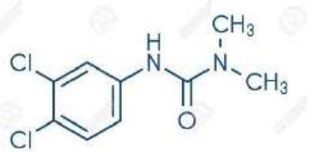
- DCBQ can take electrons from Q_A^-
- In normal conditions DCBQ will bind at the Q_B site
- DCMU is an inhibitor that blocks the Q_B site
- If Q_A is exposed (i.e. if the DE loop is not blocking it), then DCBQ can still take electrons off Q_A^-, even if the Q_B site is blocked

DCBQ = electron acceptor; reduces Q_A^-

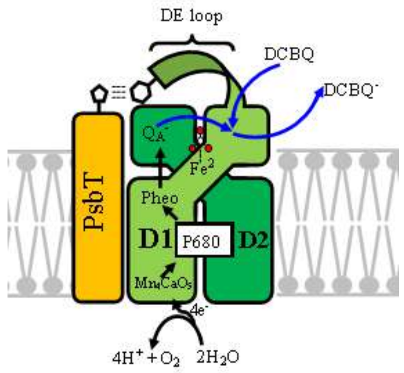


DCBQ

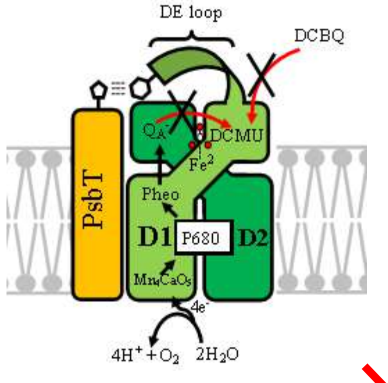
DCMU = herbicide; binds irreversibly at Q_B site



DCMU



Produces oxygen:



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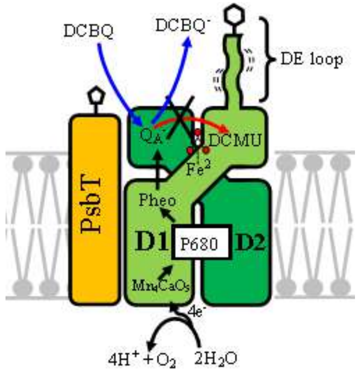
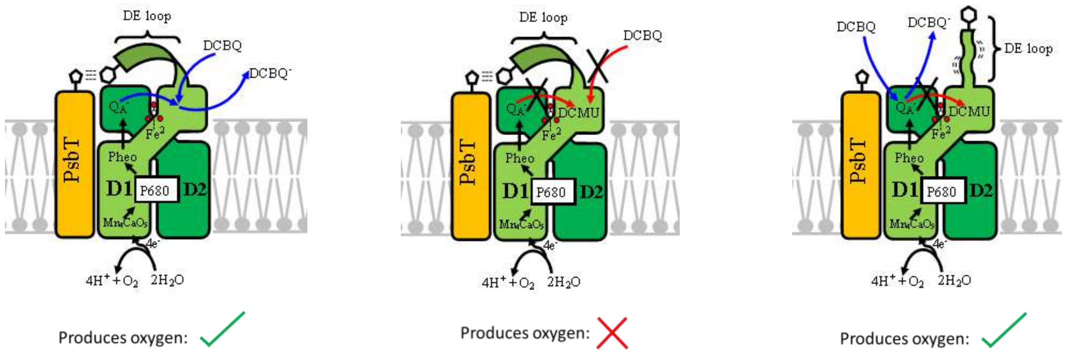
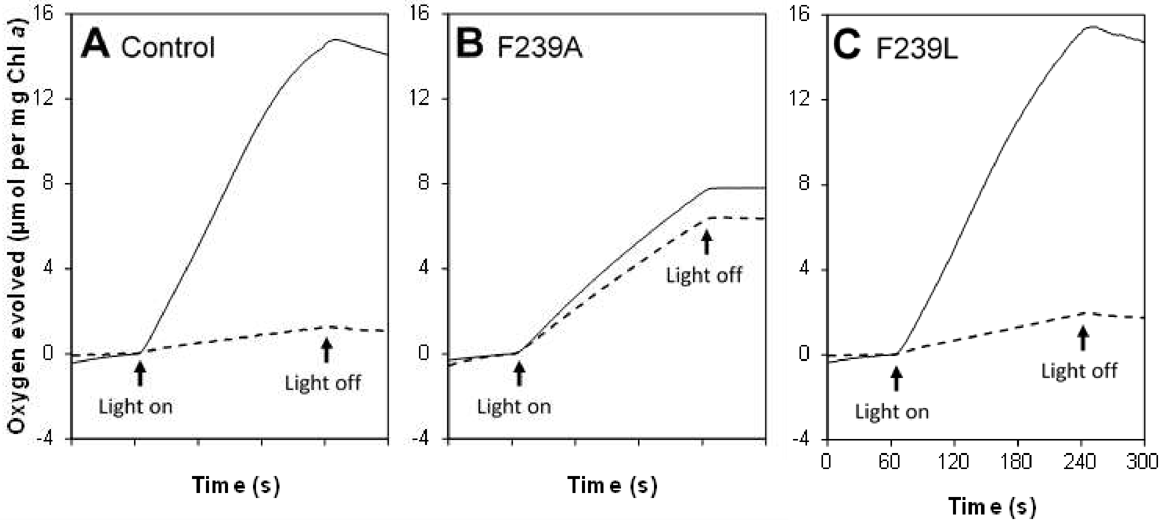


