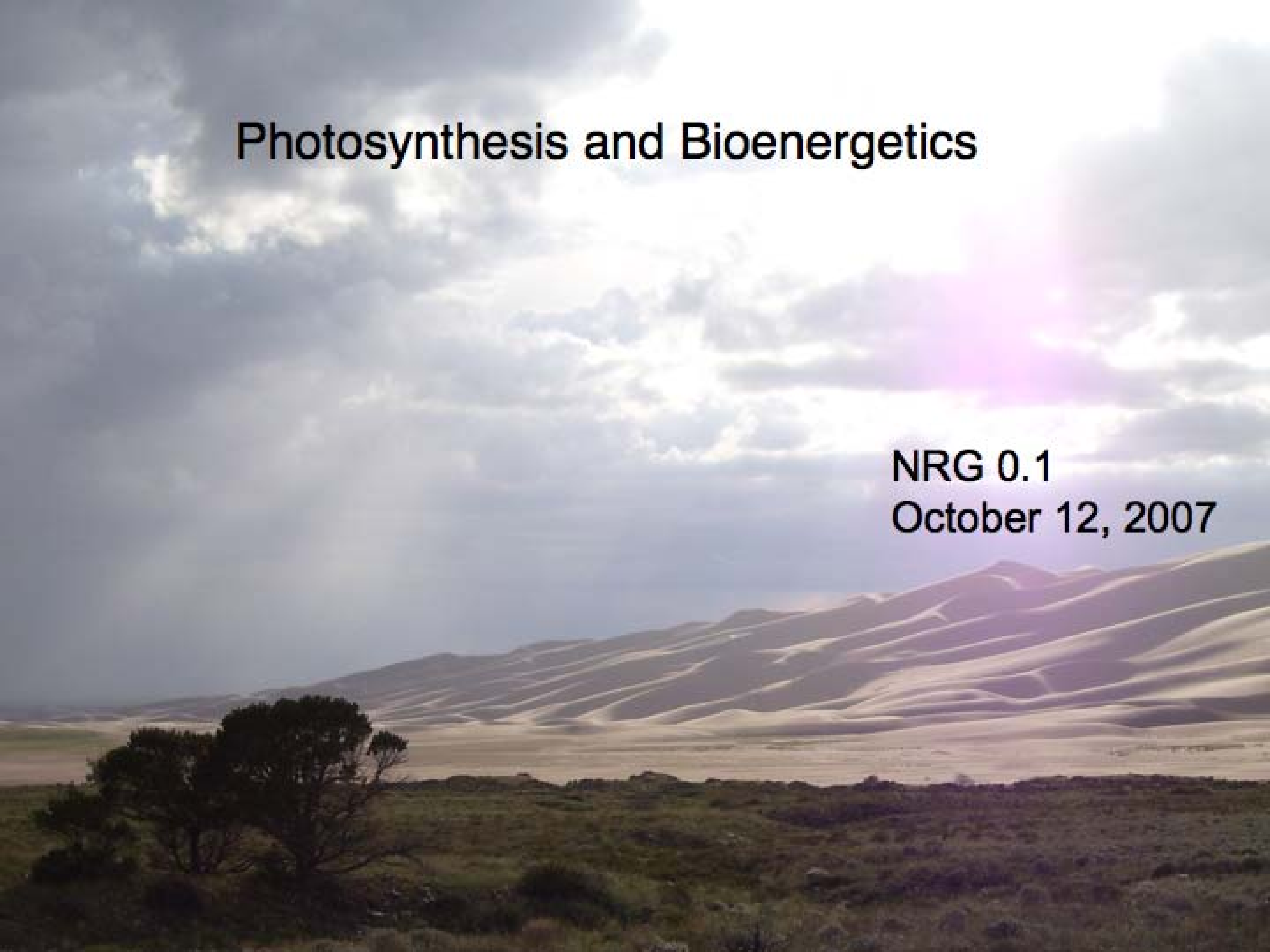
Photosynthesis and Bioenergetics

NRG 0.1
October 12, 2007



Outline of talk

I. Introduction to photosynthesis

II. Reaction centers and photosystems

III. CO_2 fixation

IV. Efficiency of photosynthesis

V. Questions and challenges

I. Introduction to Photosynthesis

What is photosynthesis?

“Photosynthesis is a process in which light energy is captured and stored by an organism, and the stored energy is used to drive cellular processes”

R. Blankenship “Molecular Mechanisms of Photosynthesis”

“The Wheat Problem”
Crookes (1900)

In 1898, Sir William Crookes, from a comparison of the rates for the production and the consumption of wheat, concluded that the “wheat-producing soil is totally unequal to the strain put upon it”, so that “England and all civilized nations stand in deadly peril of not having enough to eat.” The time scale for famine was estimated to be ~30 years.

The yield of wheat was limited by nitrogen in soil; the main sources of “fixed” nitrogen were sodium nitrate deposits in Chile.
(These deposits were subsequently claimed to last 200 years and the earlier estimates were “alarmist”).

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Crookes' charge: "It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may be turned into plenty" by developing a synthetic method to fix nitrogen.

Within 15 years, F. Haber had developed a catalytic system for reduction of N_2 to NH_3, subsequently industrialized by C. Bosch.

Photosynthesis

general reaction (van Niel)

acceptor A	$h\nu$	A^- $\longrightarrow$	reductant (donates electrons)
donor D	$\longrightarrow$ charge sep.	D^+ $\longleftarrow$	oxidant (accepts electrons)

oxygenic photosynthesis

$$nH_2O + nCO_2 + h\nu \leftrightarrow (CH_2O)_n + nO_2$$

A^- reduces CO_2 to carbohydrates $(CH_2O)_n$

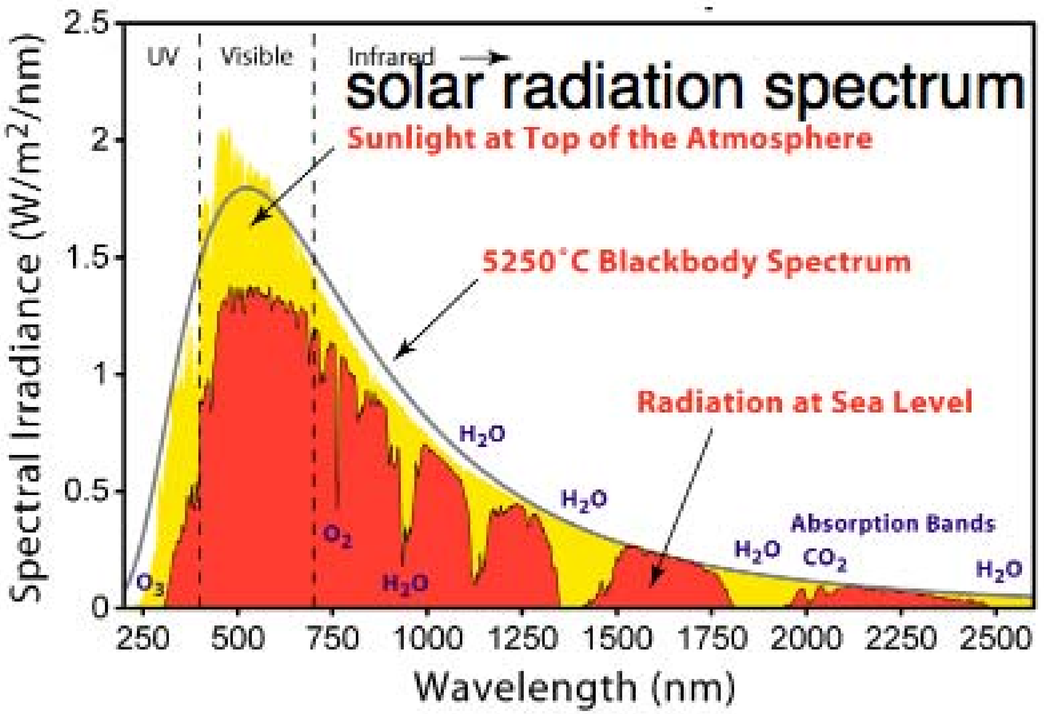
D^+ oxidizes H_2O to O_2

photosynthesis is effectively the reverse of respiration:

$$\text{glucose } (C_6H_{12}O_6) + 6O_2 \leftrightarrow 6CO_2 + 6H_2O$$

$$\Delta G^\circ = -2870 \text{ kJ/mole}$$

Energetic considerations



photon energy $= h\nu = hc/\lambda$ for a single photon

$= N_A hc/\lambda$ for one mole of photons (1 einstein)

$= 1.20 \times 10^5/\lambda$ kJ mol^{-1} $= 1.24 \times 10^3/\lambda$ eV (with λ in nm)

for $\lambda = 500$ nm, E = 240 kJ mol^{-1} = 2.5 eV

http://en.wikipedia.org/wiki/Image:Solar_Spectrum.png

Energetic requirements for living organisms

Typical basal metabolic rates ~1-10 W kg^{-1}
(minimum and maximum ~ 0.1 to 10^3 W kg^{-1})

Makarieva *et al. Proc. R. Soc.* **B272**, 2219 (2005)

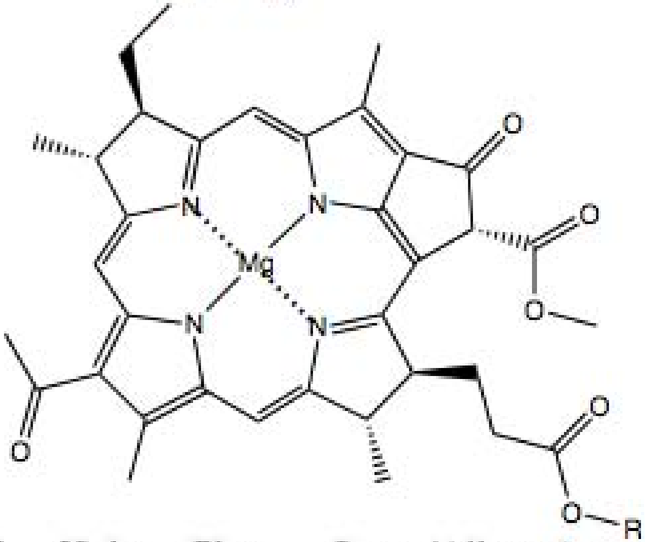
Average solar power at earth's surface ~ 164 W m^{-2}

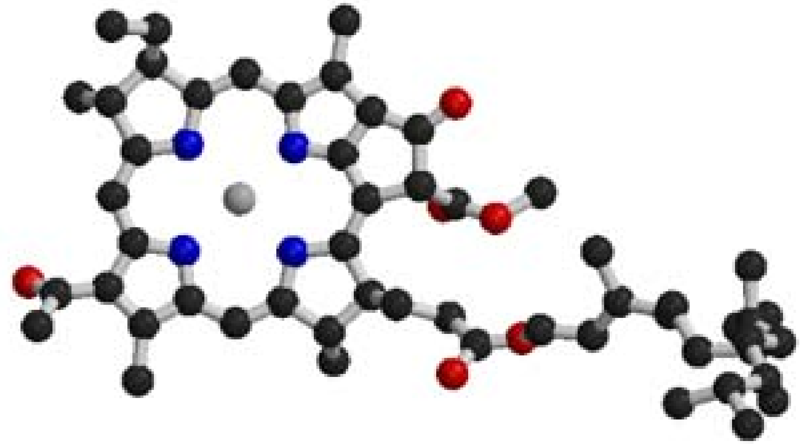
Ristinen and Kraushaar, "Energy and the Environment"

