

Primary Photochemistry of Photosynthesis

A perspective in honor of
Vlad Shuvalov

by

Govindjee

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Владимир А. Шувалов мужчина на ходу ...

Мы чтим его сегодня, а не потому, что он 70, а потому, что он знает, что такое жизнь.

И, как растения, водоросли и фотосинтезирующие бактерии преобразовать все обильные солнечную энергию в энергию, что полномочия его танцевать.

щ

Что еще мы хотим!

Продолжайте, Владимир, и научить нас о жизни.

И, как вы сделали все это возможным.

(Говинджи, 2014)

GCP



Vladimir A. Shuvalov is a man on the go...

We honor him today not because he is 70, but because he knows what life is all about
And how Plants, Algae and Photosynthetic Bacteria do their basic thing,
i.e., convert the all-abundant solar energy into energy that powers him to dance..

What more do we want..

Keep going, Vlad and teach us your tricks of life and how you made it all happen

Well, well.. From being a 6-year old handsome happy eager boy (1949) to a charming young man of 20, still quite happy (1963) at Moscow State University



Faculty of Biology and Soil
Science, MSU



From Russia to USA: Now in his 30s.. really grinning

After his PhD in 1969 on "Studying persistence of chlorophyll in photosynthetic electron transfer"; and while he was a researcher at the Academy of Science of the USSR (1969—1979), he went to the Charles F. Kettering Lab in Yellow Springs, Ohio, to work with Bacon Ke (1978-1979) and then with Bill Parson (1980-1981), at the University of Washington, Seattle



1991: USSR State Prize Winner 1997: Russian Academy of Sciences



Publication in Russian newspaper Poisk (1991)



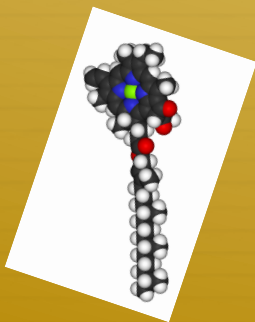
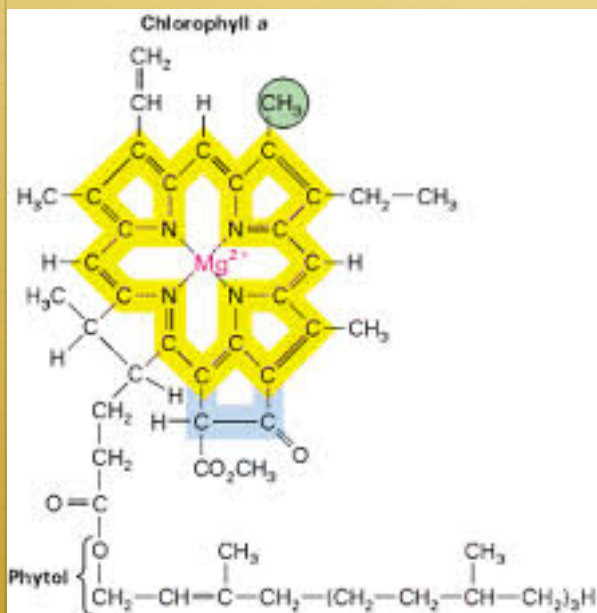
1997



OK Vlad, it was
2011: You
have really won
Slava agrees



Well, Vlad, your PhD was on **Chlorophyll**, which is the Green King that reigns our field



1. Richard Wilstätter 1872-1942; Prize in 1915; studied at Univ. of Munich)
2. Hans Fischer (1881-1945; Prize in 1930; studied at Univ. of Marburg)
3. Richard Burns Woodward (1917-1979; Prize in 1965; studied at MIT)



A Glimpse of Some of the Discoveries of Vladimir Anatoly Shuvalov

- In bRC, BPheo is an electron acceptor that precedes Q_A (Shuvalov & Klimov, 1976; cf. Dutton; and Parson, 1975)
- In BRC, BChl is an electron acceptor before BPheo (Shuvalov, Klevanik et al., 1978)
- In PSII RC, a Chl is an alternate e-acceptor to Pheo : $P^+ \text{Chl}_{D1}^-$ (Shelaev et al., 2008, 2011)
- In PSI RC, a Chl (Ao) is actually reduced within 100fs (Shelaev et al., 2010; cf. Fenton et al., 1978; Wasielewski et al., 1987))
- In bRC, $P_A^+ P_B^-$ is formed in fs (120-180 fs) within P870*