Produces oxygen:

Accessibility of the iron-quinone acceptor complex

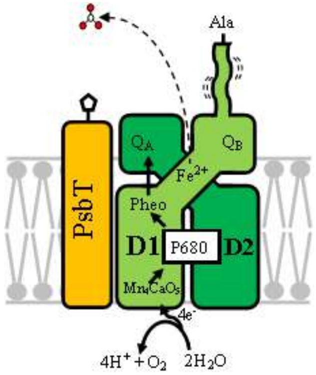
- In the control and F239L strains the addition of DCMU causing a dramatic drop in the rate of oxygen evolution
- This is not observed in the F239A strain
- This result indicates that the acceptor side is exposed in the F239A mutant, suggesting that the DE loop is mobile





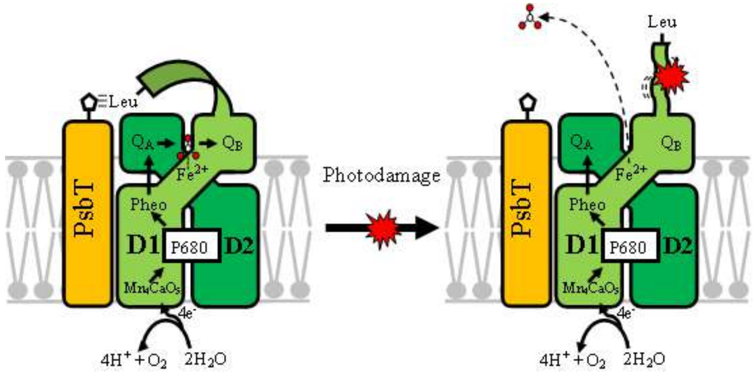
Solid line = DCBQ only
Dotted line = DCBQ and DCMU

Interpretation of mutant results



- The F239A mutant

1. DE loop is unrestricted even in the dark

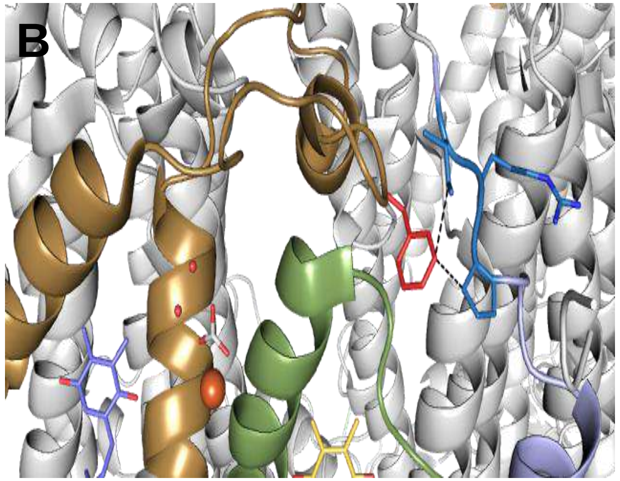


- The F239L mutant

1. DE loop is restricted in dark or low light conditions
2. In high light conditions photodamage rapidly disrupts the weakened D1:PsbT interaction (data not shown)

- Additional results (not shown) suggest that when the DE loop is unrestricted, the bicarbonate is rapidly lost from the non-heme iron

Fuse hypothesis



- The DE loop is frequently damaged
- The accumulation of damage on the DE loop disrupts its interaction with PsbT
- This allows the loop to move unrestricted, causing the bicarbonate to dissociate
- This slows down PS II and facilitates ‘safe’ charge recombination

- In this way, the DE loop and the bicarbonate act like an electrical fuse, by preventing further damage to PS II during high light (power surges)

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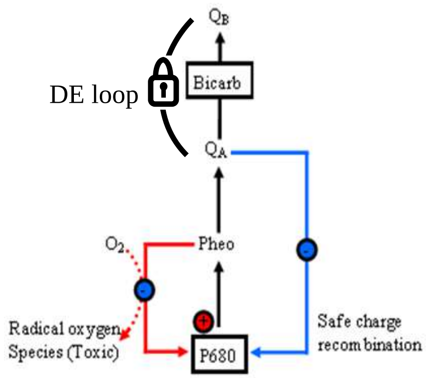

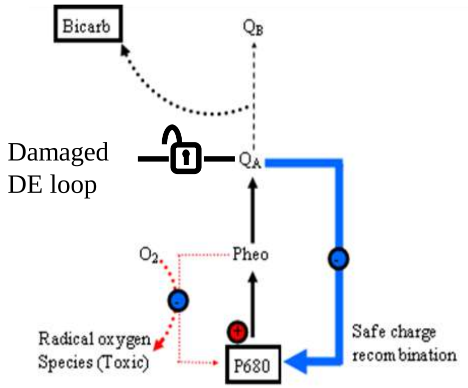

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Acknowledgements

- Prof. Julian Eaton-Rye
- Dr Rob Fagerlund
- Jackie Daniels
- All members of the Eaton-Rye lab