Energy and Evolution

BIOL0030_21-22

# Oxygenic Photosynthesis — Water as Fuel

John F. Allen

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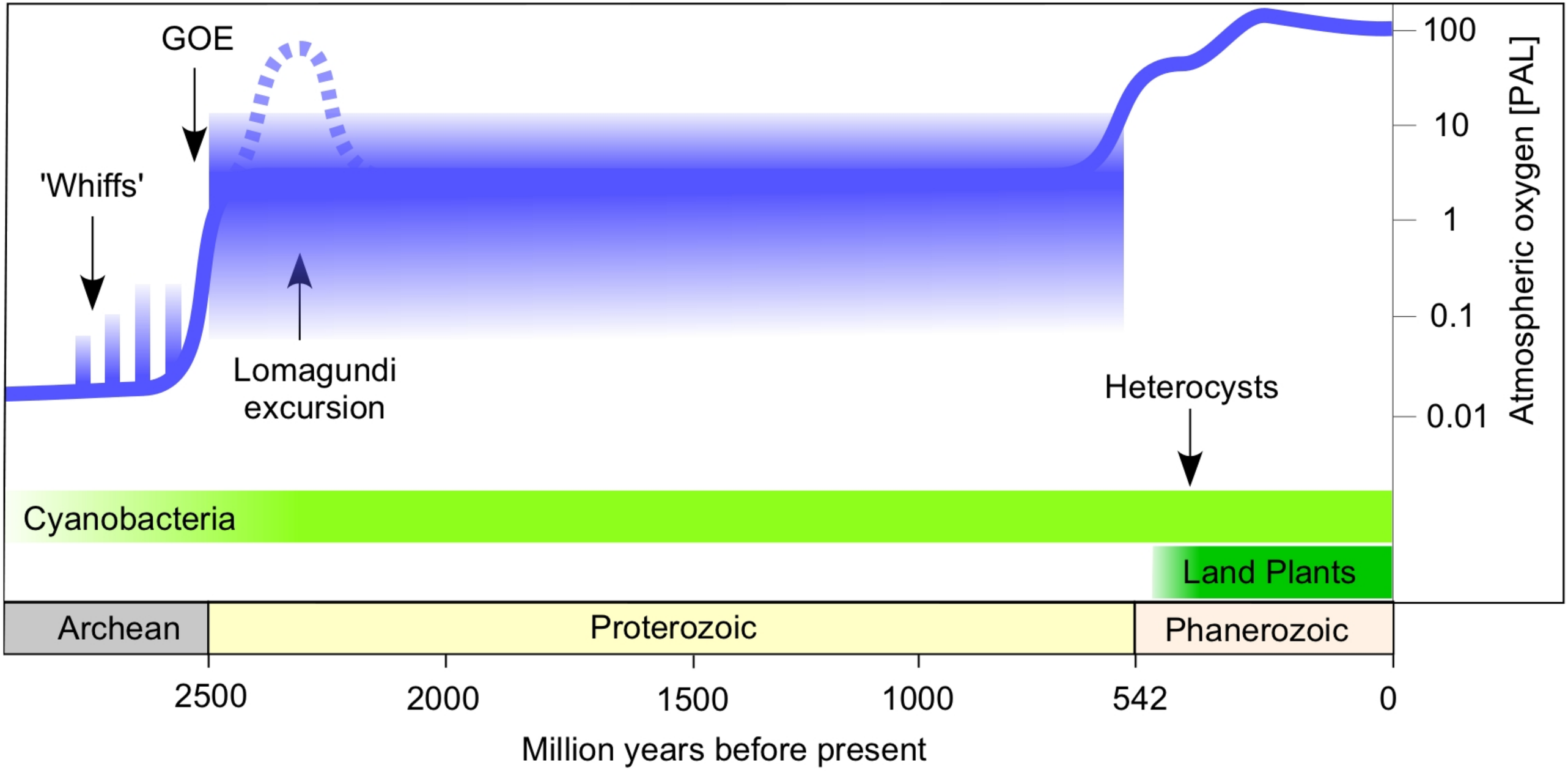
How did photosystem I and photosystem II reaction centres diverge from a common ancestor AND eventually meet again – to work together in the same membrane at the same time...?


GOE
'Whiffs'
Lomagundi
excursion
Heterocysts
Cyanobacteria
Land Plants
100
10
1
0.1
0.01
Atmospheric oxygen [PAL]
Archean
Proterozoic
Phanerozoic
2500
2000
1500
1000
542
0
Million years before present

CellPress
REVIEWS

Opinion

# Nitrogenase Inhibition Limited Oxygenation of Earth's Proterozoic Atmosphere

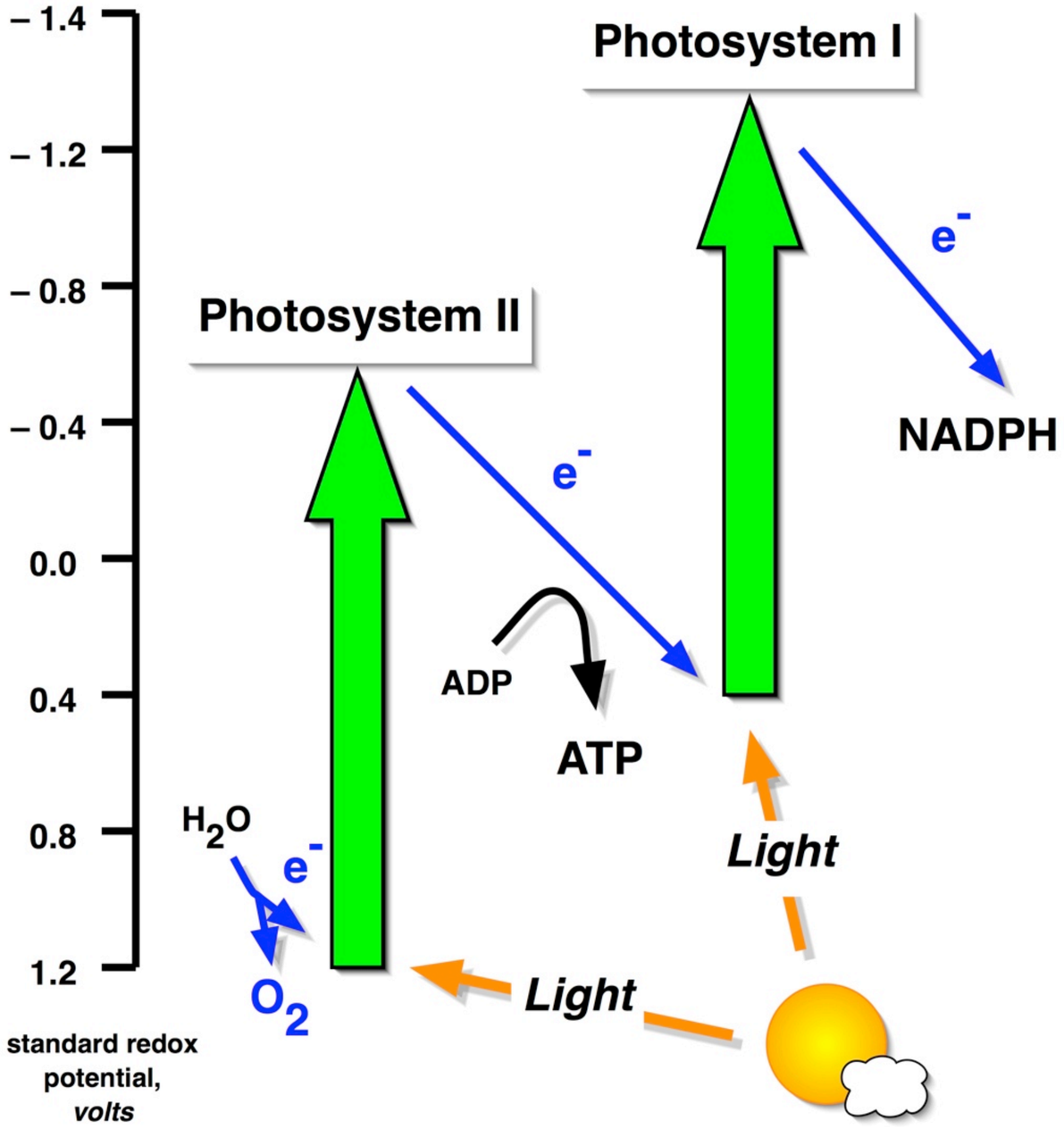
John F. Allen,[1,4,5,@,*] Brenda Thake,[2] and William F. Martin[3]

**Cyanobacteria produced the oxygen that began to accumulate on Earth 2.5 billion years ago, at the dawn of the Proterozoic Eon. By 2.4 billion years ago, the Great Oxidation Event (GOE) marked the onset of an atmosphere containing oxygen. The oxygen content of the atmosphere then remained low for almost 2 billion years. Why? Nitrogenase, the sole nitrogen-fixing enzyme on Earth, controls the entry of molecular nitrogen into the biosphere. Nitrogenase is inhibited in air containing more than 2% oxygen: the concentration of oxygen in the Proterozoic atmosphere. We propose that oxygen inhibition of nitrogenase limited Proterozoic global primary production. Oxygen levels increased when upright terrestrial plants isolated nitrogen fixation in soil from photosynthetic oxygen production in shoots and leaves.**

## Highlights

Photosynthesis in cyanobacteria introduced oxygen into Earth's atmosphere, giving the Great Oxidation Event, about 2.4 billion years ago. Atmospheric oxygen concentration then remained puzzlingly low, at most only 10% of its present value, for nearly 2 billion years.