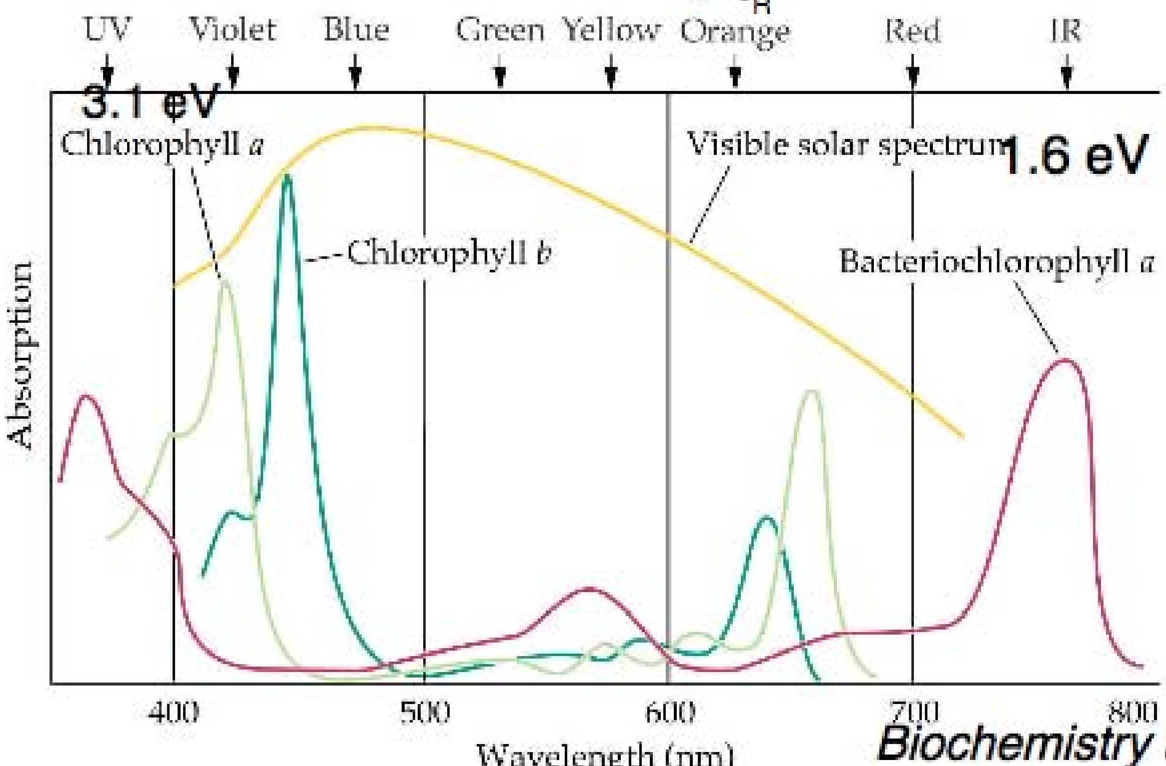
For a 1 μm microorganism (mass ~ 10^{-15} kg),
the basal metabolic rate ~ 10^{-14} W

the average incident solar power on organism~10^{-10} W
is more than sufficient to satisfy the metabolic needs

Chlorophyll: structure and absorption spectrum

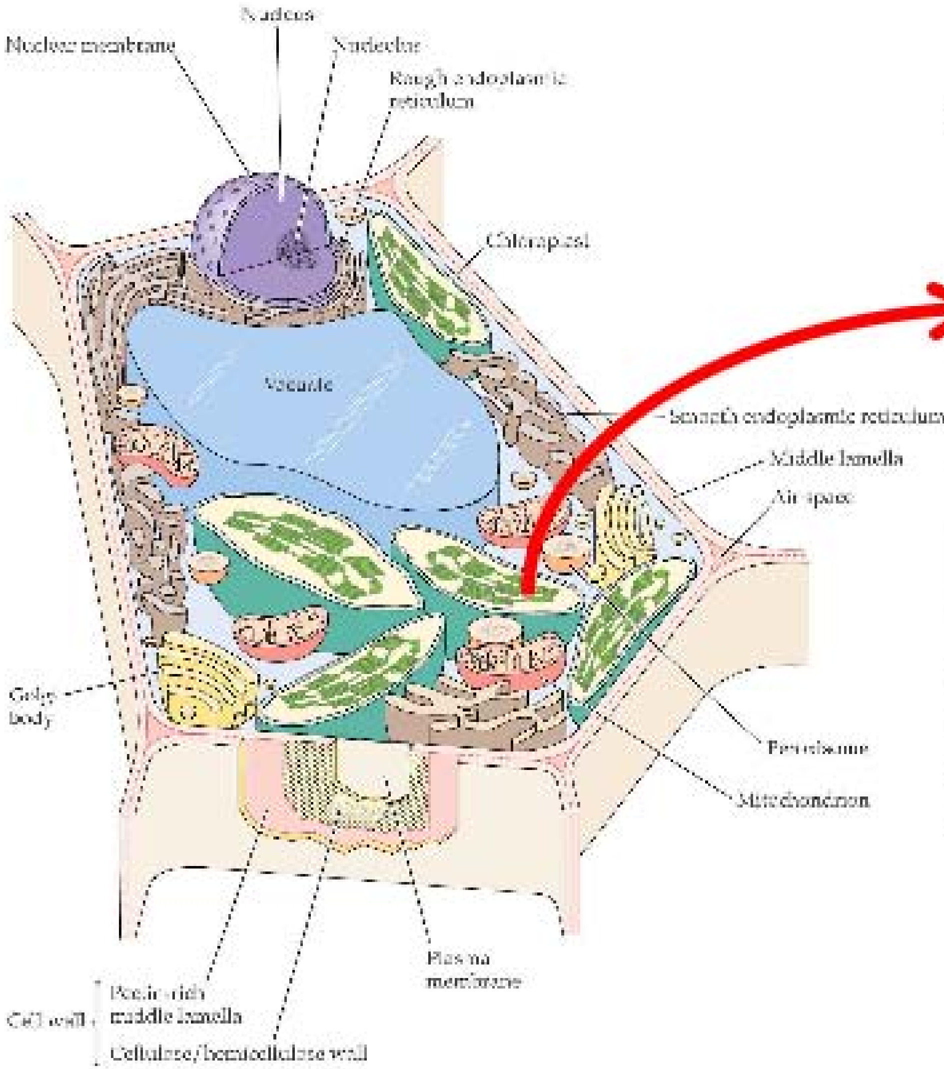




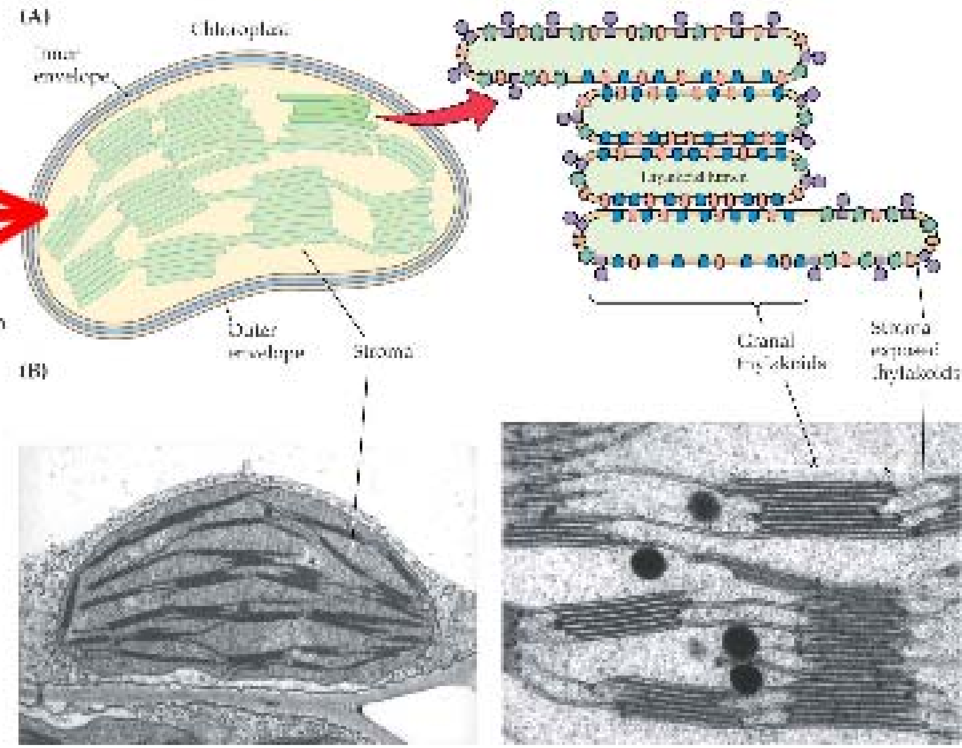


Buchanan, Gruissem, Jones
Biochemistry and Molecular Biology of Plants

Organization of photosynthetic plant cells



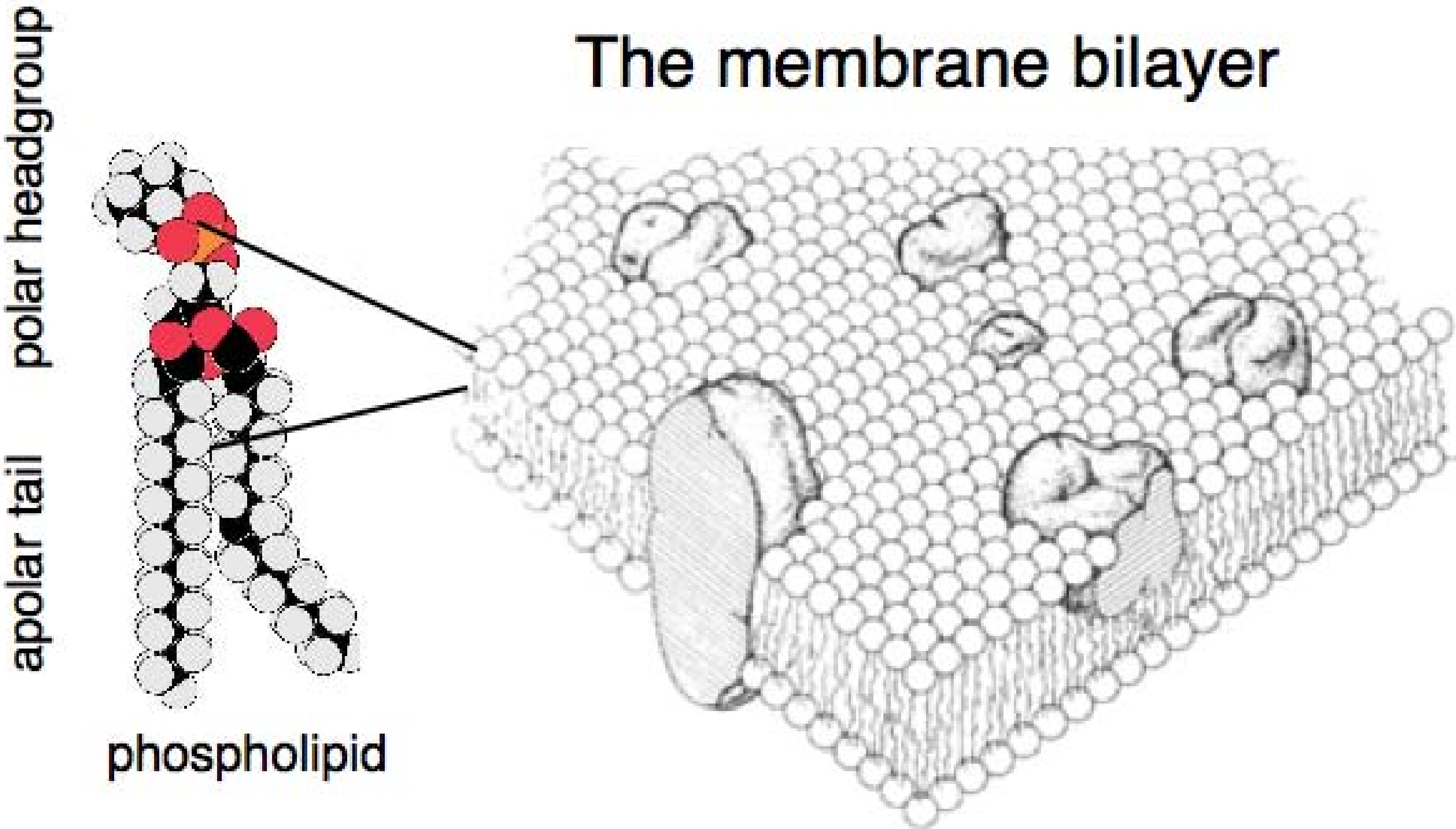
chloroplasts



Buchanan, Gruissem, Jones

Biochemistry and Molecular Biology of Plants

The membrane bilayer



S.J. Singer's fluid mosaic model *Science* **175**, 720 (1972)

Cells and organelles are surrounded by lipid-containing membrane bilayers; photosynthetic cofactors will partition into the apolar interior that is largely impermeable to water and ions. Membrane proteins embedded in the bilayer are responsible for photosynthesis, transport and many other biological functions.

II. Reaction centers and photosystems

THE PHOTOCHEMICAL REACTION IN PHOTOSYNTHESIS

and

A SEPARATION OF THE REACTIONS IN PHOTOSYNTHESIS BY MEANS OF INTERMITTENT LIGHT

By ROBERT EMERSON AND WILLIAM ARNOLD

(From the Kerckhoff Laboratories of Biology, California Institute of Technology, Pasadena)

chlorophyll organized into photosynthetic units, with one O_2 produced (one CO_2 reduced) per 2480 chl

photosynthesis involves a light reaction capable of proceeding at great speed and a dark reaction which involves a relatively long time to run its course.