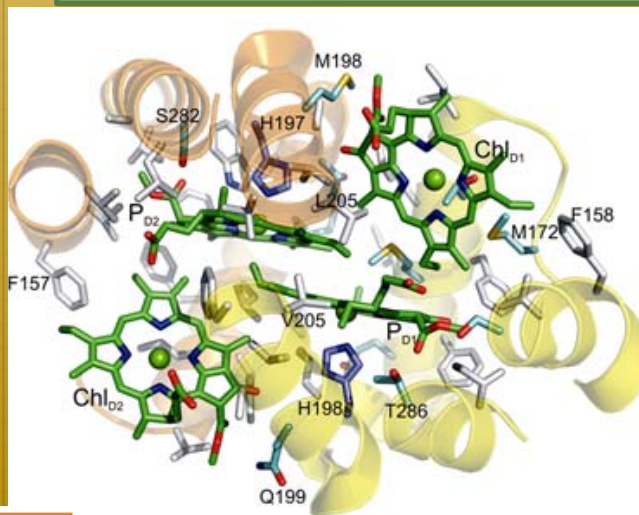
D-P-A of PSII and of PSI: Vlad really focused on all the A's; P's were done; did not want to touch D's: Chls and Pheos
Background on Chl a: Why Chl a does different things? Short answer: Redox potential; amino acid environment

Photosynth Res (2009) 99:85–98
DOI 10.1007/s11120-008-9395-x

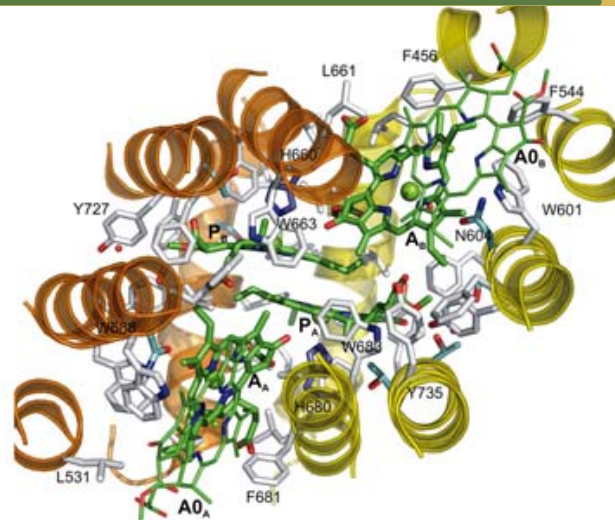
REVIEW

A viewpoint: Why chlorophyll *a*?

Lars Olof Björn · George C. Papageorgiou · Robert E. Blankenship · Govindjee



PS II RC



PS I RC

PSII: P_{D1}; P_{D2}:
His 198, His 197

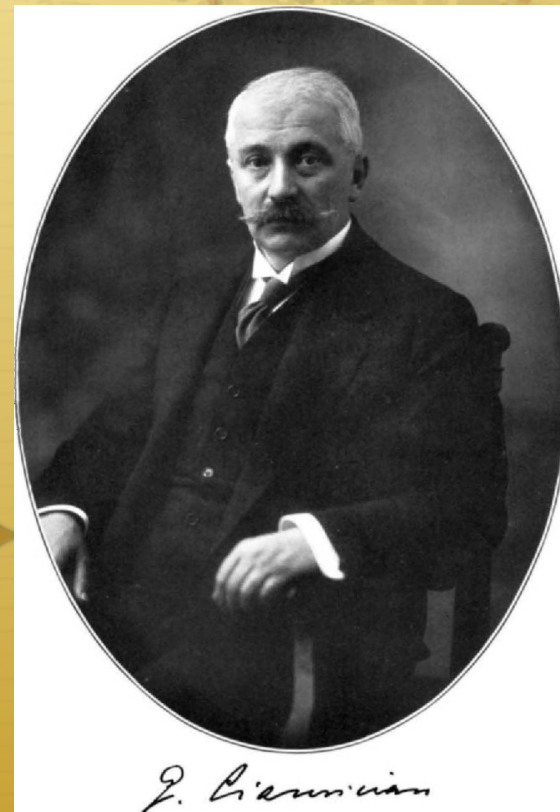
PSI: A₀:
Met 688; Tyr 696



Giacomo Luigi Ciamician (1912)
“The Photochemistry of the Future”,
Science 36 (926) 385-394.

“For our purposes the fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions. To do this it would be sufficient to be able to imitate the assimilating processes of plants.”

To imitate it, we must understand it, and Vlad Shuvalov has provided much understanding to us ..



**A bit of history before
Vlad Shuvalov began his exciting
experiments with top-of-the line
instruments built and assembled by him
and his brilliant analysis of the new
data on the
“Primary Photochemistry of
Photosynthesis”... He will talk about
them himself right after my talk**



Light absorption (fs)

Excitation Energy

Transfer to Reaction

Centers (several ps)

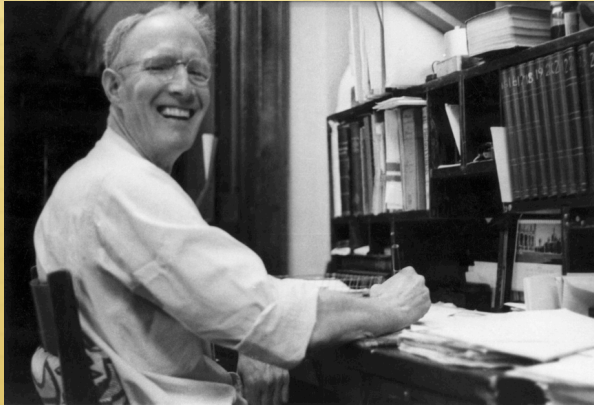
Primary Charge Separation (fs--ps)

