Photosynthesis

Transition Metal Clusters in Biology

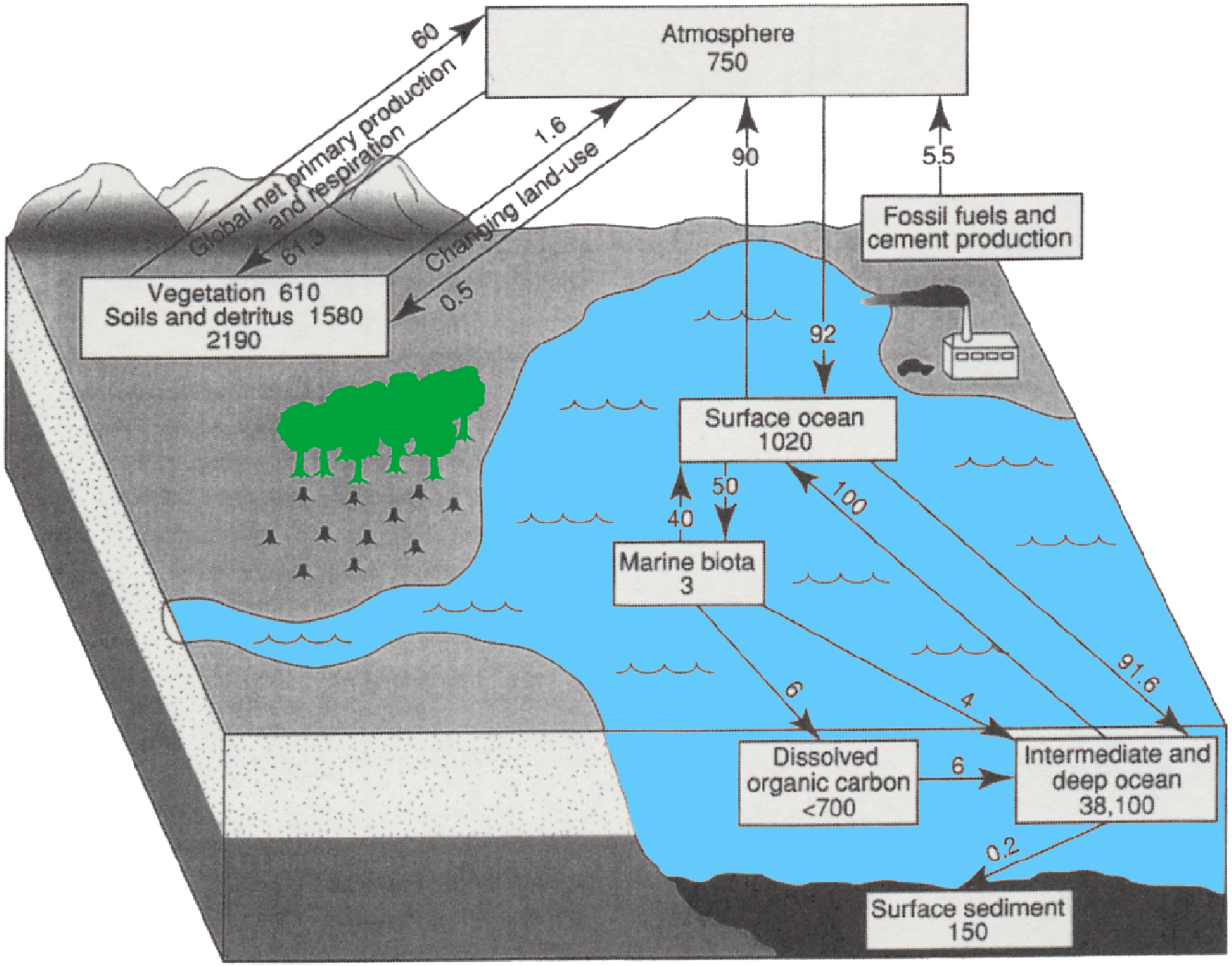
(Manganese Cluster in Oxygen Evolving Center)

Water as Reductant?

Main Elements in Biology

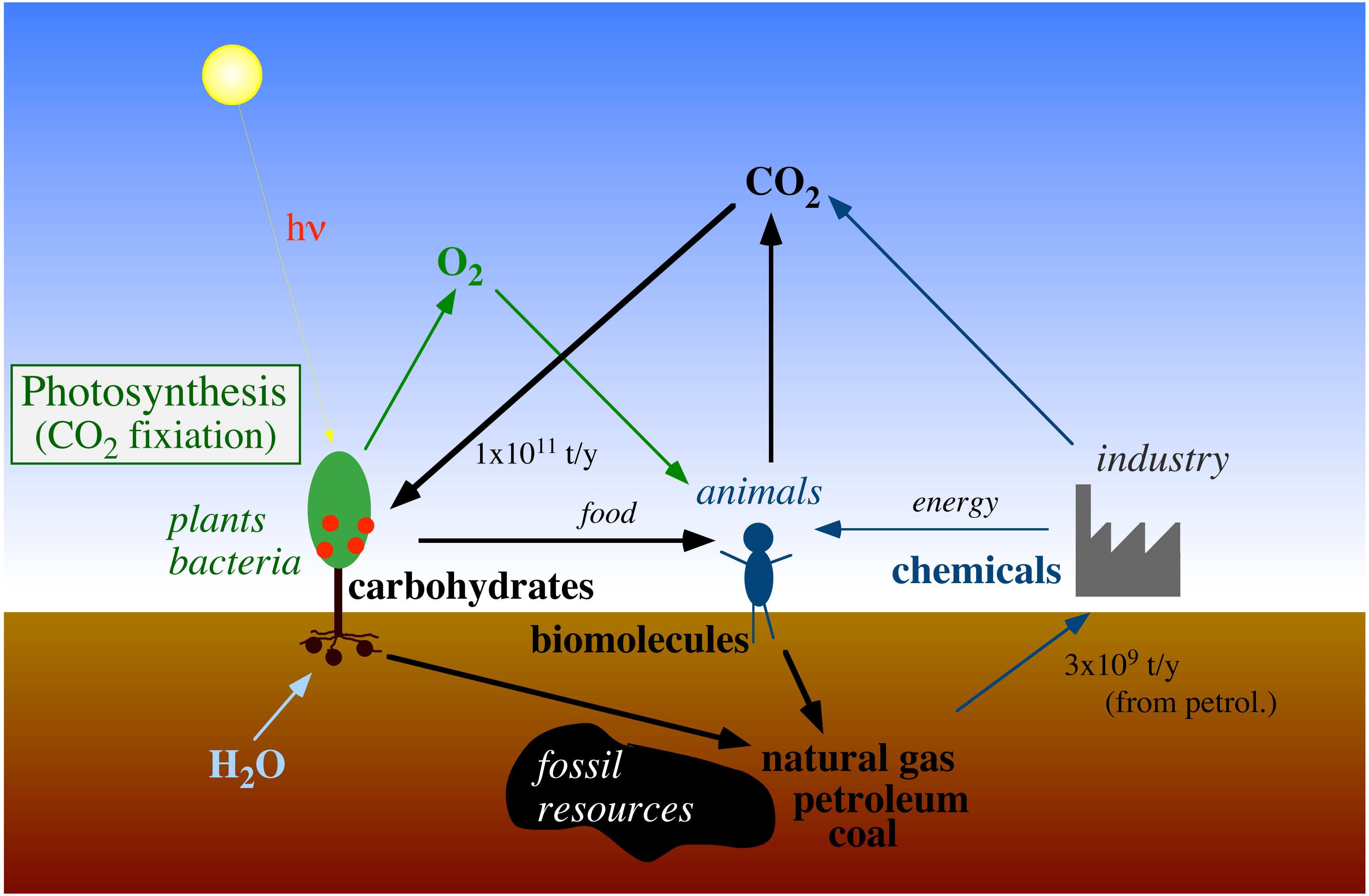
Recuded Form	CH_4	H_2	N_2	H_2O	
Biology	C	H	N	O	P
Oxidized Form	CO_2 (CO_3^{2-})	H_2O	NO_3^-	O_2	PO_4^{3-} (**P**i)

Carbon Dioxide Cycle

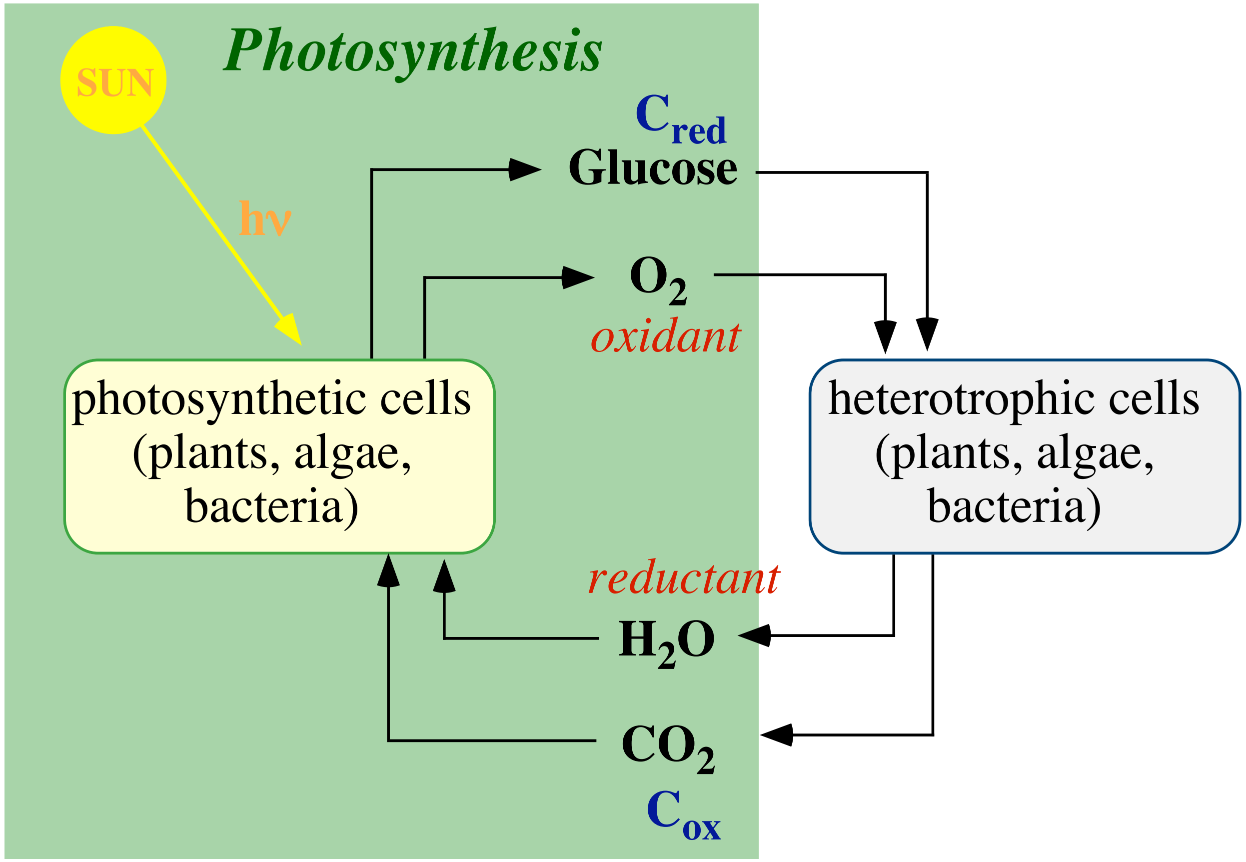


Tha carbon dioxide cycle, showing the reserviors (in GtC) and fluxes (GtC/y) in 1980-1989.
(In "Understandinh Our Environment" Ed. R. M. Harrison, RCS, 1999).

Carbon Cycle *via* Photosynthesis



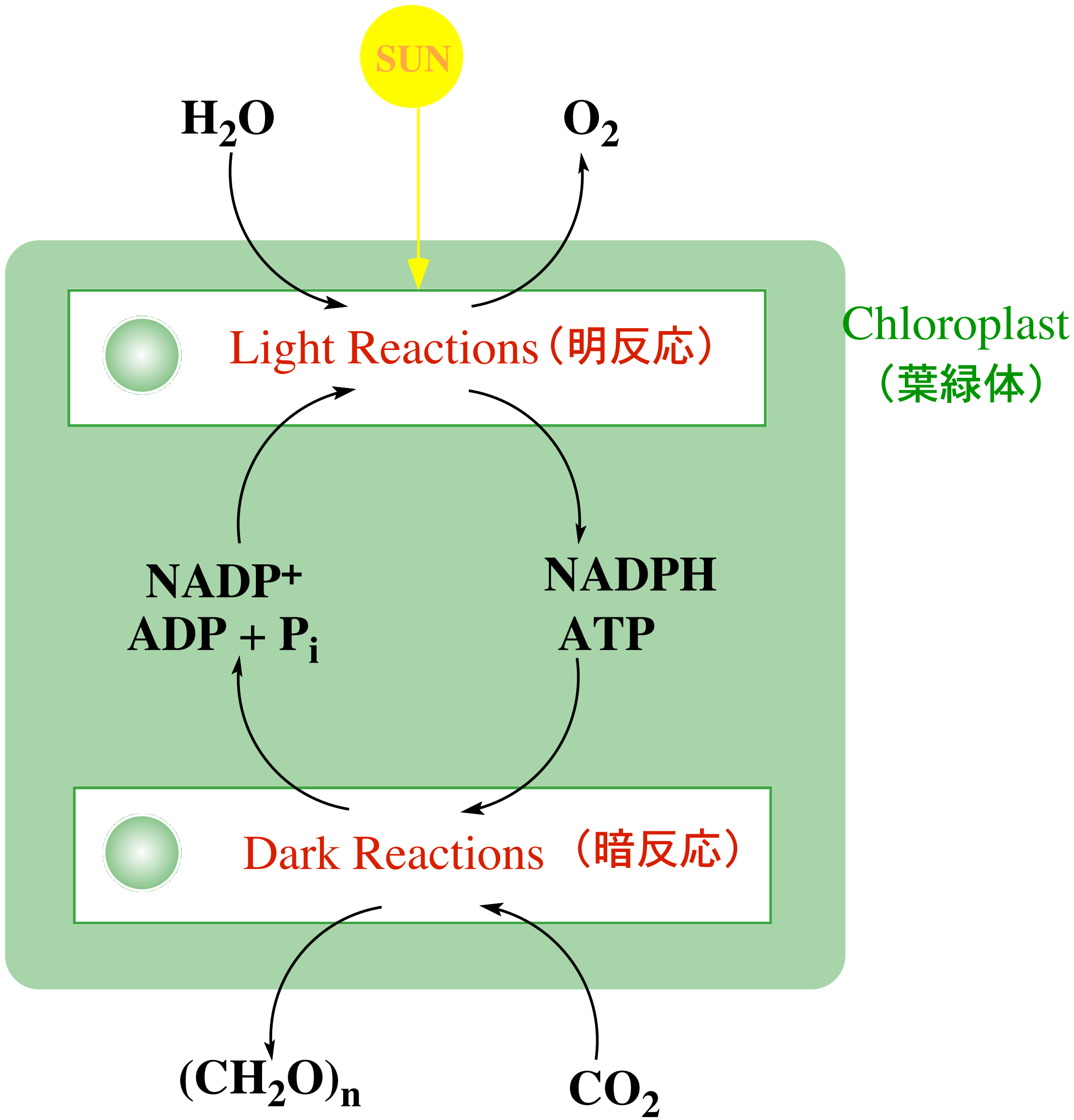
What is Photosynthesis



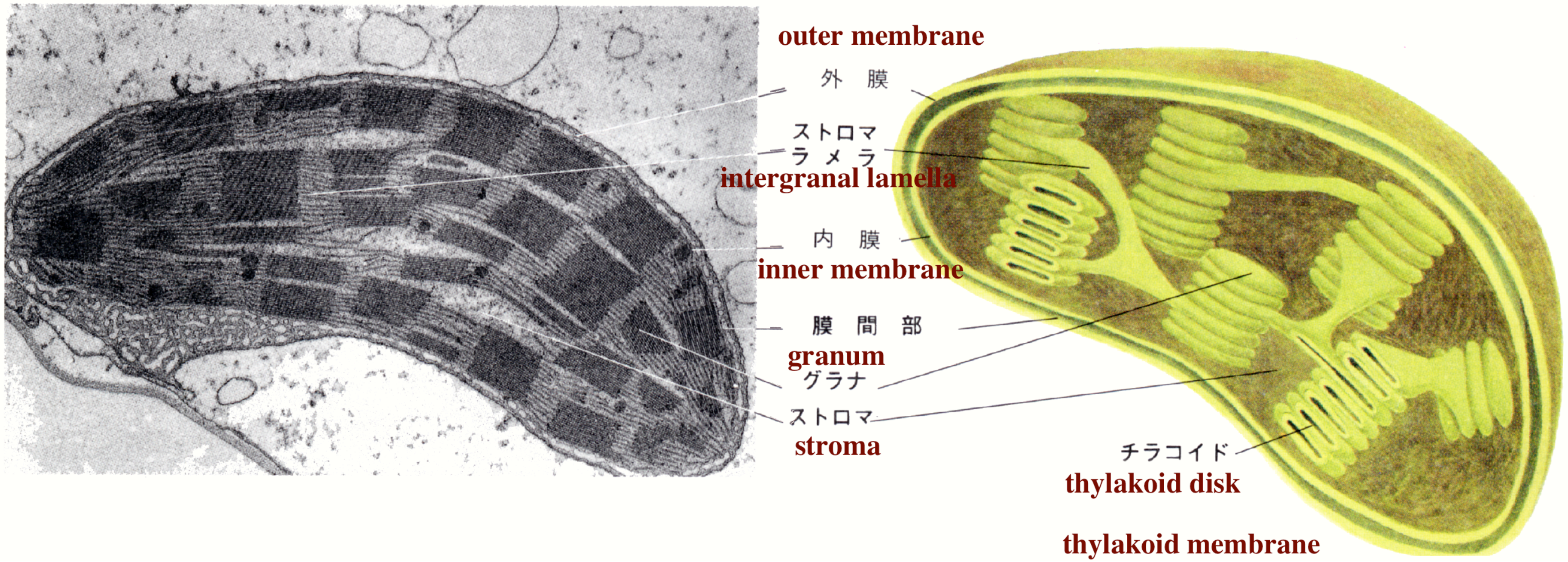
$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

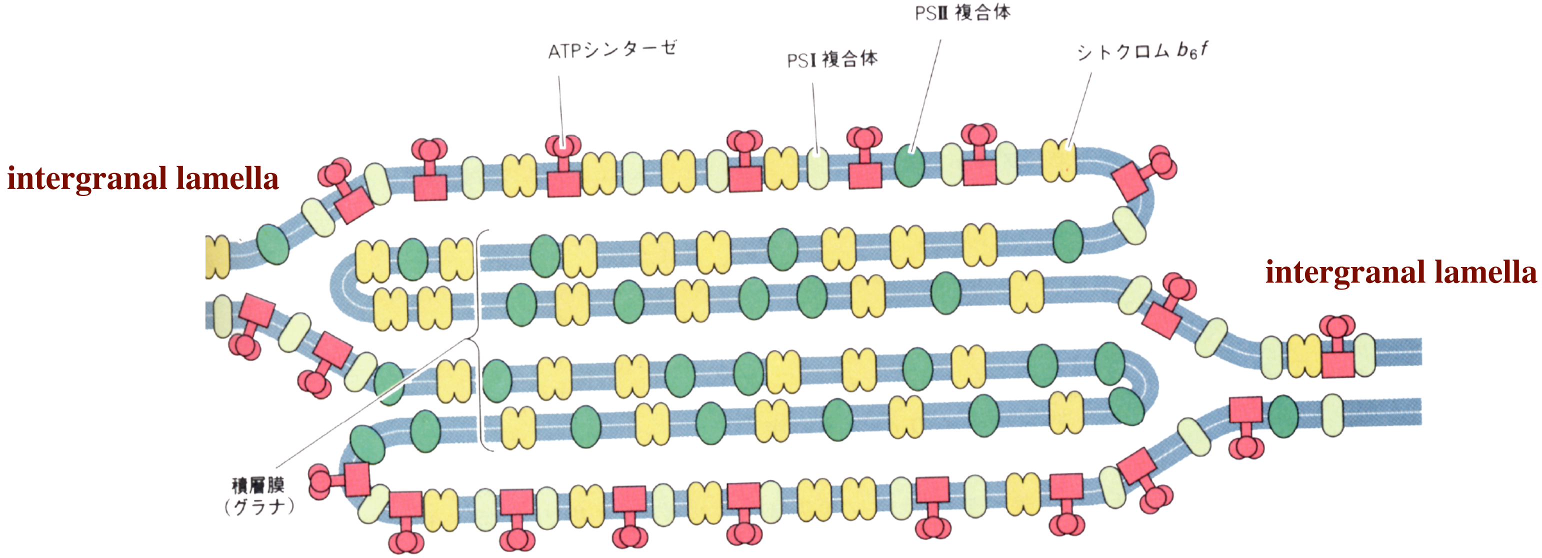
C_{ox} *reductant* ? C_{red} *oxidant*

Photosynthesis Two Phases and Takes Place in Chloroplast (Plant)



Chloroplast from Corn





Light Reactions

- Photosynthetic Electron Transfer making Charge (H^+) Separation

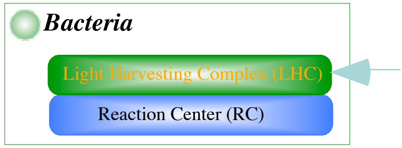
Bacteria

Light Harvesting Complex (LHC)
Reaction Center (RC)

- Photosynthetic Electron Transfer forming NADHP and ATP

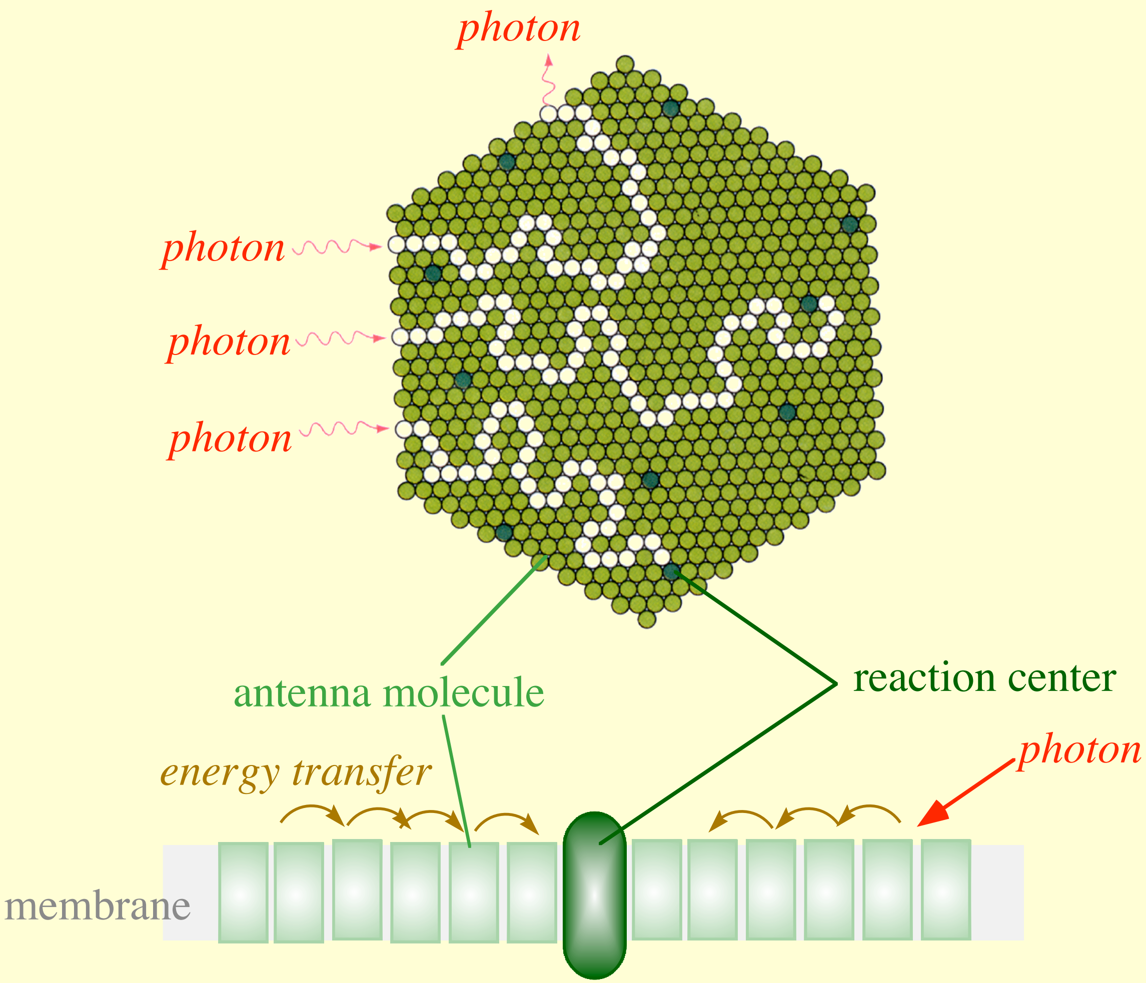
Plants

Light Harvesting Complex (LHC)
Photosystem II (PSII)
Photosystem I (PSI)

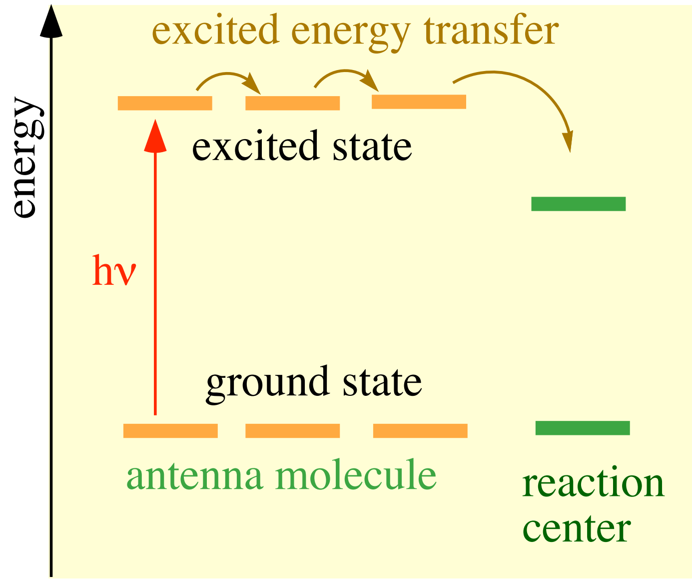


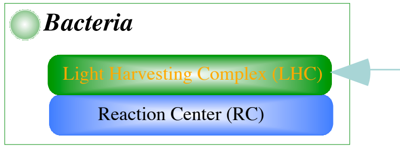
Light Harvesting Complex

LHC Diagram



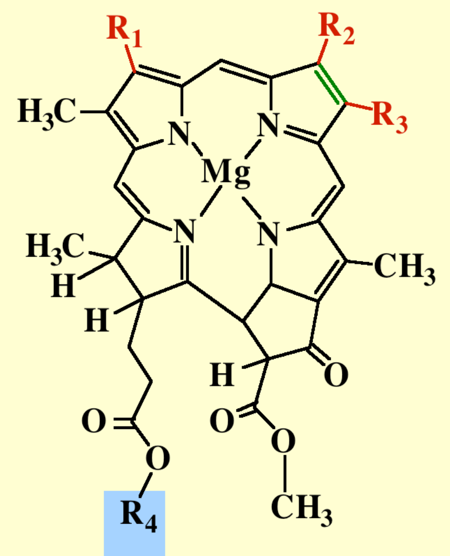
Light harvesting complex involves hundreds of antenna molecules (pigments); chlorophyll and carotenoid.