Emerson later showed ~0.1 CO_2 reduced / absorbed photon

J. Gen. Physiol. **15**, 391 and **16**, 191 (1932)

Photosynthetic bacteria: the model organism

PURPLE BACTERIA

The behavior of these colored microorganisms in the presence or absence of light is a simple means of studying the basic mechanism by which living things react to their environment

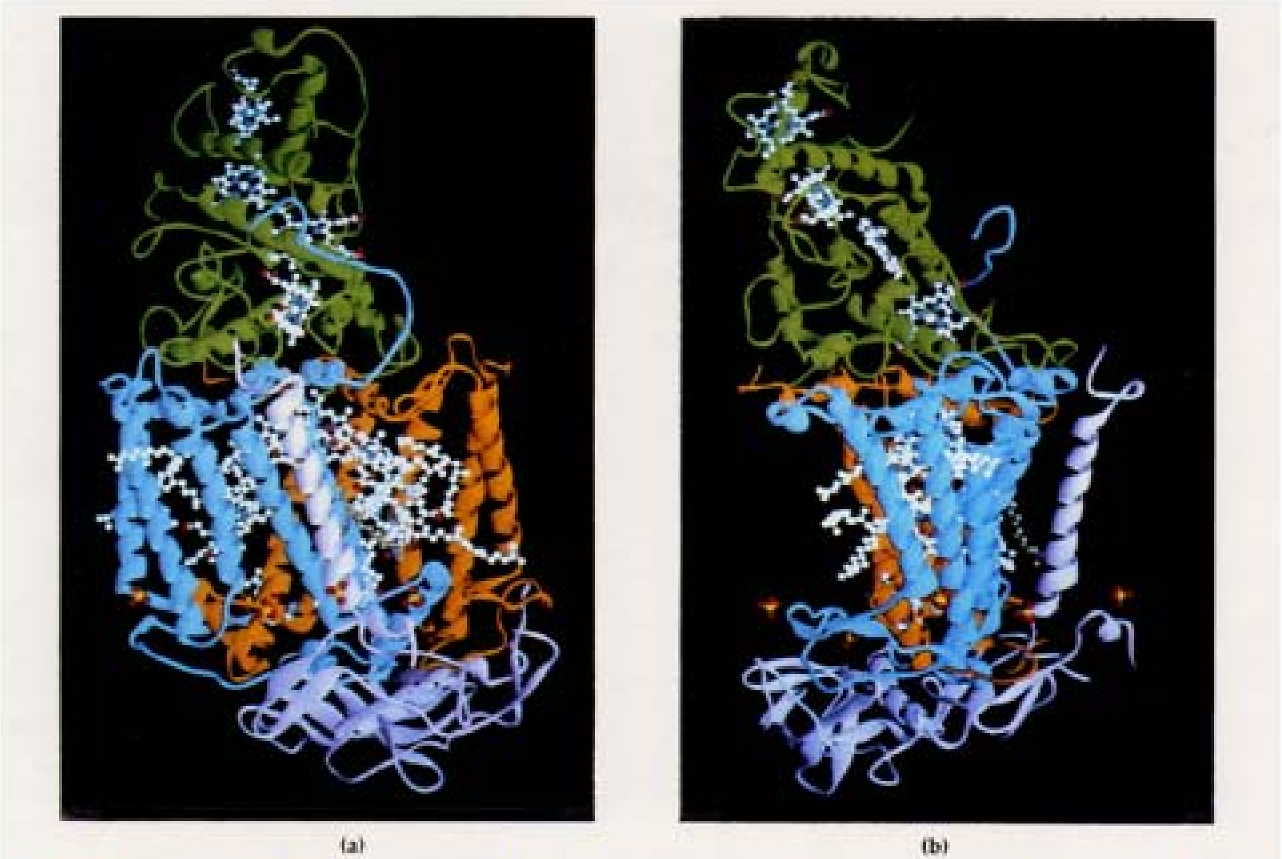
by Roderick K. Clayton and Max Delbrück

Scientific American, Nov. 1951 pp. 68-72

Clayton was Delbrück's first Caltech graduate student (Physics)

Clayton later isolated reaction centers (RC) as discrete chemical entities from the purple photosynthetic bacteria *Rb. sphaeroides*, which served as the "hydrogen atom" of photosynthesis

The first high resolution membrane protein structure
Rps. viridis photosynthetic reaction center



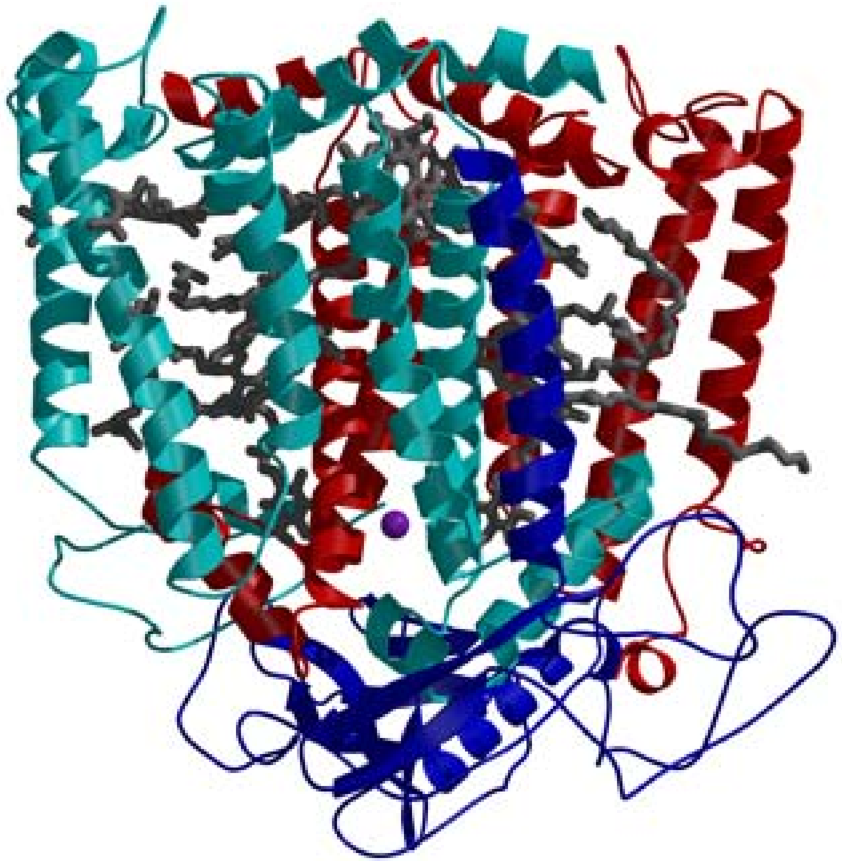
L, M, and H membrane-spanning subunits, with photosynthetic cofactors and attached cytochrome

Deisenhofer, Michel, Huber, *et al. JMB* **180**, 385 (1984)
Nature **318**, 618 (1985)

Rb. sphaeroides photosynthetic reaction center (RC)

three subunits: L, M and H

view in plane of membrane



A

PDB IDs 2PRC; 1AIJ

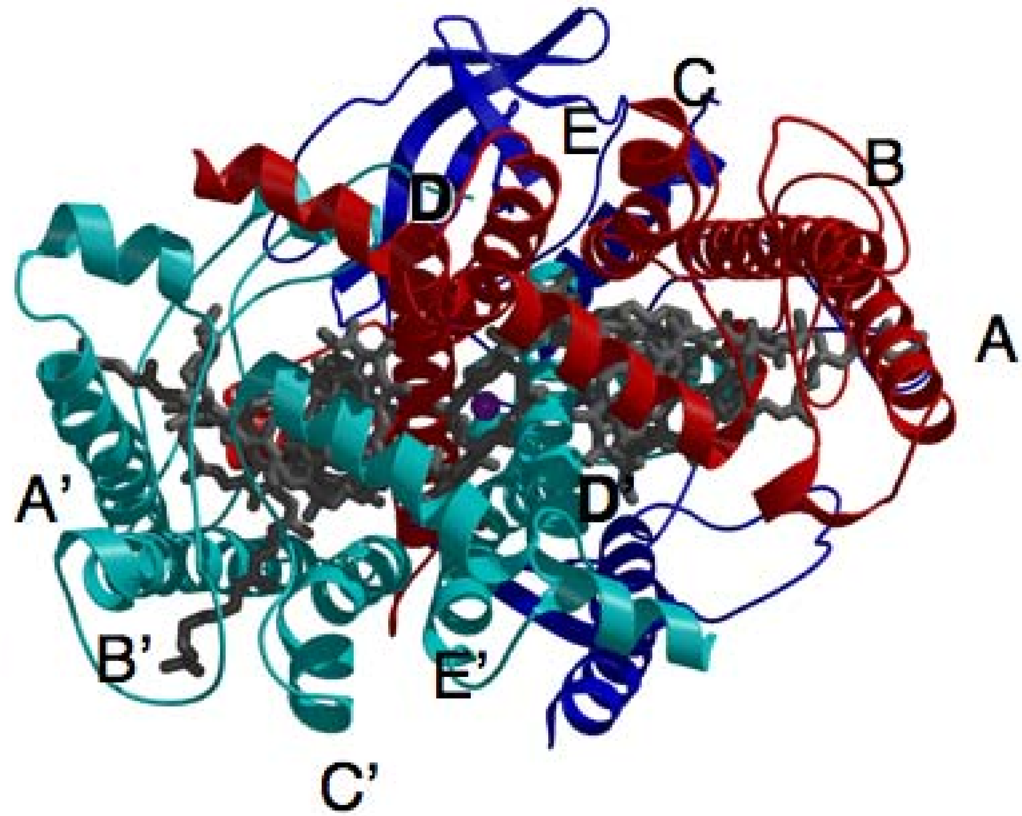
G. Feher

Rb. sphaeroides photosynthetic reaction center (RC)