Electron Transport (bottleneck: ms)

Carbon Fixation (seconds to a minute)

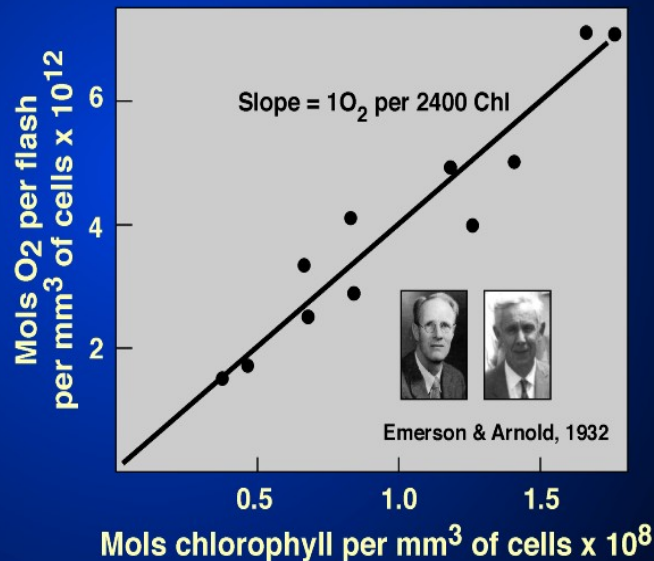


1932



The discovery of “Photosynthetic Unit” (2400 Chlorophylls per Oxygen)

- ✦ We need only suppose that for every 2480 molecules of chlorophyll there is present in the cell one unit capable of reducing one molecule of carbon dioxide each time it is suitably activated by light”



1936

Hans Gaffron (1902-1979) The “Concept of Excitation Energy Transfer” and a “photoenzyme”

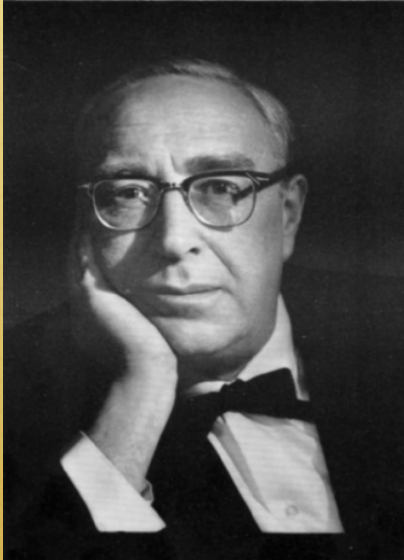
Hans Gaffron



Provided by Late Bob Clegg

Photo by Govindjee



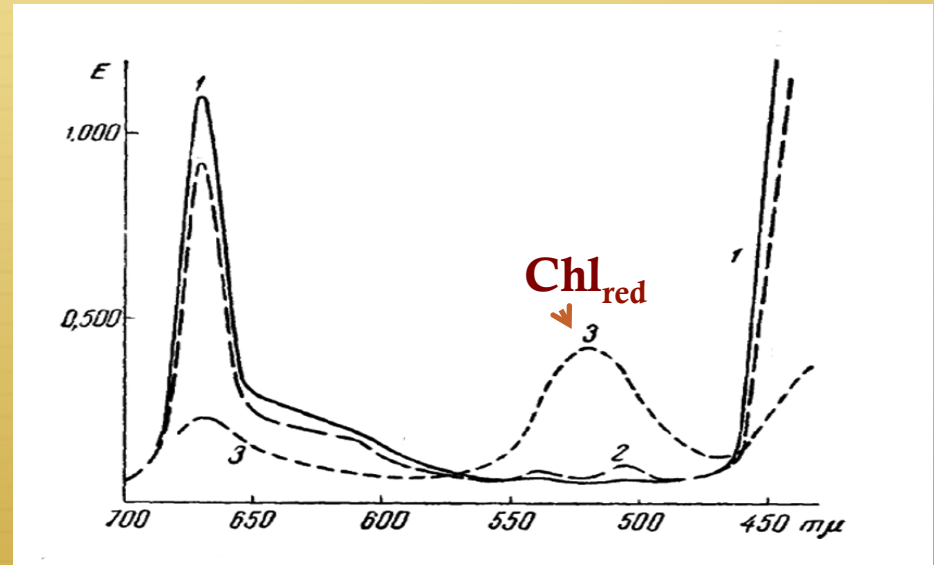


- ✦ “Reversible Oxidation and Reduction of Chlorophyll” by E. Rabinowitch and J. Weiss, *Nature* 138: 1098-1099 (1936)
- ✦ They observed reversible oxidation (and reduction) of ethyl chlorophyllide by ferric and ferrous chloride, where the oxidation was stimulated by light.