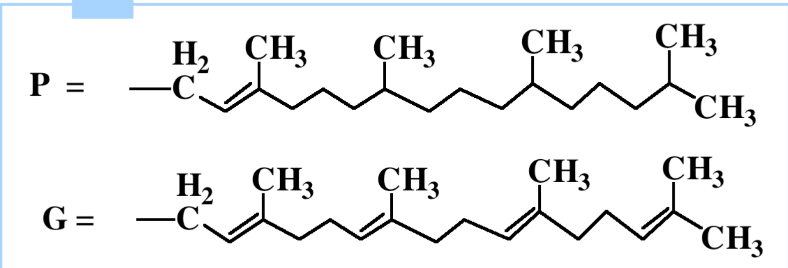


Antenna Molecules (Pigments)

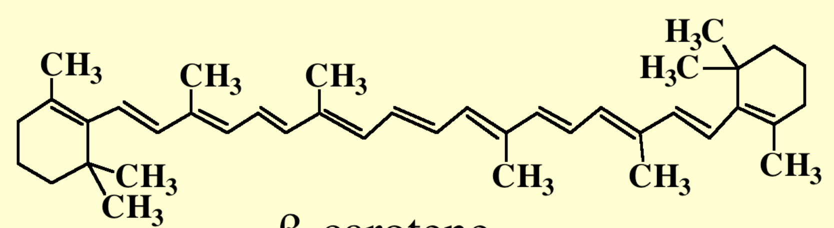
chlorophyll



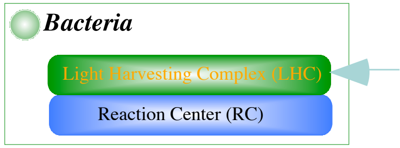
		R_1	R_2		R_3	R_4
Chl *a*	chlorophyll *a*	$-CH=CH_2$	Me	double	Et	P
Chl *b*	chlorophyll *b*	$-CH=CH_2$	$-C(=O)-H$	double	Et	P
BChl *a*	bacterio chlorophyll *a*	$-C(=O)-CH_3$	Me	single	Et	P or G
BChl *b*	bacterio chlorophyll *b*	$-C(=O)-CH_3$	Me	single	Et	P



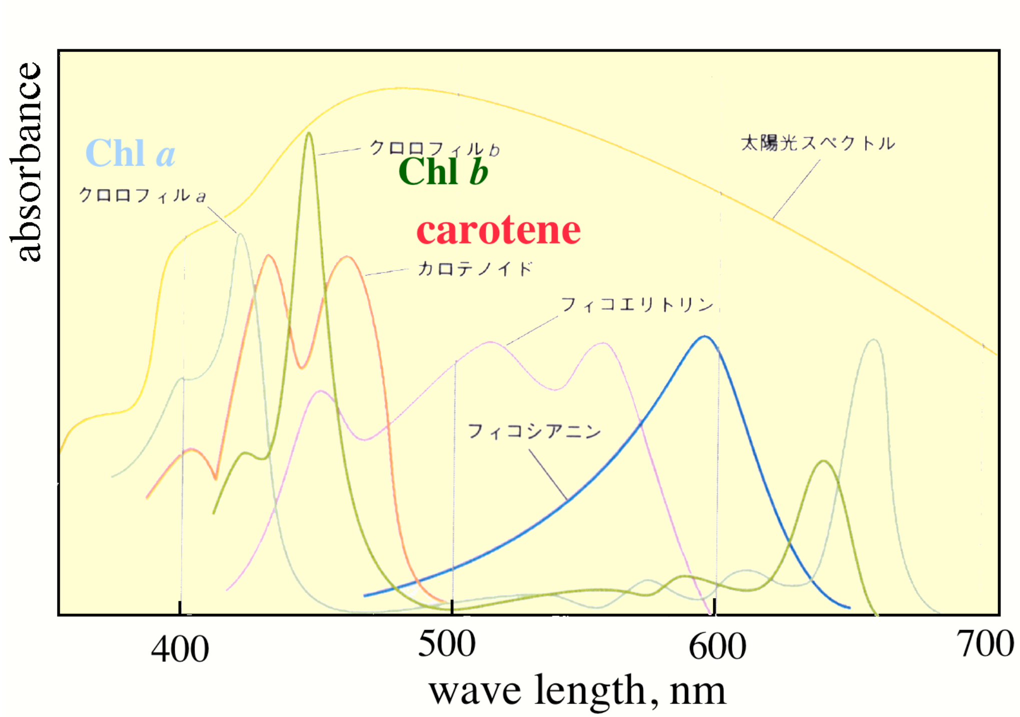
carotenoid

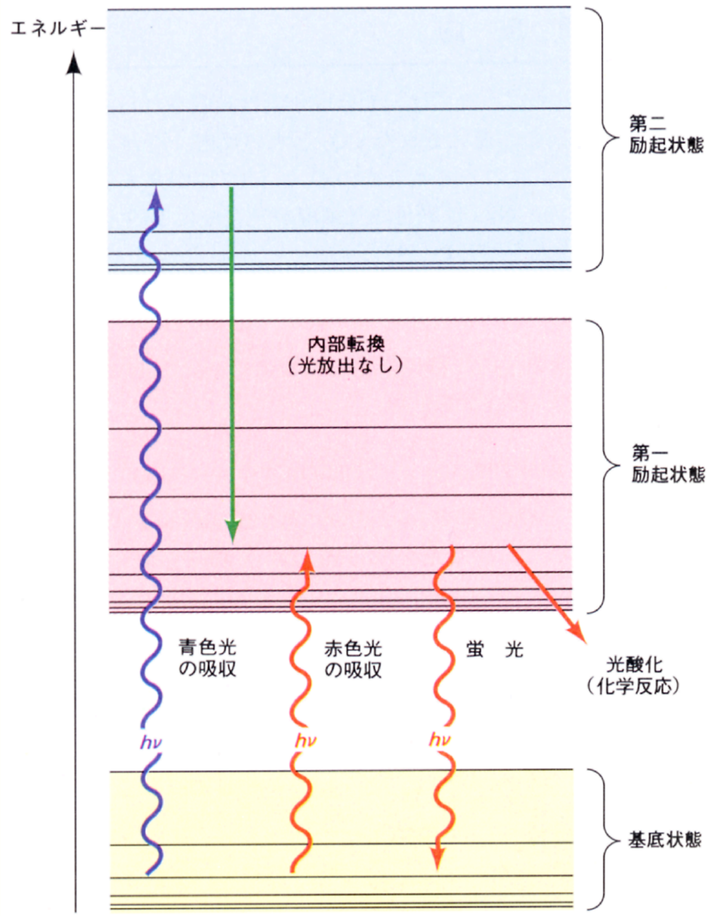


β-carotene



Antenna Molecules (Pigments)

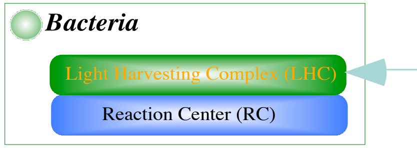




$$E = h\nu = hc/\lambda$$

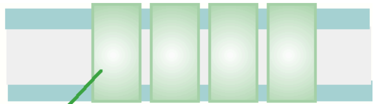
$h = 6.626 \times 10^{-34}$ j·s

$c = 2.998 \times 10^{8}$ m·s^{-1}

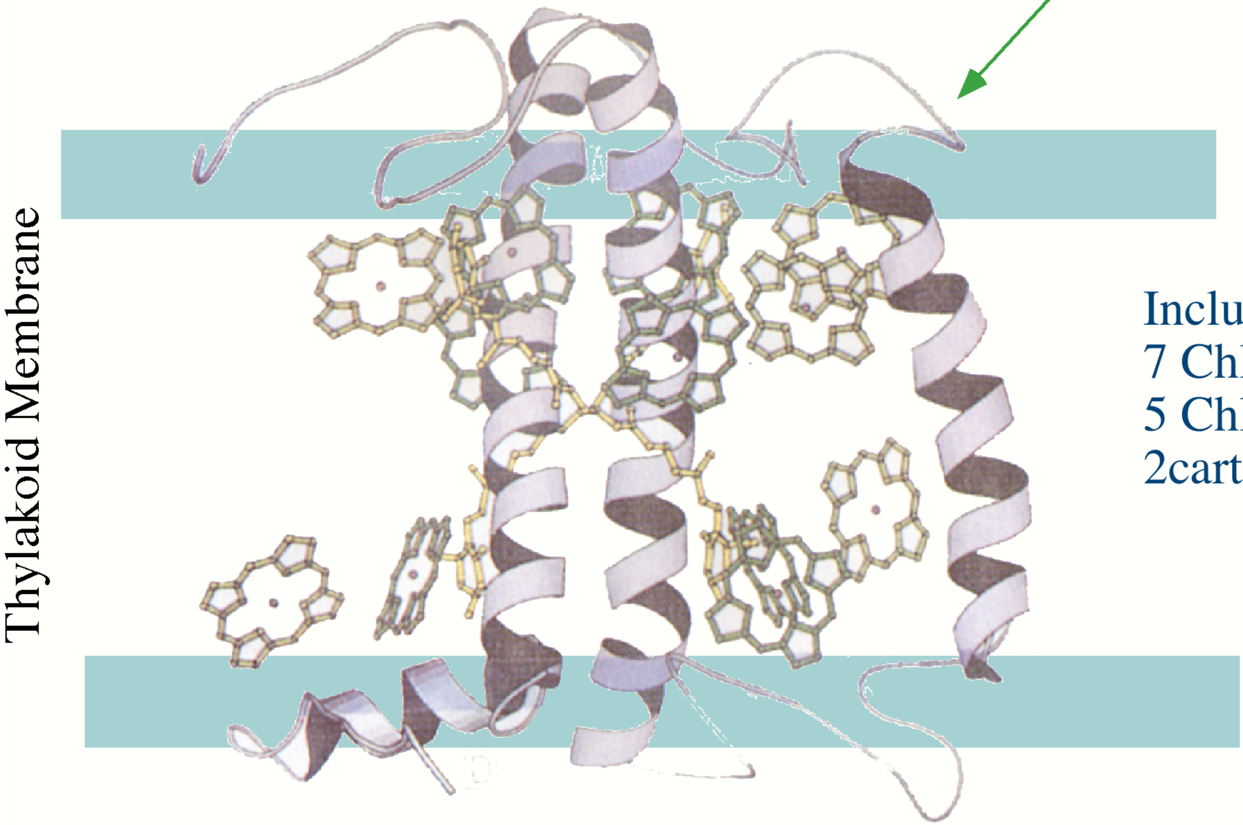


Light Harvesting Protein

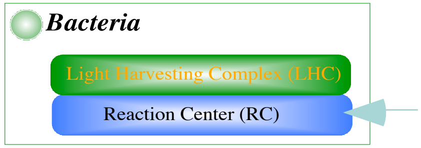
Chloroplast LHC-II Protein



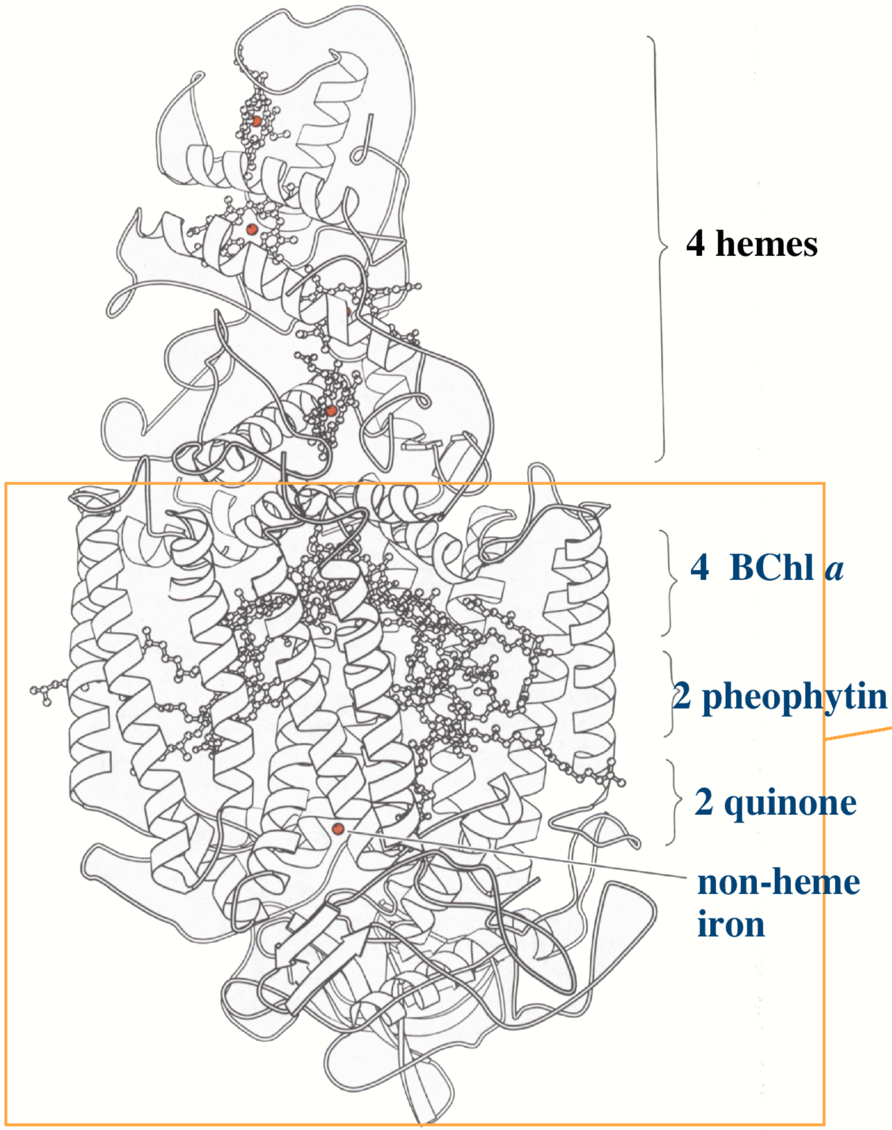
(232 aa)



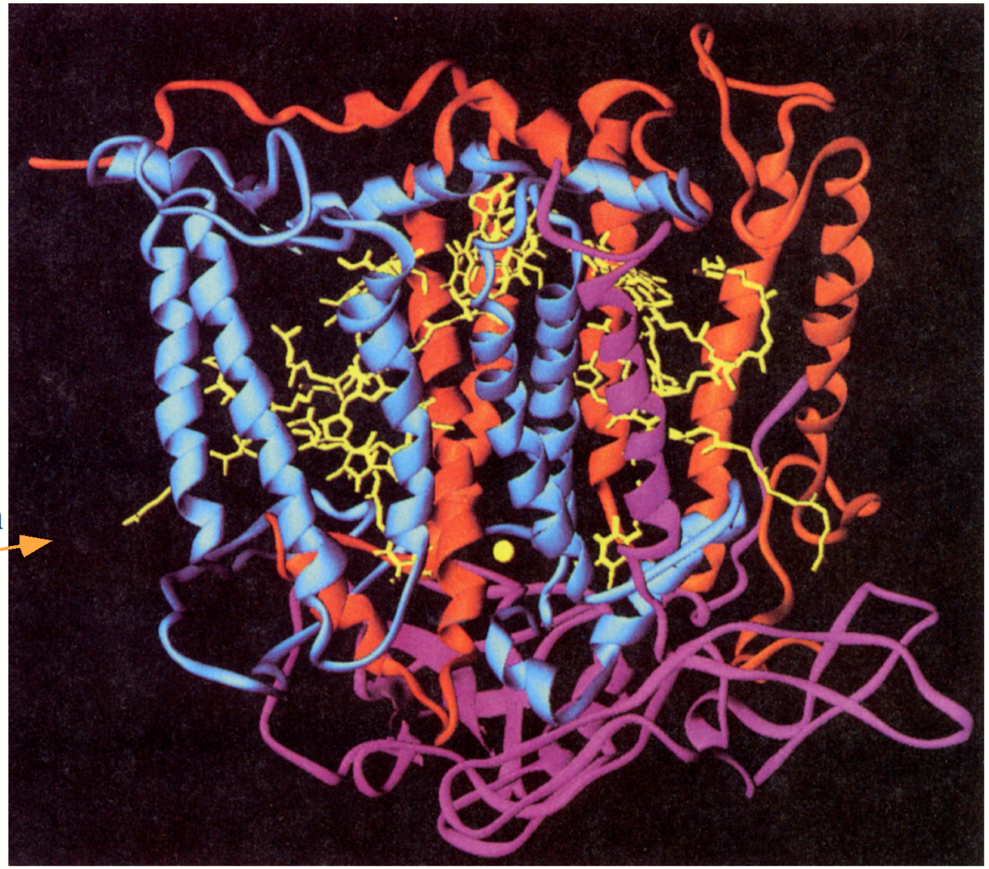
Including
7 Chl *a*
5 Chl *b*
2cartenoid



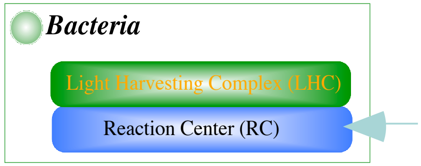
Photosynthesis Reaction Center (*R hodospseudomonas viridis*)



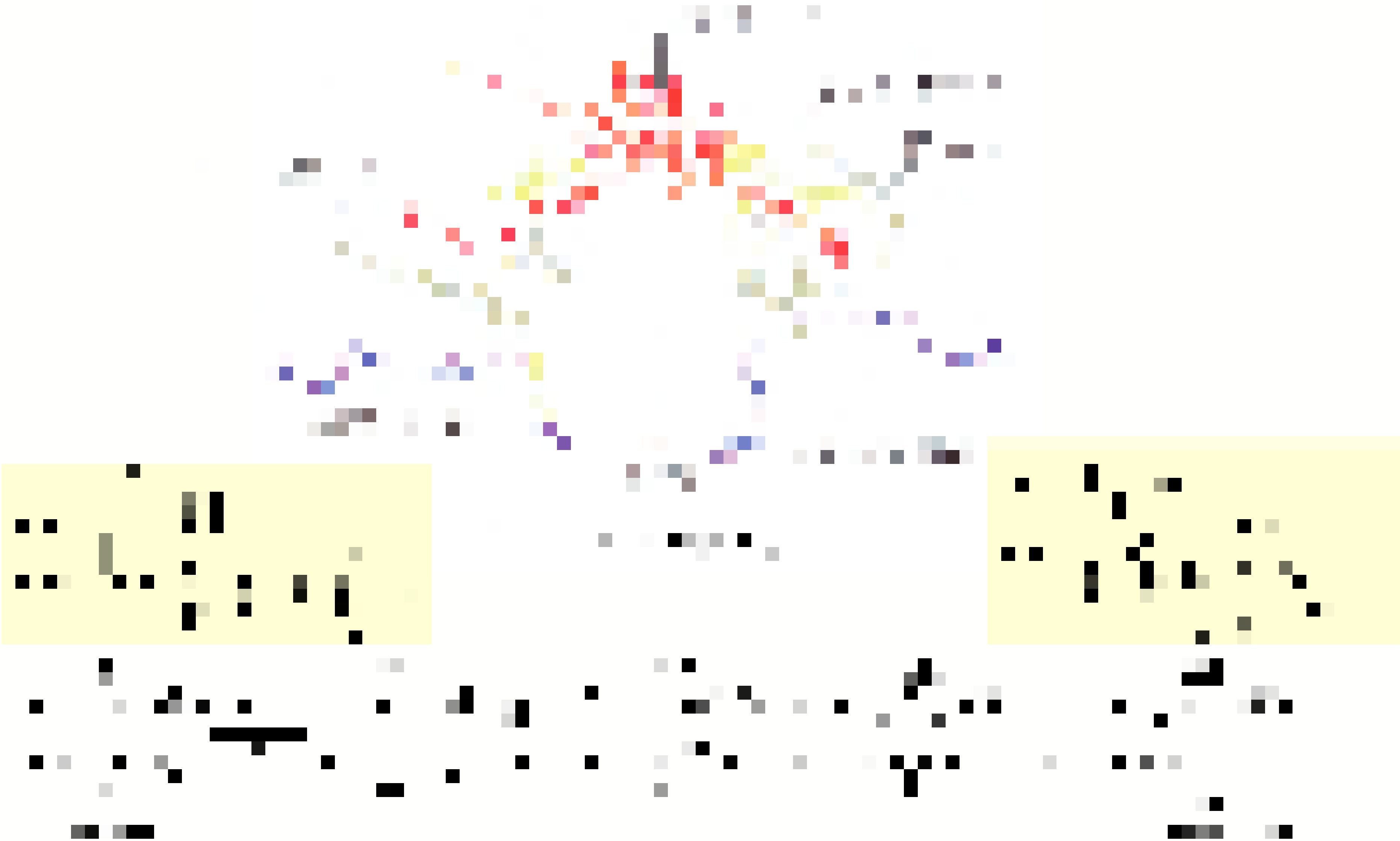
P870

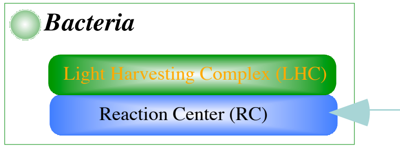


bacteriopheophytin *b* (BPheo *b*) = BChl *b* - Mg^{2+} + $2H^{+}$

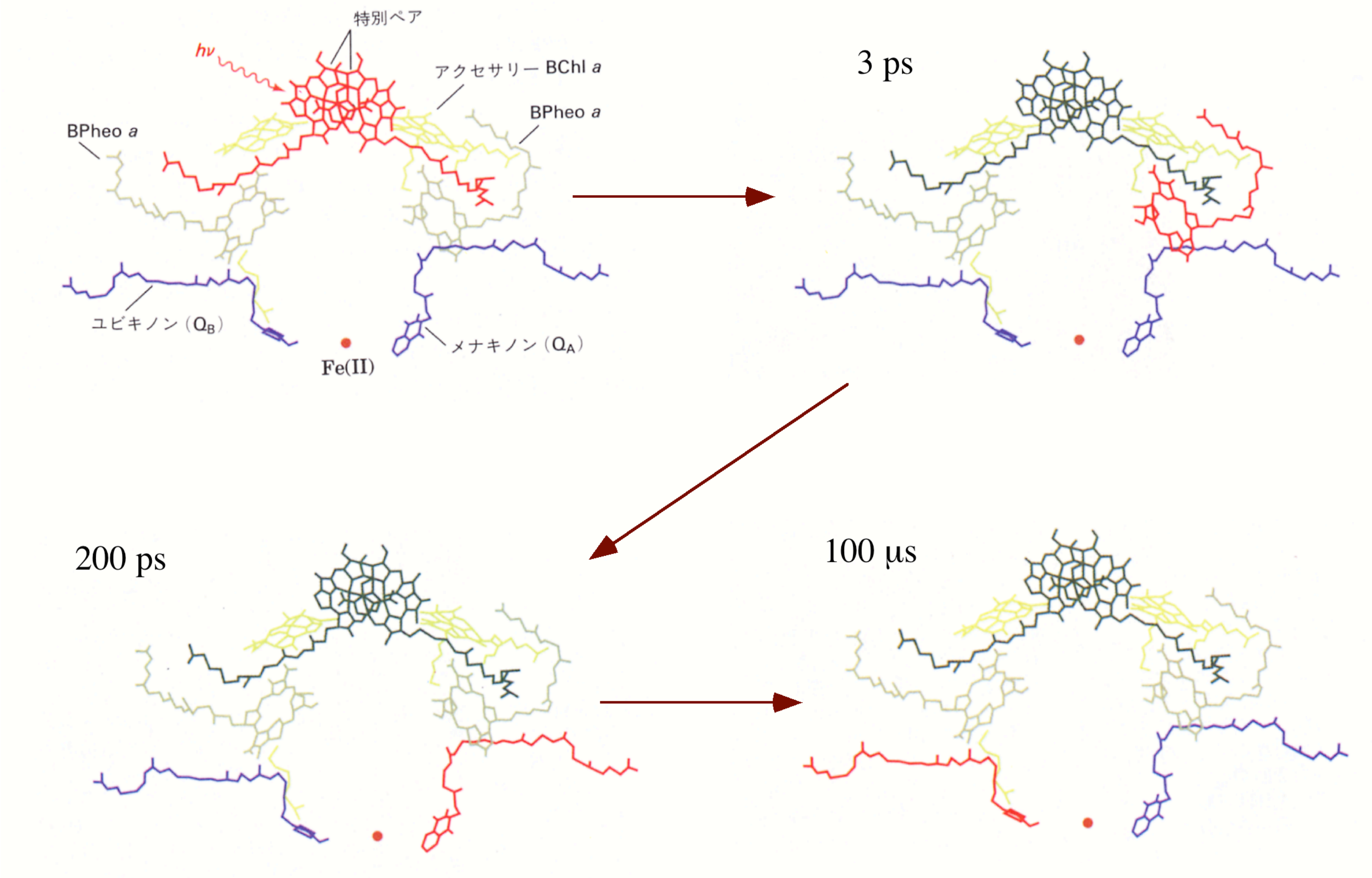


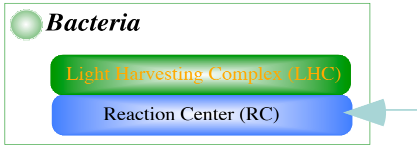
Photosynthesis Reaction Center (*R hodospseudomonas viridis*)