three subunits: L, M and H

view in plane of membrane

view down membrane normal

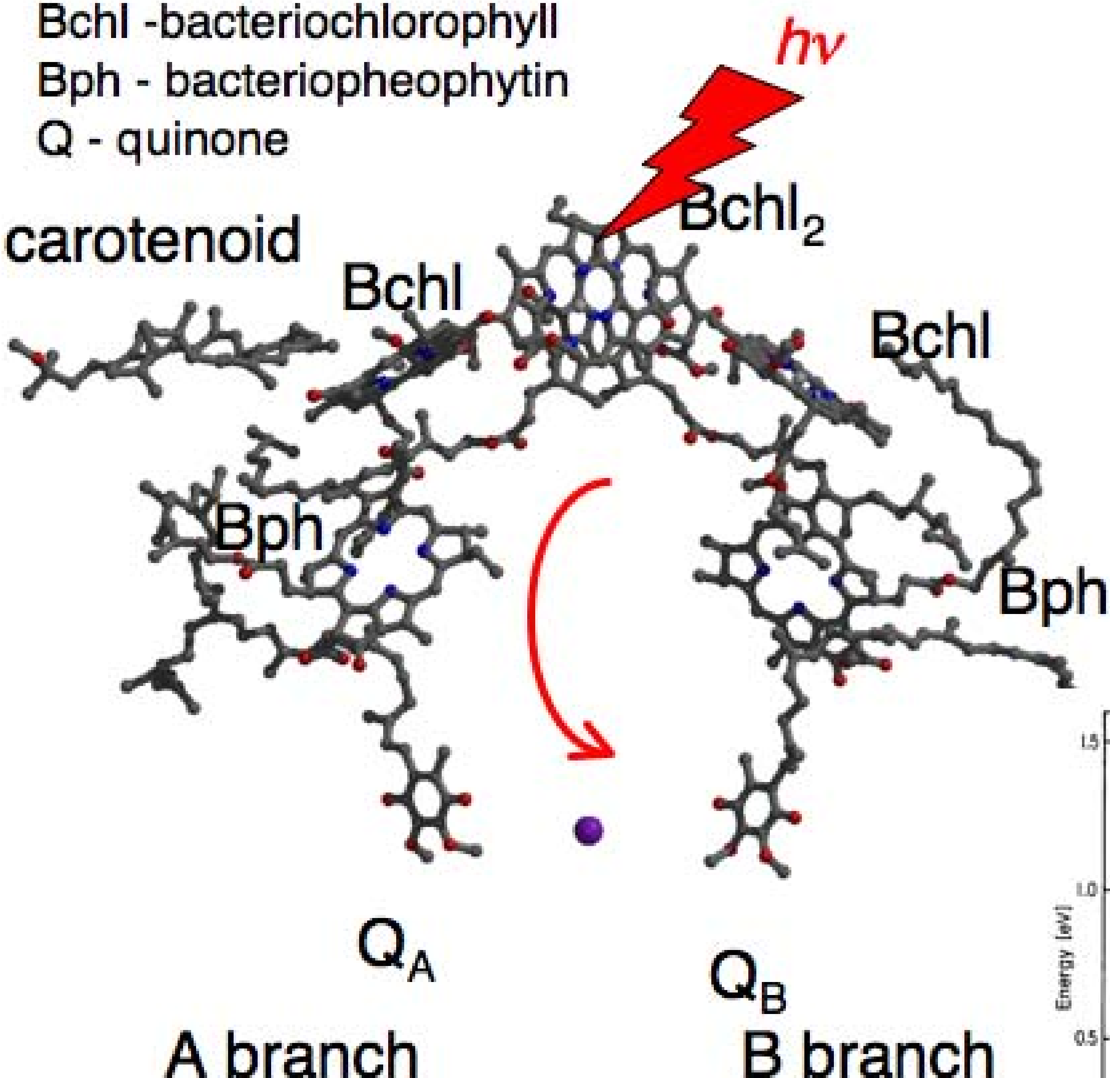


PDB IDs 2PRC; 1AIJ

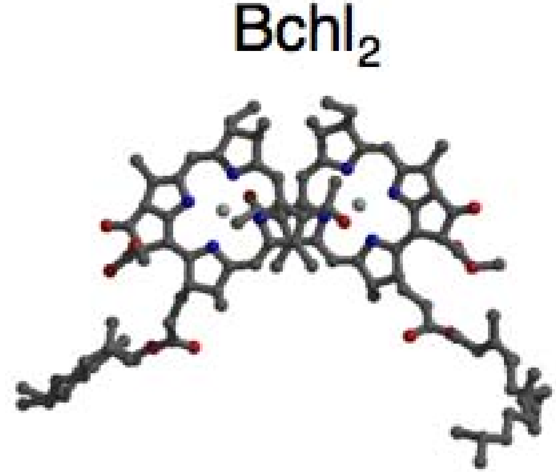
G. Feher

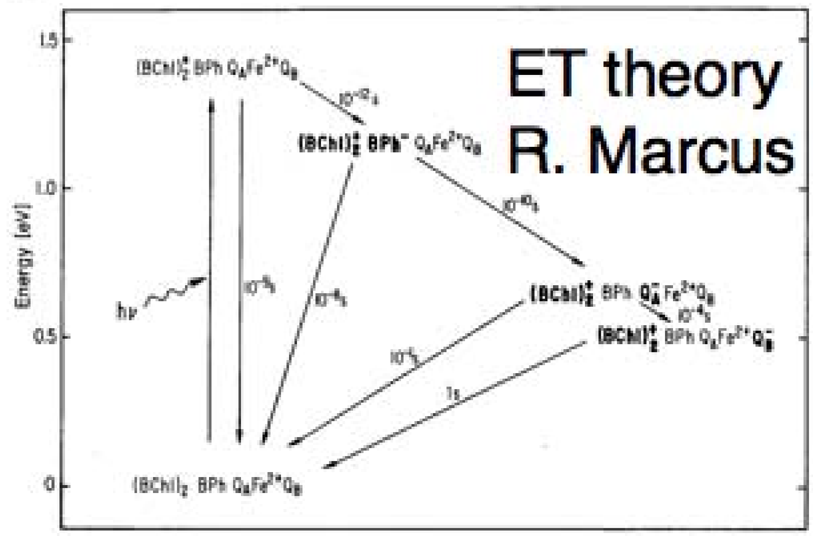
organization of cofactors in the RC

Bchl -bacteriochlorophyll
Bph - bacteriopheophytin
Q - quinone



Feher *et al.* *Nature* **339**, 111 (1989)





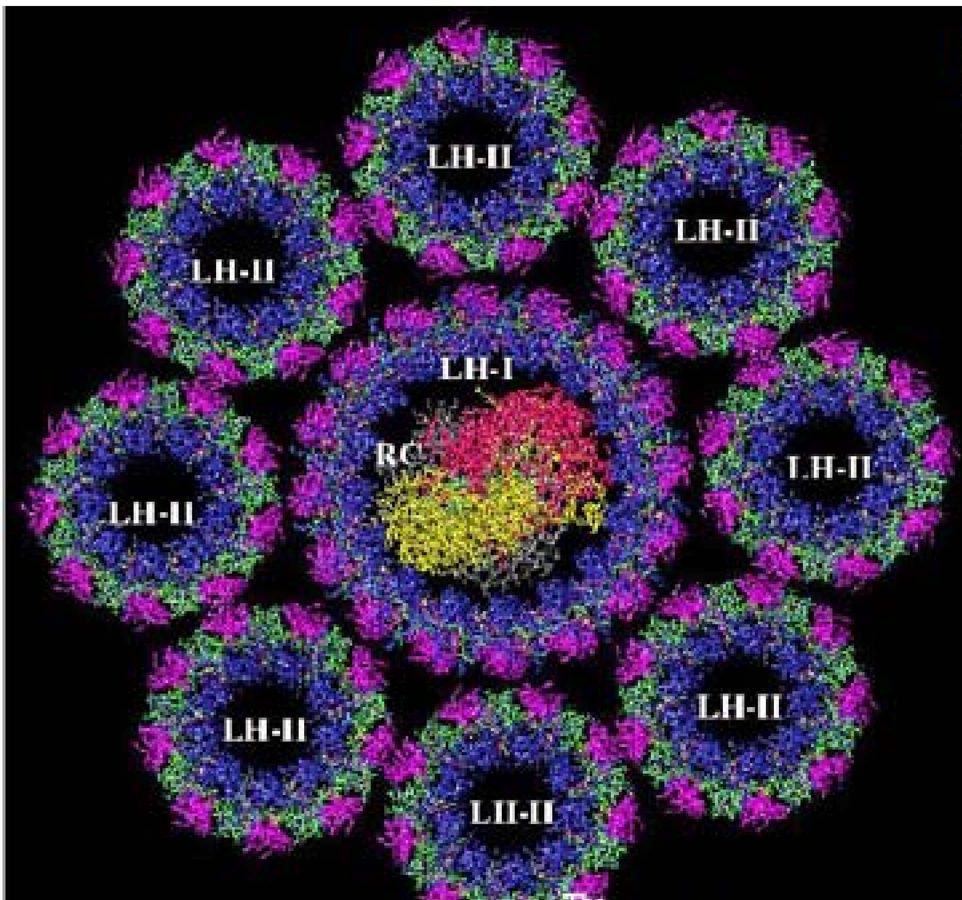
organization of photosynthetic membranes

incident solar radiation ~1 photon/RC/sec

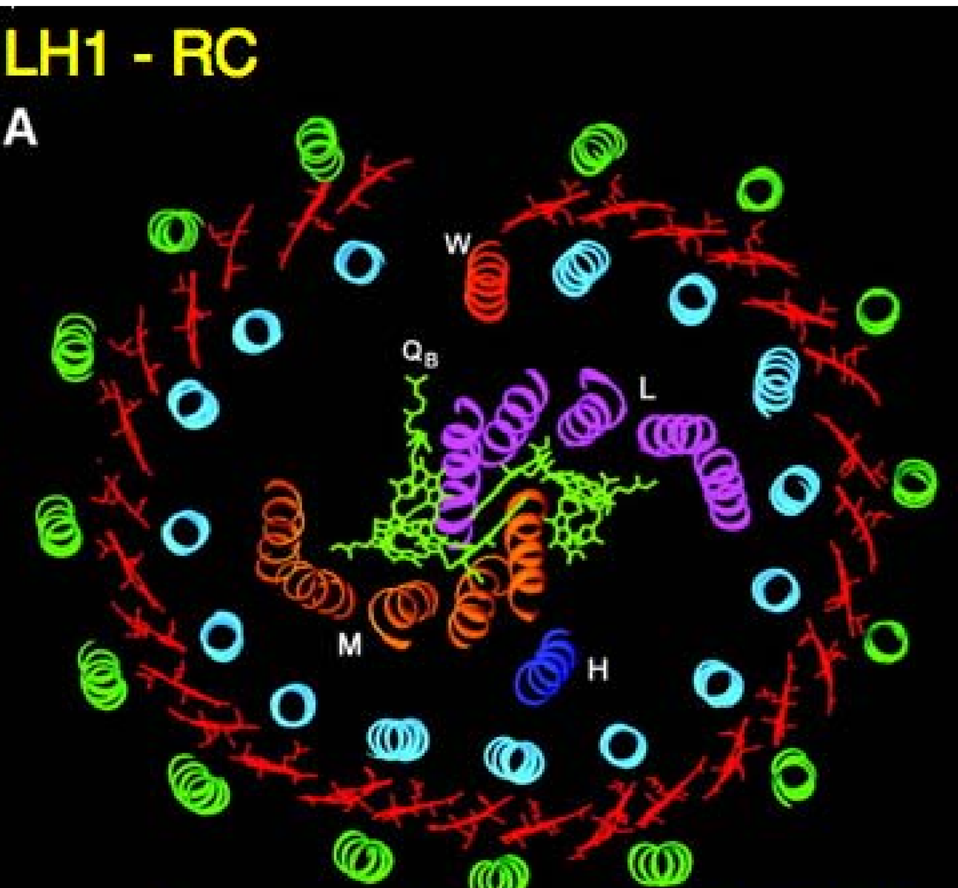
the cycling time for the RC is ~ 10^{-3} sec;

light harvesting/antennae complexes to funnel light to the RC

represent most of the “2480” chlorophylls / photosynthetic unit



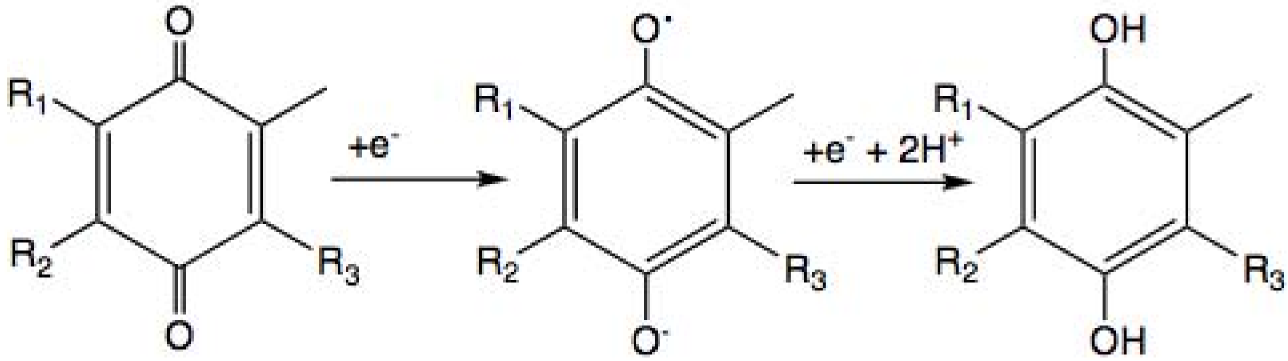
http://www.ks.uiuc.edu/Research/psu/PSU_ring.jpg



Roszak et al. Science 302, 1969 (2003)

Quinones: the final acceptor in bacterial RCs

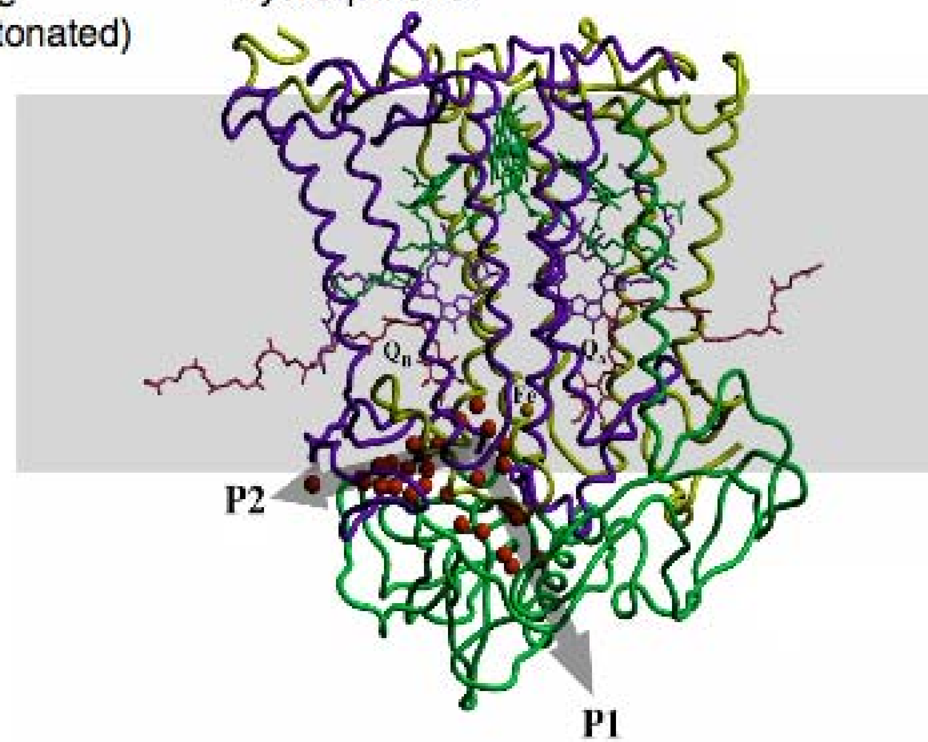
lipid soluble carriers of electrons and protons



oxidized quinone (Q_{10})