1948



Krasnovsky



Reversible photochemical reduction of chlorophyll
(Krasnovsky reaction) [from: A.A. Krasnovsky
(1948) SSSR 60: 421-424]



1947-1948

Theodor Förster (of the Förster theory of Energy Transfer) with Robert (Bob) Knox



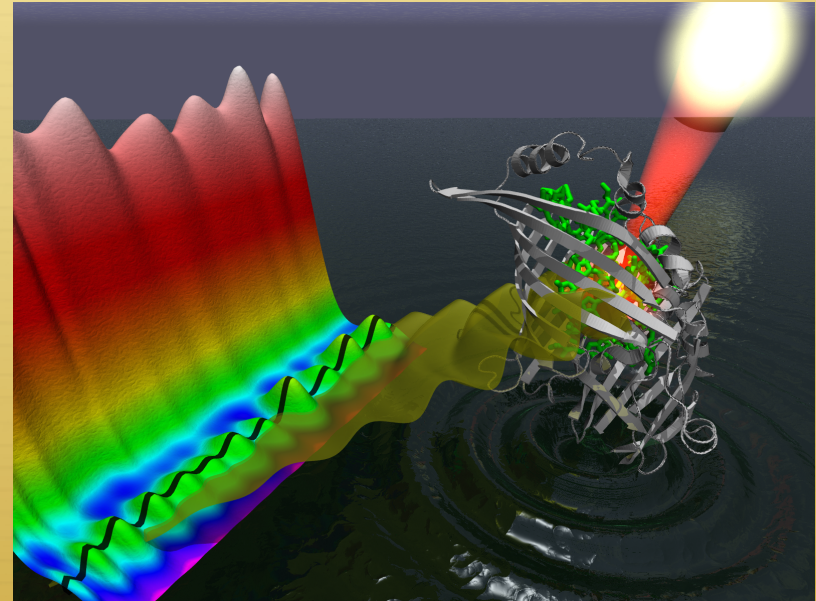
Theory: Energy transfer depends upon 3 major parameters:

- ✦ 1) $1/r^6$, where r is the distance between donor and acceptor molecules
- ✦ 2) Kappa squared, where Kappa is orientation factor
- ✦ 3) Overlap integral of emission spectrum of donor and absorption spectrum of acceptor molecule



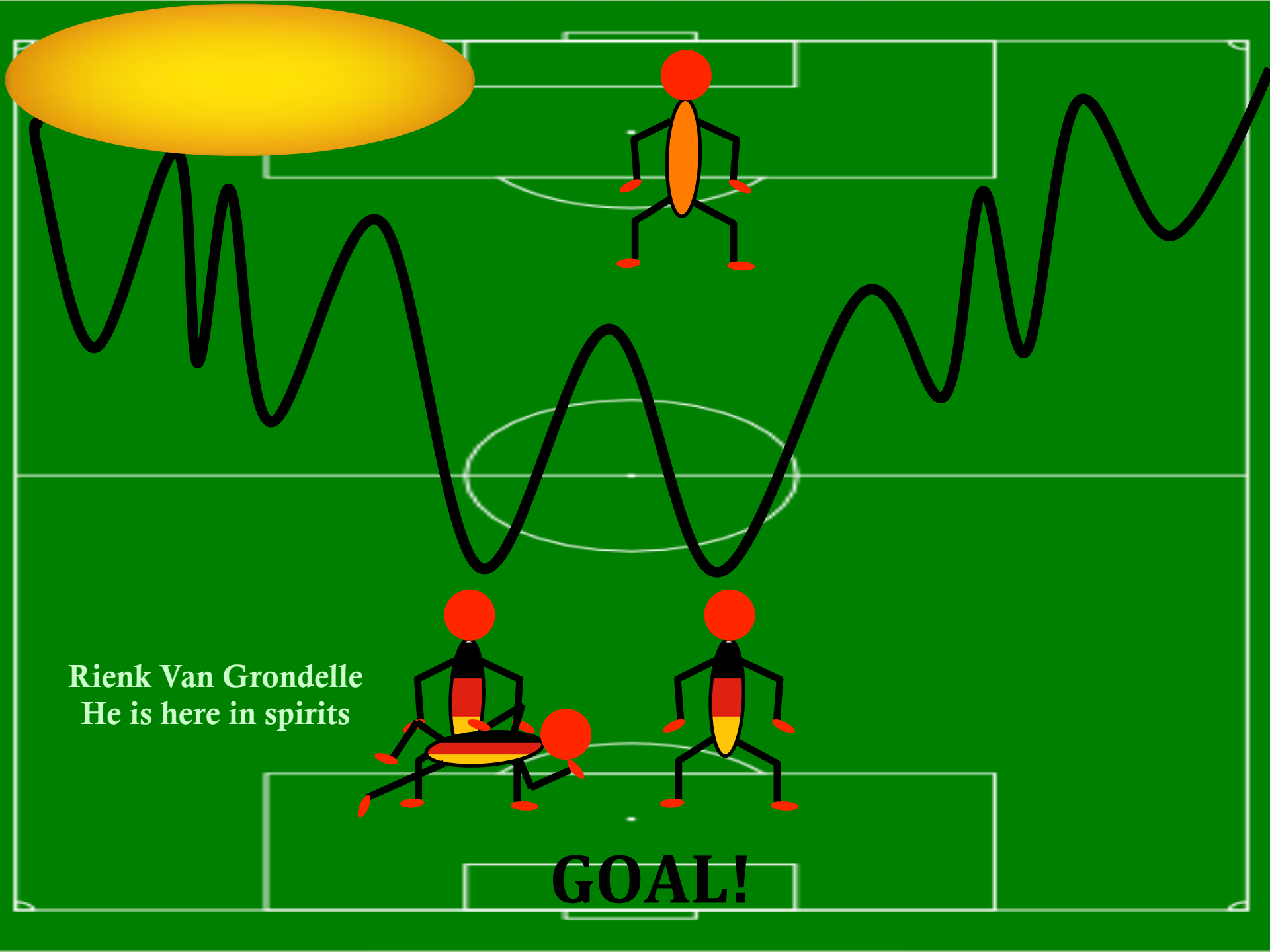
First demonstration of Coherent Excitation Energy Transfer (From Graham Fleming's group at UC Berkeley) Nature 434:625 (2005); 446: 782 (2007)