Photosynthesis Reaction Center
-Electron Transfer-

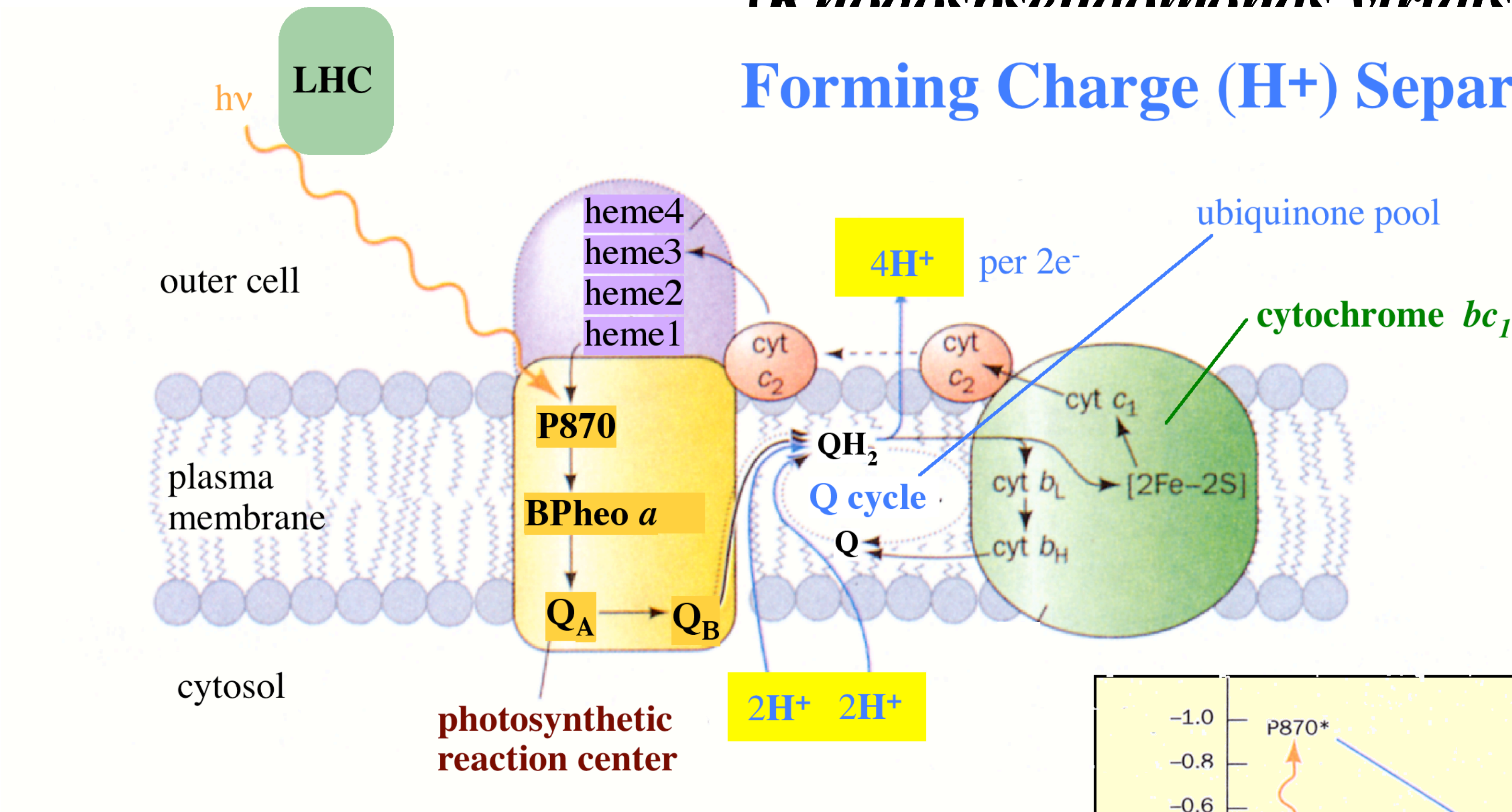


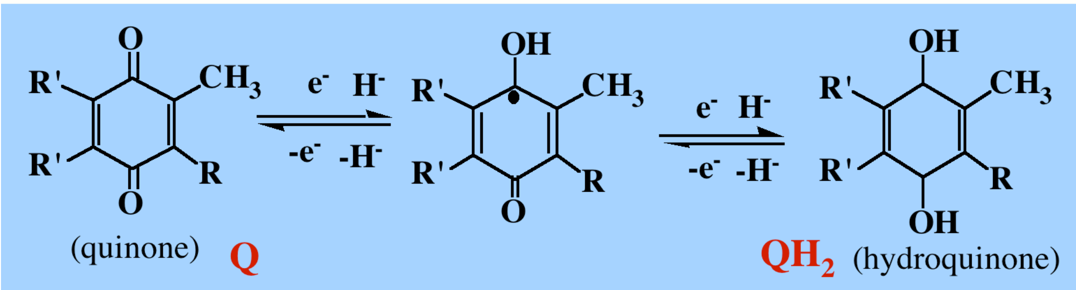


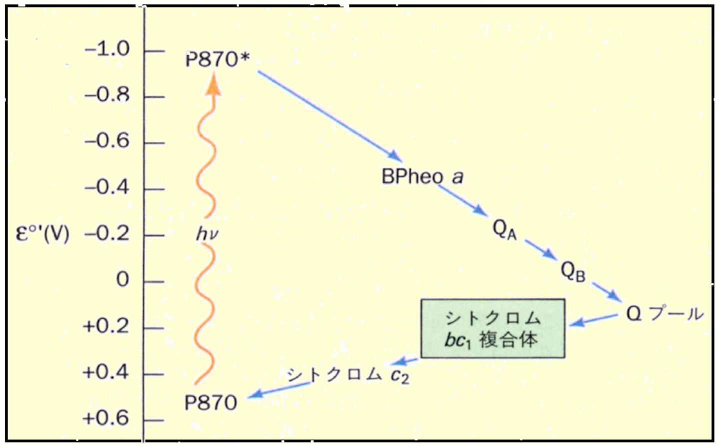
Photosynthetic Electron Transfer System

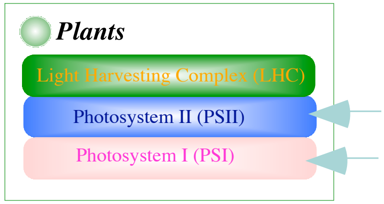
(Rhodospseudomonas viridis)

Forming Charge (H+) Separation

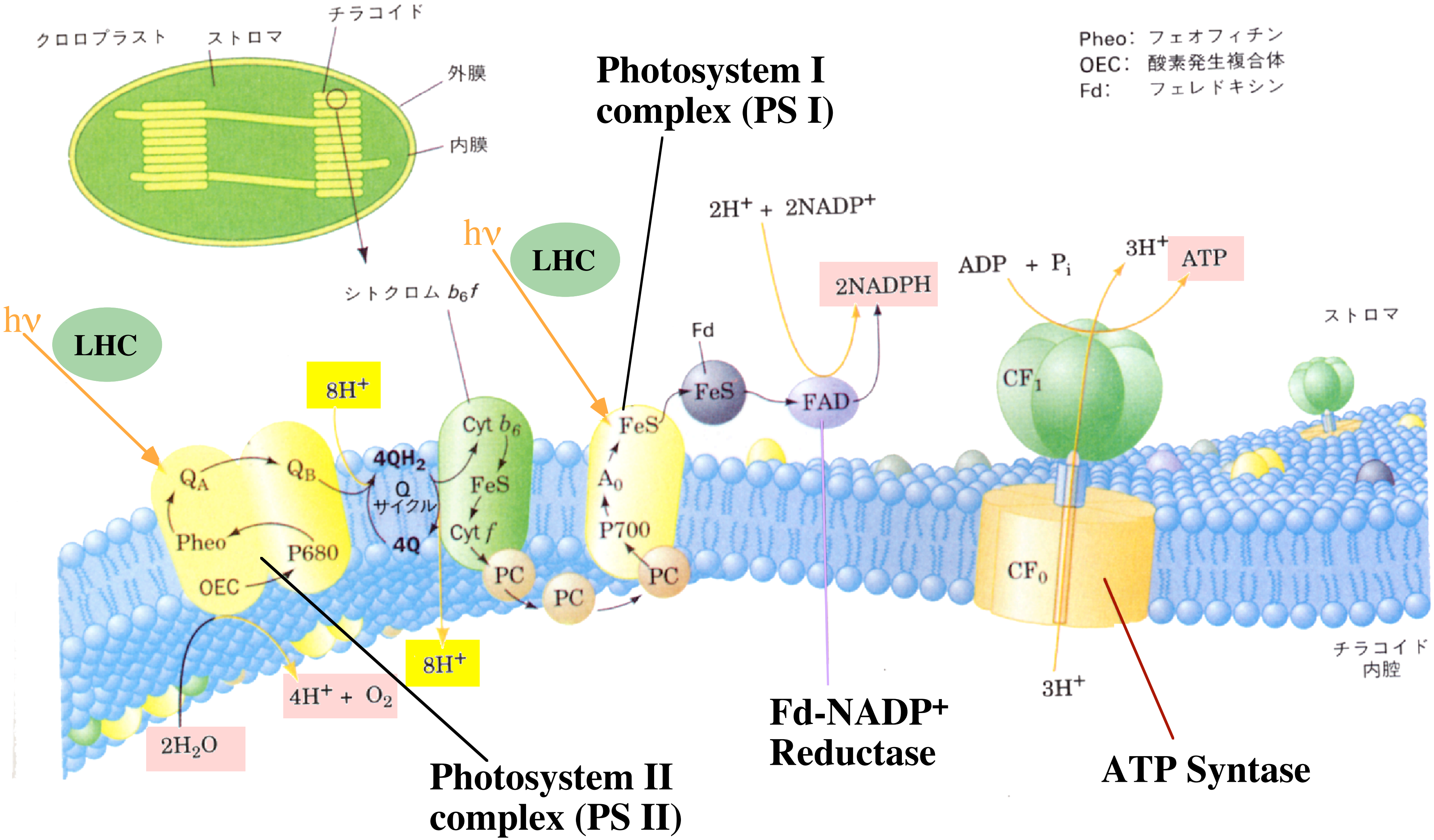


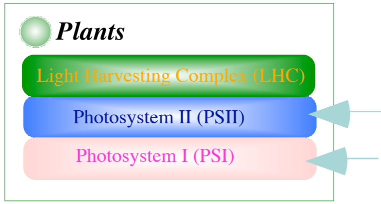




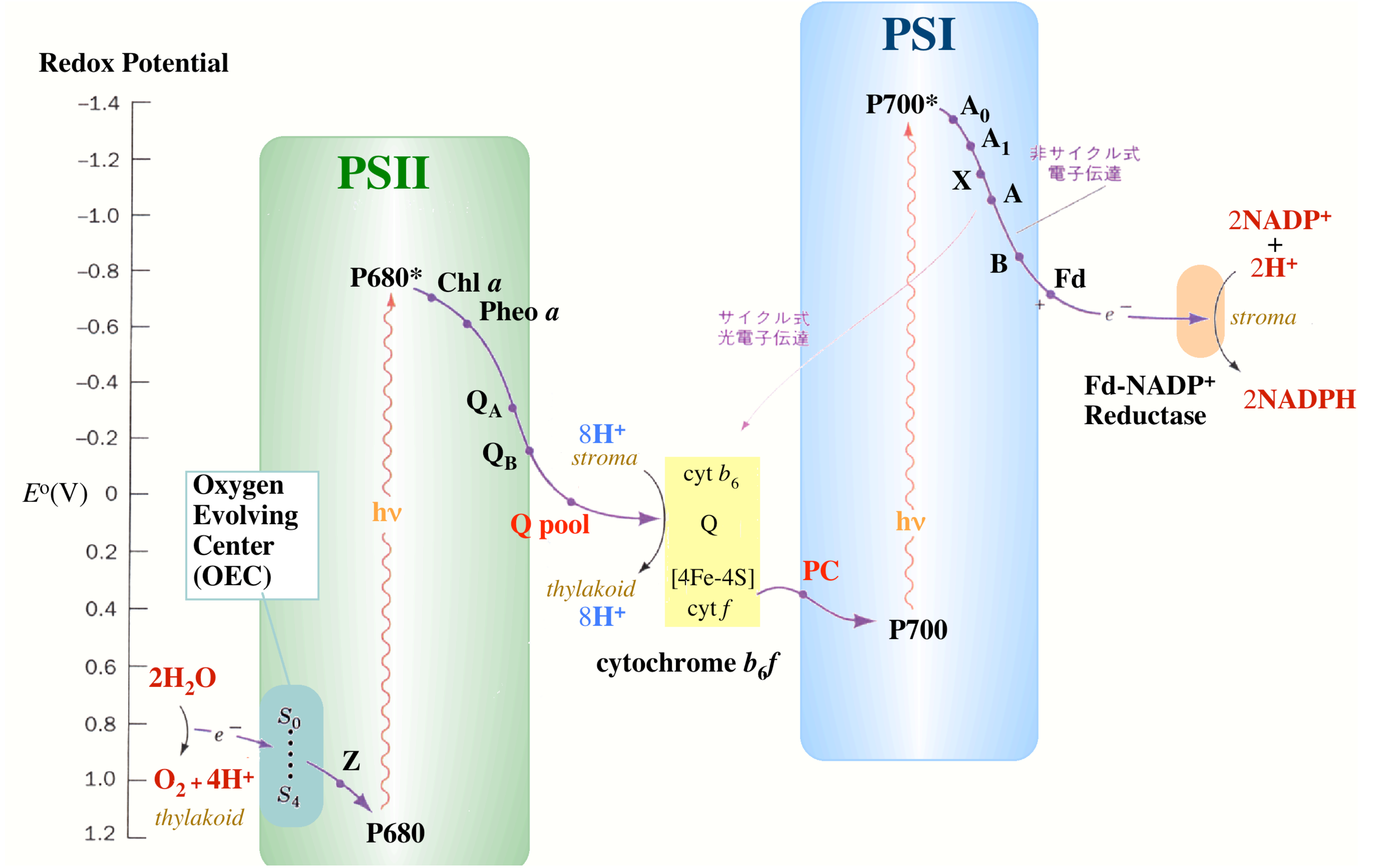


Photosynthetic Electron Transfer (Plant)

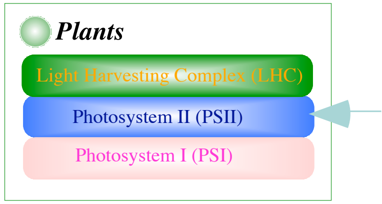


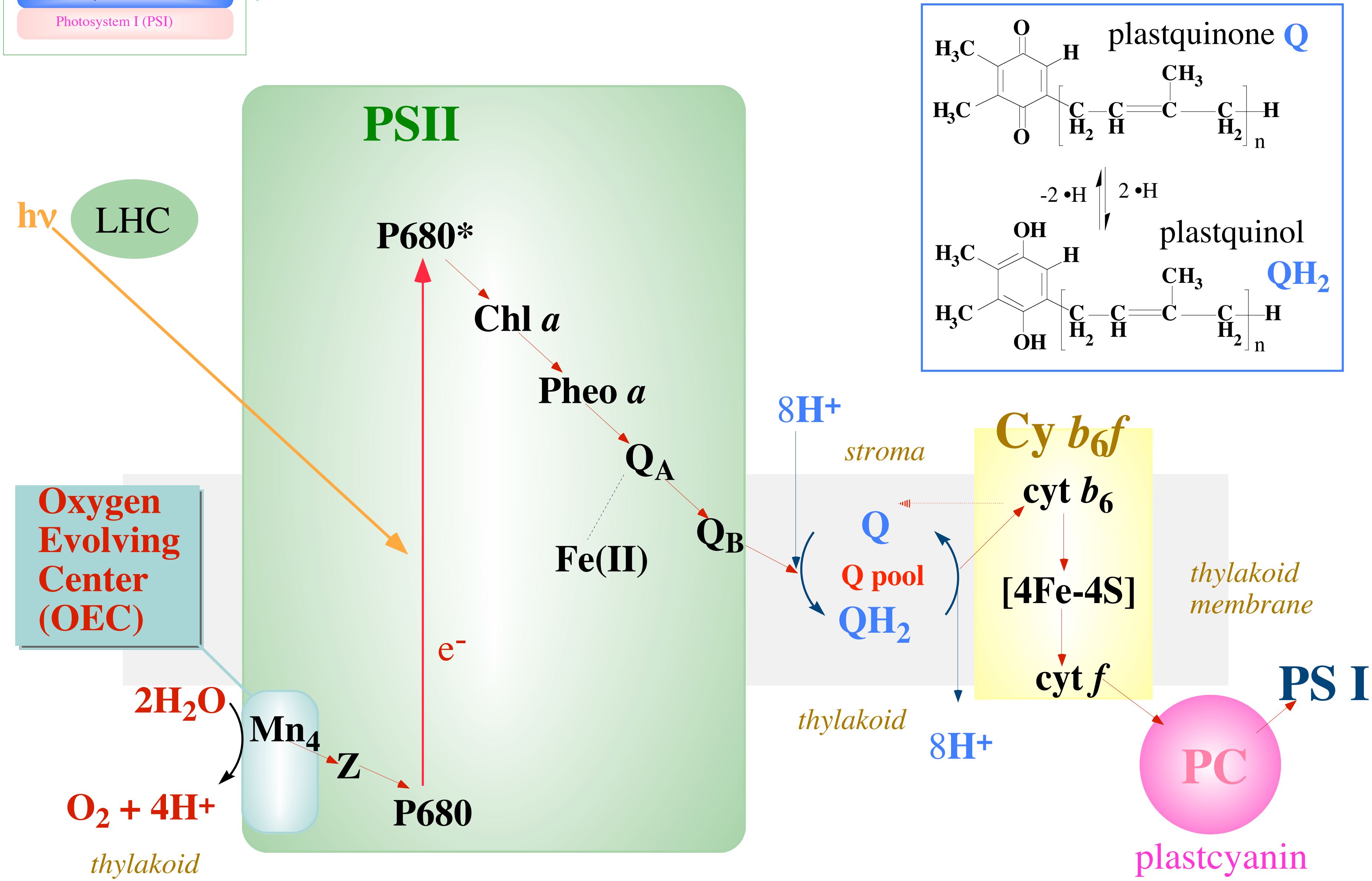


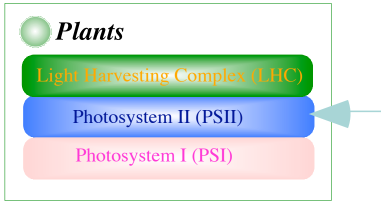
Photosynthetic Electron Transfer (Plant)



Photosystem II (PS II)

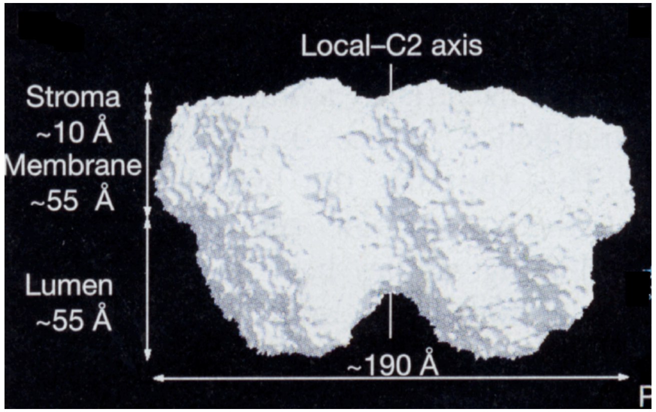


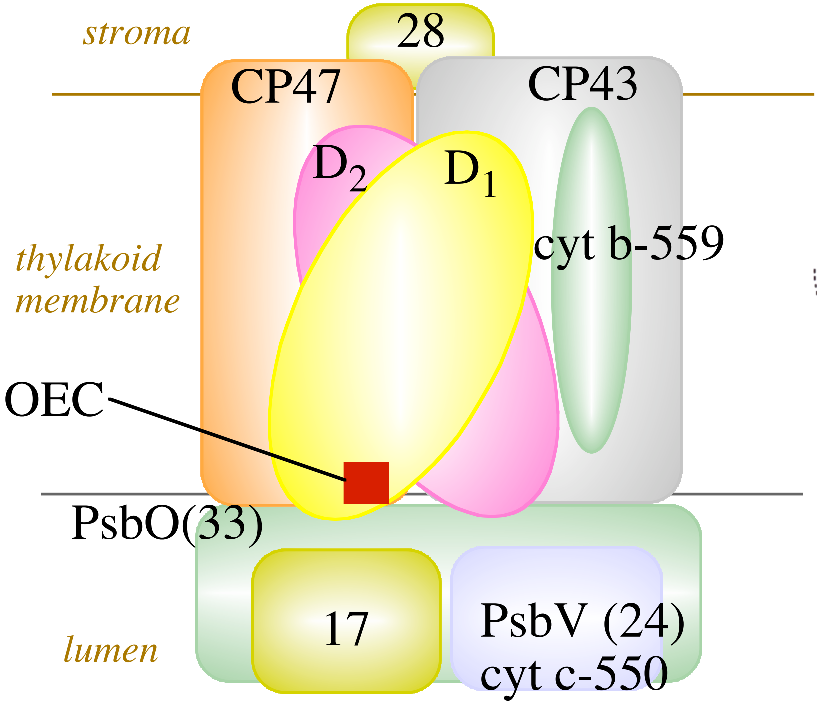


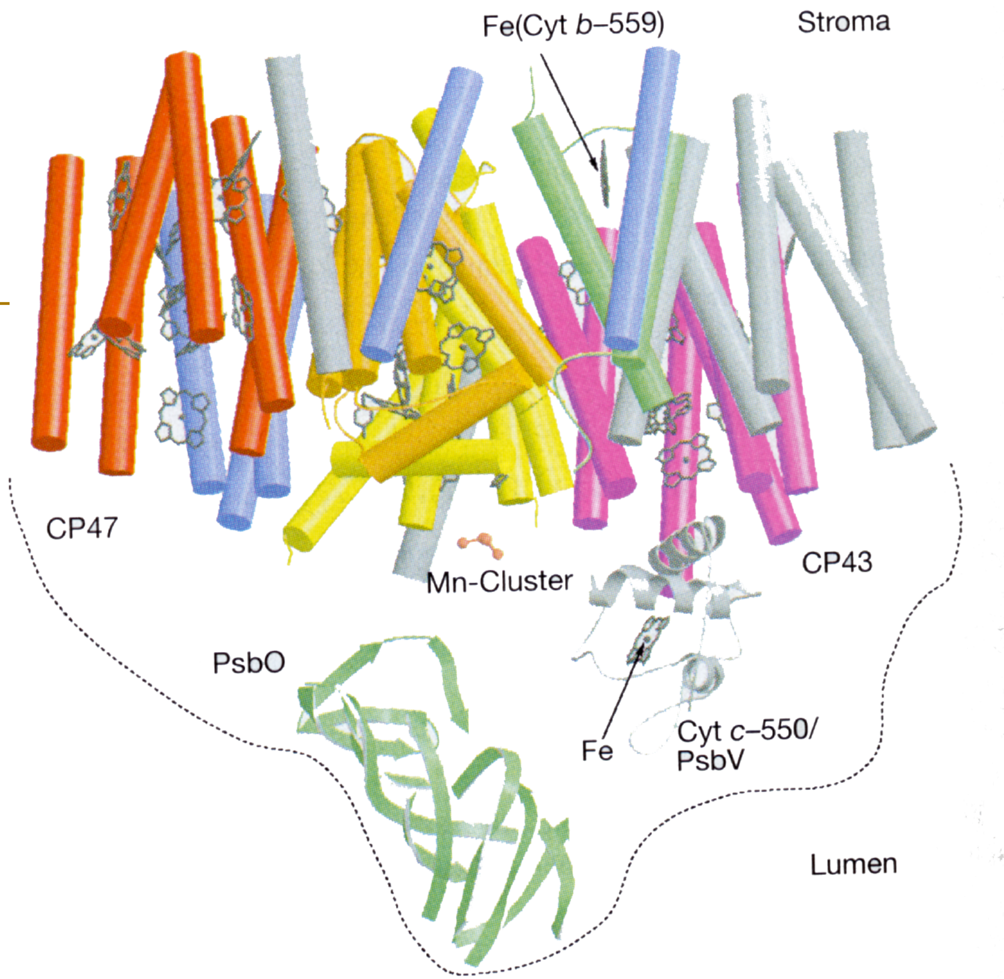


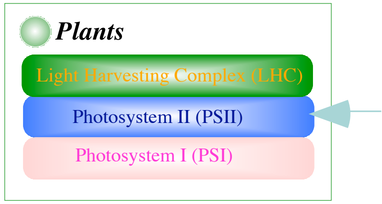
Crystal Structure of PS II from *Synechococcus elongatus* at 3.8 Å Resolution