 https://doi.org/10.1016/j.tplants.2019.07.007




The “Z-scheme”of oxygenic photosynthesis. After Hill and Bendall 1960

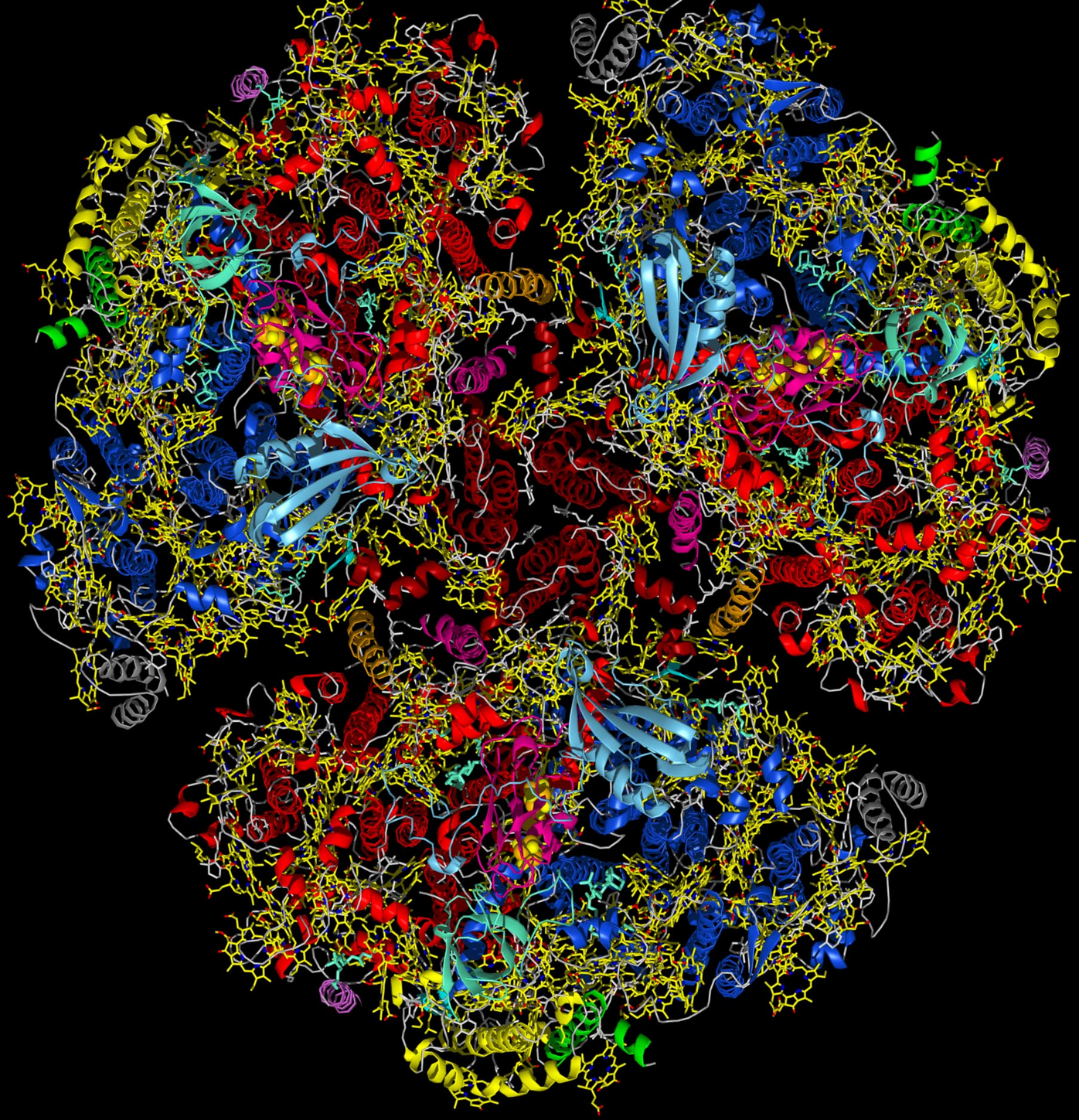
# Three-dimensional structure of cyanobacterial photosystem I at 2.5 Å resolution

**Patrick Jordan*, Petra Fromme†, Horst Tobias Witt†, Olaf Klukas*, Wolfram Saenger* & Norbert Krauß*‡**

** Institut für Chemie/Kristallographie, Freie Universität Berlin, D-14195 Berlin, Takustraße 6, Germany*
*† Max Volmer Laboratorium für Biophysikalische Chemie, Institut für Chemie, Fakultät 2; Technische Universität Berlin, D-10623 Berlin, Straße des 17. Juni 135, Germany*

**Life on Earth depends on photosynthesis, the conversion of light energy from the Sun to chemical energy. In plants, green algae and cyanobacteria, this process is driven by the cooperation of two large protein–cofactor complexes, photosystems I and II, which are located in the thylakoid photosynthetic membranes. The crystal structure of photosystem I from the thermophilic cyanobacterium *Synechococcus elongatus* described here provides a picture at atomic detail of 12 protein subunits and 127 cofactors comprising 96 chlorophylls, 2 phylloquinones, 3 $Fe_4S_4$ clusters, 22 carotenoids, 4 lipids, a putative $Ca^{2+}$ ion and 201 water molecules. The structural information on the proteins and cofactors and their interactions provides a basis for understanding how the high efficiency of photosystem I in light capturing and electron transfer is achieved.**

Nature 411, 909-917 (2001)



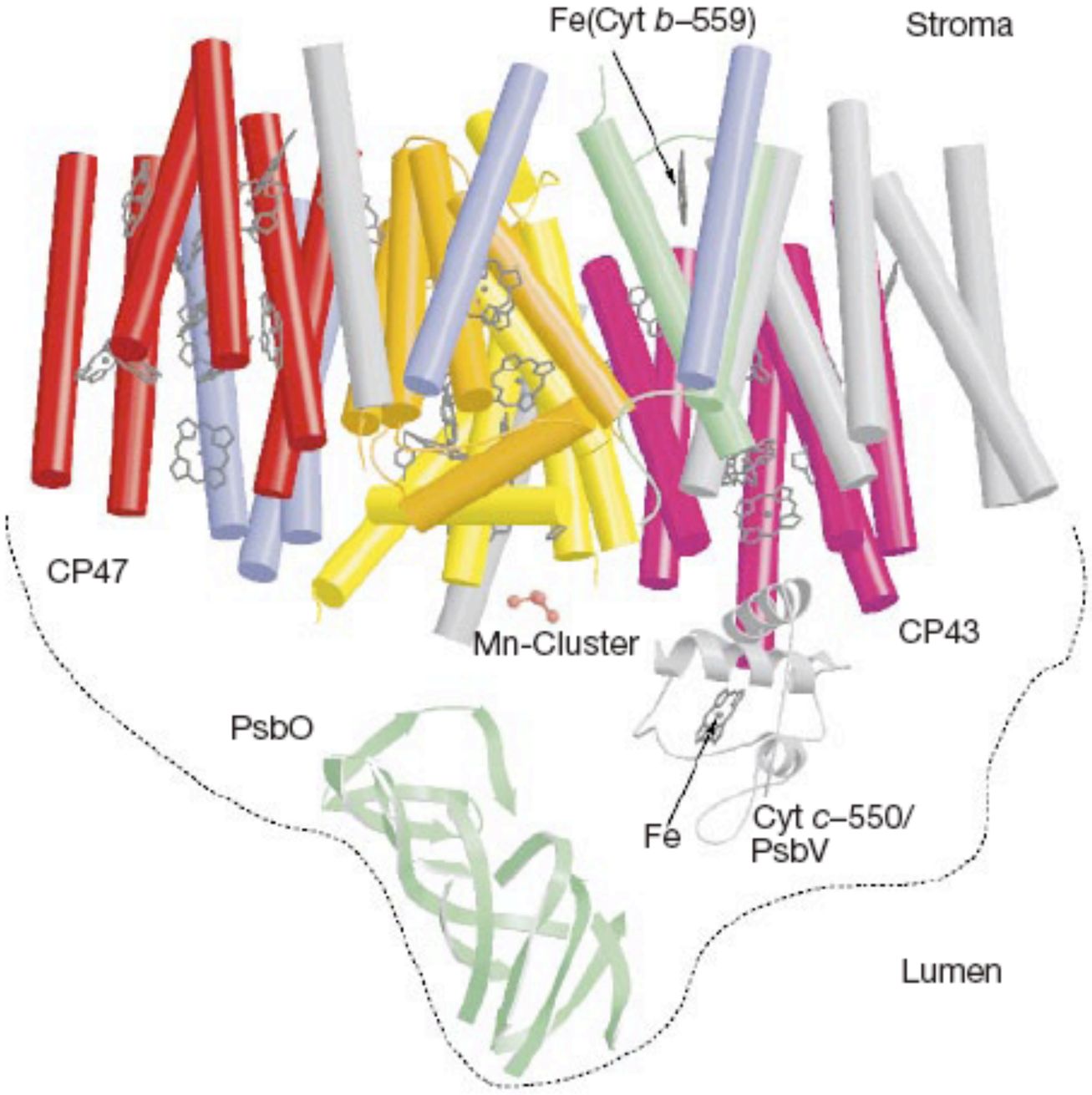
# Crystal structure of photosystem II from *Synechococcus elongatus* at 3.8 Å resolution

**Athina Zouni*, Horst-Tobias Witt*, Jan Kern*, Petra Fromme*, Norbert Krauß†, Wolfram Saenger†, Peter Orth†**

**Max-Volmer-Institut für Biophysikalische Chemie und Biochemie, Technische Universität Berlin, Straße des 17, Juni 135, D-10623, Berlin, Germany*
*† Institut für Chemie, Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany*

Oxygenic photosynthesis is the principal energy converter on earth. It is driven by photosystems I and II, two large protein–cofactor complexes located in the thylakoid membrane and acting in series. In photosystem II, water is oxidized; this event provides the overall process with the necessary electrons and protons, and the atmosphere with oxygen. To date, structural information on the architecture of the complex has been provided by electron microscopy of intact, active photosystem II at 15–30 Å resolution[1], and by electron crystallography on two-dimensional crystals of D1-D2-CP47 photosystem II fragments without water oxidizing activity at 8 Å resolution[2]. Here we describe the X-ray structure of photosystem II on the basis of crystals fully active in water oxidation[3]. The structure shows how protein subunits and cofactors are spatially organized. The larger subunits are assigned and the locations and orientations of the cofactors are defined. We also provide new information on the position, size and shape of the manganese cluster, which catalyzes water oxidation.

Nature 409, 739-743 (2001)