Quantum coherence allows reversible sampling of the sites. In contrast to the “hopping” model, this wavelike motion helps avoid kinetic traps. Protein matrix plays an active role in the energy transfer in FMO –protein from green bacteria



Like ripples in a pond, the wavelike motion of the quantum coherence allows the excited state to spread and explore many states at once..
But does it matter , we may ask?





Rienk Van Grondelle
He is here in spirits

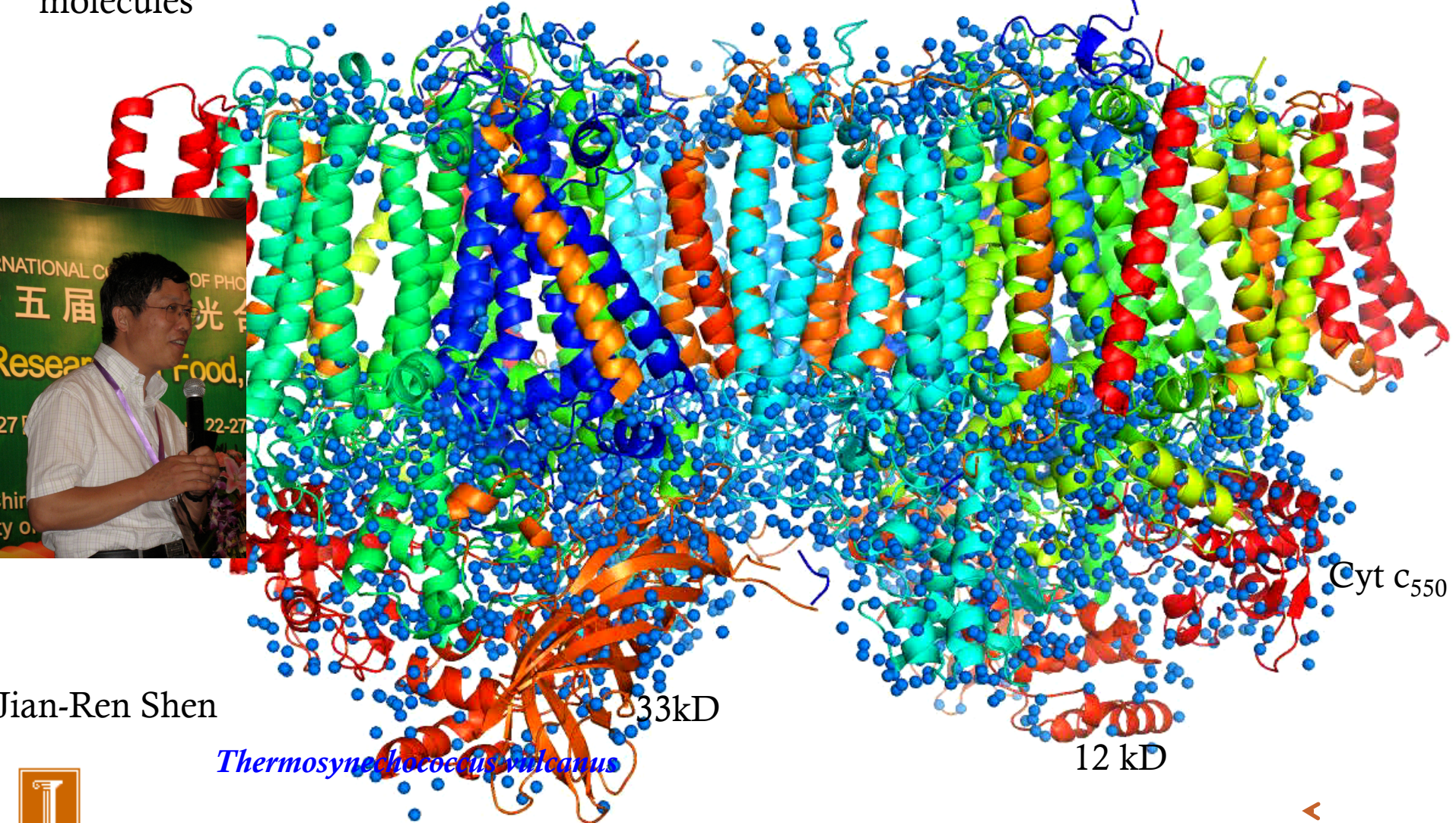
GOAL!