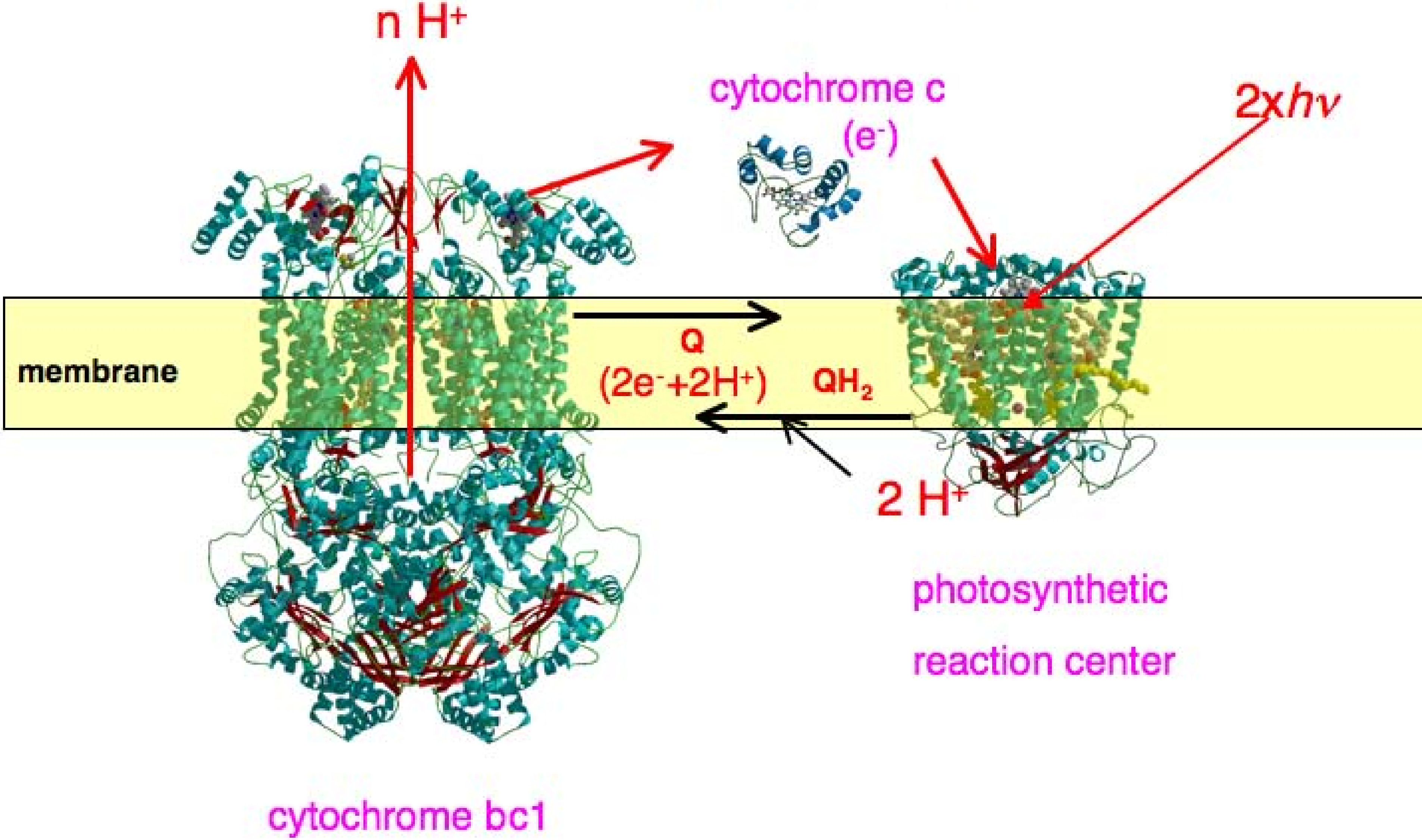
semiquinone (can be protonated)

hydroquinone



Stowell *et al.* *Science* **276**, 812 (1997)

Electron transfer circuitry in photosynthetic bacteria



overall stoichiometry of bacterial photosynthesis

RCs take up one H^+ from the cytoplasm per electron (and photon)

in cytochrome bc_1, one H^+ is taken up from the cytoplasm, but two H^+ are released to the periplasm, per electron.

net: $2H^+$ are translocated across the membrane per electron

ie - a pH gradient is generated across the membrane

reducing equivalents for biosynthesis are not generated by this cyclic process

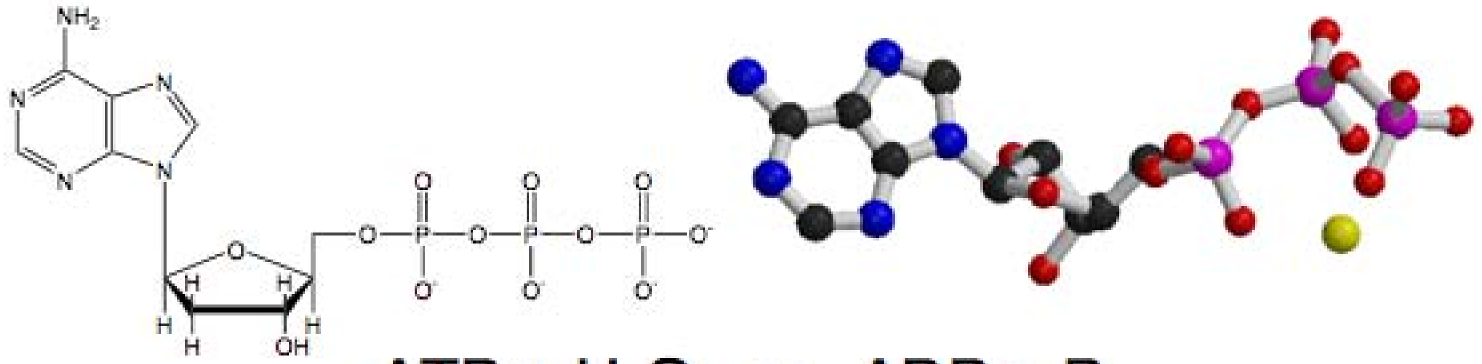
(photosynthetic bacteria use H_2, H_2S, or reduced organic compounds as metabolic reductants)

Proton gradients and ATP synthesis

Peter Mitchell (1961) proposed a chemiosmotic model where the energy released during photosynthesis (and respiration) is stored in a proton gradient across the membrane

$$\Delta\mu_{H^+} = \mu_{H^+_{in}} - \mu_{H^+_{out}} = RT\ln\frac{a_{H^+,in}}{a_{H^+,out}} + F\left(\Phi_{in} - \Phi_{out}\right) \equiv -2.303RT\Delta pH + F\Delta\Phi$$

This gradient can be used to generate adenosine triphosphate (ATP), the “energy currency” of cells, which has a favorable ΔG of hydrolysis

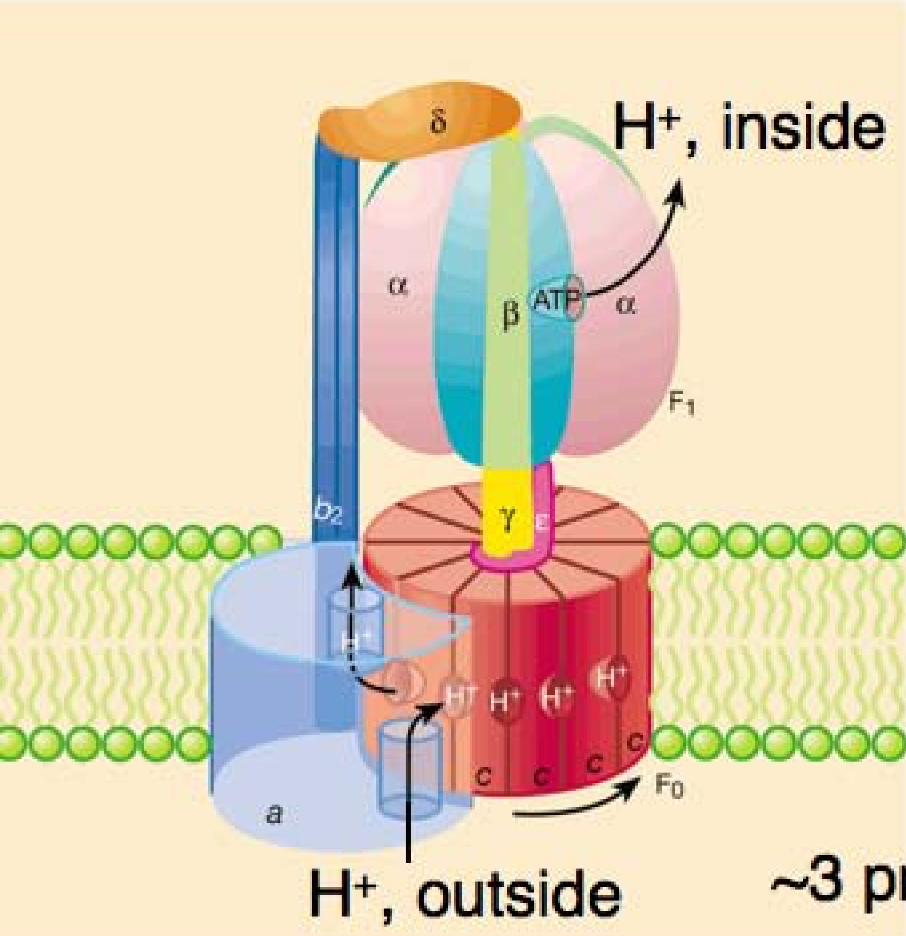


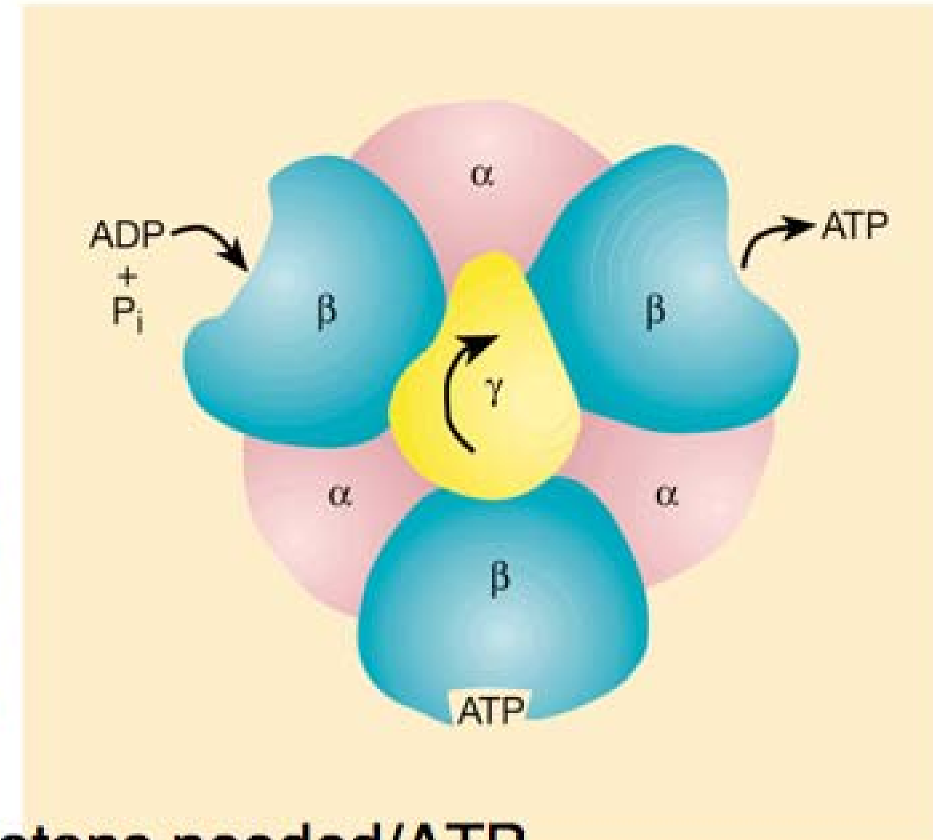
$$ATP + H_2O \leftrightarrow ADP + P_i$$

$\Delta G^{\circ\prime} \sim -30$ kJ mole^{-1} and $\Delta G' \sim -50$ kJ mole^{-1}

$\Delta\mu_{H+} \sim 15\text{-}20$ kJ mol^{-1}, so that ATP synthesis requires ≥ 3 H^+

ATP synthase: the protein responsible for the synthesis of ATP coupled to flux of protons across the membrane