Fe(Cyt b–559)
Stroma
CP47
Mn-Cluster
CP43
PsbO
Fe
Cyt c–550/
PsbV
Lumen

ARTICLE

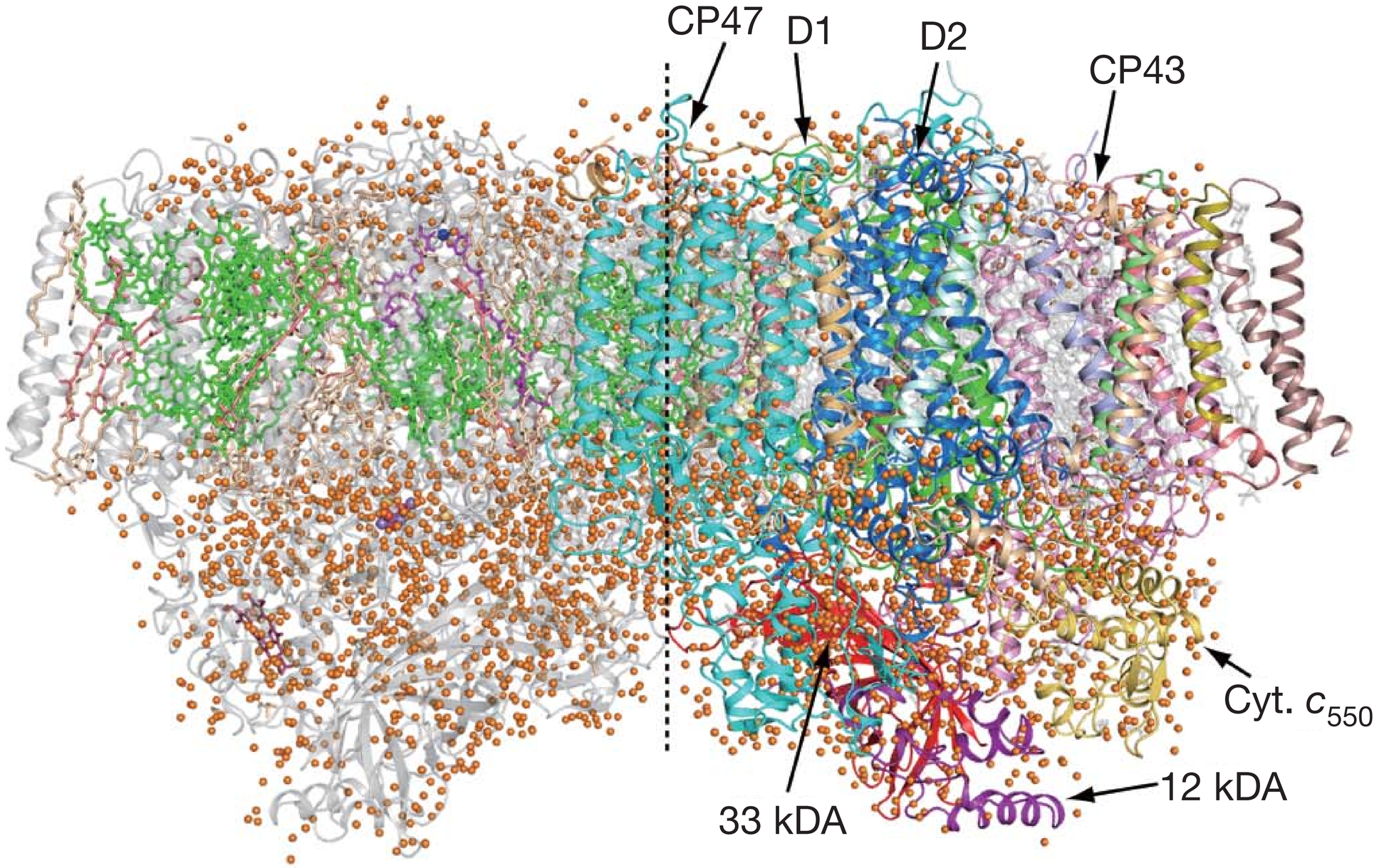
doi:10.1038/nature09913

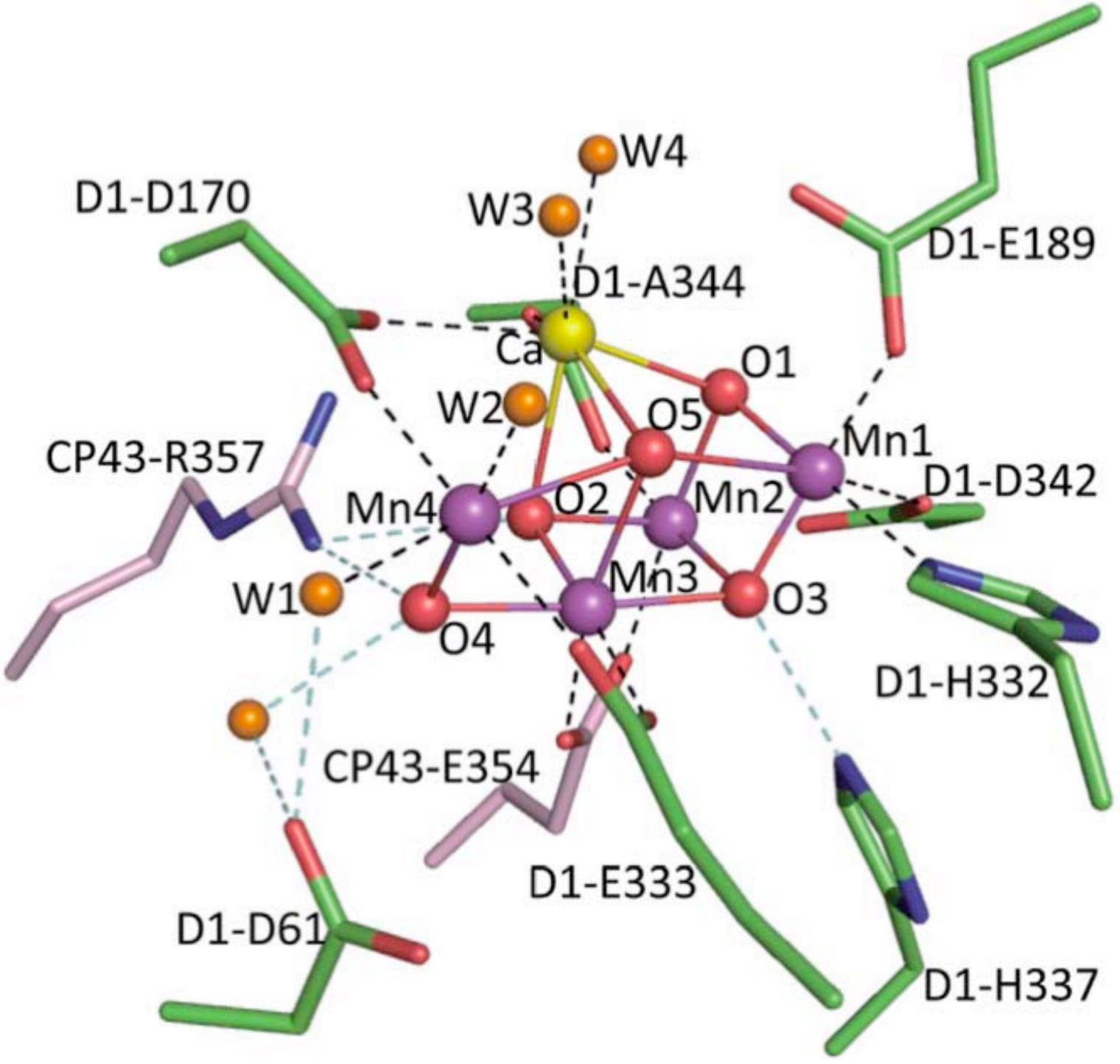
# Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å

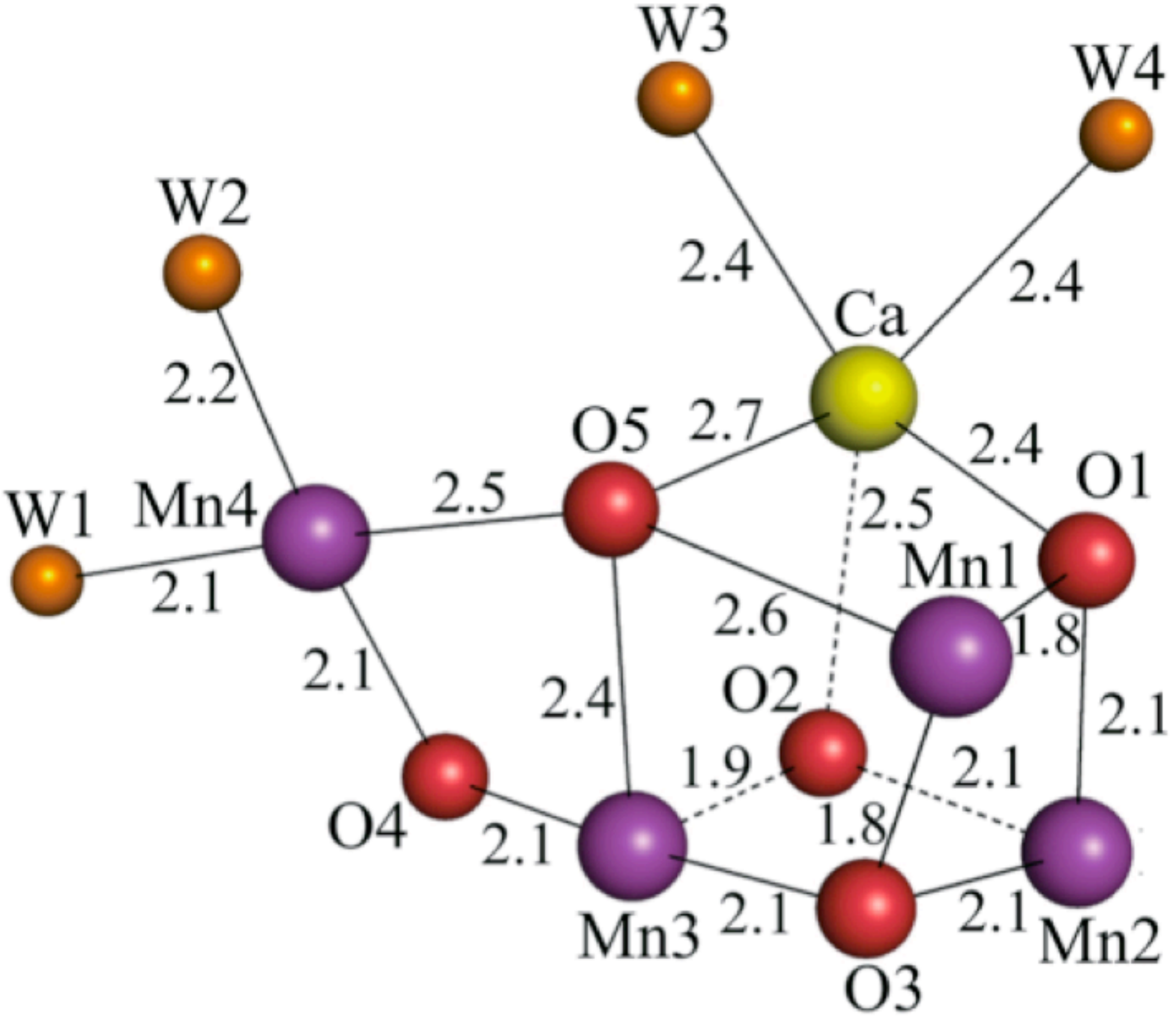
Yasufumi Umena[1]†*, Keisuke Kawakami[2]†*, Jian-Ren Shen[2] & Nobuo Kamiya[1]†

**Photosystem II is the site of photosynthetic water oxidation and contains 20 subunits with a total molecular mass of 350 kDa. The structure of photosystem II has been reported at resolutions from 3.8 to 2.9 Å. These resolutions have provided much information on the arrangement of protein subunits and cofactors but are insufficient to reveal the detailed structure of the catalytic centre of water splitting. Here we report the crystal structure of photosystem II at a resolution of 1.9 Å. From our electron density map, we located all of the metal atoms of the $Mn_4CaO_5$ cluster, together with all of their ligands. We found that five oxygen atoms served as oxo bridges linking the five metal atoms, and that four water molecules were bound to the $Mn_4CaO_5$ cluster; some of them may therefore serve as substrates for dioxygen formation. We identified more than 1,300 water molecules in each photosystem II monomer. Some of them formed extensive hydrogen-bonding networks that may serve as channels for protons, water or oxygen molecules. The determination of the high-resolution structure of photosystem II will allow us to analyse and understand its functions in great detail.**

Nature 473, 55-60 (2011)


CP47
D1
D2
CP43
Cyt. $c_{550}$
12 kDA
33 kDA


W4
W3
D1-D170
D1-A344
D1-E189
Ca
O1
W2
O5
Mn1
CP43-R357
D1-D342
Mn4
O2
Mn2
Mn3
W1
O3
O4
D1-H332
CP43-E354
D1-E333
D1-D61
D1-H337


W3
W4
W2
2.4
2.4
Ca
2.2
2.7
O5
2.4
O1
W1
Mn4
2.5
2.5
Mn1
2.1
2.6
1.8
2.1
2.4
O2
2.1
1.9
2.1
O4
1.8
2.1
Mn3
2.1
2.1
Mn2
O3