Crystal Structure of Oxygen-evolving Photosystem II dimer at a 1.9 Å Resolution

By Yasufi Umena , Keisuke Kawakami , Jian-Ren Shen and Nobuo Kamiya (2011)
Nature 473, 55-60

Blue balls are water molecules

CP47 (Cyan); D1(blue); D2 (green);CP43(lime green)



Jian-Ren Shen



1952

Energy transfer, the trap (P) and oxidation of Chl:

PhD thesis of L.N.M. Duysens



In Duysens' 1952 thesis
“On excitation energy
transfer” the important
reaction center concept of
P870 (in vivo) for
oxidation of just a few
molecules of BChl (Chl)
was born---and so was the

Concept of two types of
Chl a's –precursor to the
PSII and PSI Chl a's



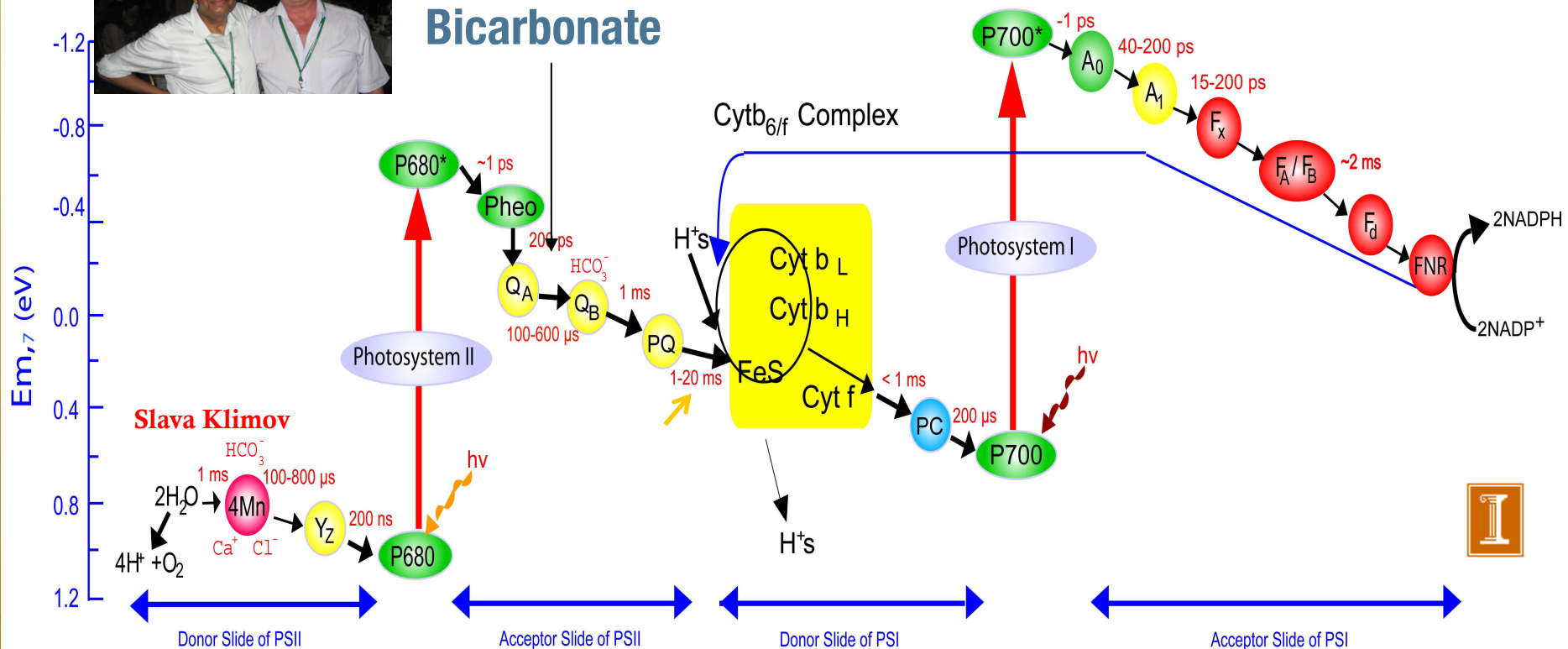


The Z-Scheme

Govindjee et al. (2005)



Bicarbonate



**Bessel Kok discovered P700 in 1956-1957; in 1959, he showed the two-light effect on it– and much more..
Later, the Kok-Joliot Oxygen Clock**

Jack Myers (1987) Bessel Kok
(1918-1979) Biograph Mem
of the Natl Acad of Sci,
Washington, DC, pp. 125-147