A. Zouni et al. *Nature* 2001, *409*, 739-743

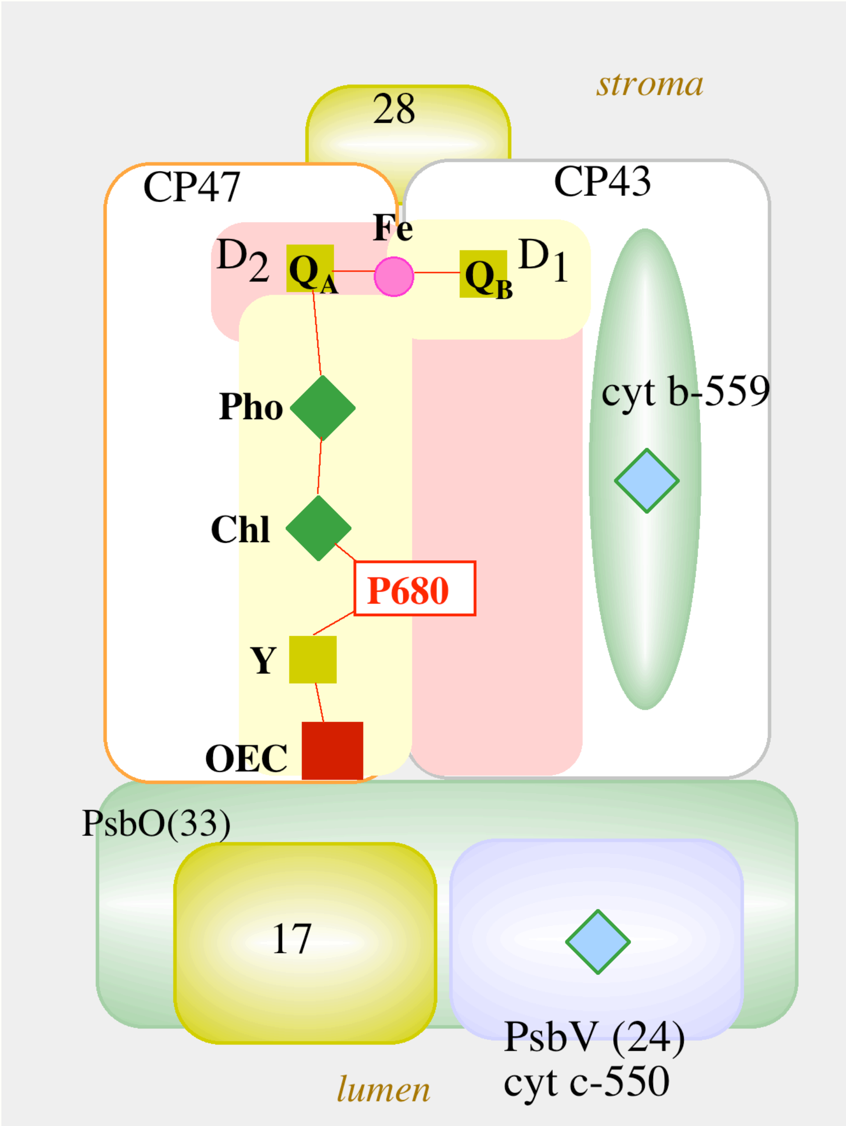


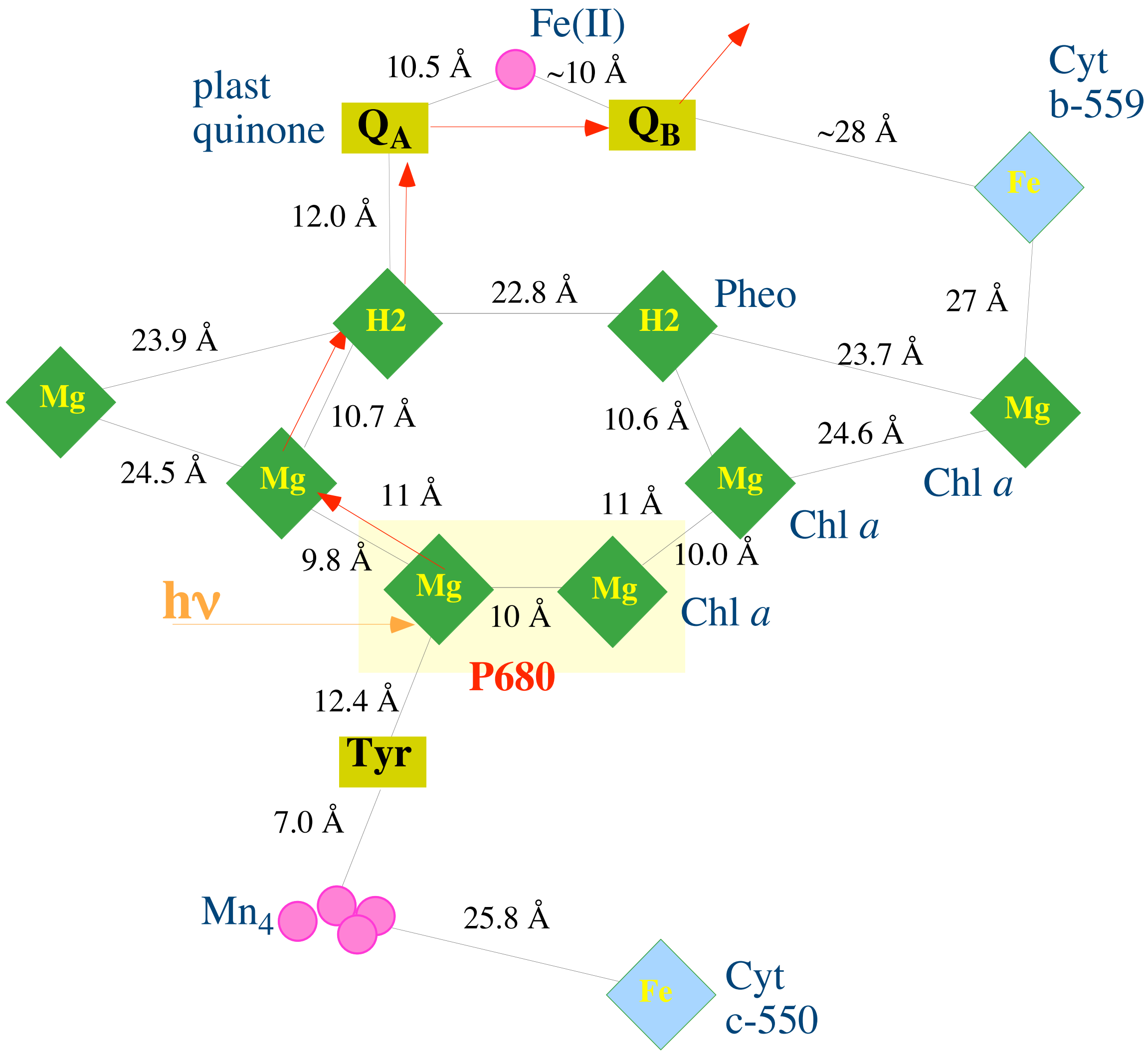


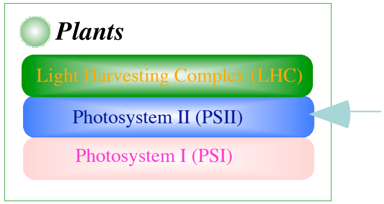




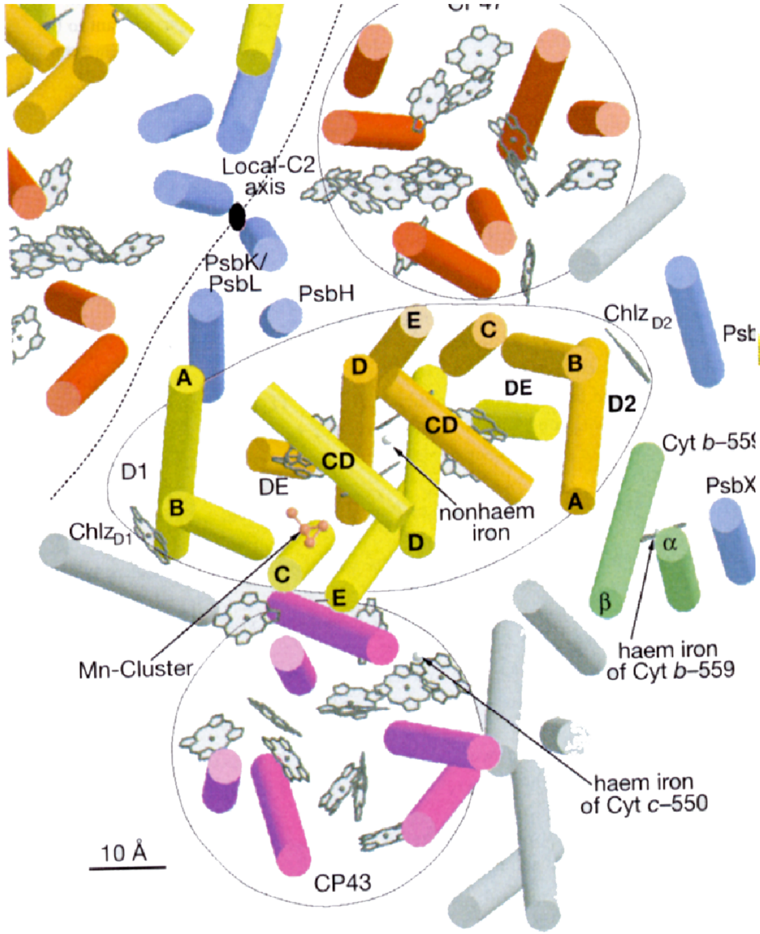
Crystal Structure of PS II from *Synechococcus elongatus* at 3.8 Å Resolution

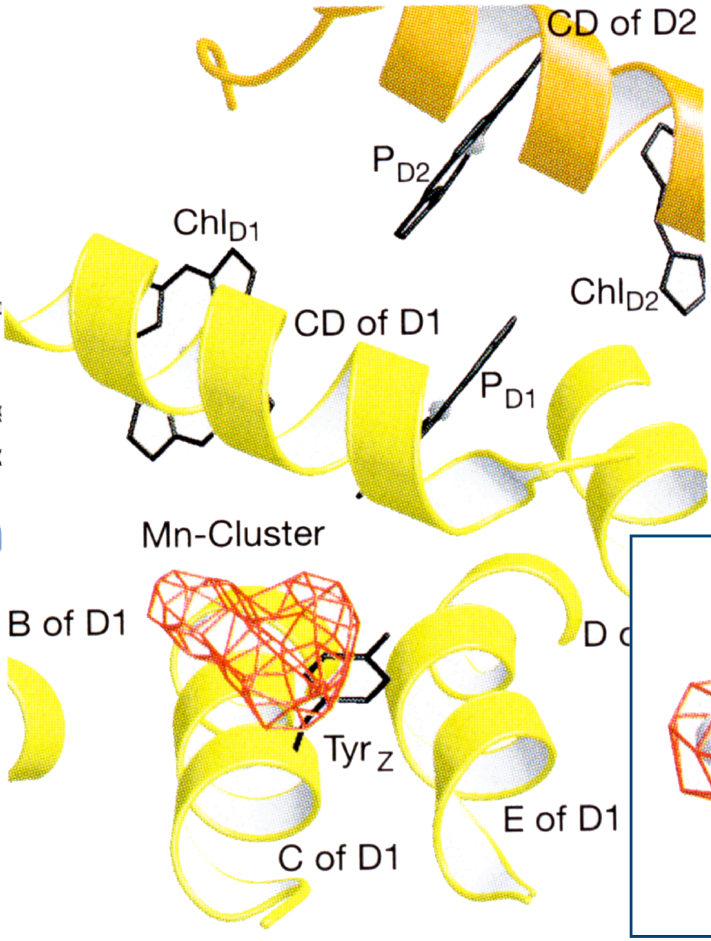


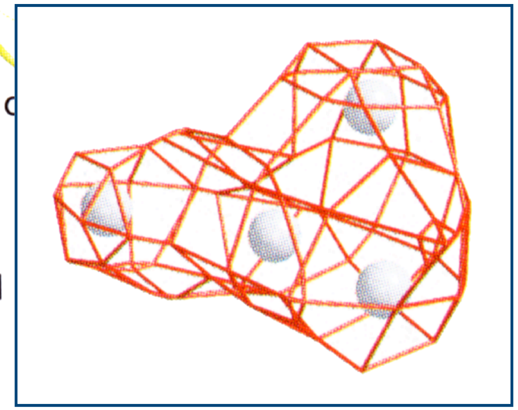


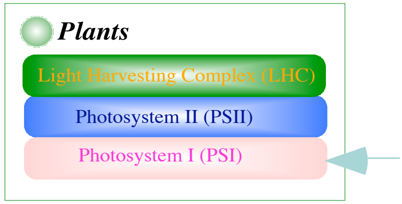


Crystal Structure of PS II
from *Synechococcus elongatus*
at 3.8 Å Resolution
Oxygen Evolving Center Still Not Clear

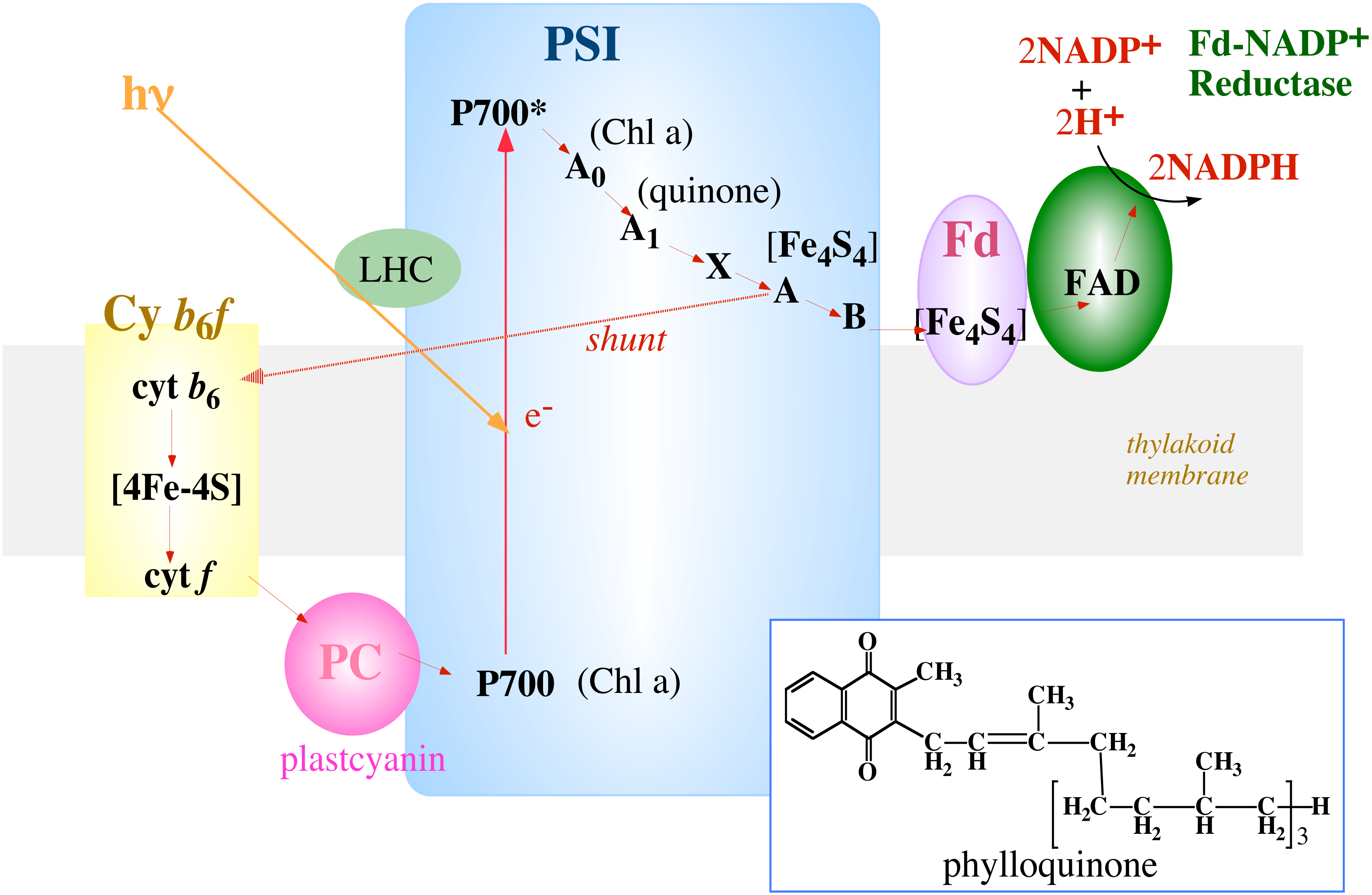






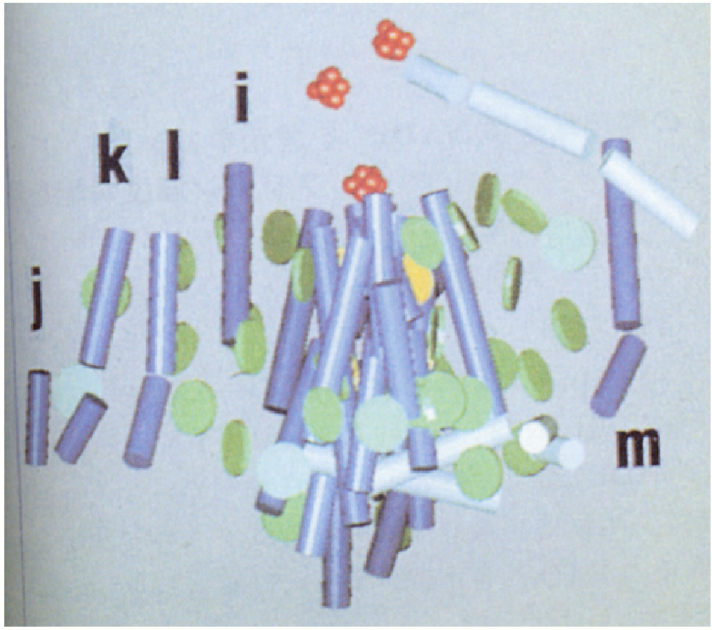


Photosystem I (PS I)



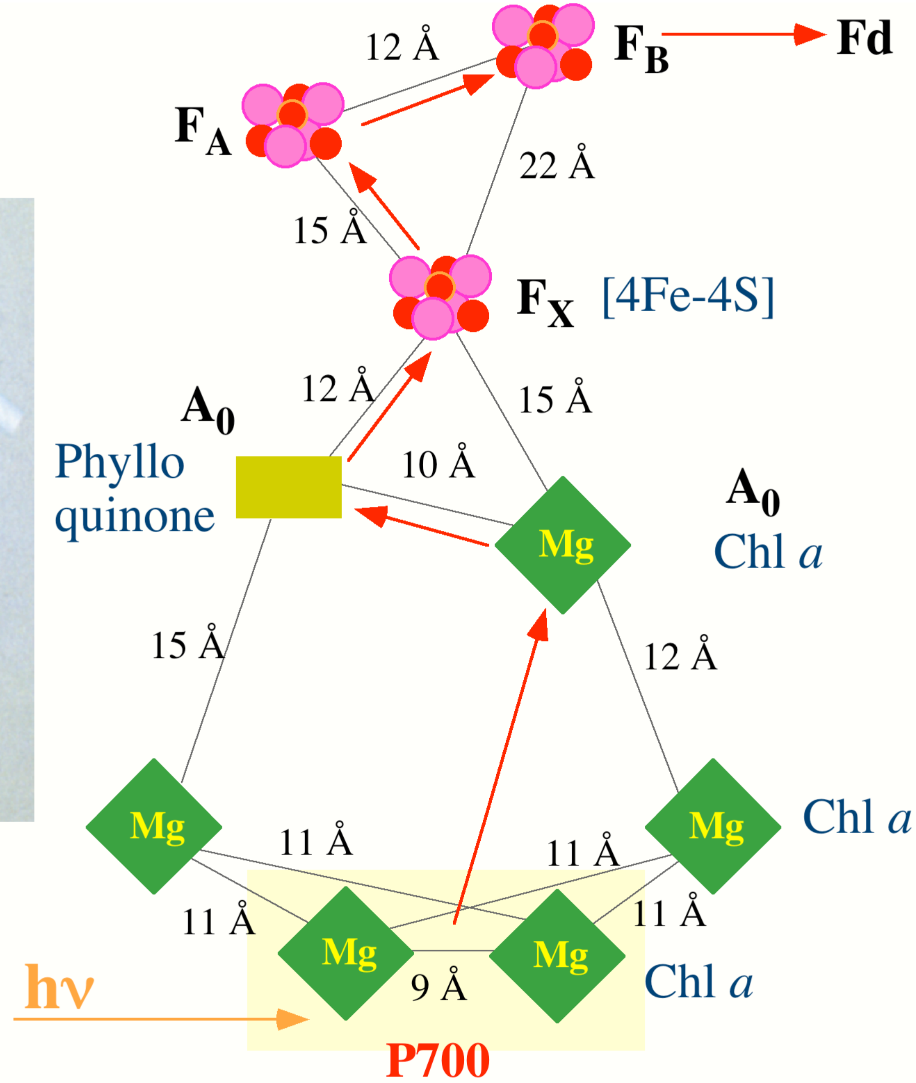
Photosystem I (PS I)

stroma

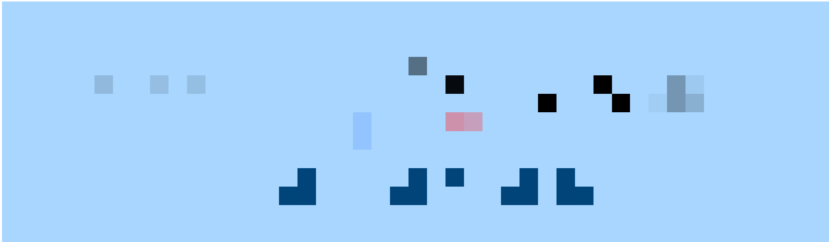


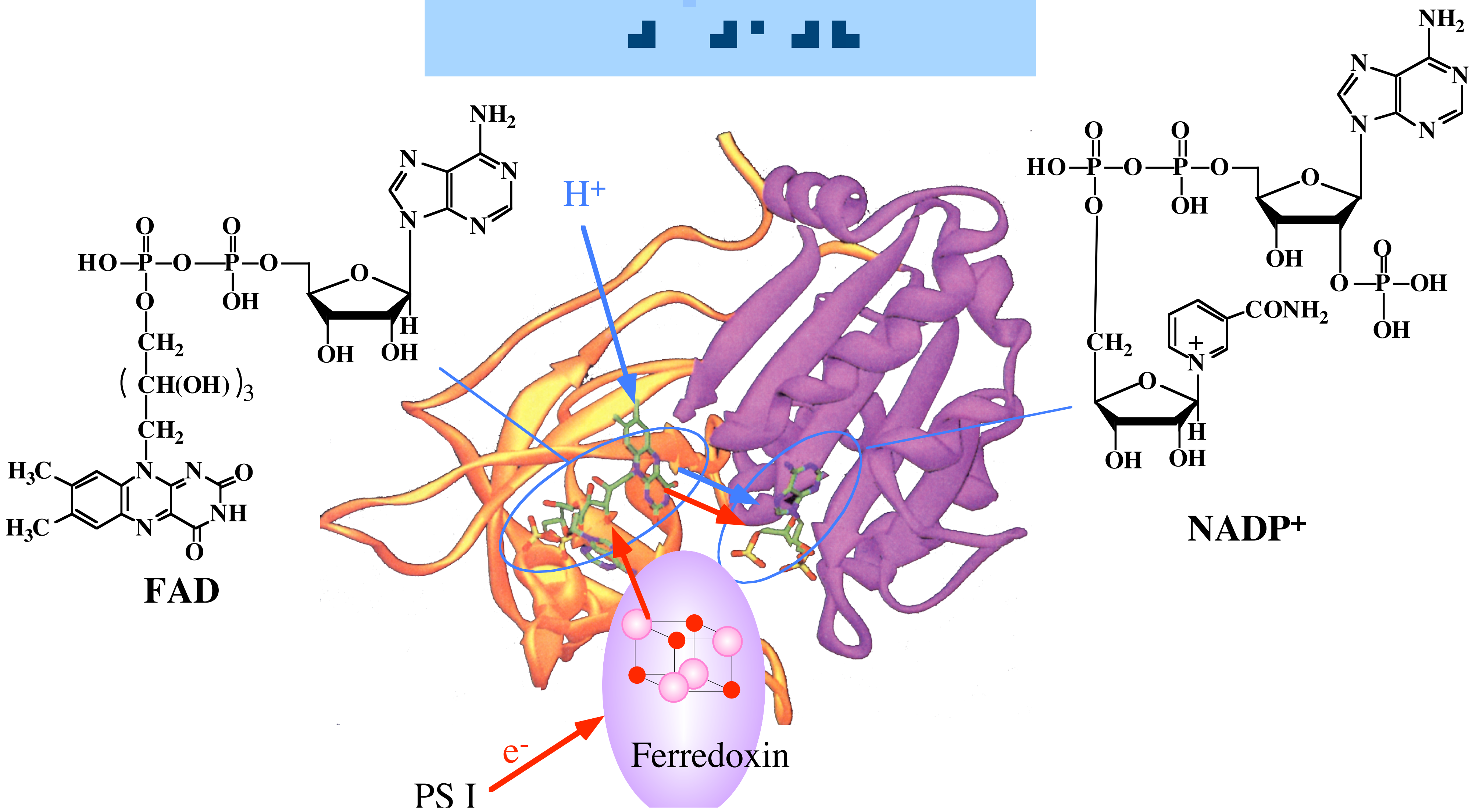
thylakoid

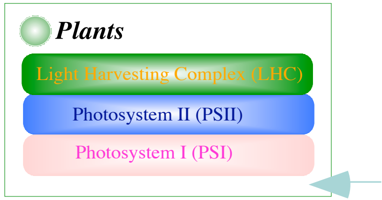
PS I (*Synechococcus sp.*)
6 Å resolution



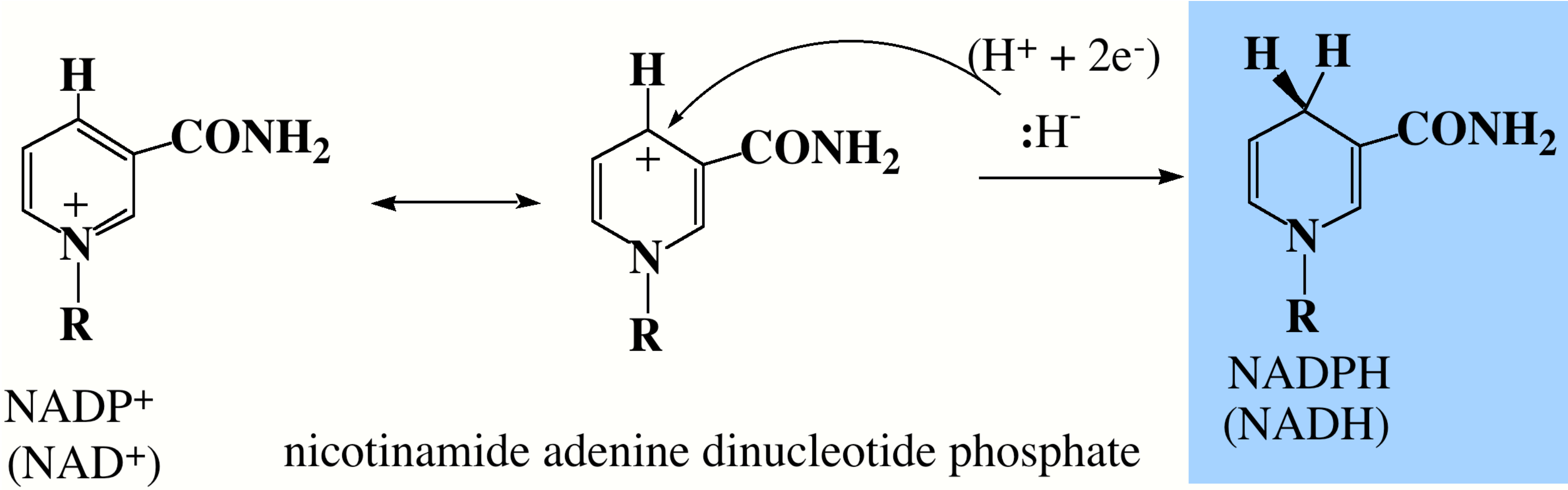
Ferredoxin-NADP+ Reductase (FRN)