WATER OXIDATION

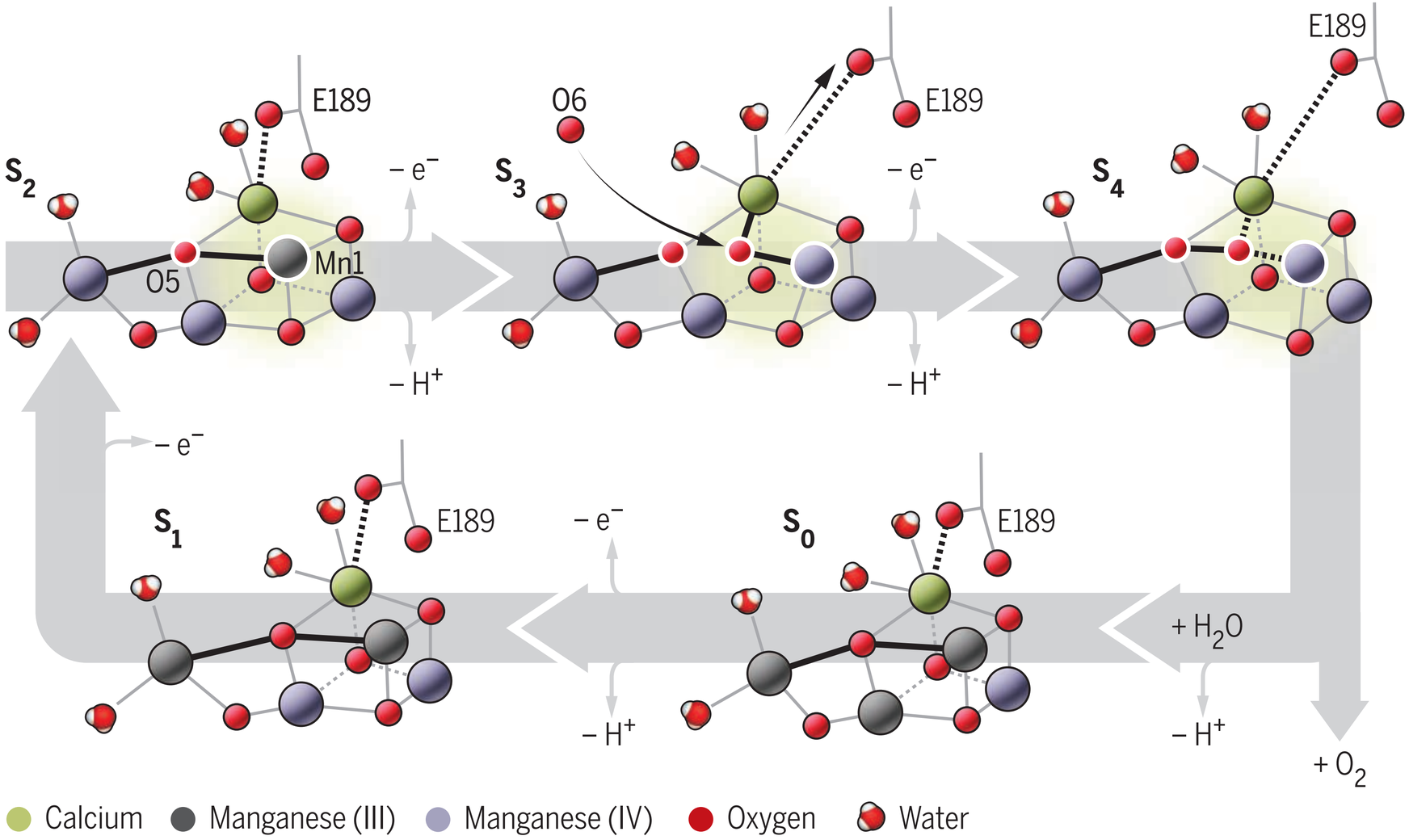
# An oxyl/oxo mechanism for oxygen-oxygen coupling in PSII revealed by an x-ray free-electron laser

Michihiro Suga[1,2]*†, Fusamichi Akita[1,2]*, Keitaro Yamashita[3]‡, Yoshiki Nakajima[1], Go Ueno[3], Hongjie Li[1,4], Takahiro Yamane[1], Kunio Hirata[3], Yasufumi Umena[1], Shinichiro Yonekura[1], Long-Jiang Yu[1], Hironori Murakami[5], Takashi Nomura[3,4], Tetsunari Kimura[6], Minoru Kubo[3,4], Seiki Baba[5], Takashi Kumasaka[5], Kensuke Tono[3,5], Makina Yabashi[3,5], Hiroshi Isobe[1], Kizashi Yamaguchi[7,8], Masaki Yamamoto[3], Hideo Ago[3]†, Jian-Ren Shen[1]†

Photosynthetic water oxidation is catalyzed by the $Mn_4CaO_5$ cluster of photosystem II (PSII) with linear progression through five S-state intermediates ($S_0$ to $S_4$). To reveal the mechanism of water oxidation, we analyzed structures of PSII in the $S_1$, $S_2$, and $S_3$ states by x-ray free-electron laser serial crystallography. No insertion of water was found in $S_2$, but flipping of D1 $Glu^{189}$ upon transition to $S_3$ leads to the opening of a water channel and provides a space for incorporation of an additional oxygen ligand, resulting in an open cubane $Mn_4CaO_6$ cluster with an oxyl/oxo bridge. Structural changes of PSII between the different S states reveal cooperative action of substrate water access, proton release, and dioxygen formation in photosynthetic water oxidation.

## The S states in the oxygen-evolution reaction

The oxygen-evolving complex is photo-oxidized through a series of S states to produce molecular oxygen from water. In the final steps before O=O bond formation, a new oxygen, O6, binds to the vacant site at Mn1. After a final photo-oxidation event, O5 and O6 appear poised to form an O=O bond, releasing molecular oxygen, reducing the cluster, and beginning the catalytic cycle anew. Glutamatic acid at position 189 is noted as E189.



nature COMMUNICATIONS

ARTICLE

https://doi.org/10.1038/s41467-020-19852-0 OPEN

# Light-driven formation of manganese oxide by today's photosystem II supports evolutionarily ancient manganese-oxidizing photosynthesis

Petko Chernev[1,3], Sophie Fischer[1], Jutta Hoffmann[1], Nicholas Oliver[1], Ricardo Assunção[1], Boram Yu[1], Robert L. Burnap[2], Ivelina Zaharieva[1], Dennis J. Nürnberg[1], Michael Haumann[1] & Holger Dau[1✉]

Water oxidation and concomitant dioxygen formation by the manganese-calcium cluster of oxygenic photosynthesis has shaped the biosphere, atmosphere, and geosphere. It has been hypothesized that at an early stage of evolution, before photosynthetic water oxidation became prominent, light-driven formation of manganese oxides from dissolved Mn(2+) ions may have played a key role in bioenergetics and possibly facilitated early geological manganese deposits. Here we report the biochemical evidence for the ability of photosystems to form extended manganese oxide particles. The photochemical redox processes in spinach photosystem-II particles devoid of the manganese-calcium cluster are tracked by visible-light and X-ray spectroscopy. Oxidation of dissolved manganese ions results in high-valent Mn(III, IV)-oxide nanoparticles of the birnessite type bound to photosystem II, with 50-100 manganese ions per photosystem. Having shown that even today's photosystem II can form birnessite-type oxide particles efficiently, we propose an evolutionary scenario, which involves manganese-oxide production by ancestral photosystems, later followed by downsizing of protein-bound manganese-oxide nanoparticles to finally yield today's catalyst of photosynthetic water oxidation.

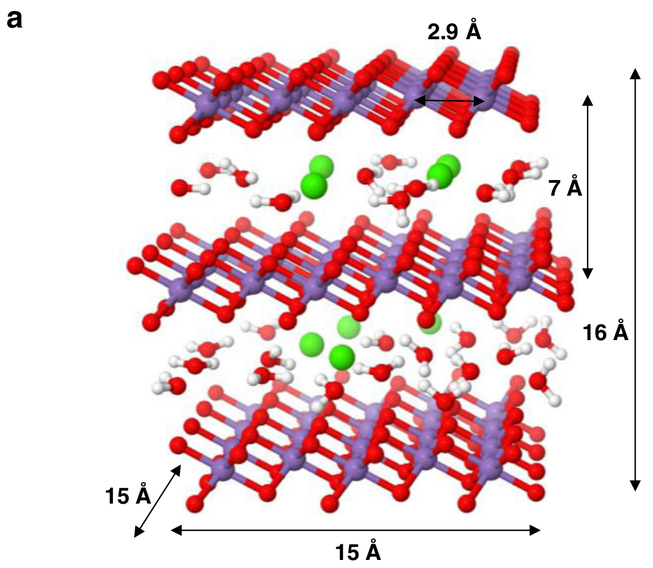



**Fig. 6 Evolution of oxygenic photosynthesis and relation to geological Mn-oxide deposits. a** Structural model of a birnessite fragment with 64 Mn ions (based on published atomic coordinates, protons were added for illustration only). Atom color coding: violet, Mn(III/IV) ions; red, O or OH; green, $Ca^{2+}$; gray, H.

# Time-resolved comparative molecular evolution of oxygenic photosynthesis

Thomas Oliver [a], Patricia Sánchez-Baracaldo [b], Anthony W. Larkum [c], A. William Rutherford [a], Tanai Cardona [a,*]

[a] *Department of Life Sciences, Imperial College London, London, UK*
[b] *School of Geographical Sciences, University of Bristol, Bristol, UK*
[c] *University of Technology Sydney, Ultimo, NSW, Australia*