Photo by Tiny Pulles

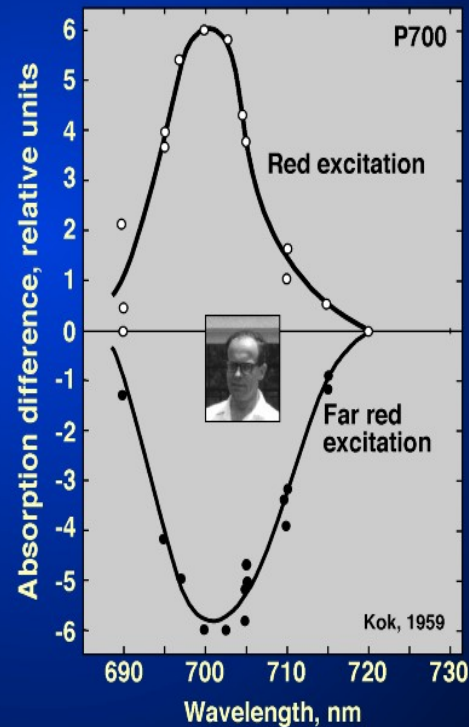




Photo:
Courtesy
of Tiny
Pulles

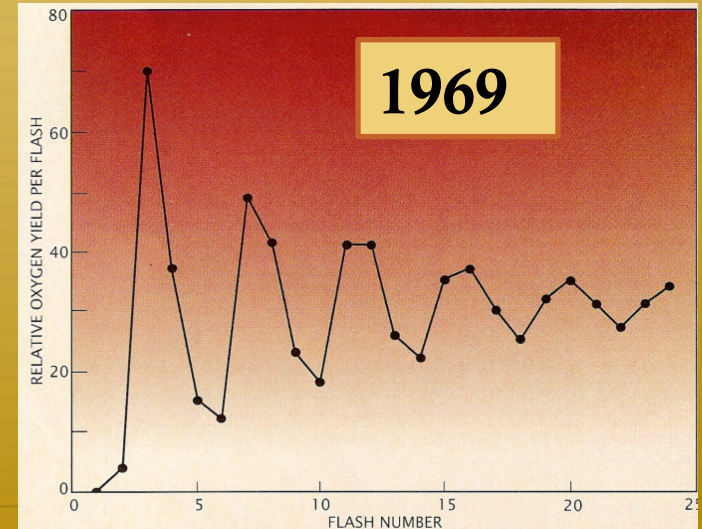
Pierre Joliot

- Discoverer of the Oxygen Clock in Photosynthesis

P. Joliot (2003) Period-four oscillations of the flash-induced oxygen formation in Photosynthesis. *Photosynthesis Research* 76: 65–72

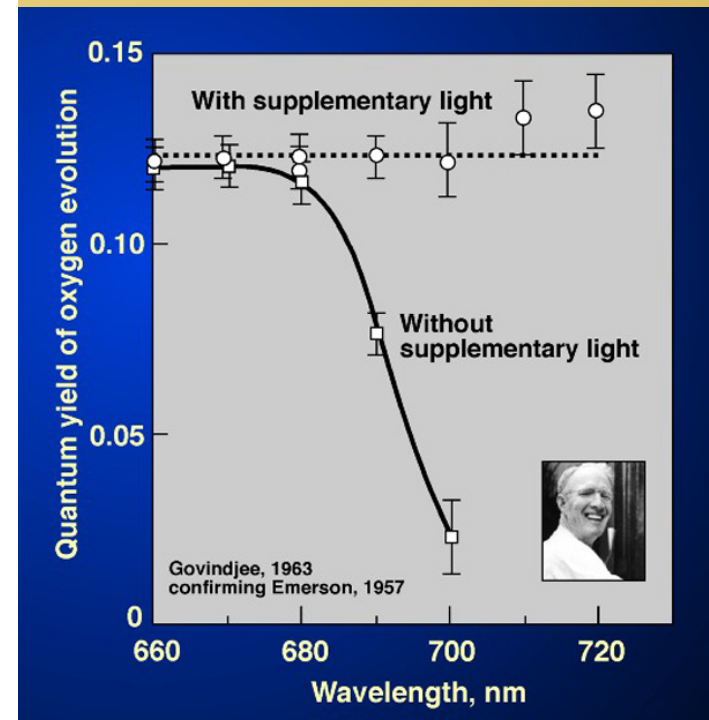
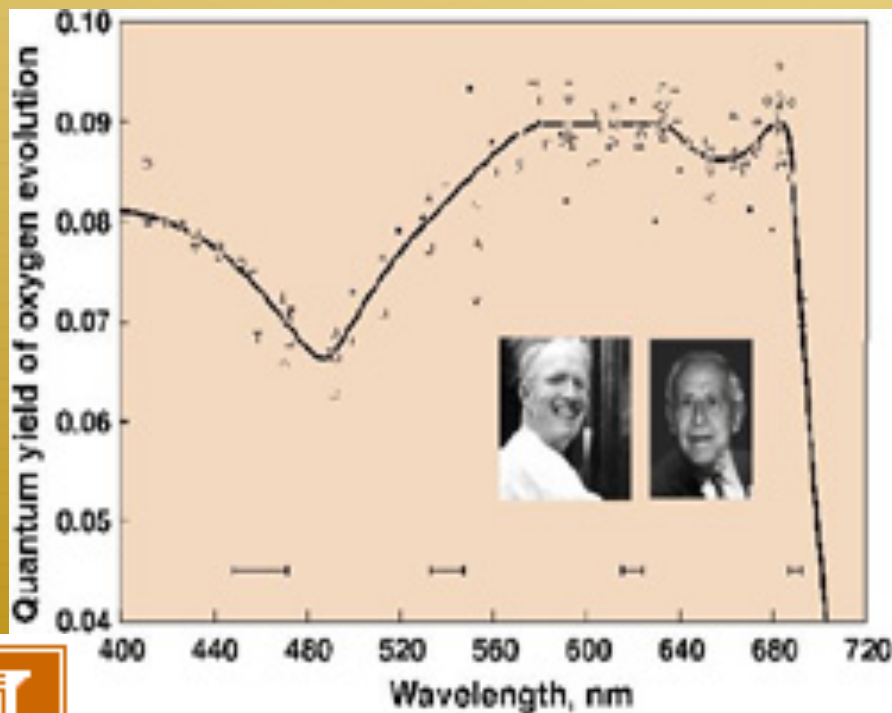
Source of figure:
Govindjee and W.J. Coleman
(1990)