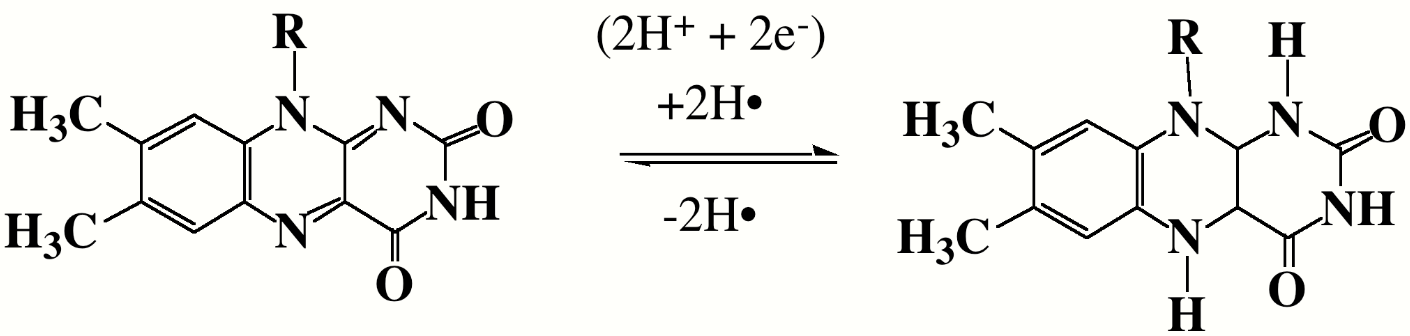


Ferredoxin-NADP+ Reductase



NADP+ (NAD+)

nicotinamide adenine dinucleotide phosphate



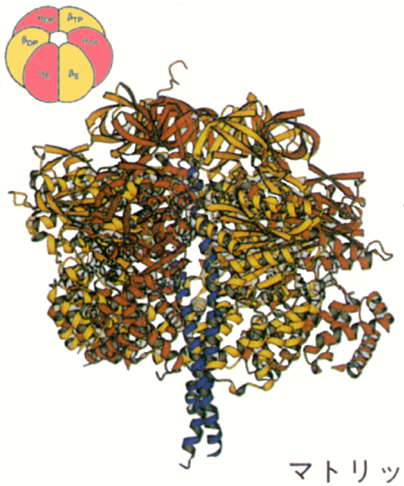
FAD

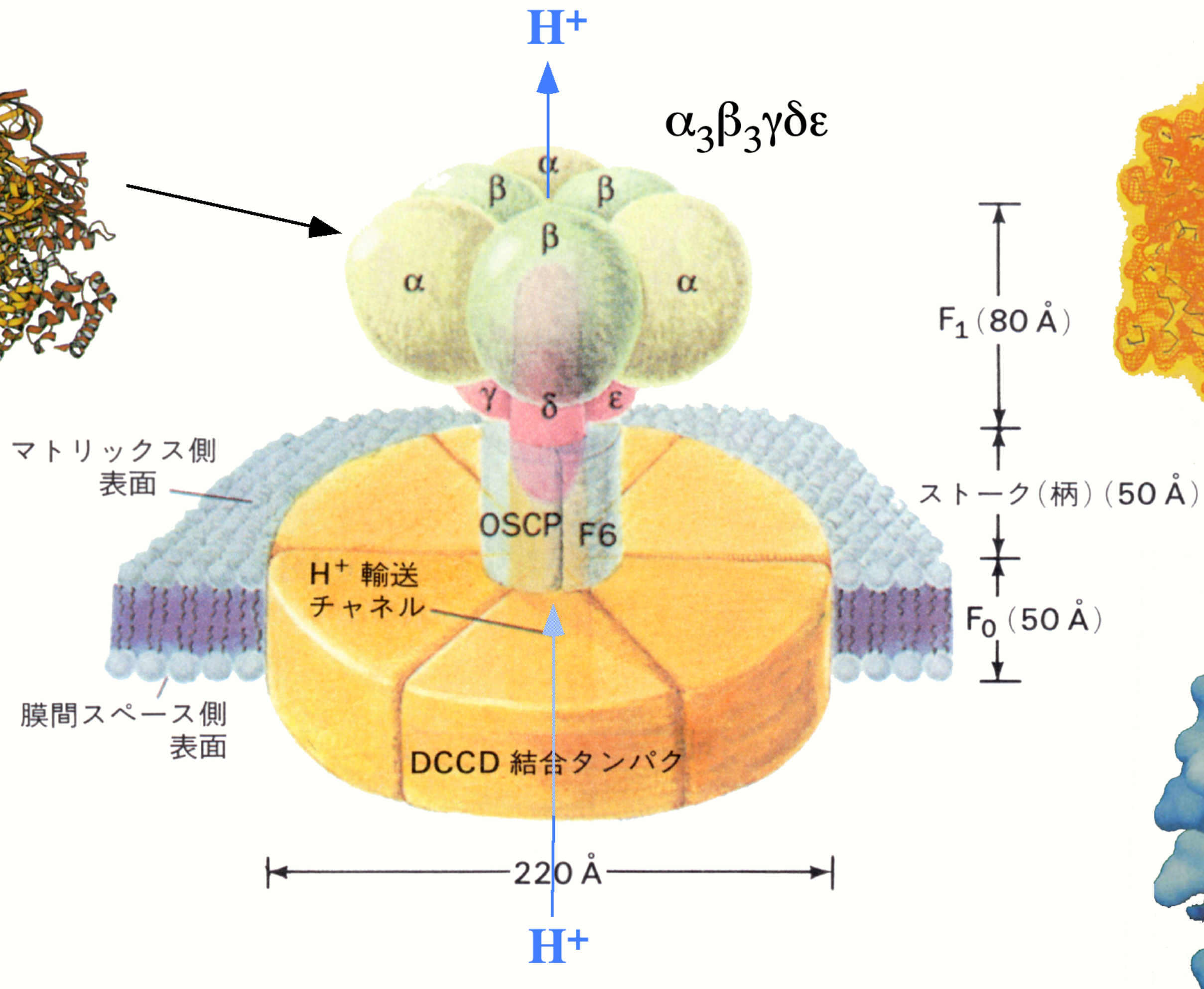
flavin adenine dinucleotide

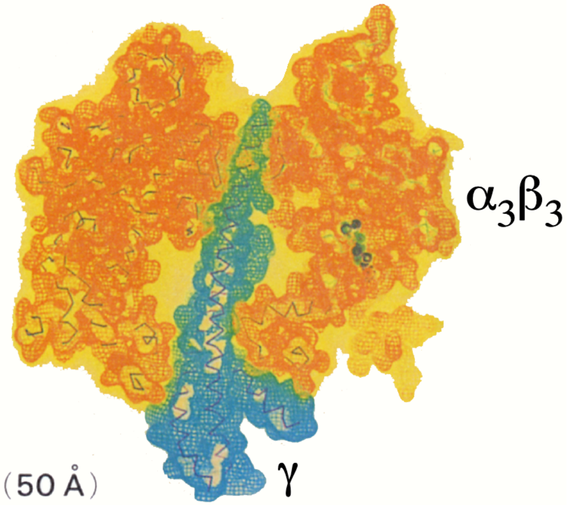
FAD_{red}

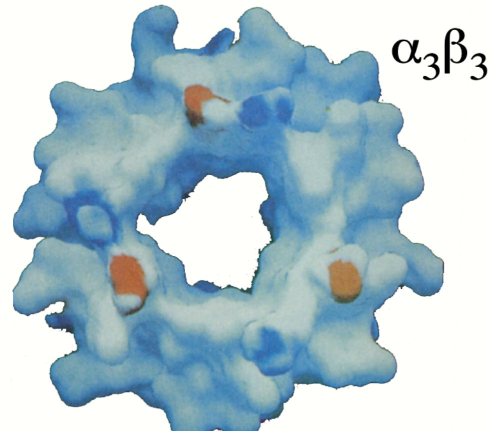
ATP Synthase

$$ADP + P_i \xrightarrow[H^+ \text{ pump}]{\text{energy}} ATP + H_2O$$



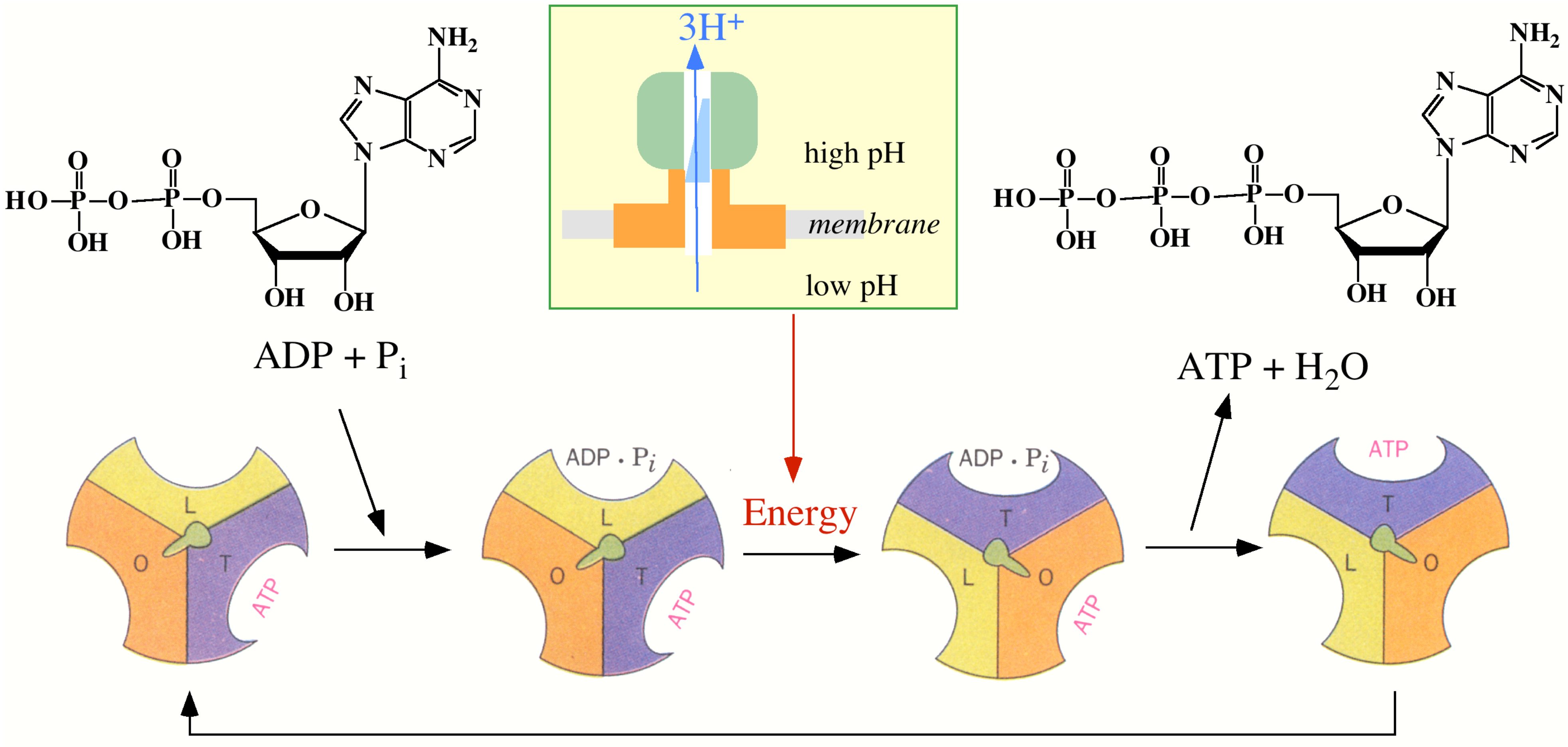






ATP Synthase

$$ADP + P_i \xrightarrow[H^+ \text{ pump}]{\text{energy}} ATP + H_2O$$

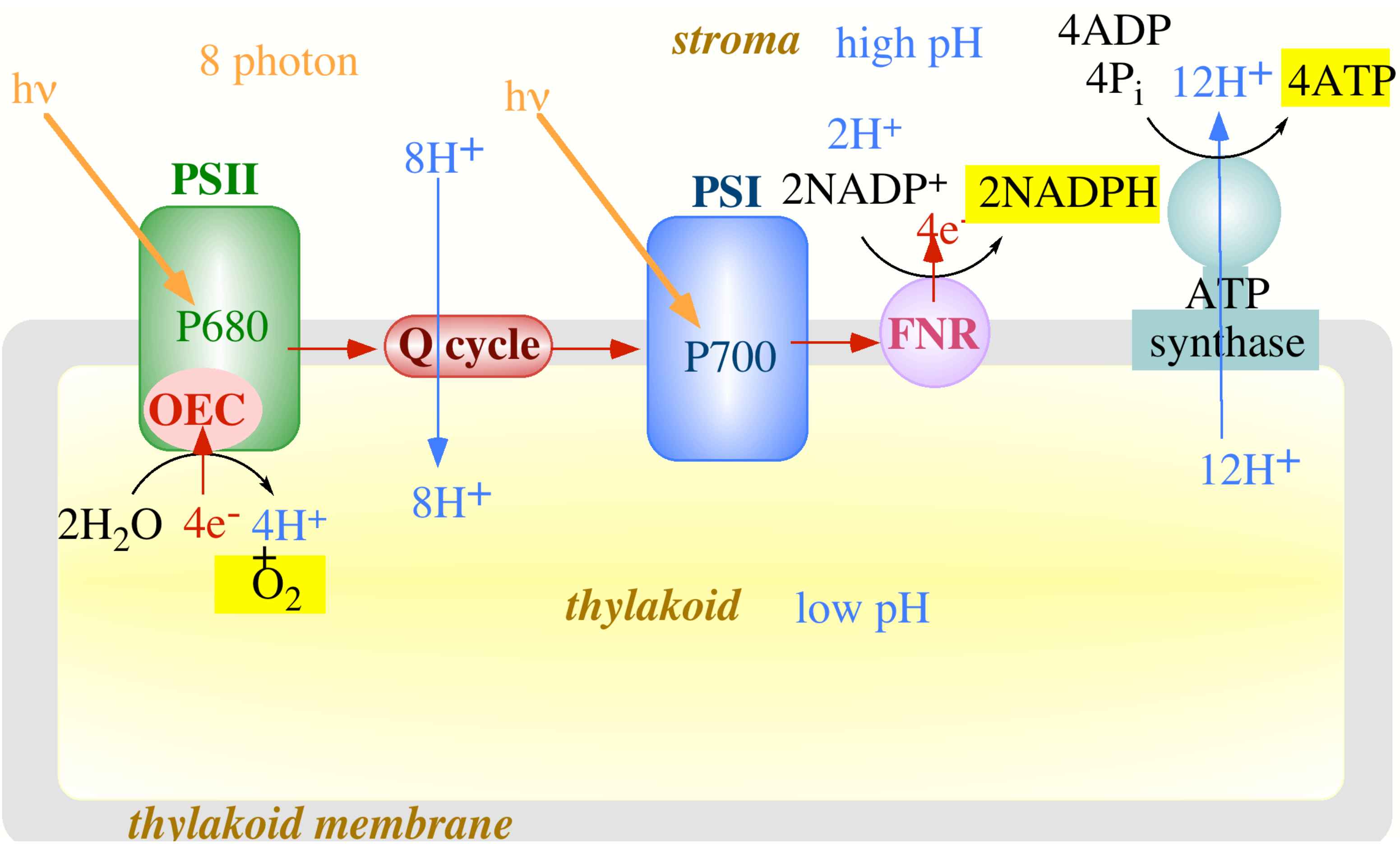


L = loose, T = tense, O = open

Summary of Light Reactions in Chloroplast

$$2H_2O + 2NADP^+ \underset{}{\overset{h\nu}{\rightleftharpoons}} 2NADP + O_2 + 2H^+ \quad (\Delta G^o = 438\ kJ{\cdot}mol^{-1})$$

$$4ADP + 4P_i \overset{h\nu}{\rightleftharpoons} 4ATP + 4H_2O \quad (\Delta G^o = 122\ kJmol^{-1})$$



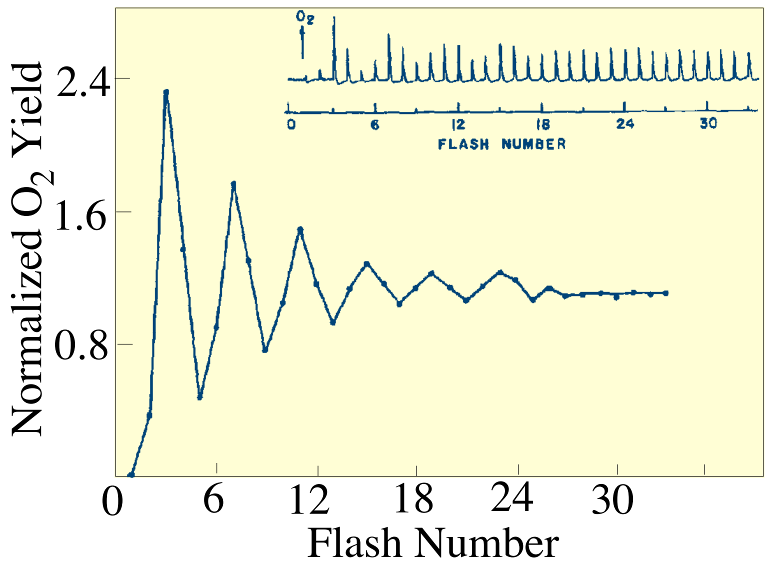
Manganese Cluster Chemistry
in Relation to
Oxygen Evolving Center in PS II

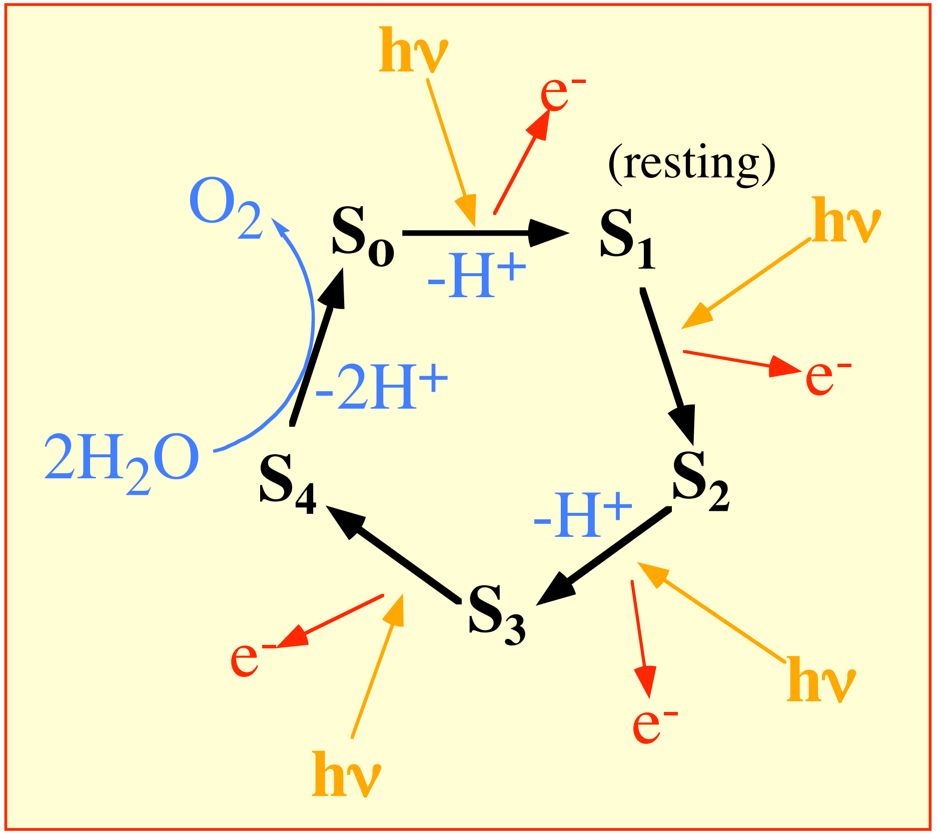
Oxygen Evolving Mechanism

$$2H_2O \xrightarrow{h\nu} O_2 + 4e^- + 4H^+$$

1971 by P. Joliet & B. Kok

Dioxygen Evolution in Flashing Light

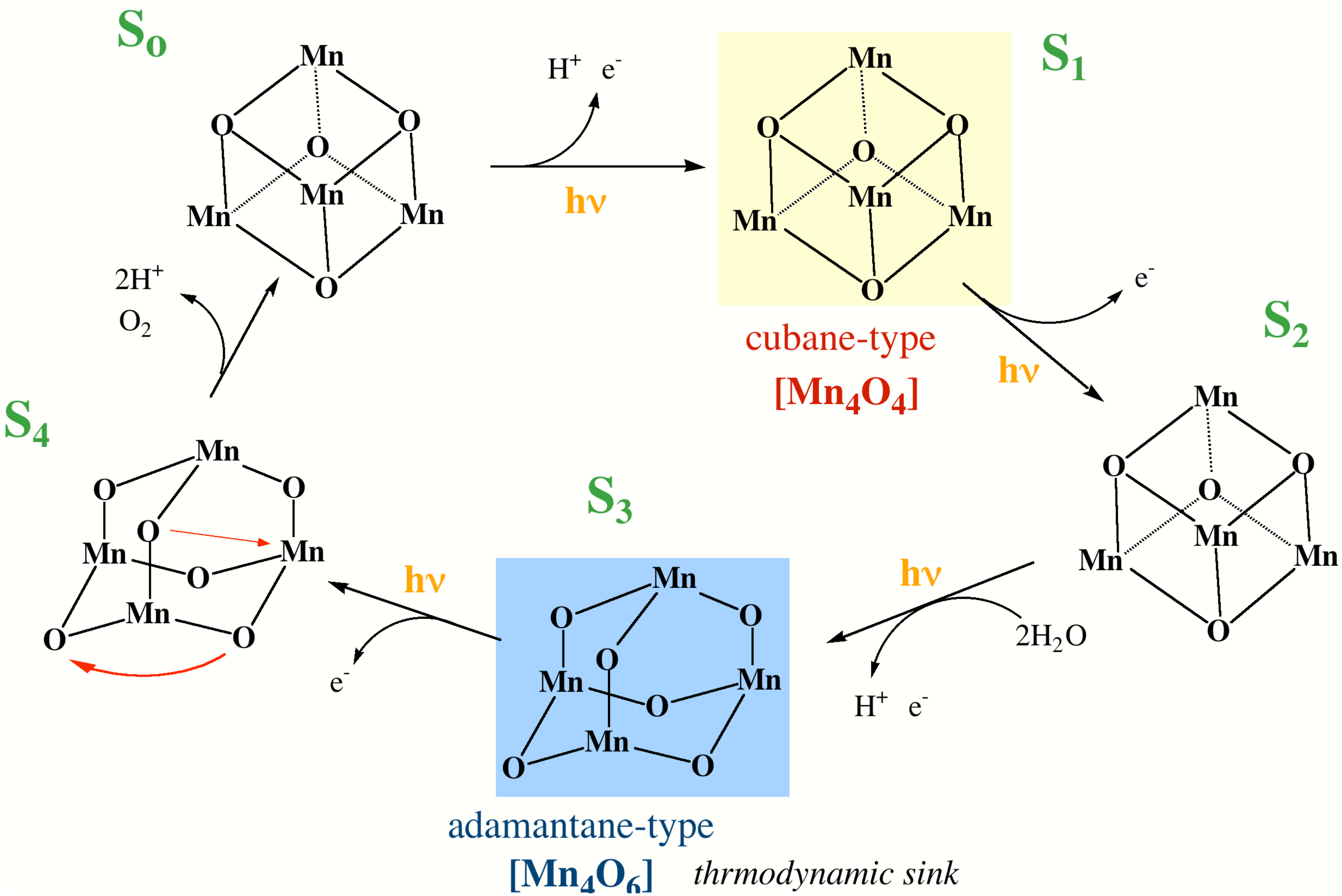




OEC Involves Four Mn Ions (4Mn)