~3 protons needed/ATP

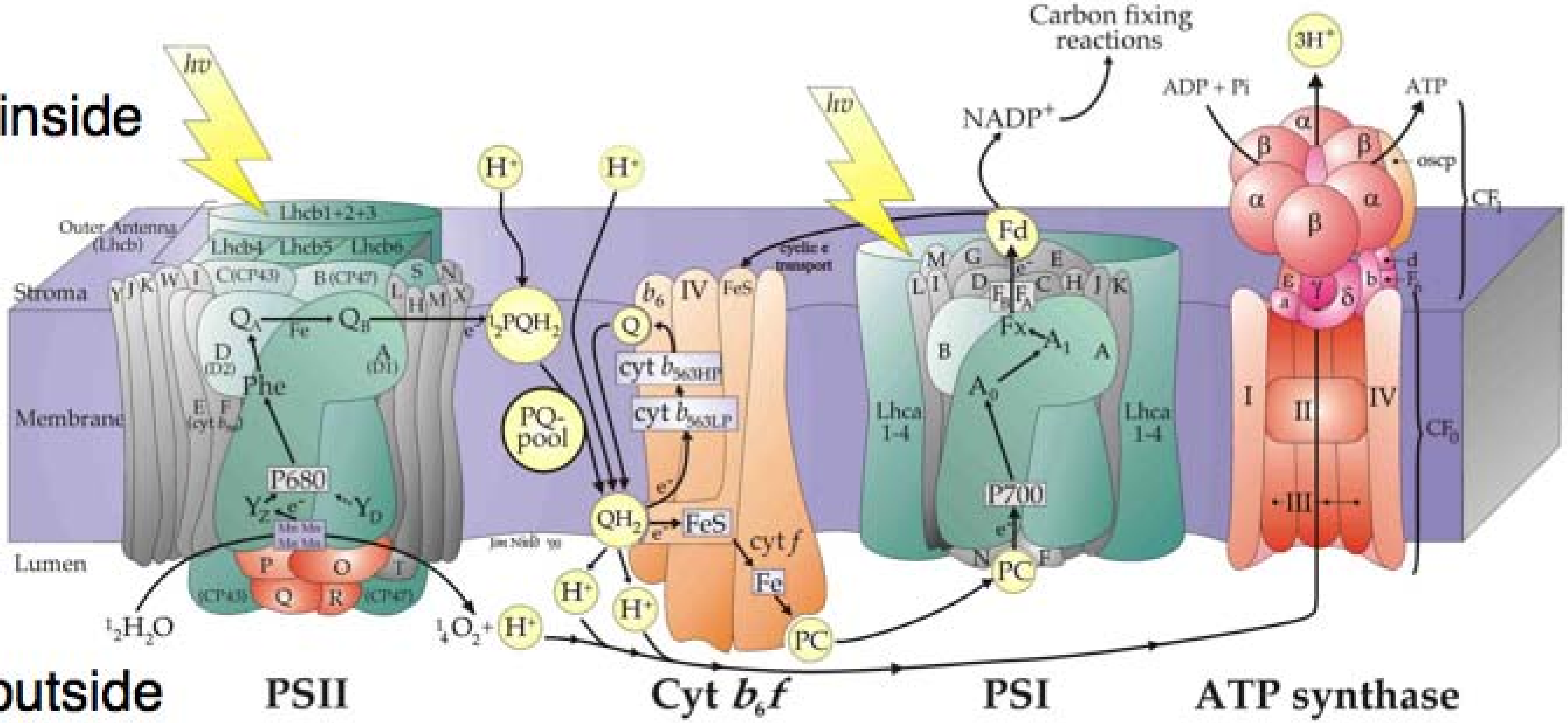
Paul Boyer and John Walker

movie of single F1 ATP synthase with fluorescent actin label

http://www.res.titech.ac.jp/~seibutu/projects/fig/f1rot_2.mov

Yoshida laboratory, Noji *et al.* *Nature* **386** 299-302 1997

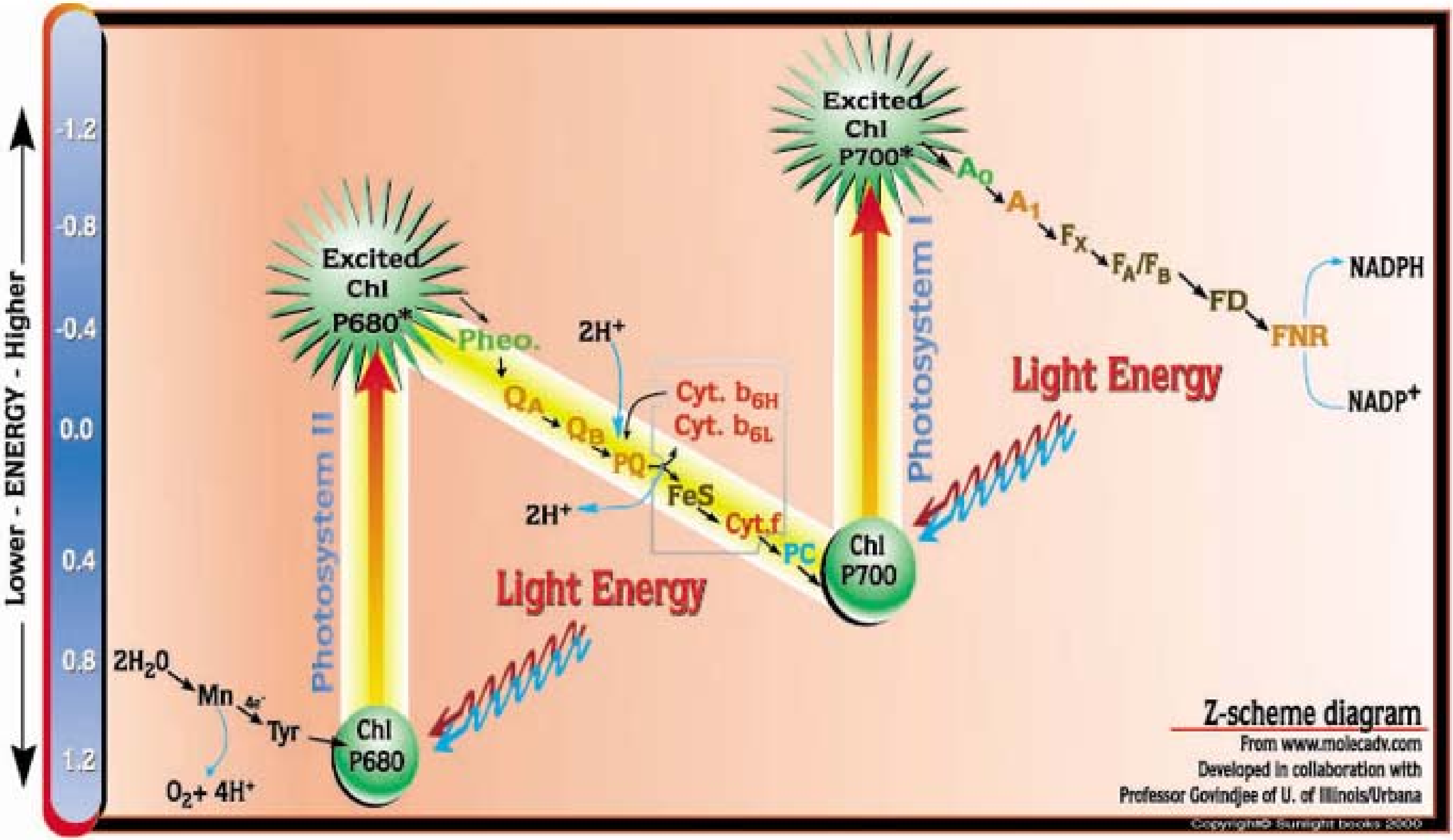
Photosynthesis in plants: two photosystems PSI and PSII



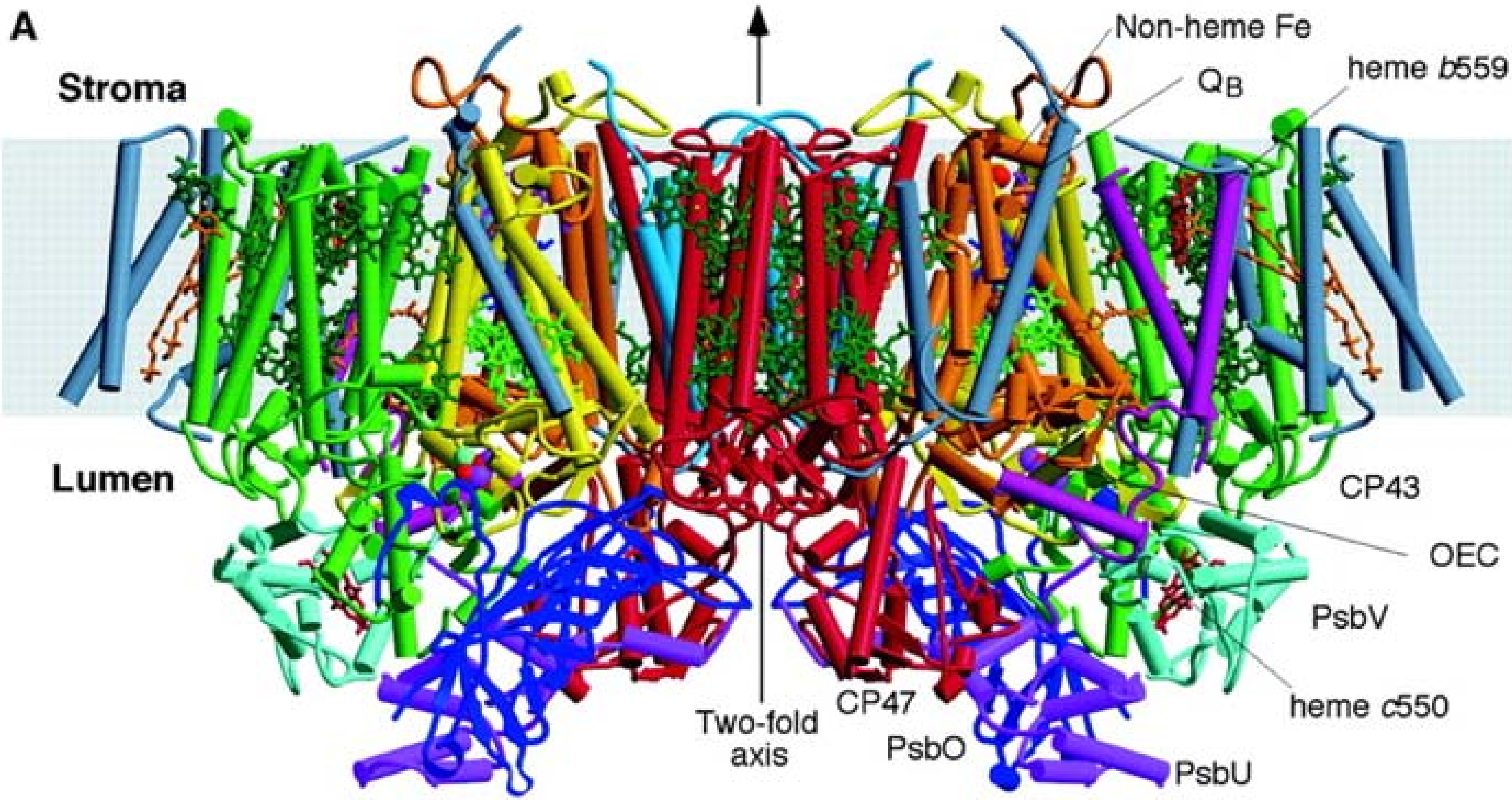
PSI and PSII are linked in a non-cyclic fashion to generate an H^+ gradient, reducing power (NADPH) and O_2