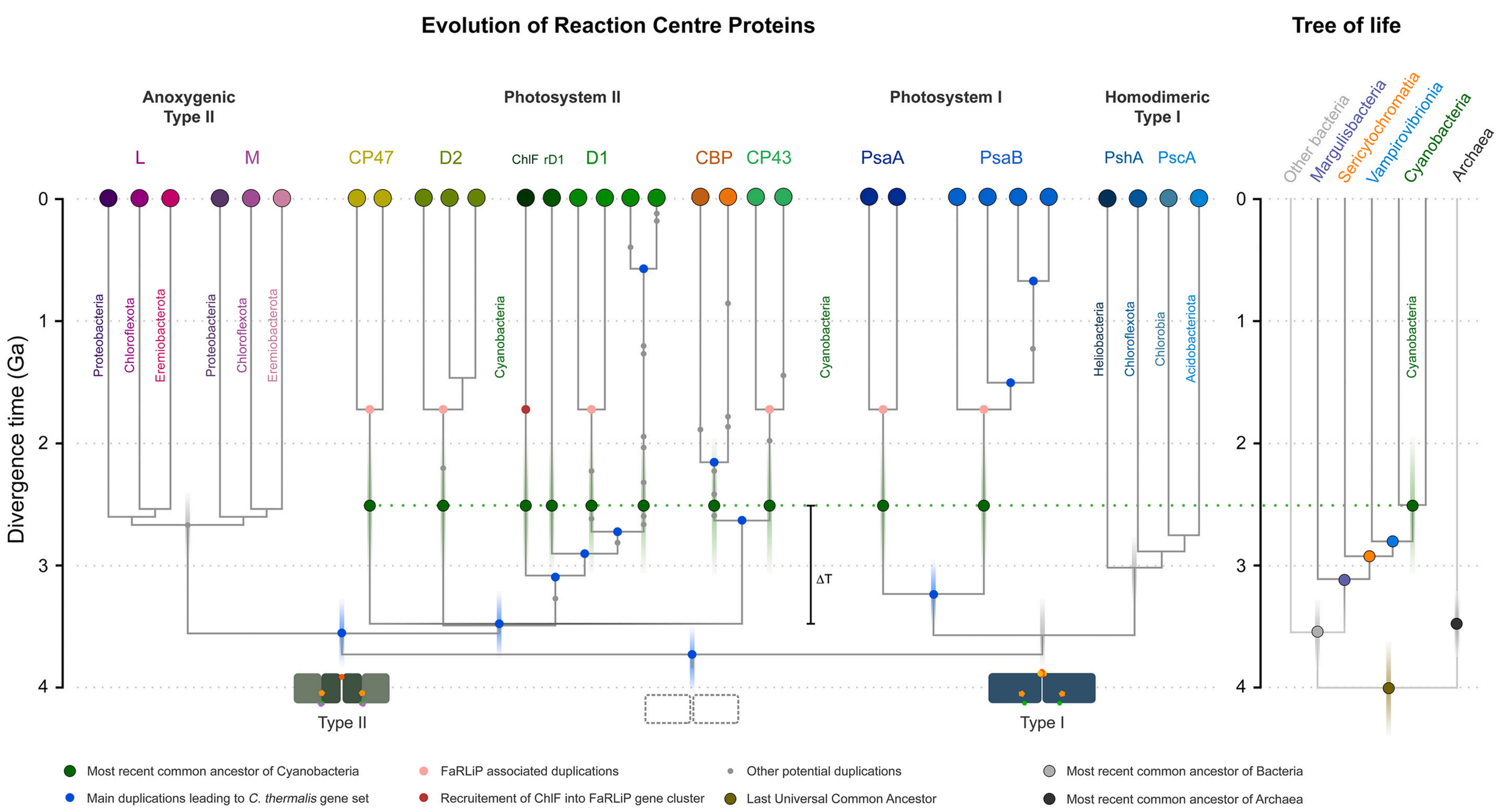
ARTICLE INFO

*Keywords:*
Origin of photosynthesis
Origin of life
Cyanobacteria
Photosystem
Reaction centre
Water oxidation

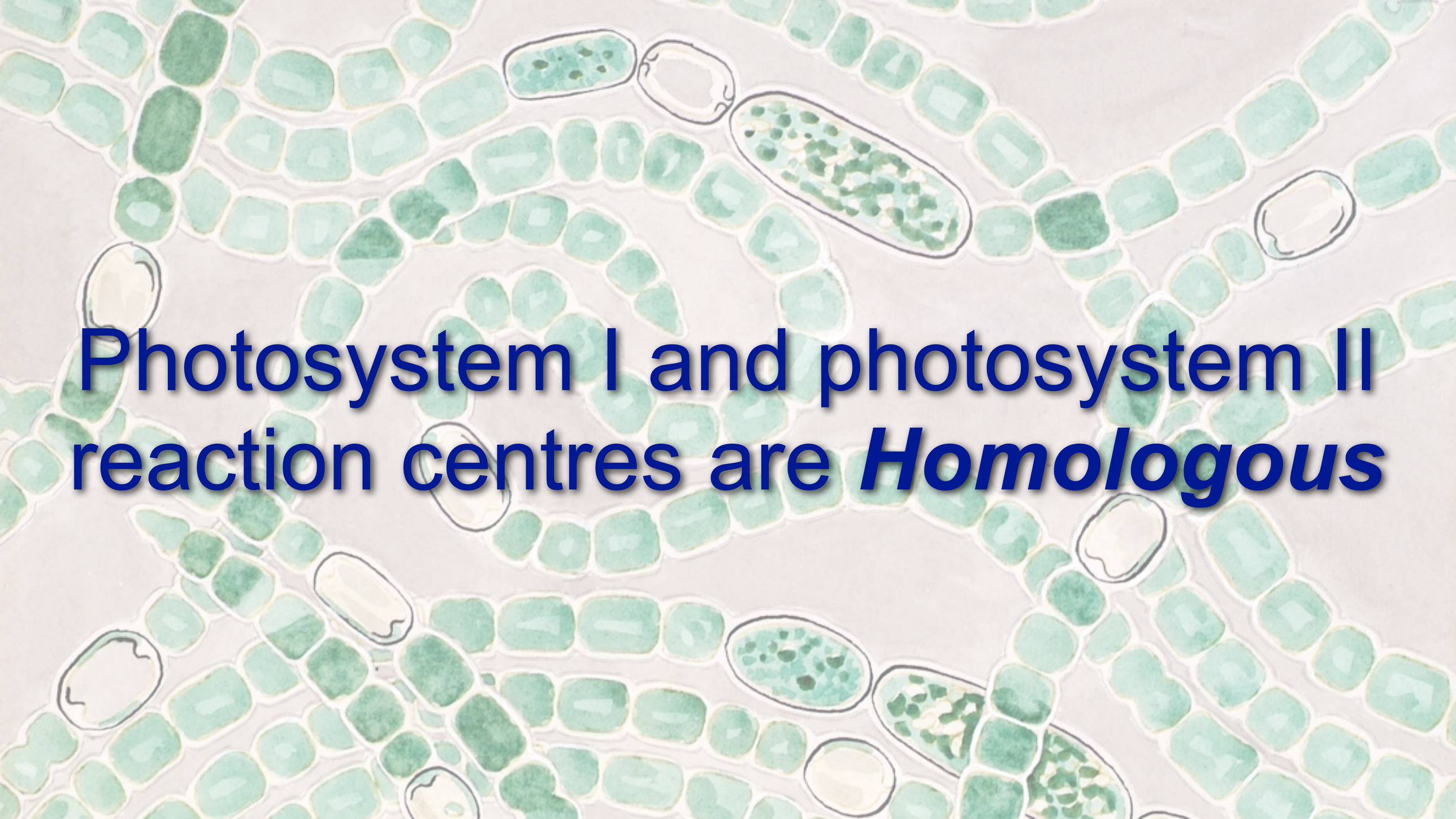
ABSTRACT

Oxygenic photosynthesis starts with the oxidation of water to $O_2$, a light-driven reaction catalysed by photosystem II. Cyanobacteria are the only prokaryotes capable of water oxidation and therefore, it is assumed that the origin of oxygenic photosynthesis is a late innovation relative to the origin of life and bioenergetics. However, when exactly water oxidation originated remains an unanswered question. Here we use phylogenetic analysis to study a gene duplication event that is unique to photosystem II: the duplication that led to the evolution of the core antenna subunits CP43 and CP47. We compare the changes in the rates of evolution of this duplication with those of some of the oldest well-described events in the history of life: namely, the duplication leading to the Alpha and Beta subunits of the catalytic head of ATP synthase, and the divergence of archaeal and bacterial RNA polymerases and ribosomes. We also compare it with more recent events such as the duplication of Cyanobacteria-specific FtsH metalloprotease subunits and the radiation leading to Margulisbacteria, Sericytochromatia, Vampirovibrionia, and other clades containing anoxygenic phototrophs. We demonstrate that the ancestral core duplication of photosystem II exhibits patterns in the rates of protein evolution through geological time that are nearly identical to those of the ATP synthase, RNA polymerase, or the ribosome. Furthermore, we use ancestral sequence reconstruction in combination with comparative structural biology of photosystem subunits, to provide additional evidence supporting the premise that water oxidation had originated before the ancestral core duplications. Our work suggests that photosynthetic water oxidation originated closer to the origin of life and bioenergetics than can be documented based on phylogenetic or phylogenomic species trees alone.

BBA - Bioenergetics 1862 (2021) 148400 https://doi.org/10.1016/j.bbabio.2021.148400

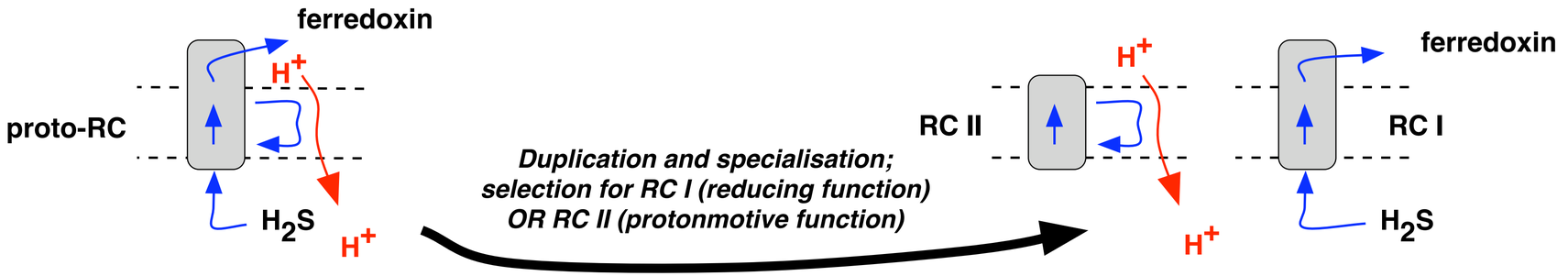



BBA - Bioenergetics 1862 (2021) 148400 https://doi.org/10.1016/j.bbabio.2021.148400

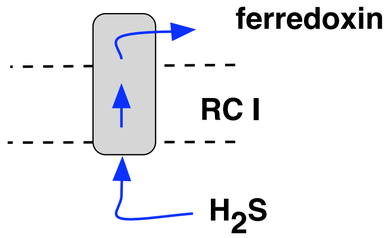

Photosystem I and photosystem II
reaction centres are *Homologous*

How did photosystem I and photosystem II reaction centres diverge from a common ancestor AND eventually meet again – to work together in the same membrane at the same time...?