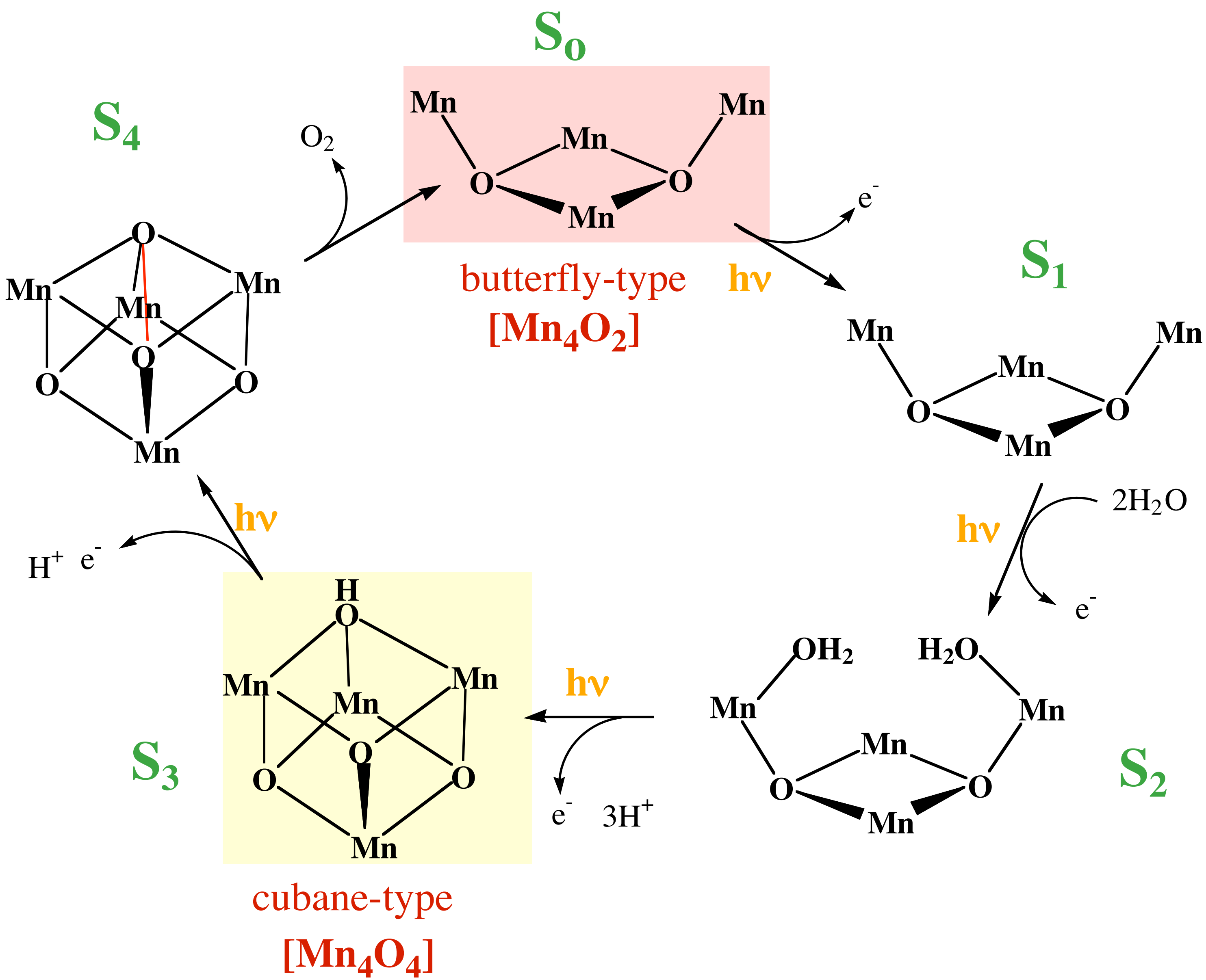
A Proposed Mechanism of OEC

G. W. Brudvig, R. H. Crabtree, *Proc. Natl. Acad. Sci. USA*, **1986**, *83* 4586



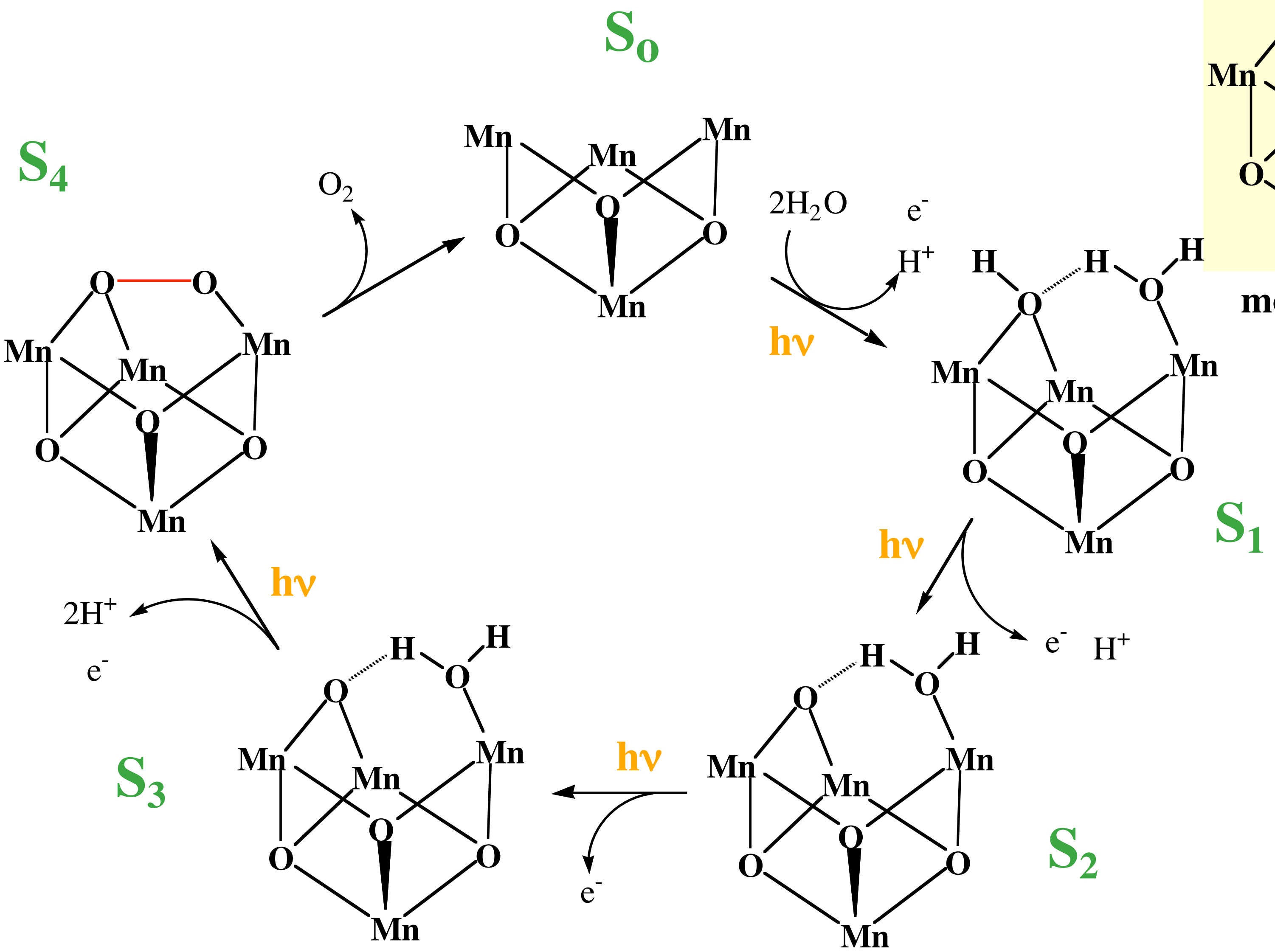
A Proposed Mechanism of OEC

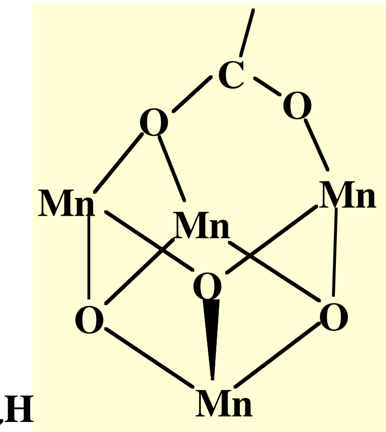
J. B. Vincent, G. Christou, *Inorg. Chim. Acta* **1987**, *136*, L41



Modified Proposed Mechanism of OEC

J. B. Vincent, R. H. Christou, *Adv. Inorg. Chem.*, **1989**, *33*, 197
D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.*, **1994**, *116*, 8376

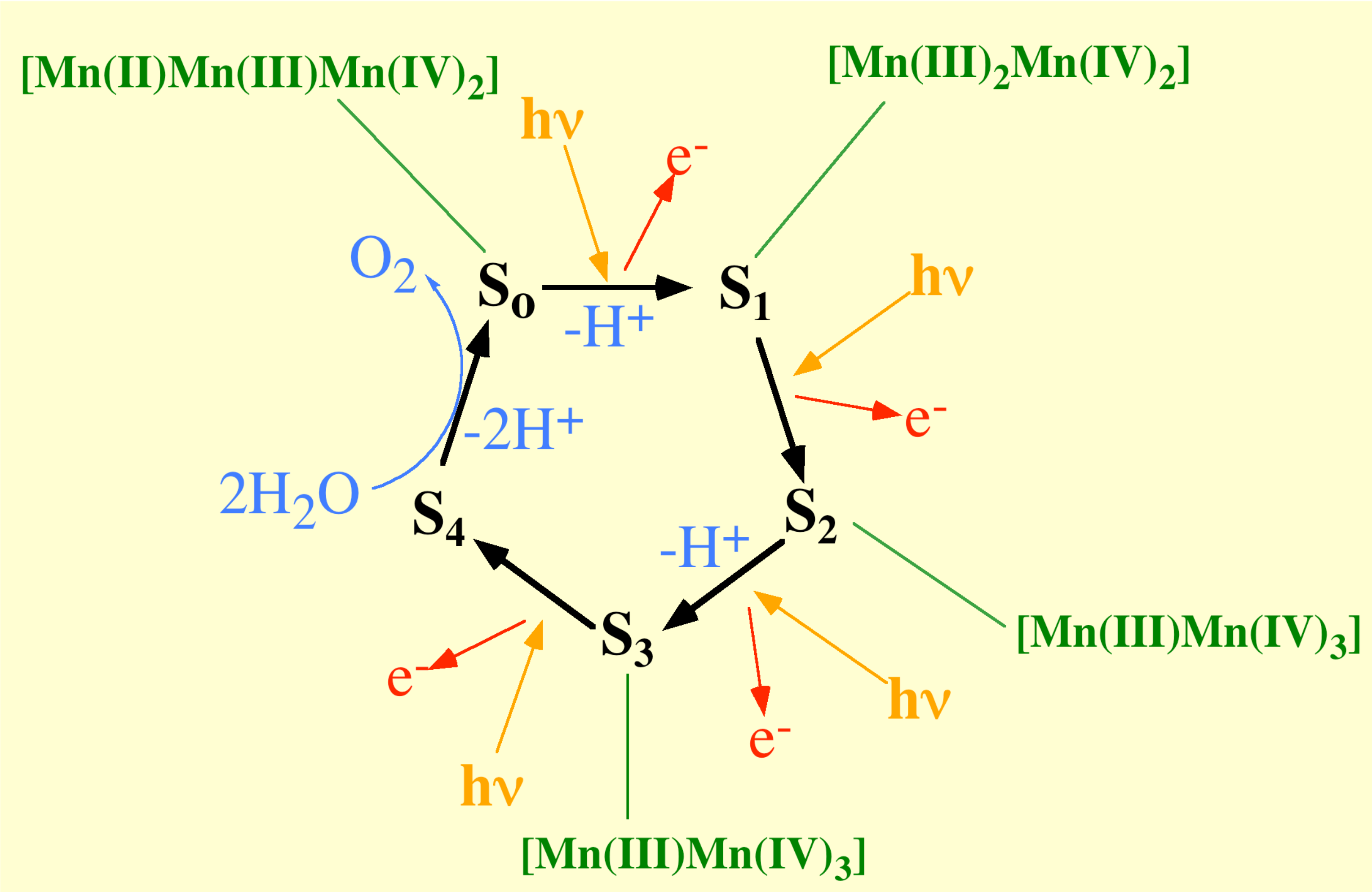




model compound

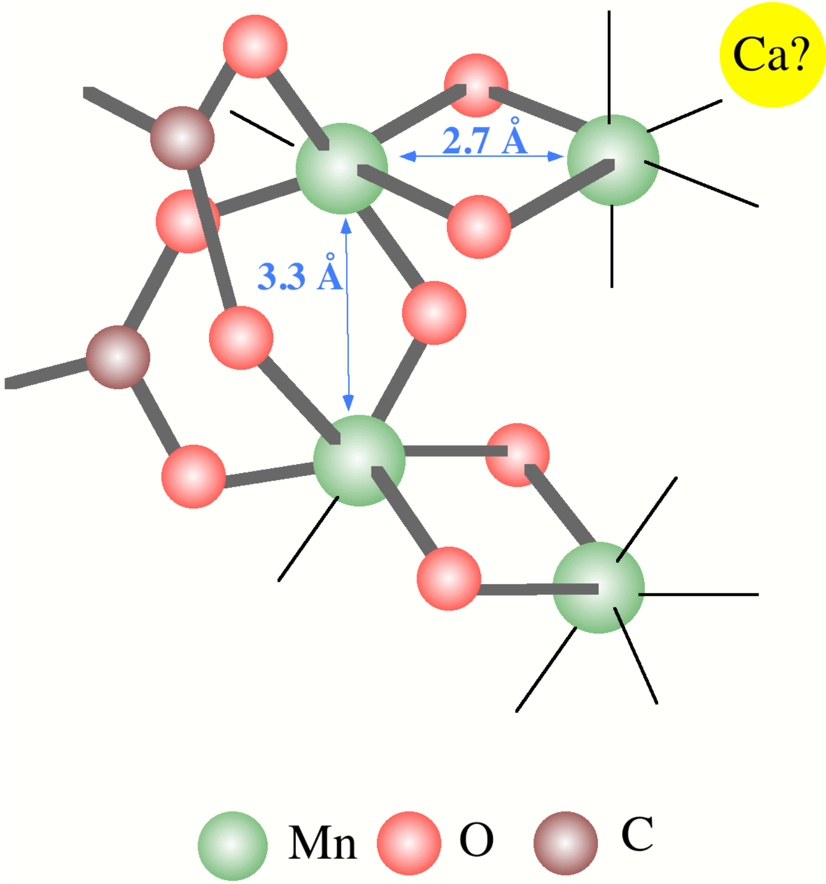
EPE Studies Revealed the Oxidation States of Mn4 Cluster in OEC

V. K. Yachandra, *Chem. Rev.*, **1996**, *96*, 2927

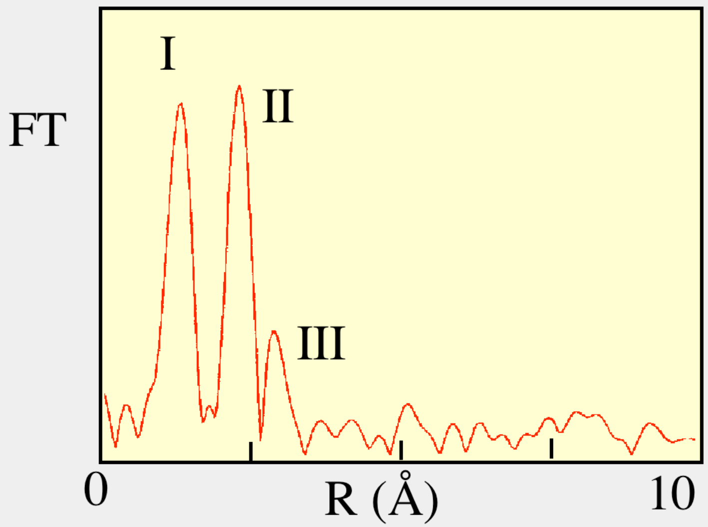


C-shape Dimer-to-Dimer Structure was Proposed from Detailed EXAFS Studies

V. K. Yachandra, *Science*, **1993**, *260*, 675



EXAFS Fourier Transform for OCE from *Synechococcus* in S_1 State

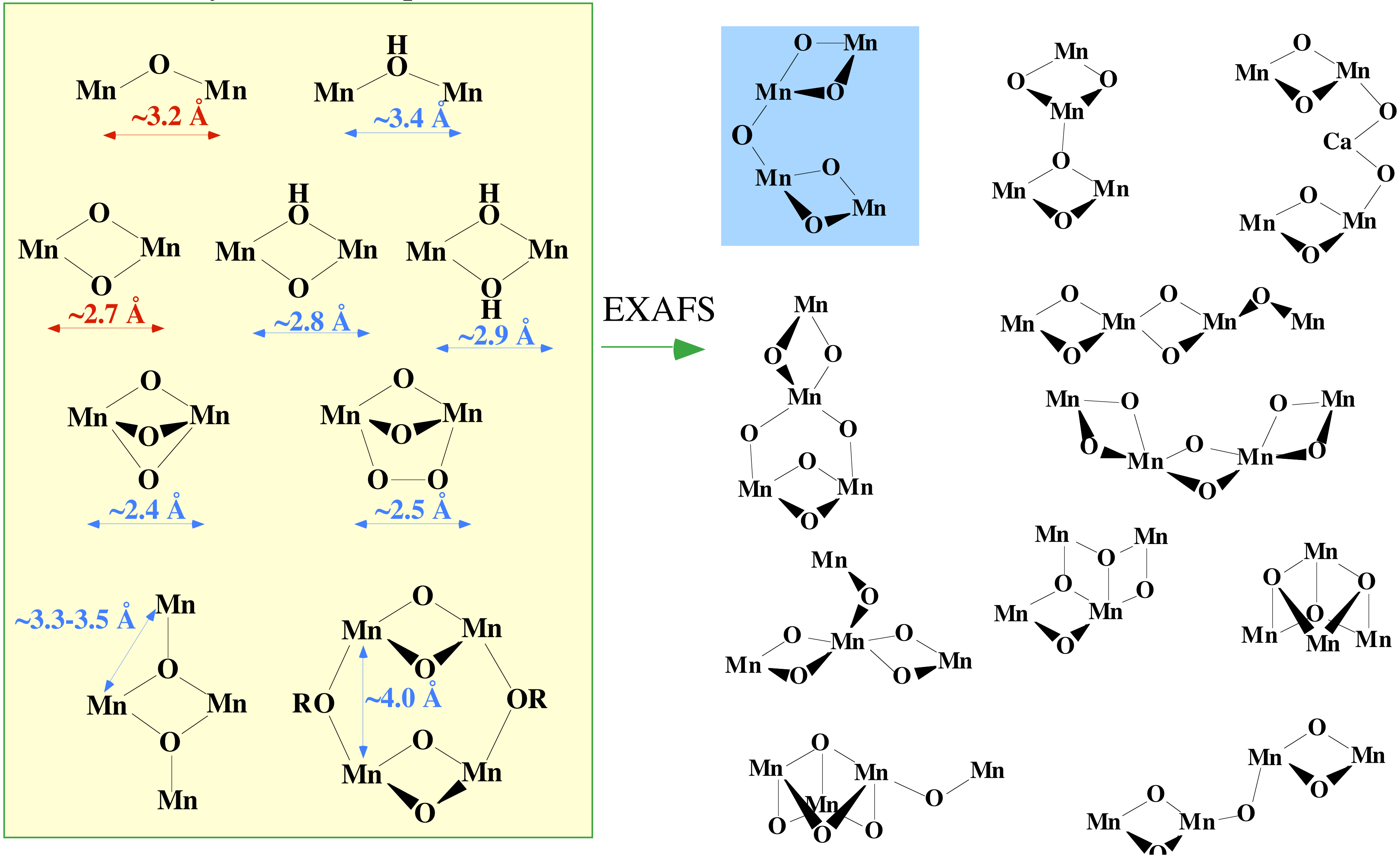


I	Mn–O	r = 1.82 Å,	N = 1.5-2.5
	Mn–O/N	r = 1.95-2.15 Å,	N = 2-4
II	Mn–Mn	r = 2.72 Å,	N = 1-1.5
III	Mn–Mn/Ca	r = 3.3 Å,	N = 0.5(Mn), 0.25(Ca)

C-shape Dimer-to-Dimer Structure was Proposed from Detailed EXAFS Studies

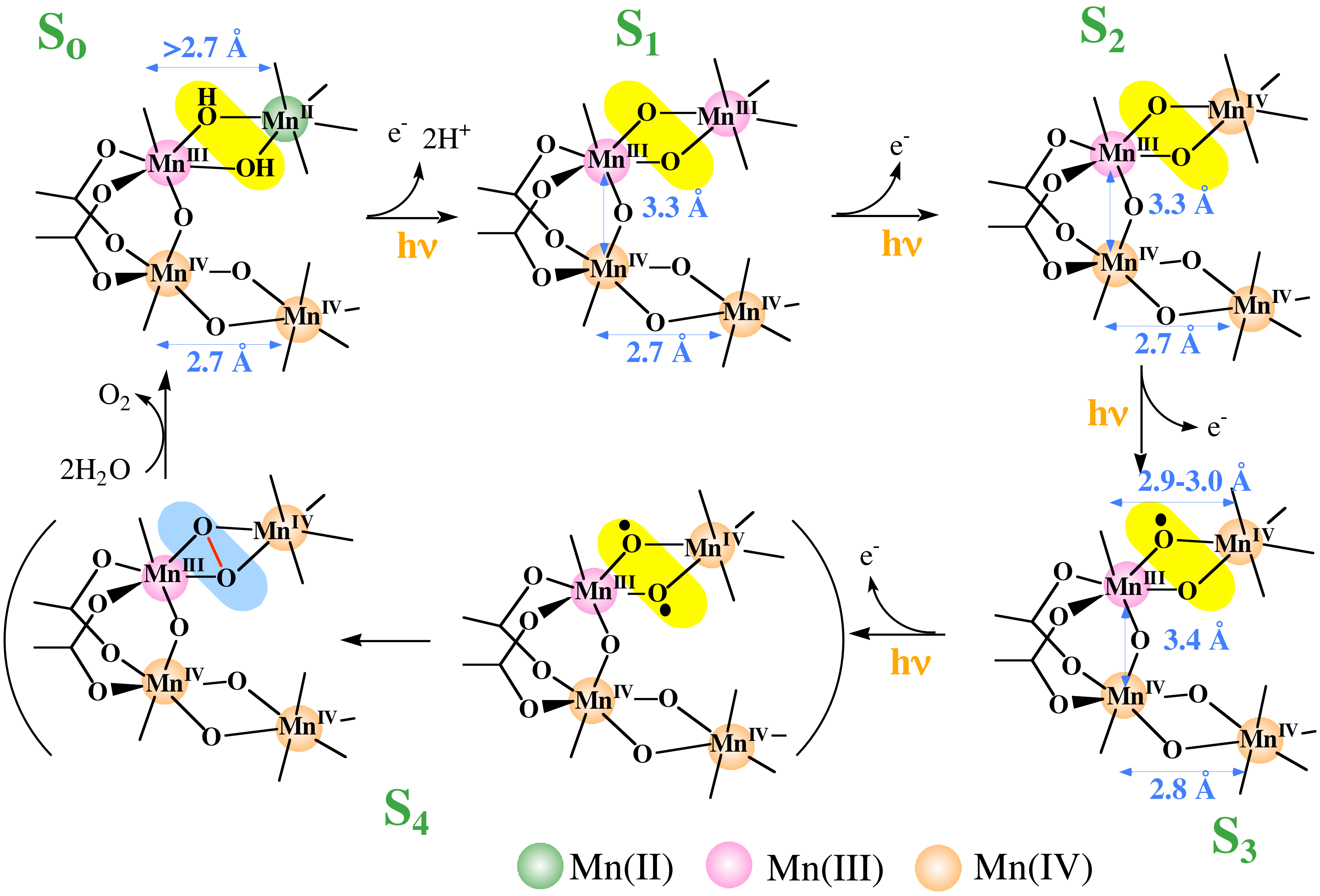
Structural Parameters from Synthetic Compounds

Structural Candidates for OEC



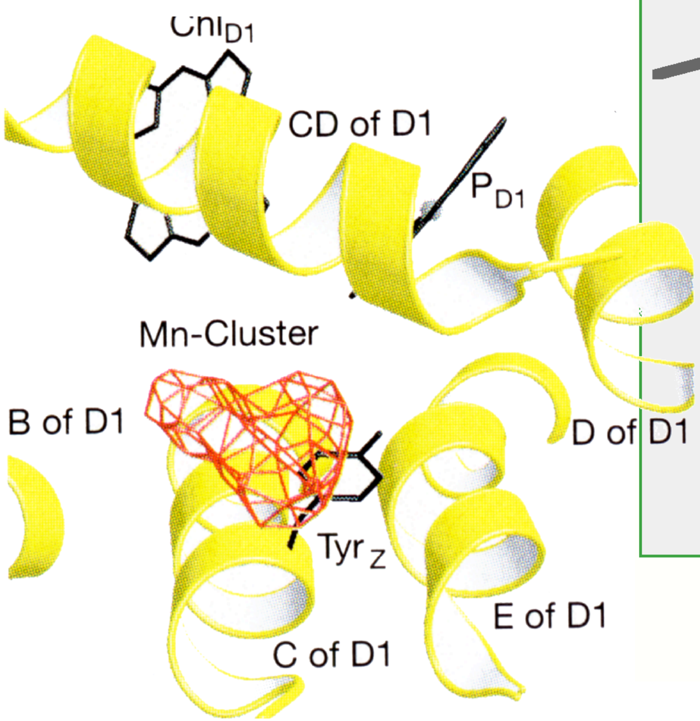
A Proposed Mechanism of OEC

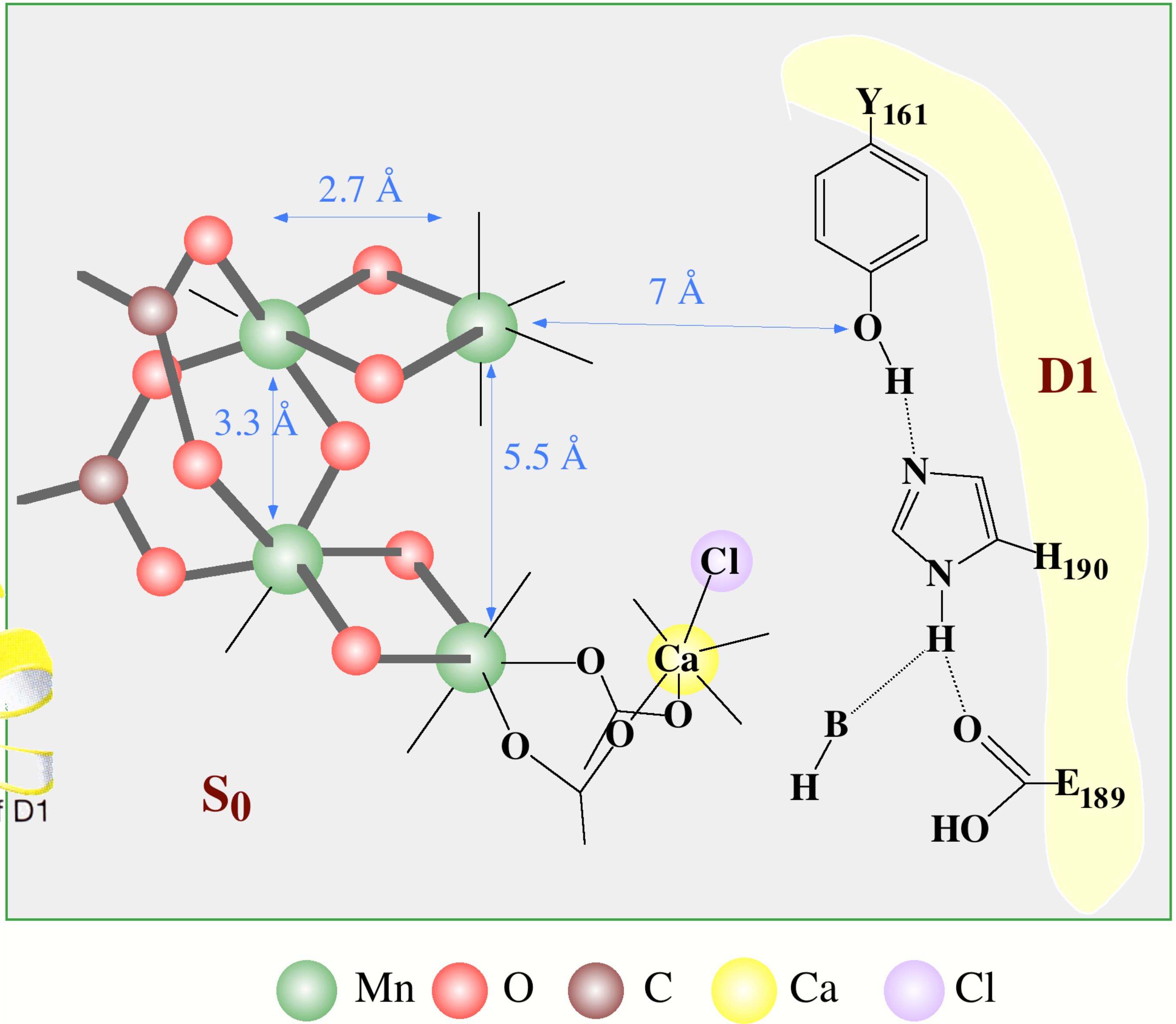
V. K. Yachandra, *Chem. Rev.*, **1996**, *96*, 2927