http://www.bio.ic.ac.uk/research/barber/photosystemII.html

Z-scheme for non-cyclic photosynthesis electron transfer

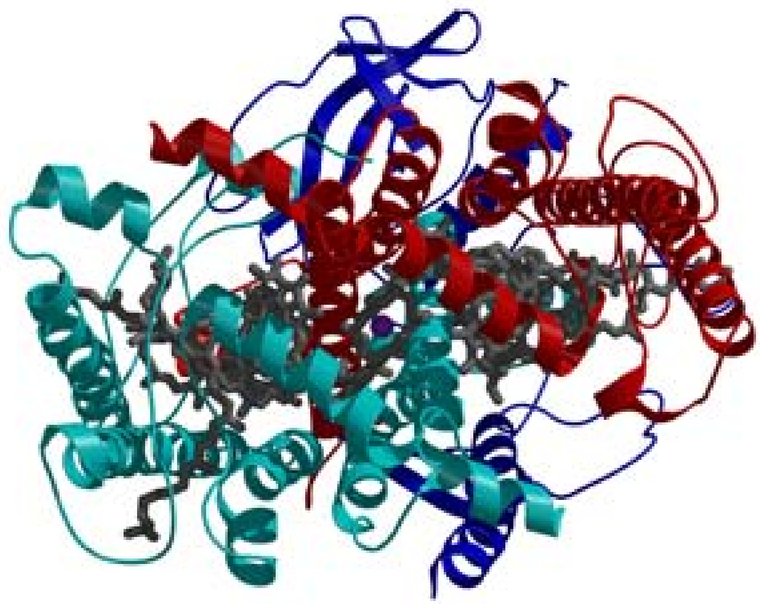


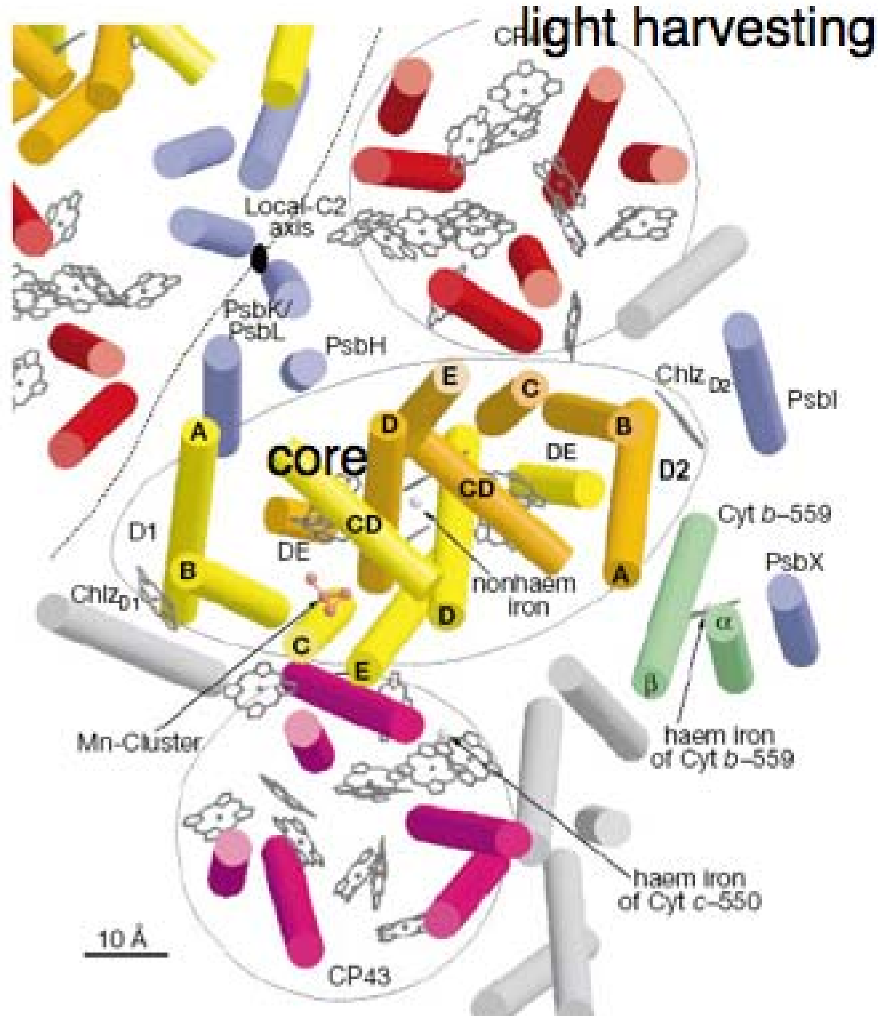
The structure of PSII from *Th. elongatus*



Ferreira, Iverson *et al.* *Science* **303**, 1831 (2004)

The core of PSII (also PSI) resembles the bacterial RC



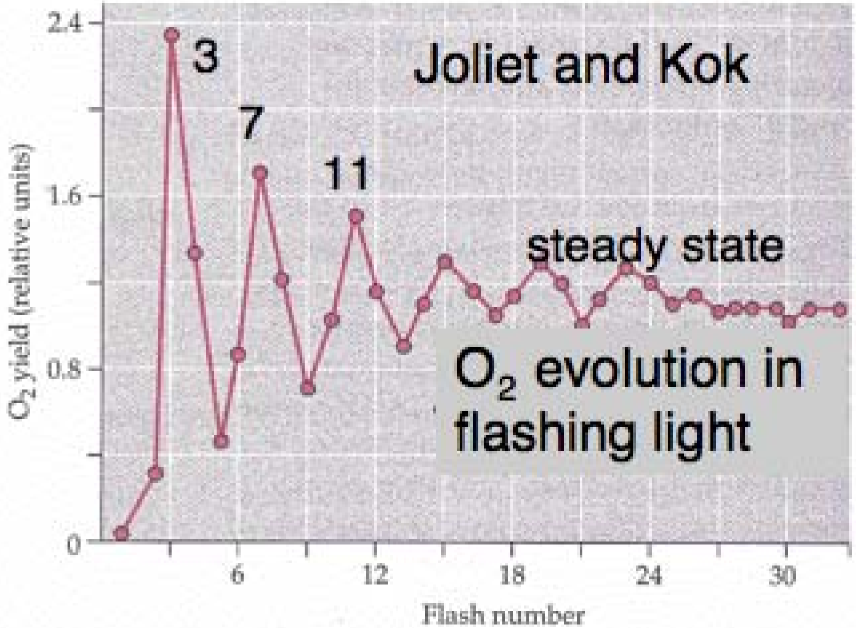


light harvesting

PDB ID 1FE1

Zouni et al Nature 409, 739 (2001)

Oxygen evolution during photosynthesis
the tetra-manganese O_2 evolving complex



Ferreira, Iverson *et al. Science* **303**, 1831 (2004)

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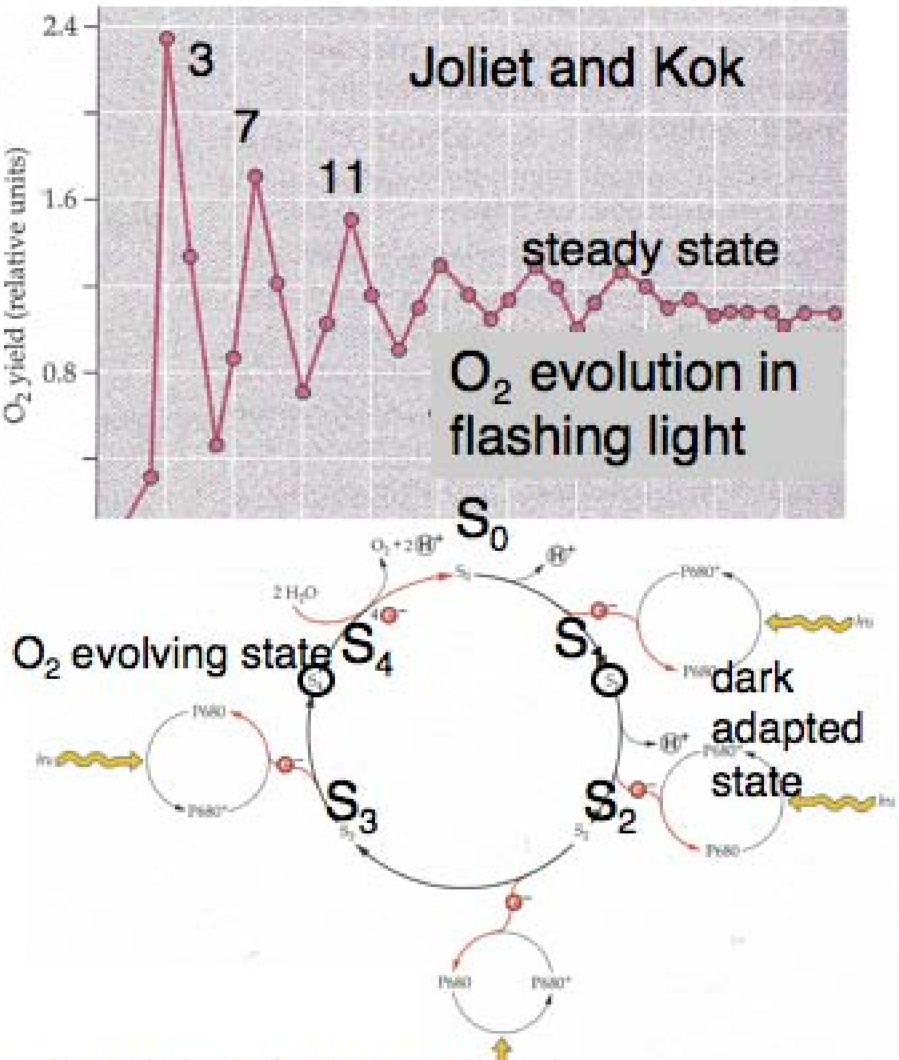

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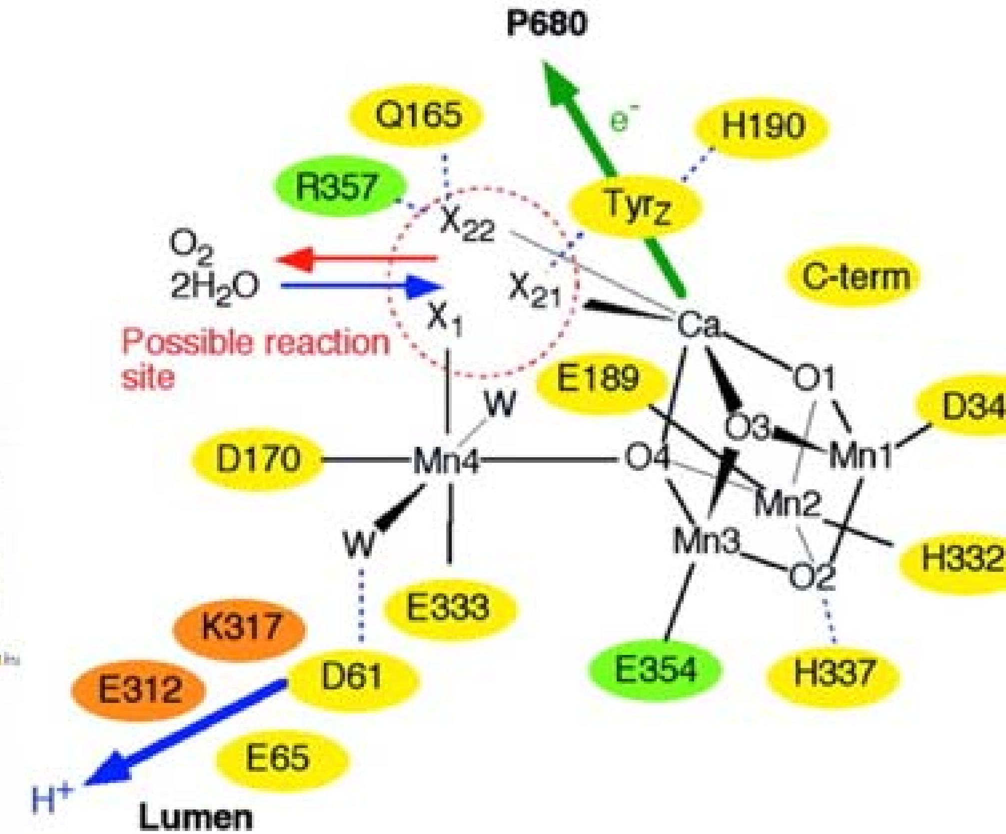


Ferreira, Iverson *et al. Science* **303**, 1831 (2004) net results of the light reactions in plant photosynthesis

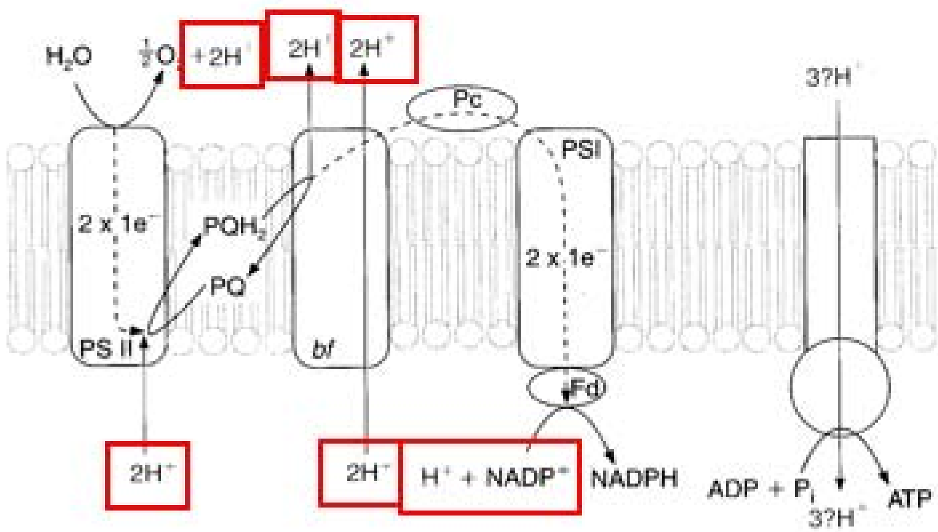
production of both H^+ gradient and reducing power (NADPH)

overall balanced reaction:

$$2H_2O + 2NADP^+ + 8h\nu \leftrightarrow O_2 + 2NADPH + 2H^+$$

this is a 4 electron process, with $2h\nu$ absorbed/electron

proton translocation stoichiometry:



net: $6H^+$ per 2 electrons; expect $\sim \leq 2$ ATP/NADPH

III. CO_2 fixation

The ATP and NADPH generated during photosynthesis are used to drive cellular processes

Of central significance is the ability to synthesize cellular materials using CO_2 as the carbon source