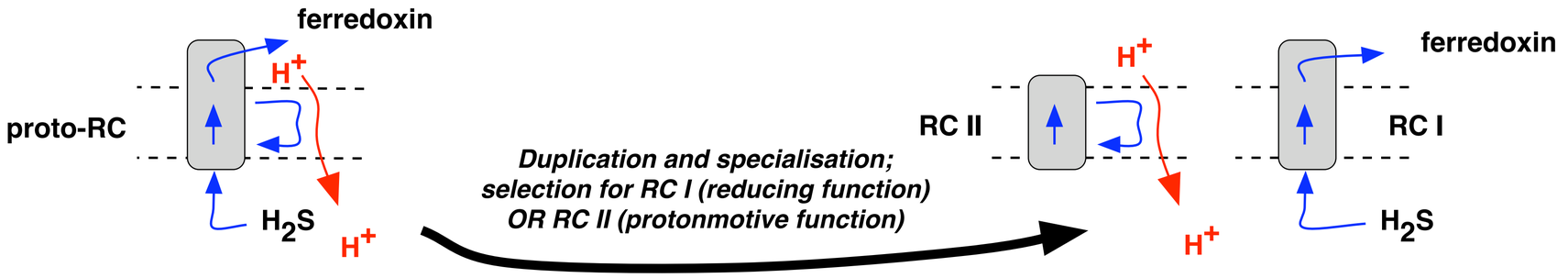
# The Redox Switch Hypothesis for the first cyanobacterium and for the origin of oxygenic photosynthesis

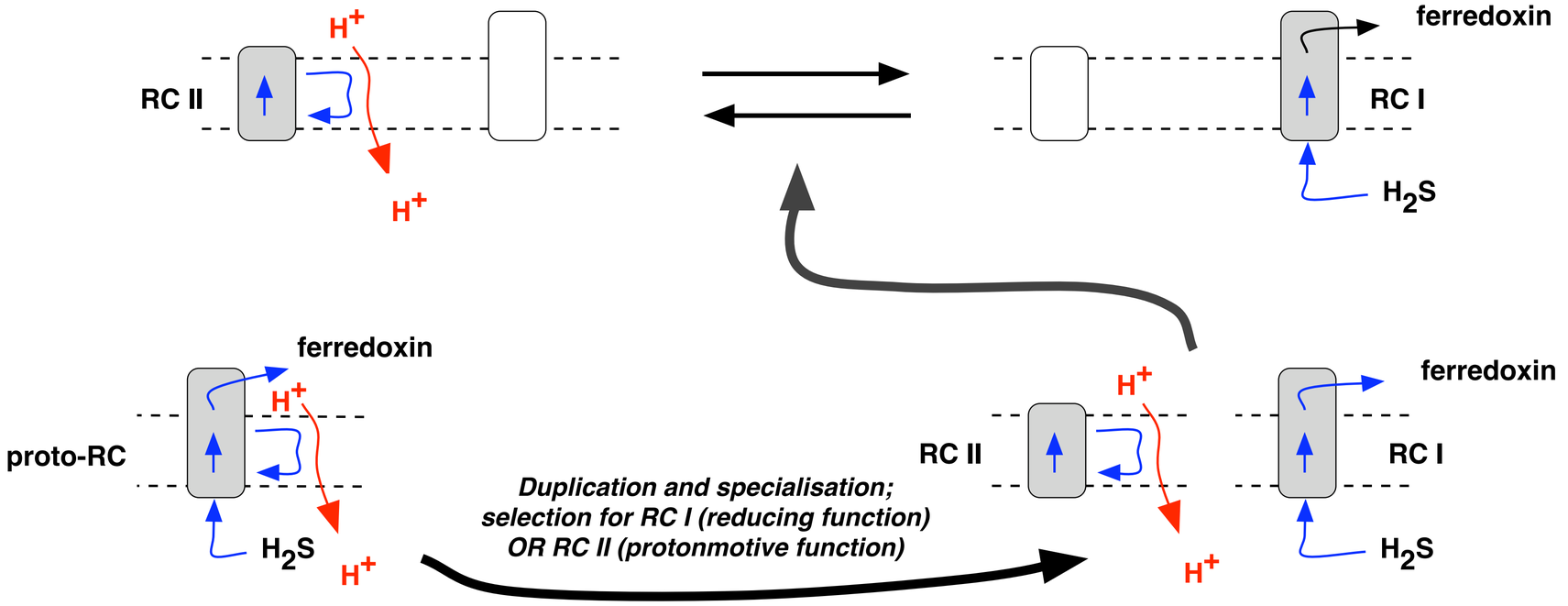

ferredoxin
H+
proto-RC
H2S
H+
Duplication and specialisation;
selection for RC I (reducing function)
OR RC II (protonmotive function)
H+
RC II
H+
ferredoxin
RC I
H2S

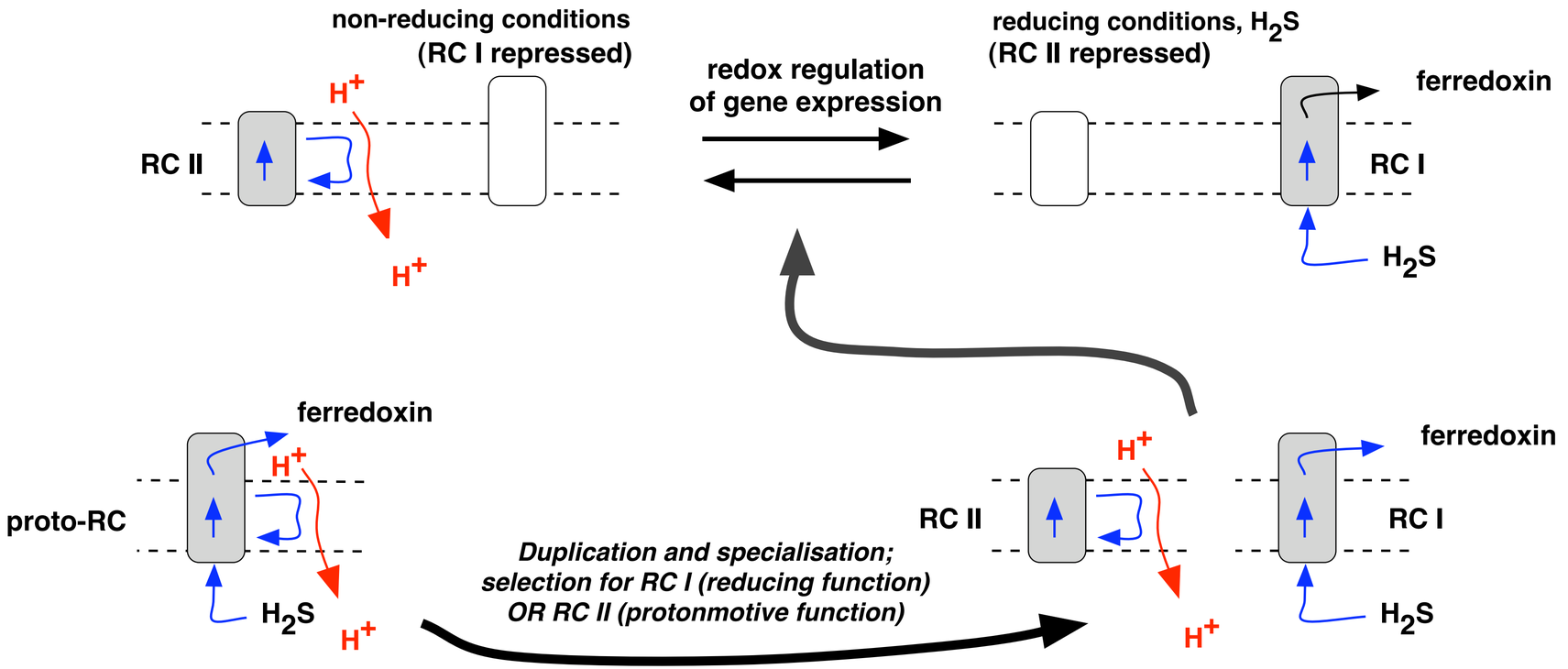
**Bacteria with RC I**
***Chlorobium, Heliobacterium***