Recently Proposed Structure of OEC Active Site

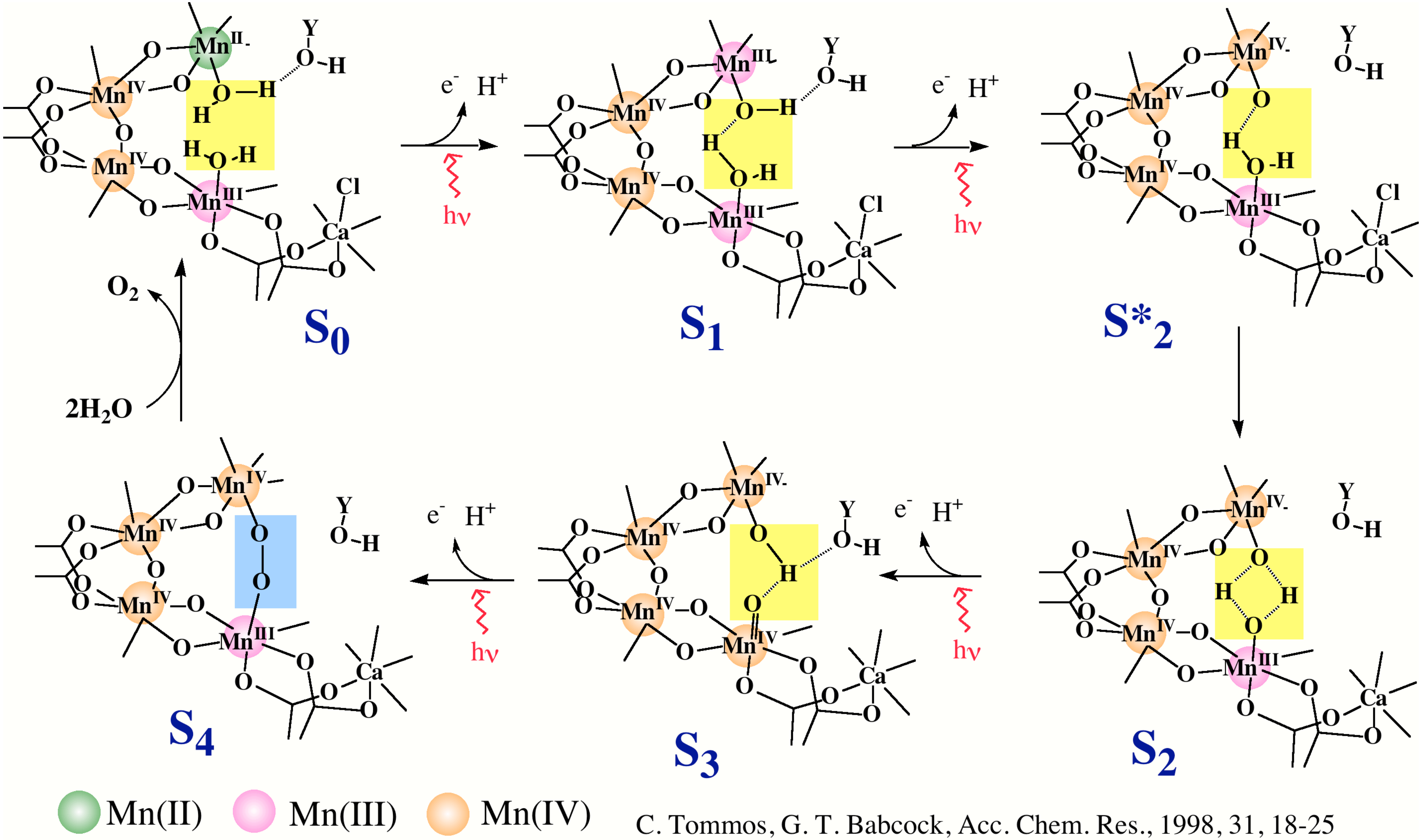
C. Tommos, G. T. Babcock, *Acc. Chem. Res.*, **1998**, *31*, 18





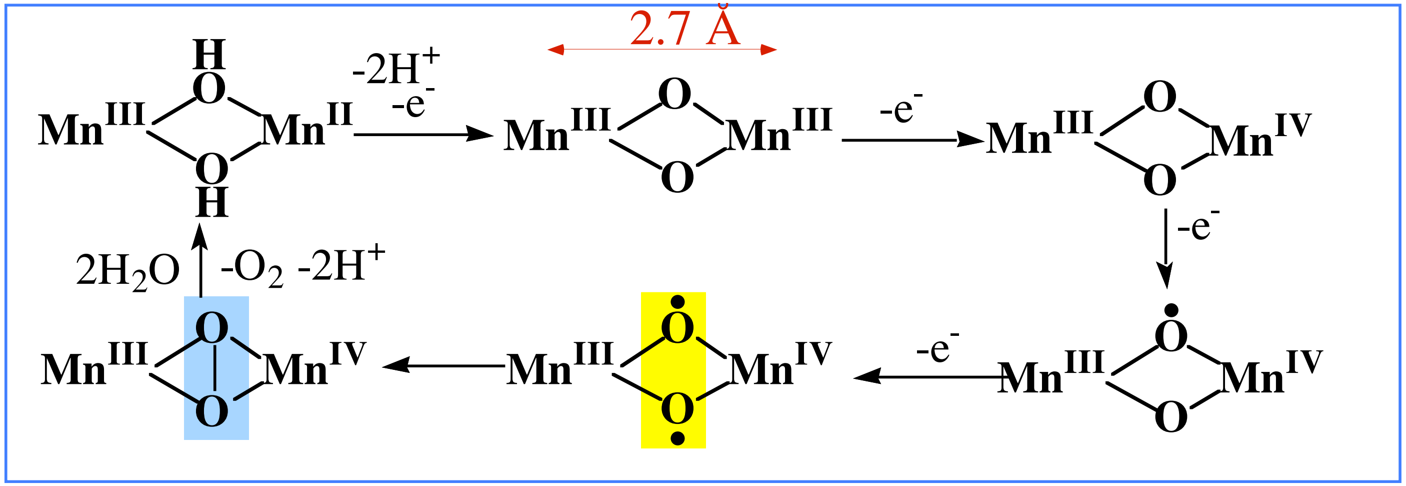
Proposed Cycle for OEC in PSII

by G. T. Babcock 1998

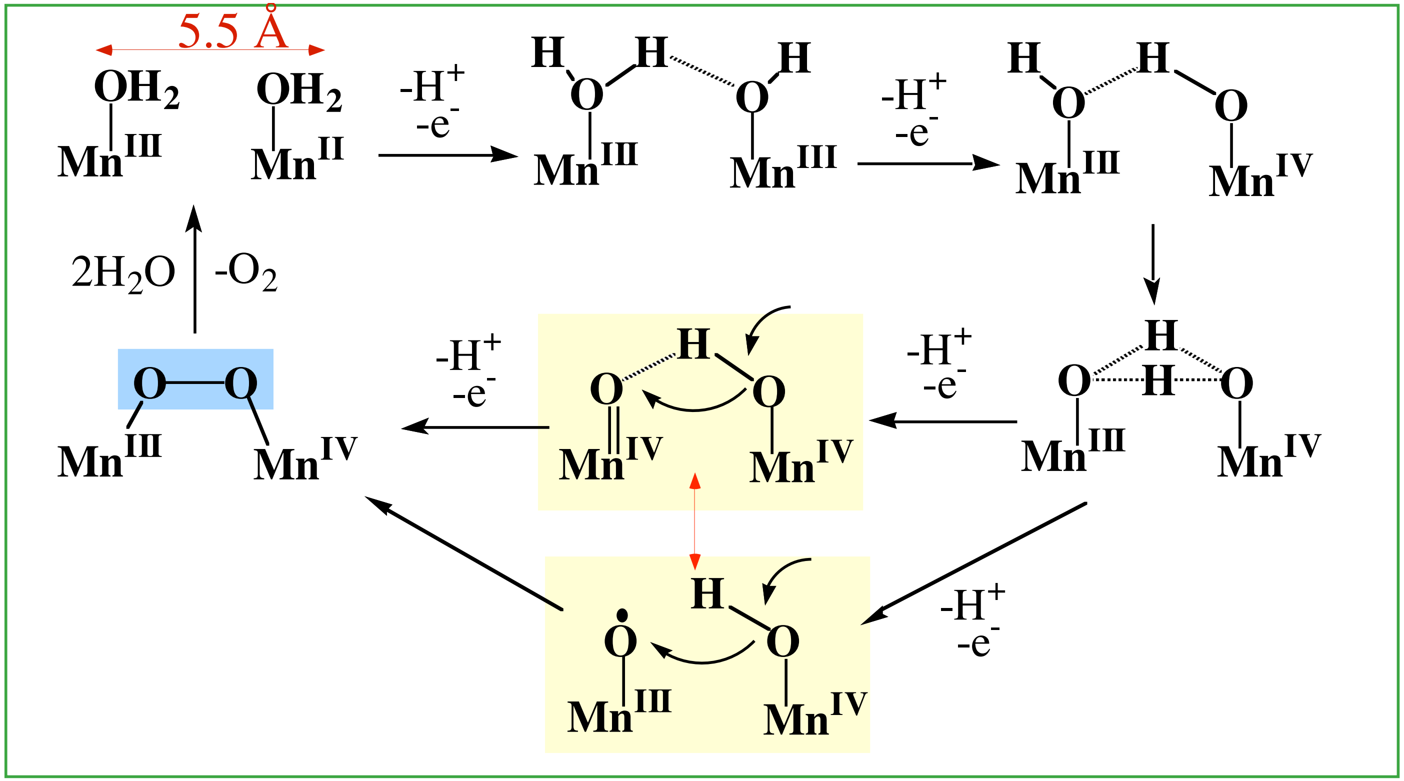


C. Tommos, G. T. Babcock, Acc. Chem. Res., 1998, 31, 18-25

Two Proposed Mechnisms with C-Shape Mn4 Center



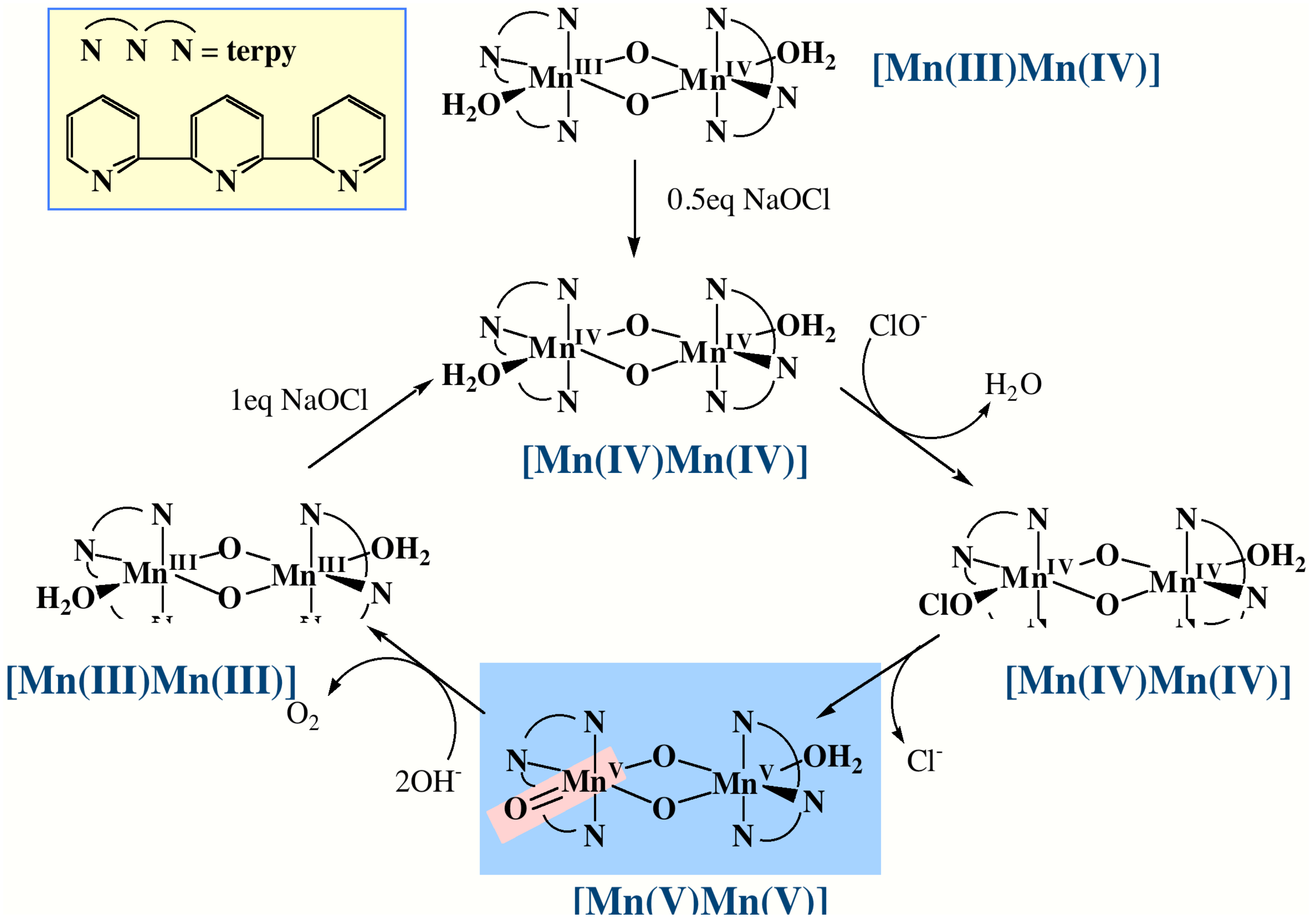
Yachandra



Babcock

Functional Model System of OEC Center by Dinuclear Mn Complex

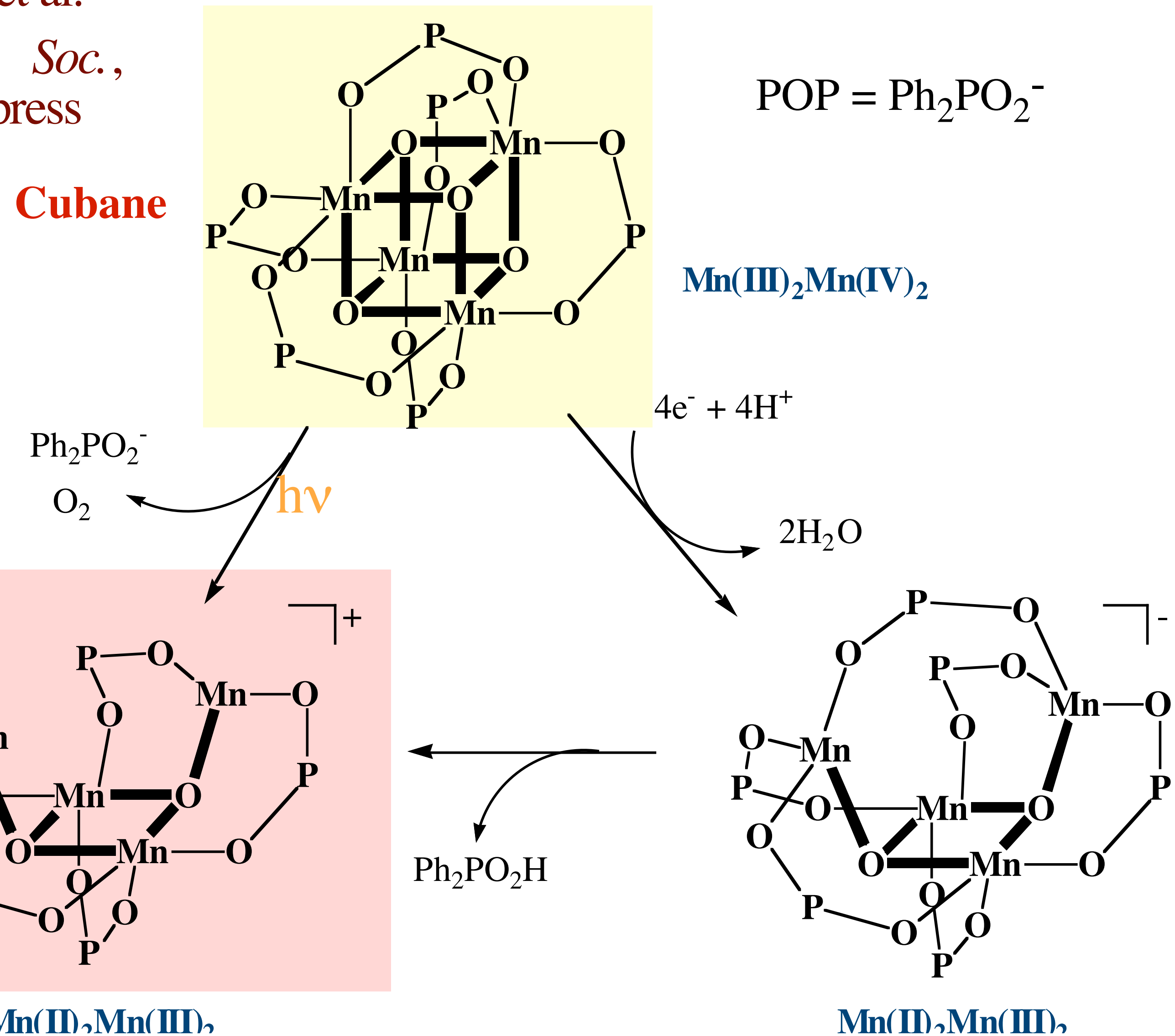
R. H. Crabtree et al.
Science, **1 999**, *2 83*, 1524



Functional Model System of OEC Center by Tetranuclear Mn Complex

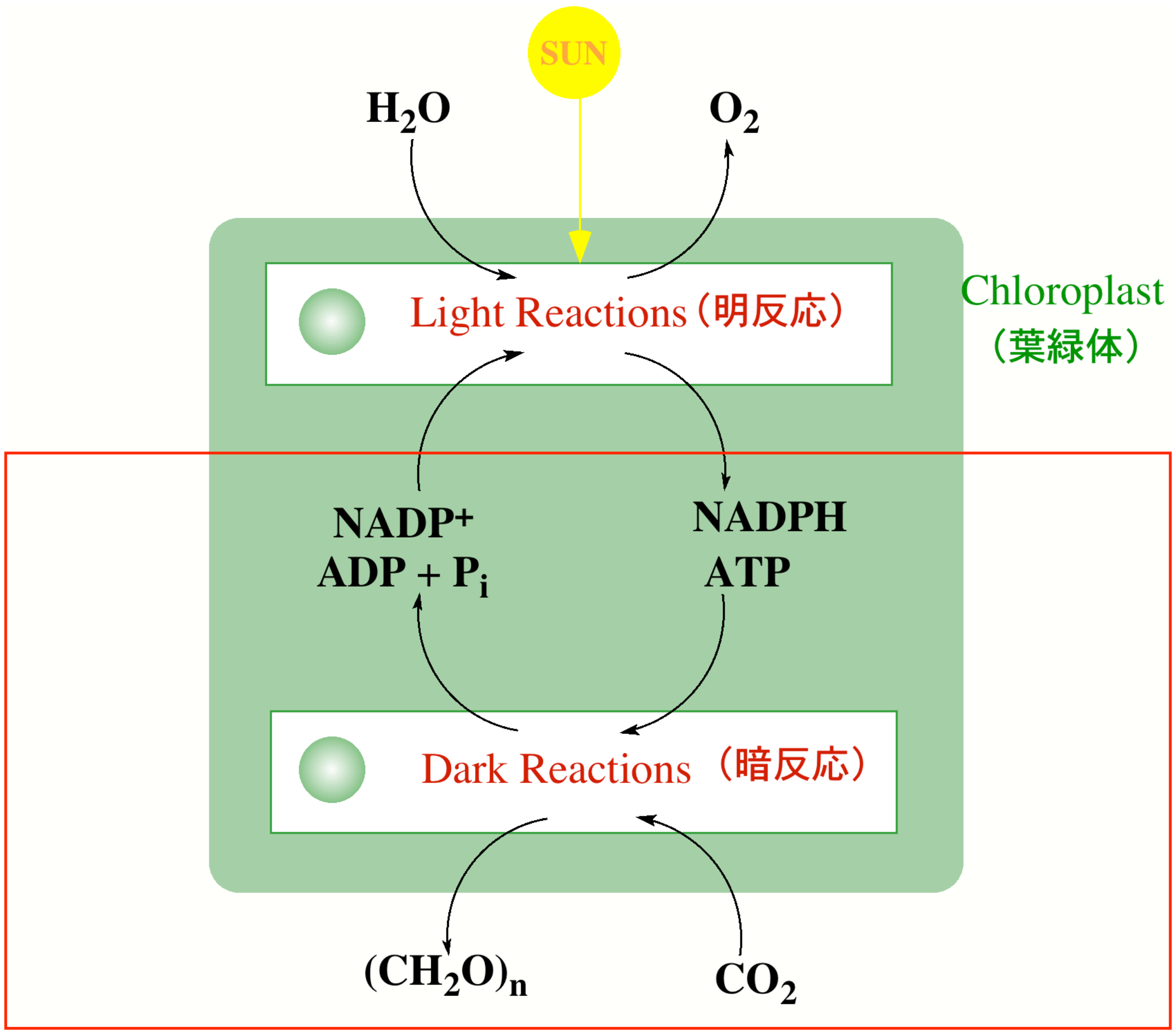
G. C. Dismukes et al.

J. Am. Chem. Soc., **2000,** in press



Butterfly

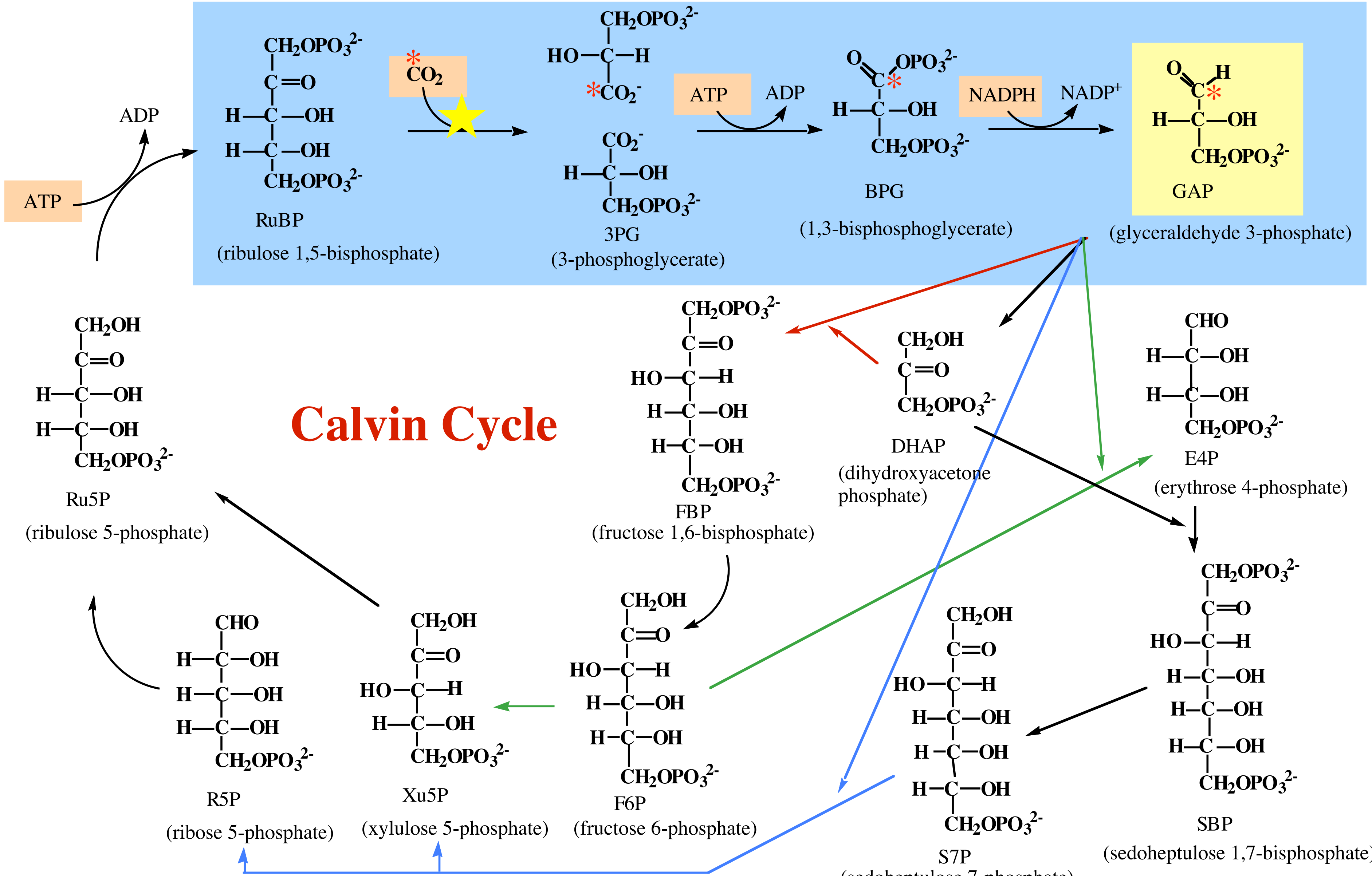
Dark Reactions of Photosynthesis



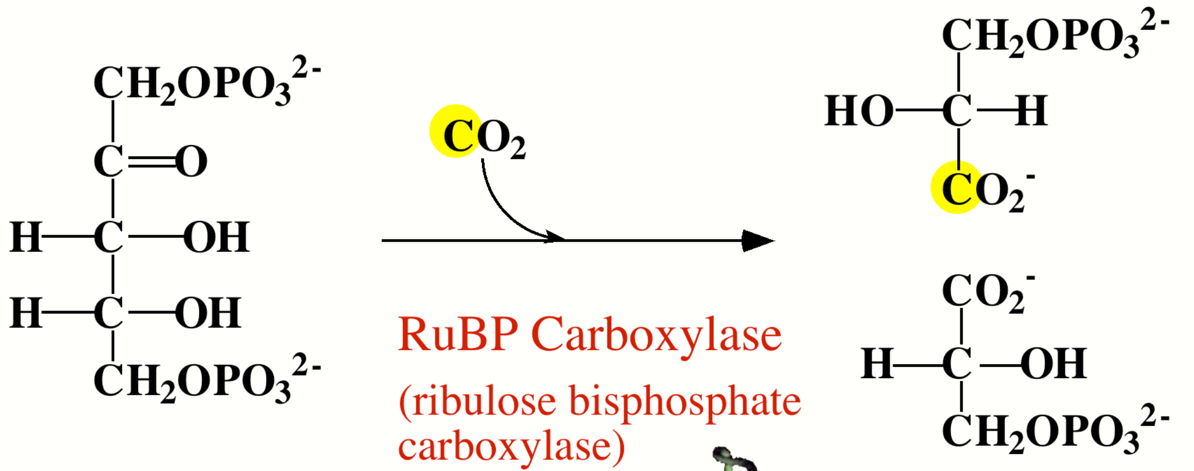
Dark Reactions (plants)

Dark Reactions (Calvin Cycle)

$$3CO_2 + 9ATP + 6NADPH + 5H_2O + 6H^+ \longrightarrow GAP + 9ADP + 6NADP^+ + 8P_i$$

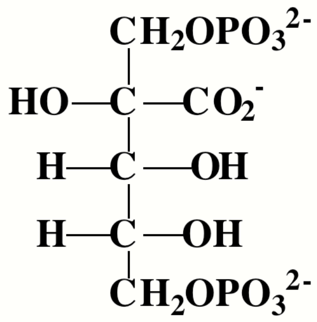


Dark Reactions (Calvin Cycle)