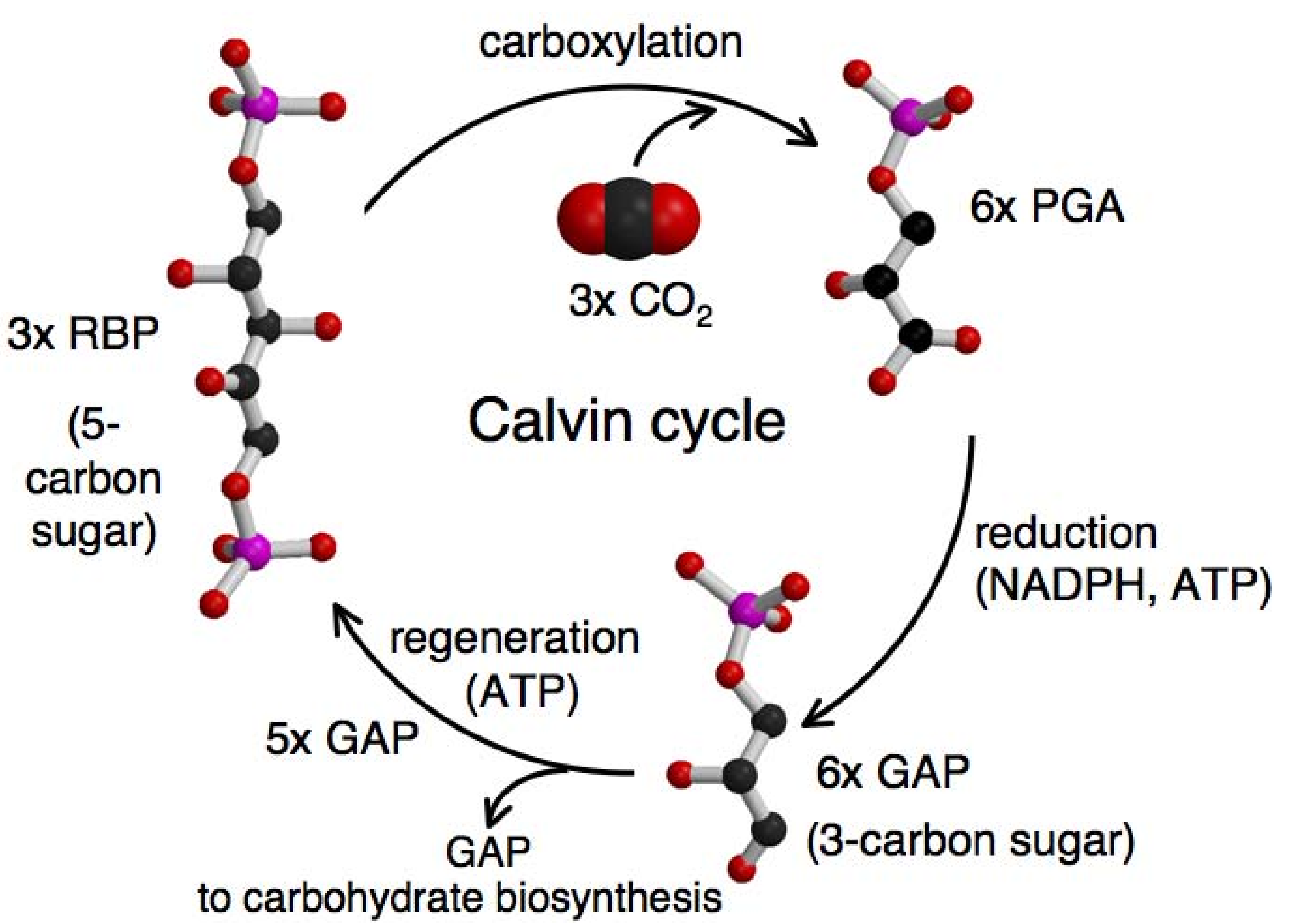
The Calvin cycle is the most important CO_2 fixation process:

$$6\ CO_2 + 18\ ATP + 12\ NADPH \rightarrow C_6H_{12}O_6$$

(per CO_2, 3 ATP, 2NADPH and 8 $h\nu$)

Availability of radioisotopes, especially ^{11}C and ^{14}C, revolutionized analysis of biological CO_2 fixation (and metabolic processes generally).

S. Ruben, M.D. Kamen, A. Benson


carboxylation
6x PGA
3x CO_2
3x RBP
(5-
carbon
sugar)
Calvin cycle
reduction
(NADPH, ATP)
regeneration
(ATP)
5x GAP
6x GAP
(3-carbon sugar)
GAP
to carbohydrate biosynthesis

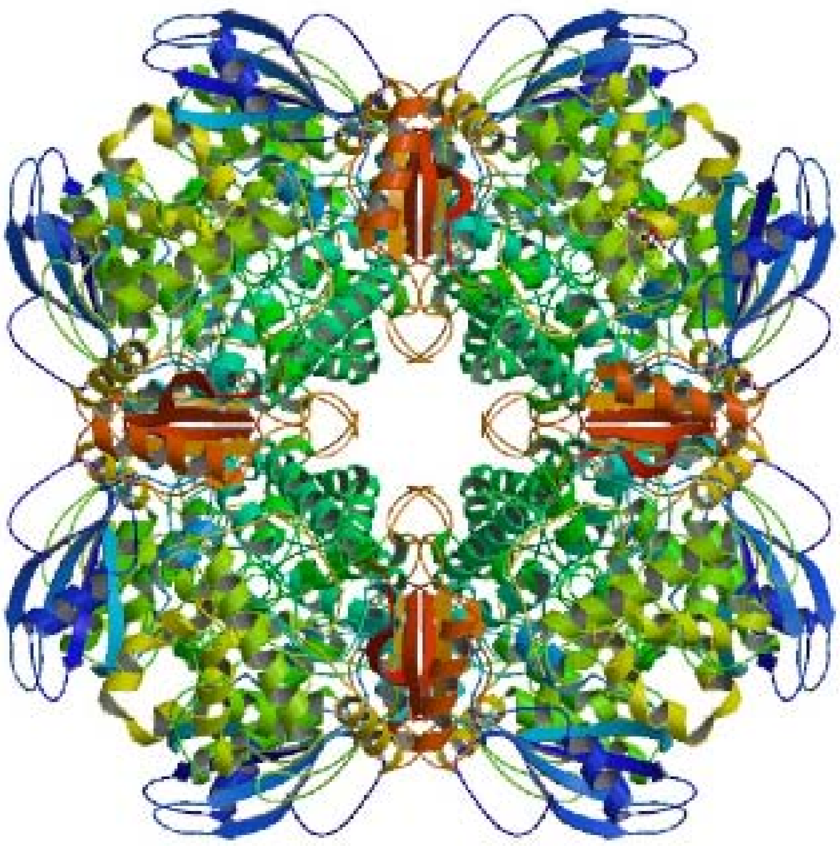
Ribulose bisphosphate carboxylase (rubisco):
the worlds most abundant protein (probably)

THE PROTEINS OF GREEN LEAVES

IV. A HIGH MOLECULAR WEIGHT PROTEIN COMPRISING A LARGE PART OF THE CYTOPLASMIC PROTEINS*

BY S. J. SINGER,† LUTHER EGGMAN, JEAN M. CAMPBELL, AND SAM G. WILDMAN‡

(From the Gates and Crellin Laboratories of Chemistry and the Kerckhoff Laboratories of Biology, California Institute of Technology, Pasadena, California)

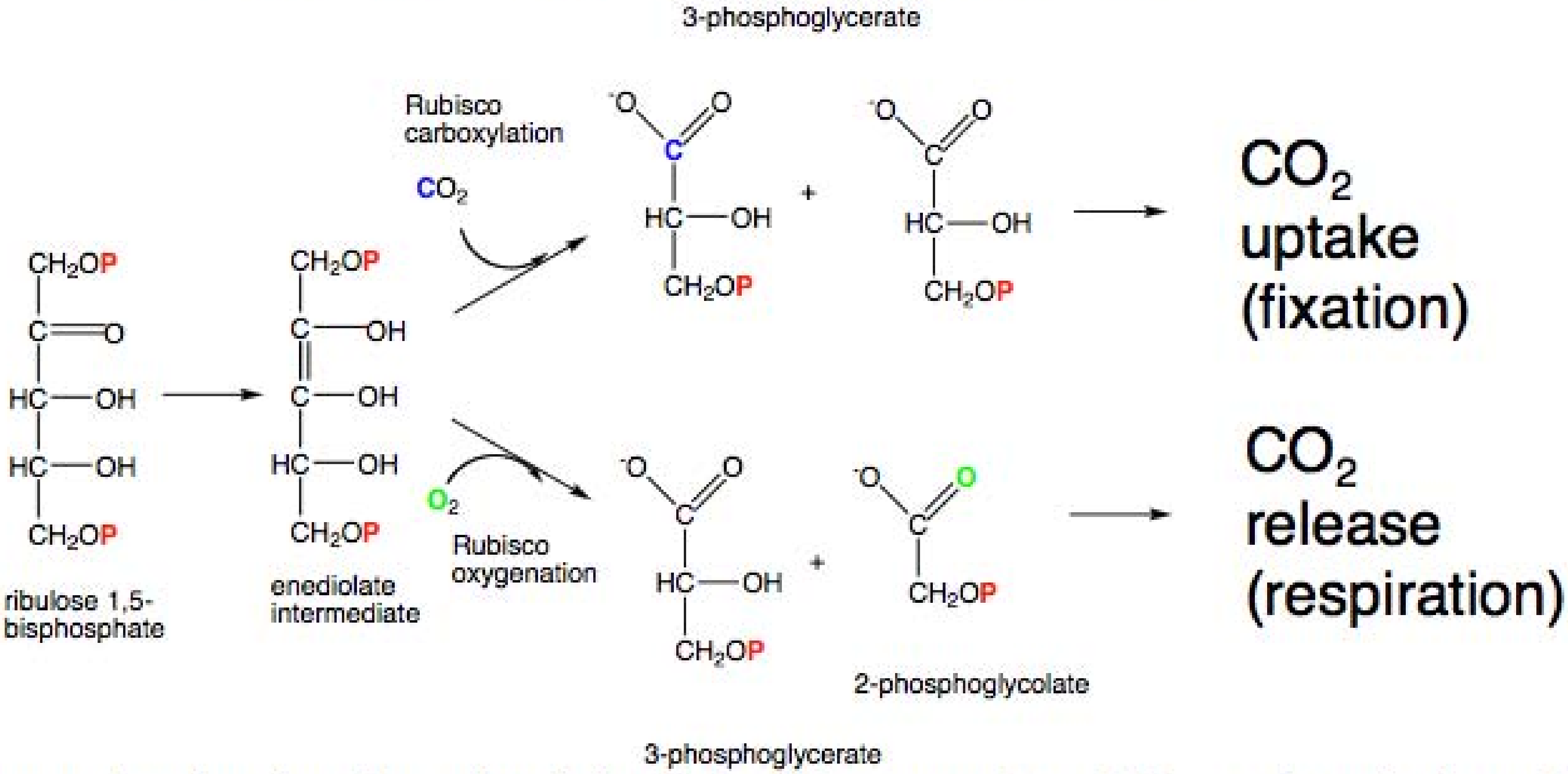


(*J. Biol. Chem.* **197**, 233 (1952))

PDB 1RLC
D. Eisenberg

photorespiration: reaction of O_2 with RuBP instead of CO_2

reduction of photosynthetic efficiency



photorespiration involves the light dependent uptake of O_2 and evolution of CO_2; ie it inhibits photosynthesis and increases the associated energy costs;under current atmospheric conditions, carboxylation:oxygenation = 3:1

in some systems, the photosynthetic efficiency is reduced by up to 50%
has motivated efforts to reduce RuBisCo oxygenation rates

IV. Efficiency of photosynthesis

energy required to synthesize basic CH_2O unit from CO_2 and H_2O:

$\sim -\Delta G^{\circ}$ glucose oxidation/6

$\sim$ 480 kJ/mole $\sim$ 5 eV

$\sim$ 8 photons of red light needed for each CH_2O unit

$\sim 8 * 1.7$ eV = 13.6 eV

5/13.6 $\sim$ 35% of absorbed photons

overall photosynthetic efficiency of incident radiation

~35% of absorbed radiation stored in CH_2O

~25% of incident sunlight in right wavelength range

~70% of incident sunlight is absorbed by dense foliage

total efficiency of incident radiation

$$\sim 0.35 \times 0.25 \times 0.70 = 6\%$$

conversion of solar energy to chemical energy stored in biomass

under normal conditions, efficiencies are much less;
the annual conversion efficiencies of crops such as corn, wheat, etc. (C3) are typically 0.1 - 0.4 %, while sugar cane (C4) can store up to 1% of the incident visible radiation.
Whitmarsh and Govindjee http://www.life.uiuc.edu/govindjee/paper/gov.html

V. Questions and Challenges

- mechanism of O_2 evolution by PSII
- improving the efficiency of rubisco
- energy transfer in light harvesting complexes
- how does photosynthesis work as a system?
- artificial photosynthesis

References

R. B. Buchanan, W. Gruissem, J.L. Jones "Biochemistry and Molecular Biology of Plants" (Wiley, 2002)

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J. Abelson "The Birth of Oxygen" Bull. American Academy, pp. 28-33, Spring (2007)

O. Morton "Eating the Sun: How Plants Power the Planet" (Fourth Estate, 2007)