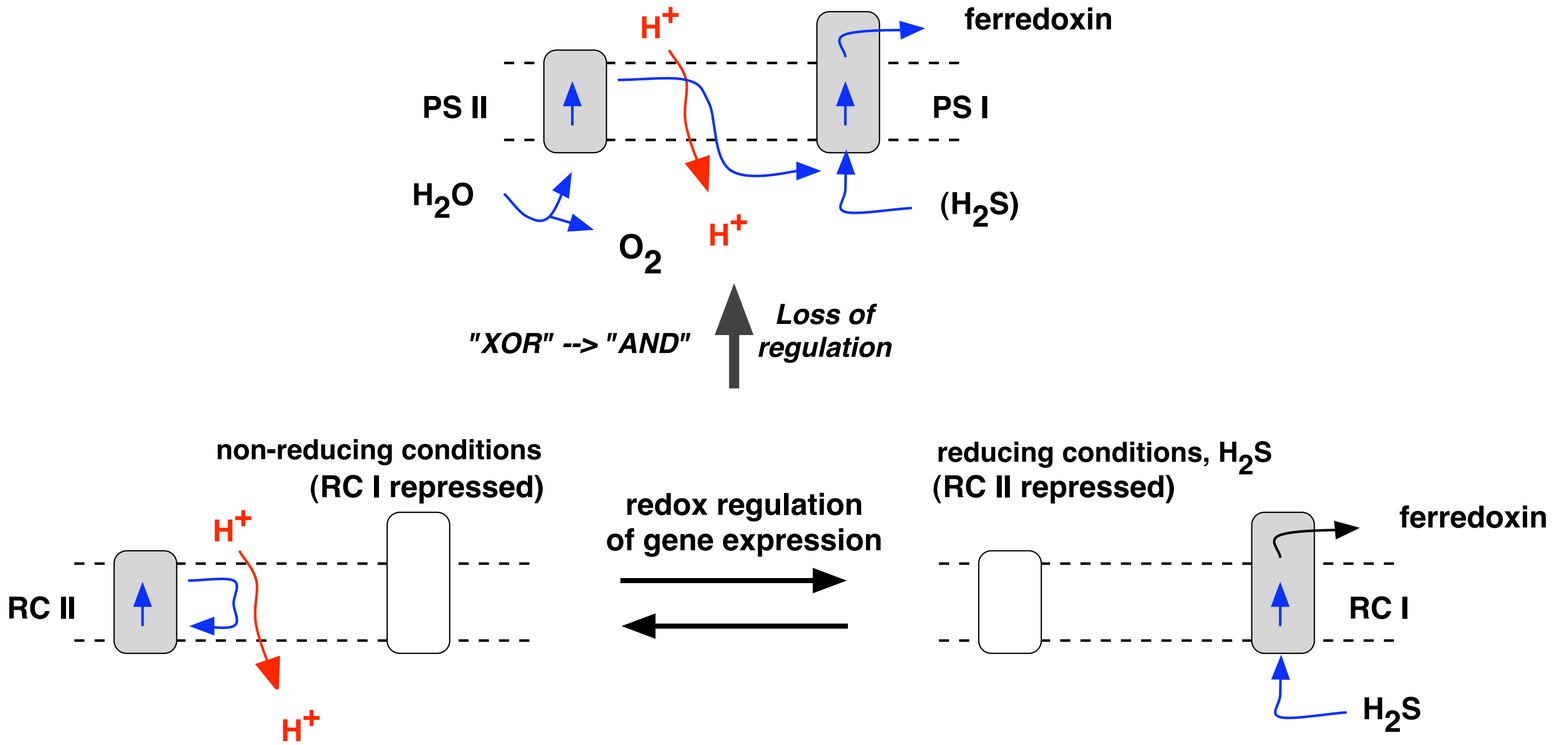

***Loss of RC II***

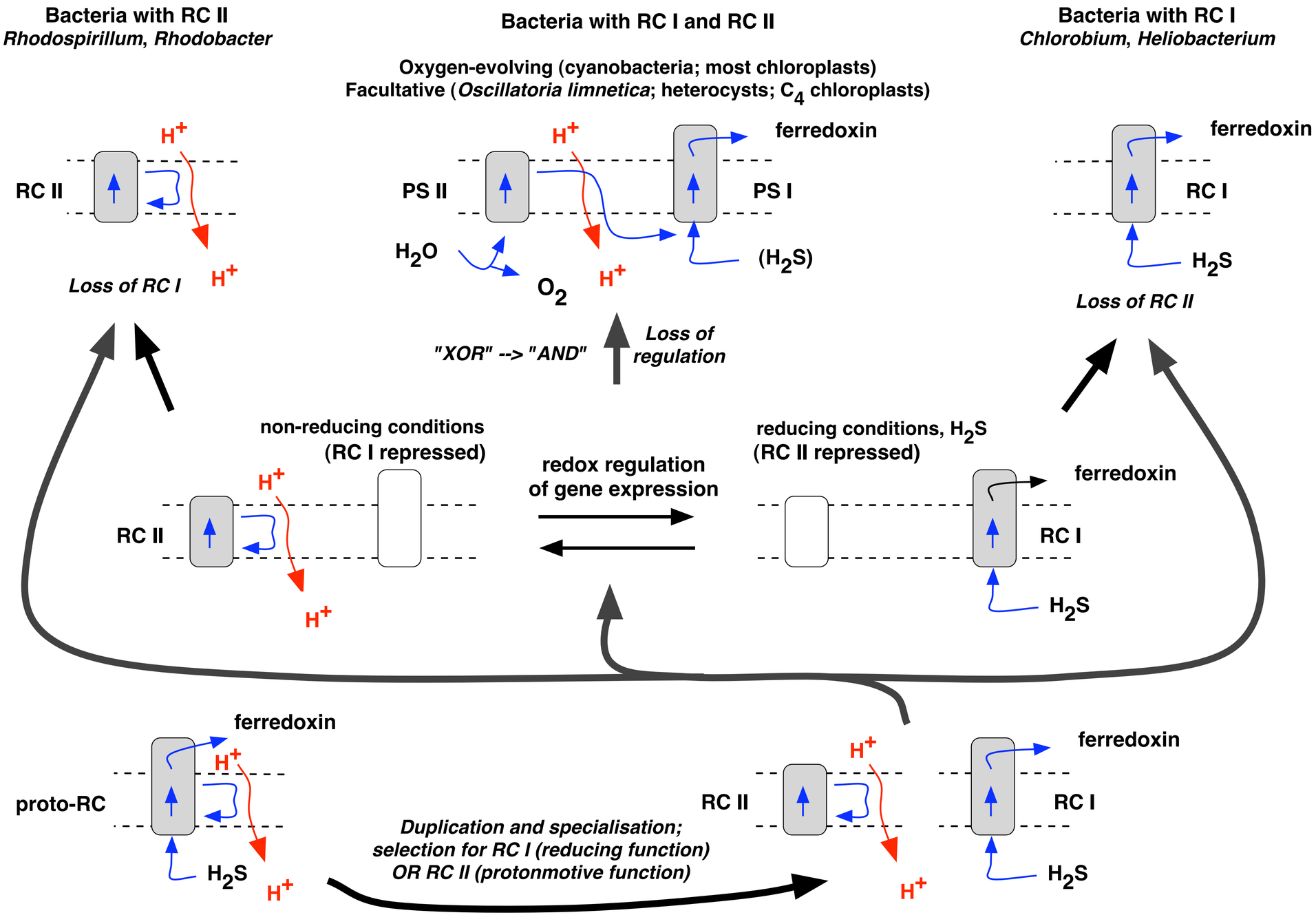



RC II
H+
H+
ferredoxin
RC I
H2S
proto-RC
ferredoxin
H+
H2S
H+
Duplication and specialisation;
selection for RC I (reducing function)
OR RC II (protonmotive function)
RC II
H+
H+
ferredoxin
RC I
H2S


non-reducing conditions
(RC I repressed)
RC II
H+
H+
redox regulation
of gene expression
reducing conditions, H2S
(RC II repressed)
ferredoxin
RC I
H2S
ferredoxin
proto-RC
H+
H2S
H+
Duplication and specialisation;
selection for RC I (reducing function)
OR RC II (protonmotive function)
RC II
H+
H+
ferredoxin
RC I
H2S

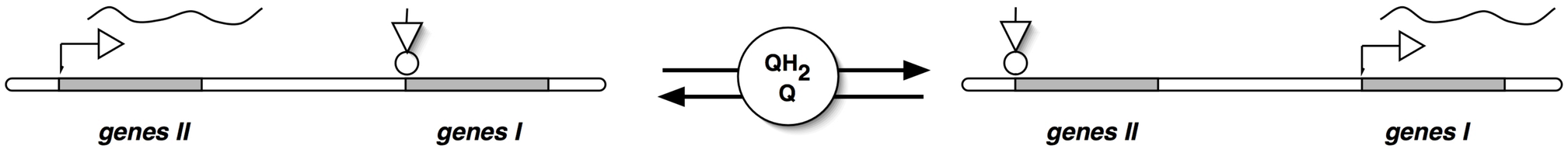

non-reducing conditions
(RC I repressed)
RC II
H+
H+
redox regulation
of gene expression
reducing conditions, H2S
(RC II repressed)
ferredoxin
RC I
H2S


H+
ferredoxin
PS II
PS I
H2O
(H2S)
O2
H+
"XOR" --> "AND"
Loss of regulation
non-reducing conditions
(RC I repressed)
reducing conditions, H2S
(RC II repressed)
redox regulation
of gene expression
H+
ferredoxin
RC II
RC I
H+
H2S




Allen, J.F. (2005) A redox switch hypothesis for the origin of two light reactions in photosynthesis. FEBS Letters 579, 963-968

# Proposed evolutionary continuity of quinone-level redox control of gene expression…

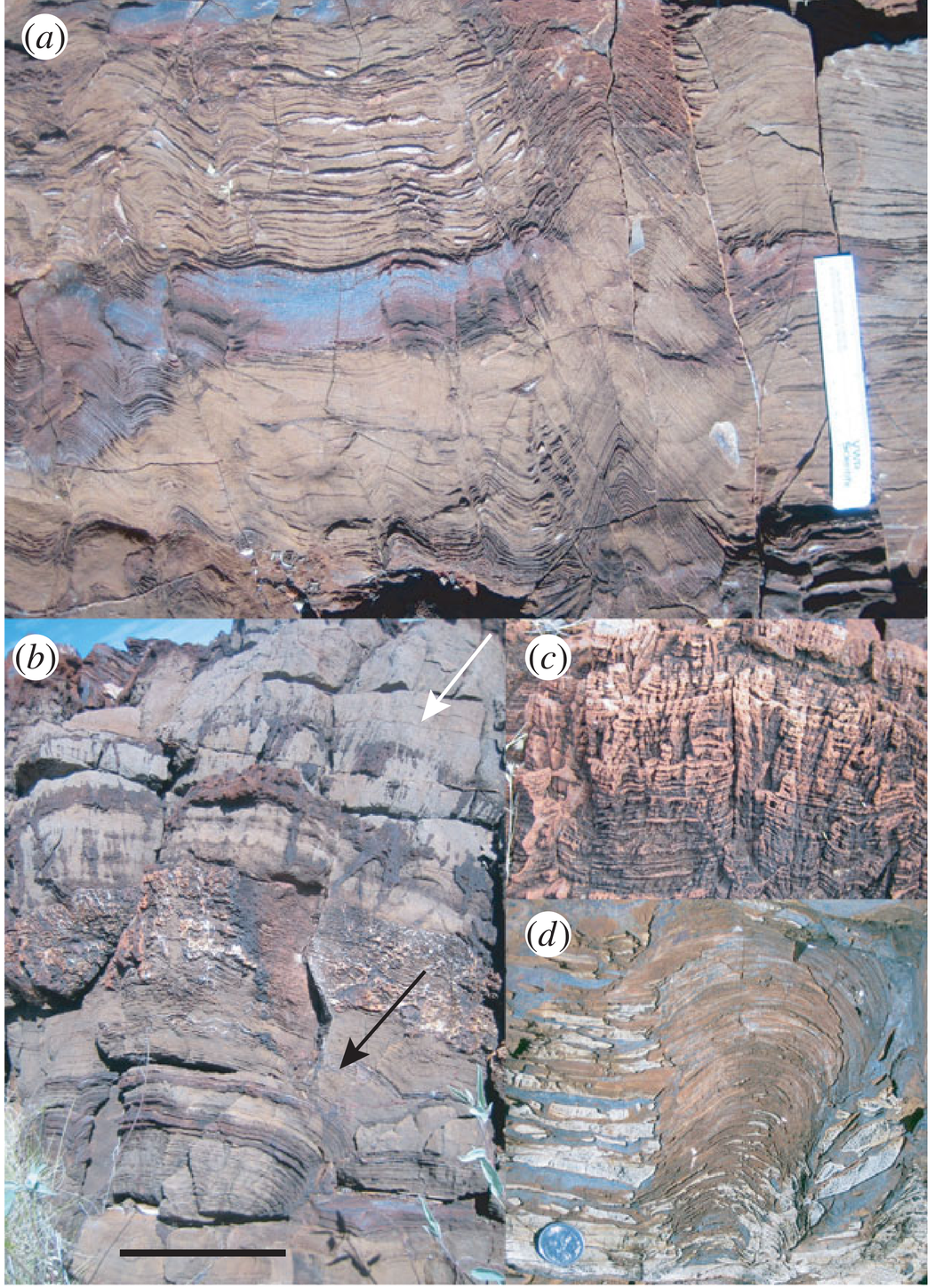

genes II
genes I
QH2
Q
genes II
genes I


Stromatolites….

**Cenozoic Landscape**

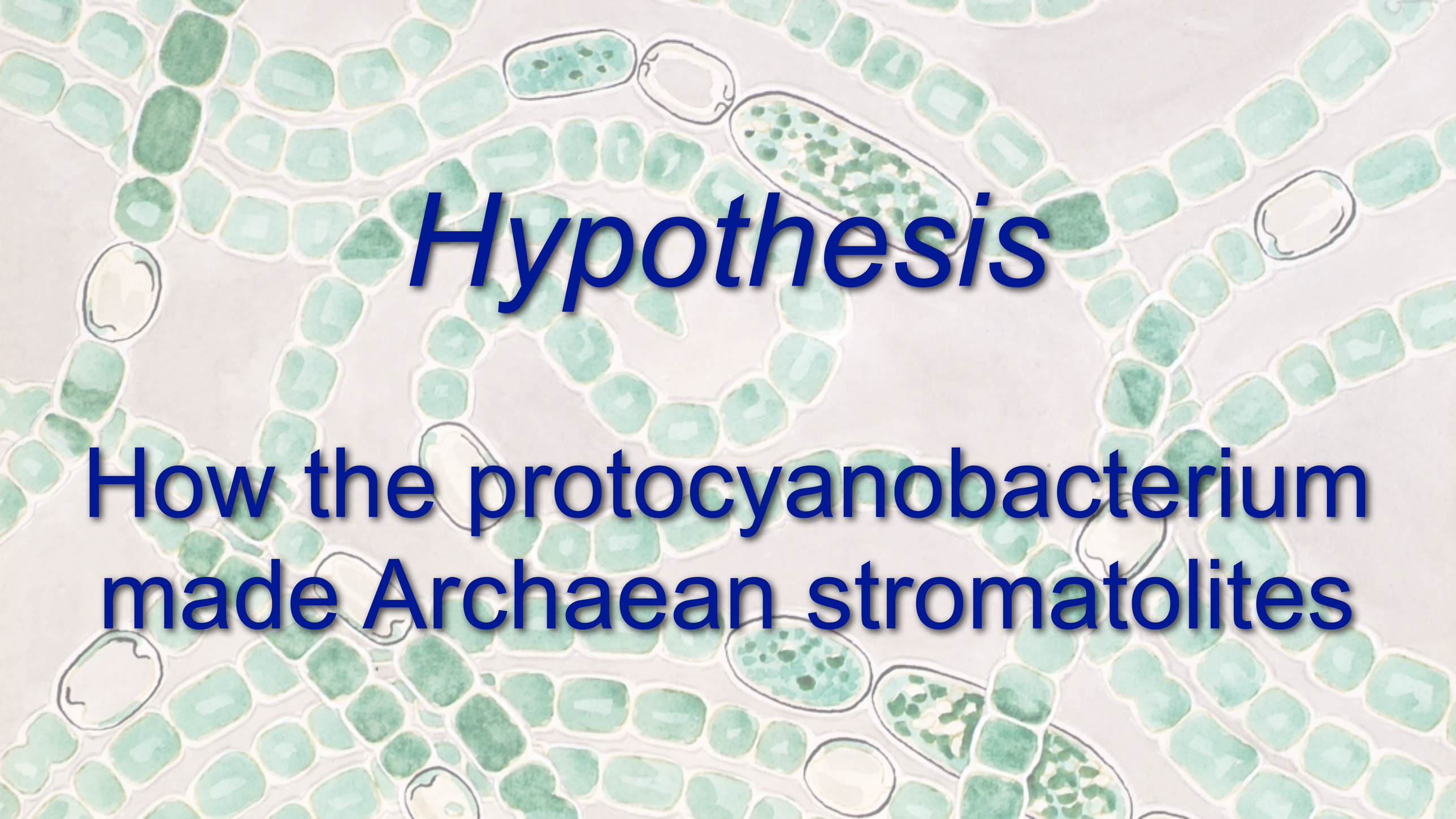
Stromatolites at Hamelin Pool, Western Australia