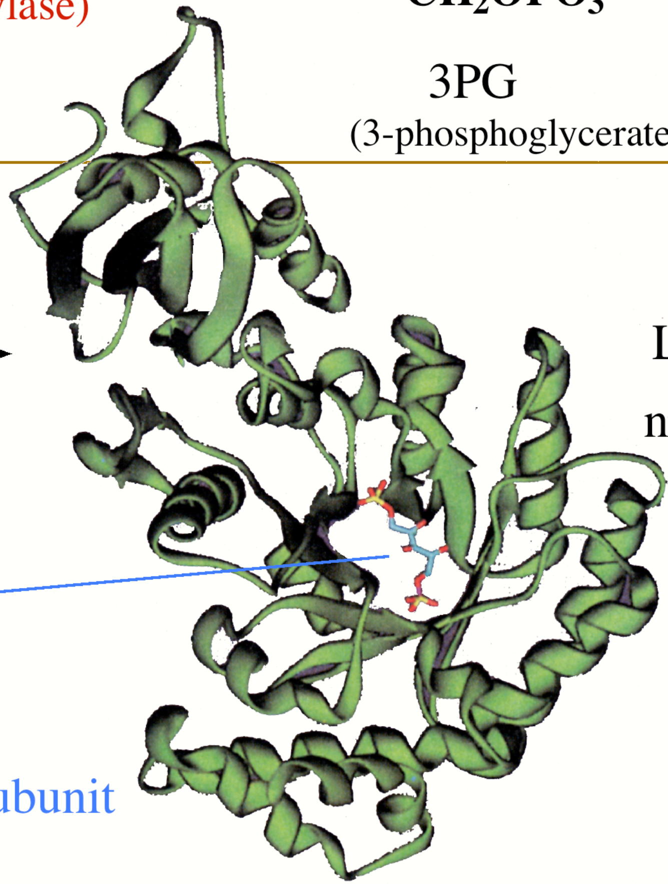


RuBP
(ribulose bisphosphate)

3PG
(3-phosphoglycerate)



CABP
(2-carboxy arabinitol 1,5-bisphosphate)



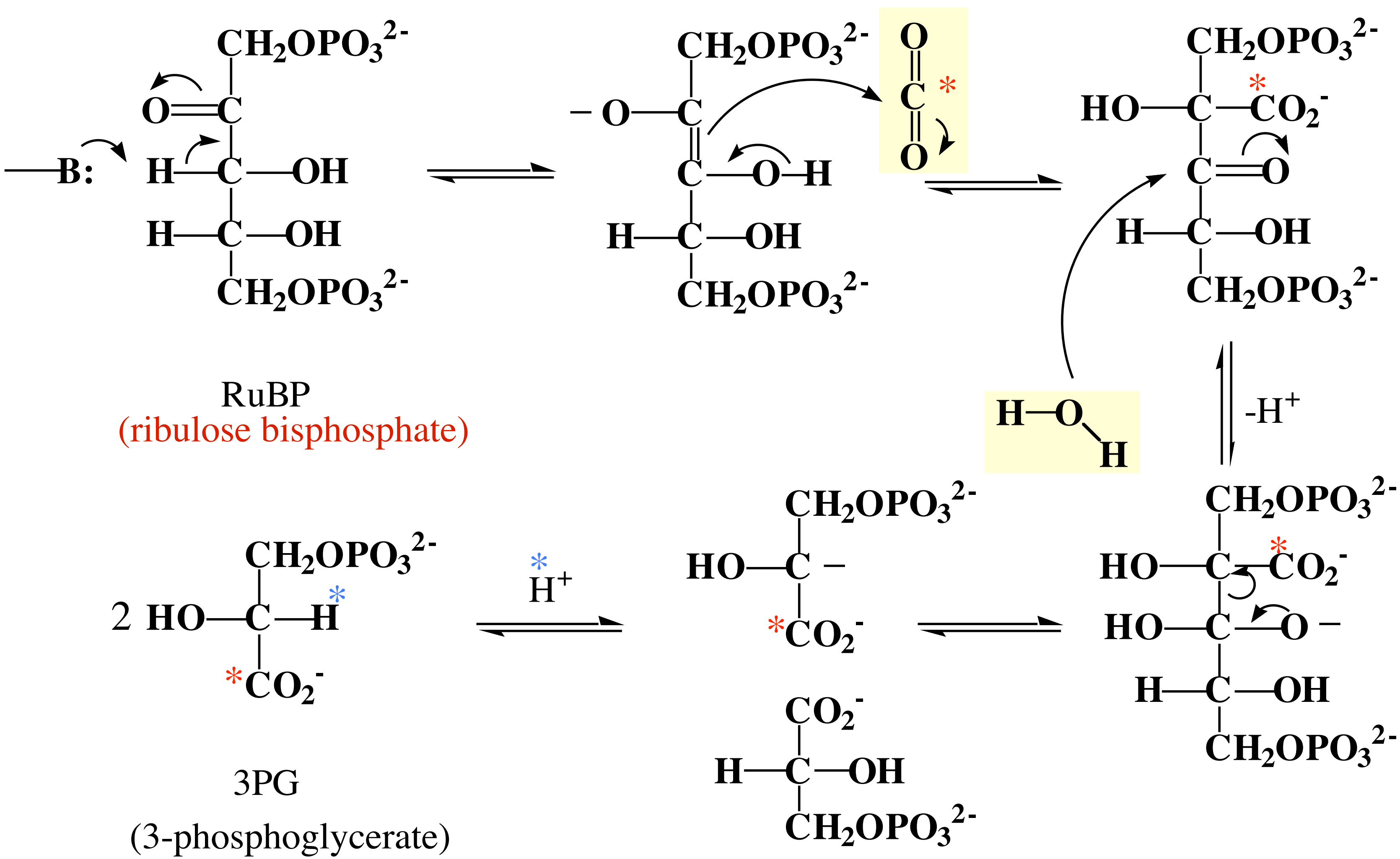
L subunit

L_8S_8 subunits
need Mg^{2+} (M^{2+})

Dark Reactions (Calvin Cycle)

Reaction Mechanism of RuBP Carboxylase

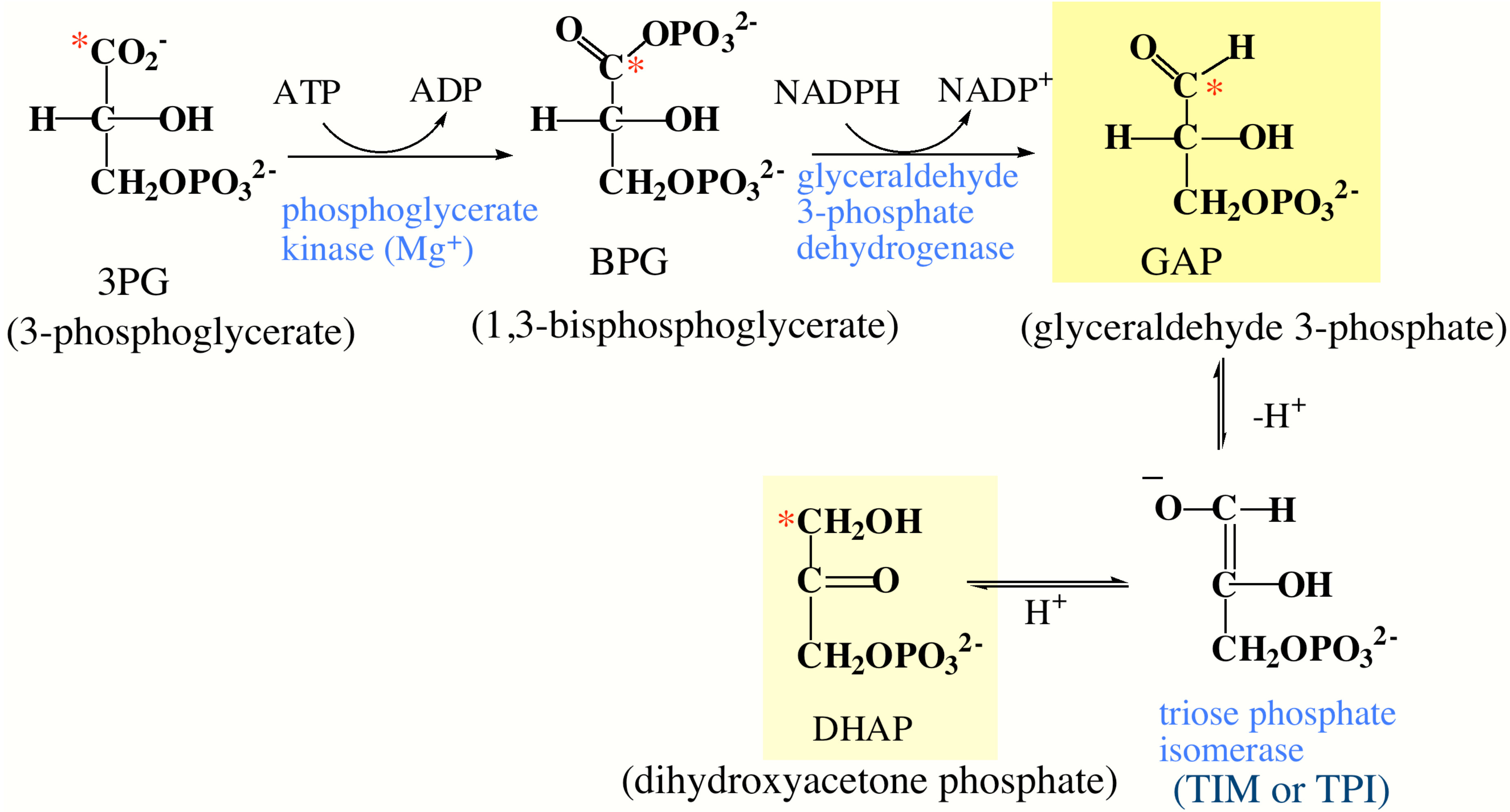
$$RuBP + CO_2 + H_2O \longrightarrow 2\ 3PG$$



Dark Reactions (plants)

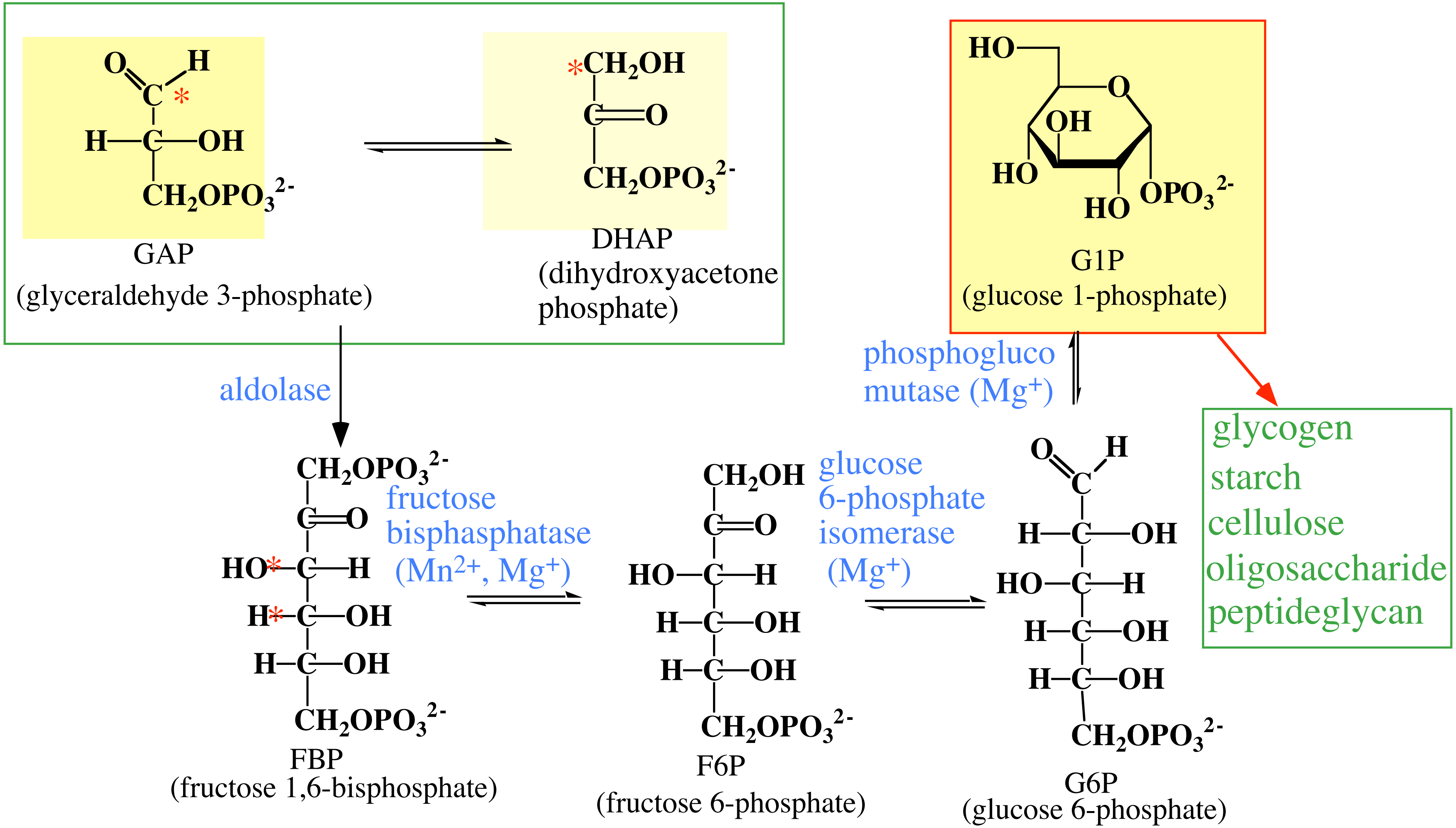
Dark Reactions (Calvin Cycle)

Route from 3PG to GAP

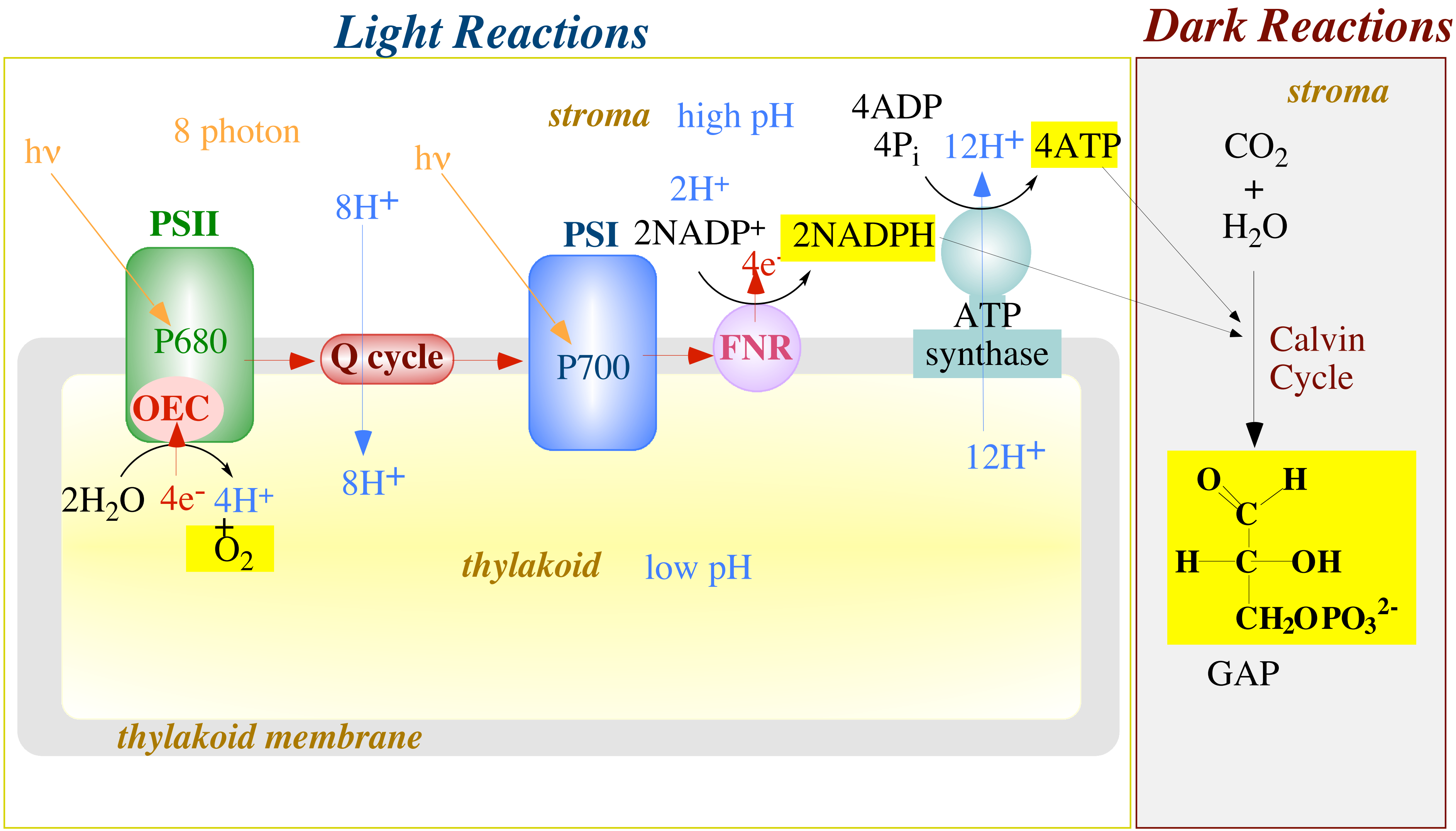


Dark Reactions (plants)

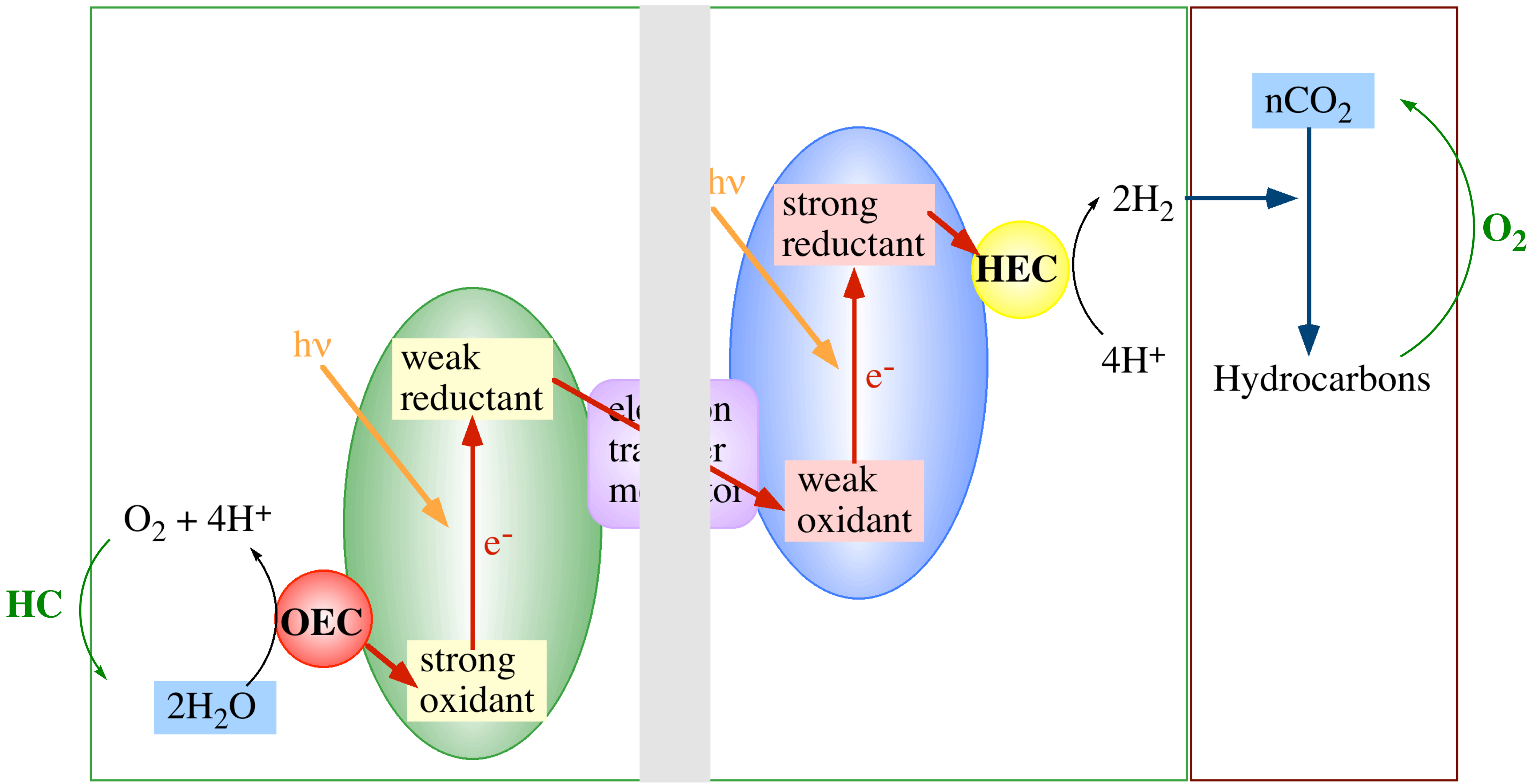
Dark Reactions (from GAP)



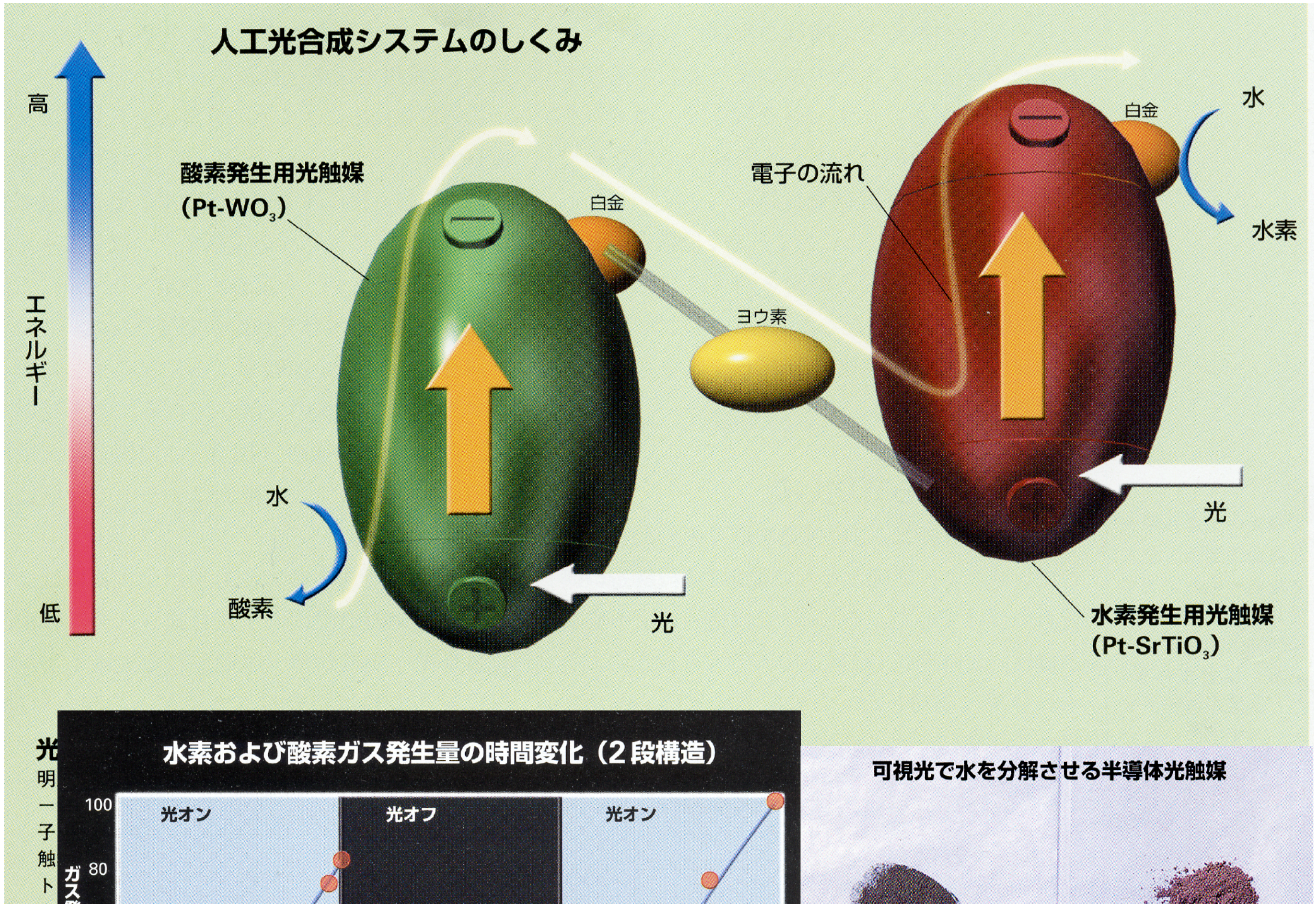
Summary of Photosynthesi in Chloroplast

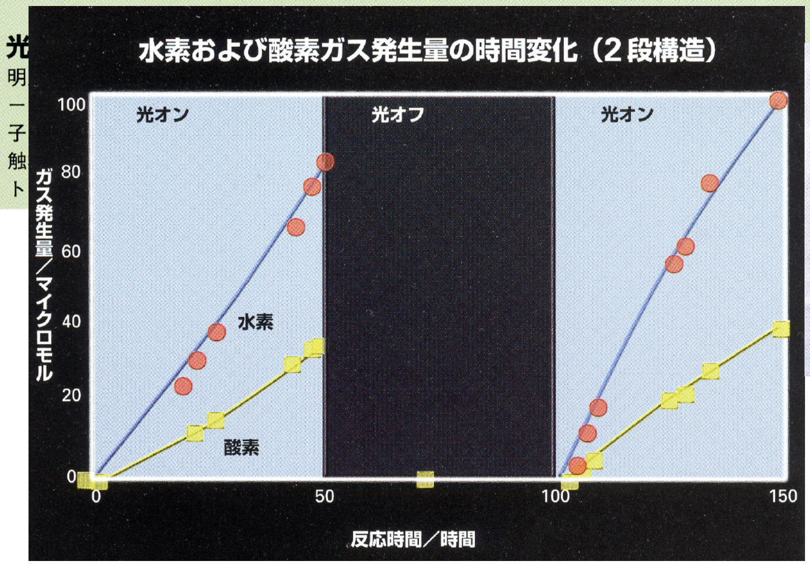


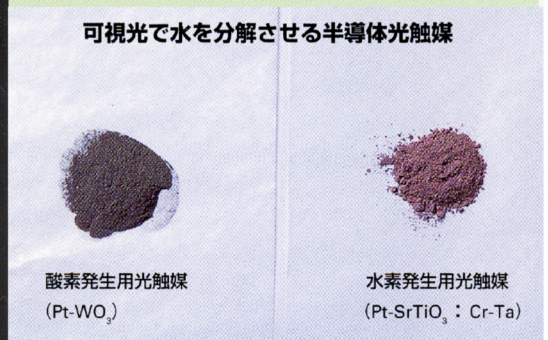
Concepts of Artificial Photosynthesis



Artificial Photosynthesis







Thanks a lot!