Photograph 4 October 2007 by Catherine Colas des Francs-Small, The University of Western Australia




Knoll AH, Bergmann KD, Strauss JV. 2016 Life: the first two billion years. Phil. Trans. R. Soc. B 371: 20150493.

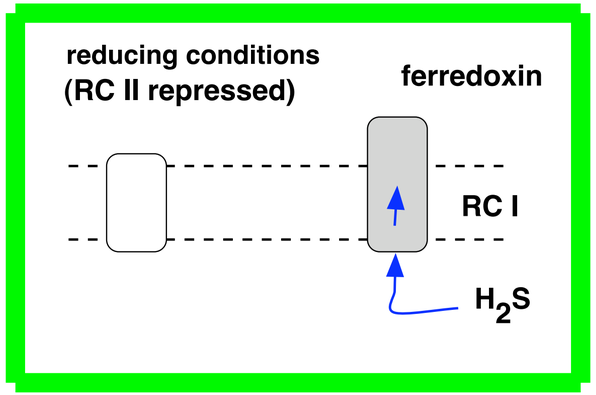
Stromatolites interpreted as evidence for microbial life in Archean rocks. (*a*) Irregular and conoidal stromatolites in carbonates of the 3450 Ma Strelley Pool Formation, Warrawoona Group, Western Australia; (*b*) a second view of Strelley Pool carbonate, showing the prevalence of decimeter-scale (originally) aragonite crystals growing upward from the seafloor (white arrow) in close association with precipitated stromatolites (black arrow); (*c*) laminated seafloor precipitates in the Strelley Pool Formation that blur the lines between biogenic and physically generated laminites; and (*d*) unambiguously biogenic stromatolite in the approximately 2720 Ma Tumbiana Formation, Fortescue Group, Western Australia. Ruler in (*a*) is 15 cm; scale bar in (*b*) is 20 cm for (*b*), 4 cm for (*c*) and 15 cm for (*d*).

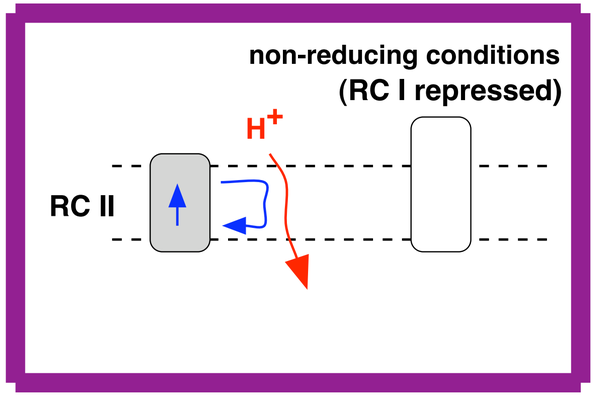

Hypothesis
How the protocyanobacterium made Archaean stromatolites

# Protocyanobacterium

# A model for seeding of stromatolites.

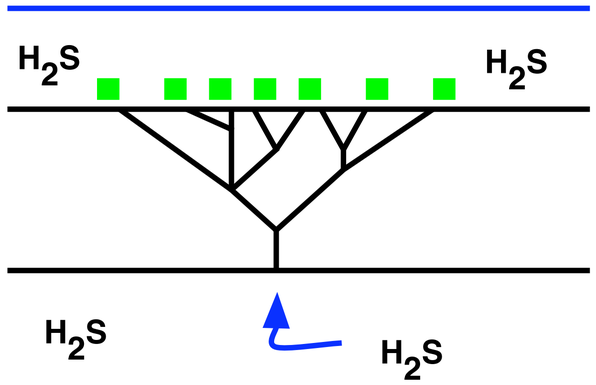
Two modes of photosynthetic metabolism in a single organism – the Protocyanobacterium



# A model for formation and growth of stromatolites.

Two modes of photosynthetic metabolism in a single organism – the Protocyanobacterium




Sequential concentration and dilution of hydrothermally-derived $H_2S$ results in alternation of type I and type II photosynthesis, and in alternation of photoautotrophy and photoheterotrophy. Sequential deposition of layers of cellular material from each mode of metabolism produces a laminar substrate that raises the growing microbial mat incrementally nearer to the surface of the water and source of light.

Allen JF (2016) A Proposal for Formation of Archaean Stromatolites before the Advent of Oxygenic Photosynthesis. Front. Microbiol. 7:1784. doi: 10.3389/fmicb.2016.01784

# Acknowledgements

ATTIC MISCELLANY.

Political Portraiture No. 1.


DOCTOR PHLOGISTON.

The PRIESTLEY palladium or the

Political Priest

# Joseph Priestley

@JPriestley1733

Clergyman, natural philosopher, chemist, educator, and political theorist. These opinions are mine own. On the sabbath, I rest.

Birmingham, UK

**208** TWEETS

**1,976** FOLLOWING

**857** FOLLOWERS

Following

The attack on Joseph Priestley's home, Fairhill, at Sparkbrook, Birmingham on 14 July 1791

https://en.wikipedia.org/wiki/Priestley_Riots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The Priestleys' home in Northumberland County, Pennsylvania


Priestley Medal obverse

| Awarded for | Distinguished service in the field of chemistry |
|---|---|
| Date | 1923 |
| Presented by | American Chemical Society (ACS) |

**Acknowledgements**

***Anabaena cylindrica***
1946 Watercolour by G. E. Fogg
Courtesy of Mrs Brenda Thake, Queen Mary University of London

**Portrait of Joseph Priestley by William Artaud** By permission of the Trustees of Dr Williams's Library.
https://www.dwl.ac.uk
Shown courtesy of Dr Isabel Rivers, Queen Mary University of London

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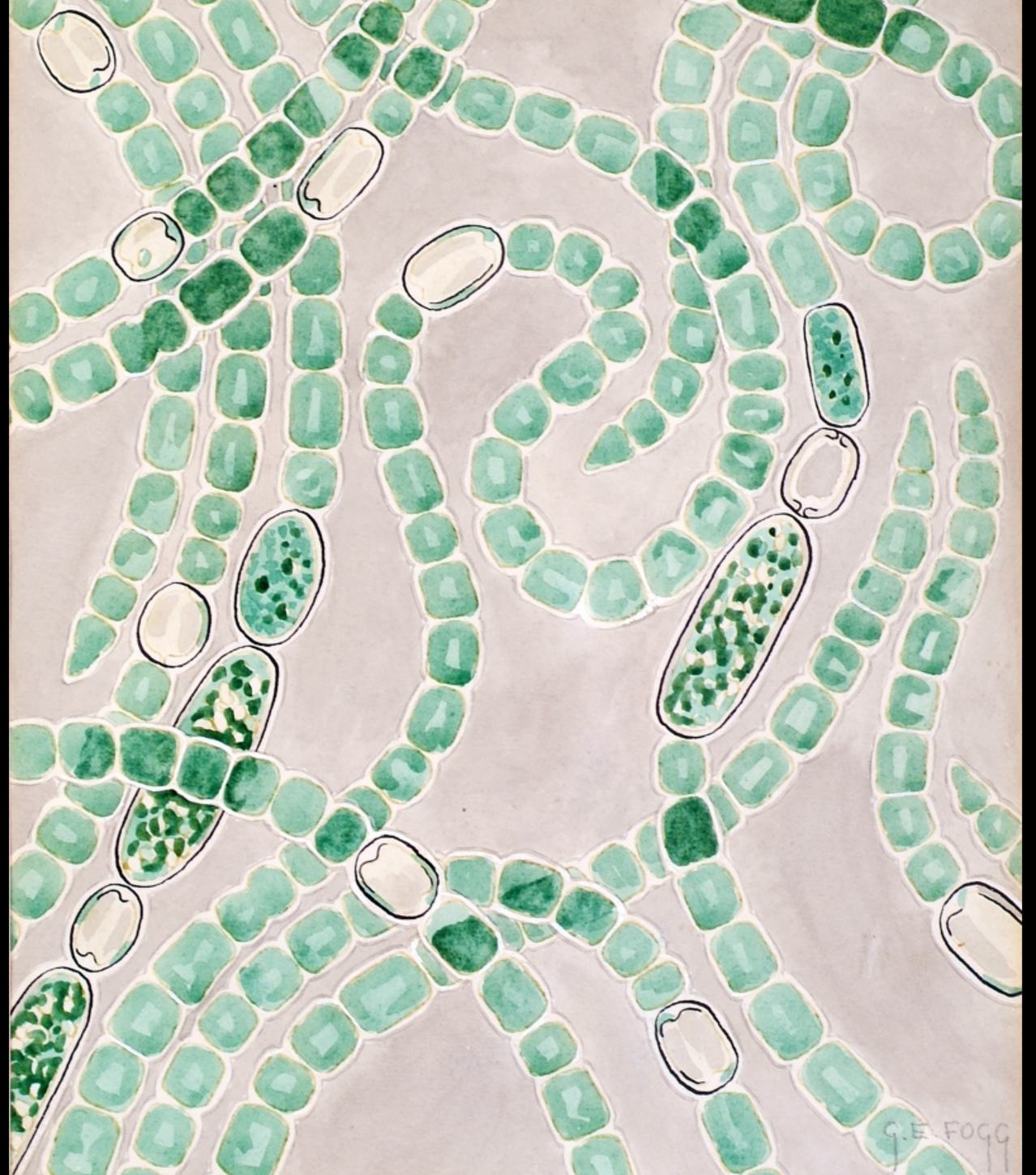
• Iskander Ibrahim
• Wilson de Paula
• Liang Wang

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# Energy and Evolution

BIOL0030_21-22

# Thank you for your attention

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