How Plants Make Oxygen.
Scientific American 262: 50-58



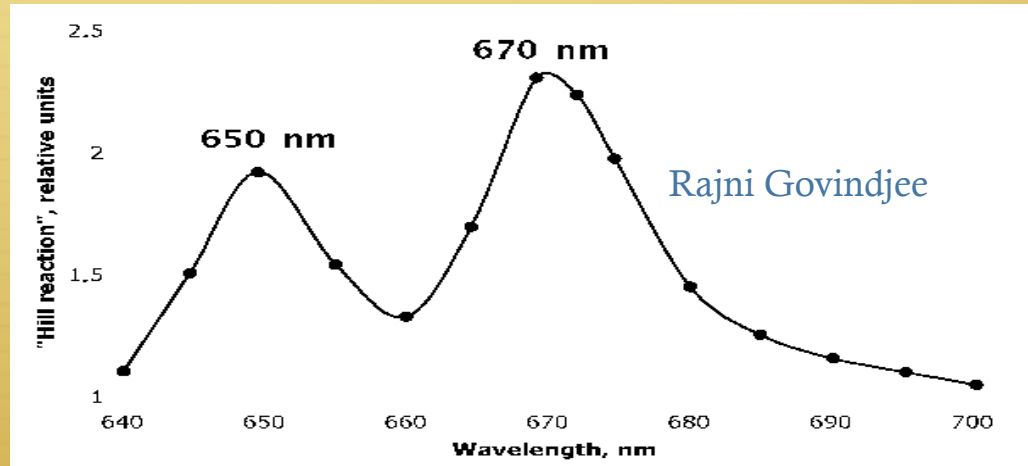
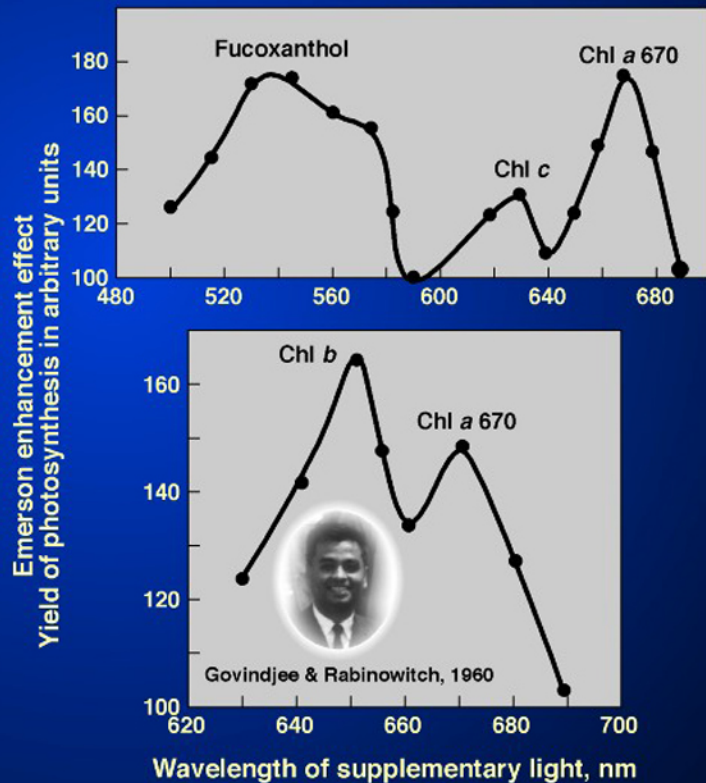
1943; 1957

The Red Drop; and the Emerson Enhancement Effect: Two Light Reaction and Two Pigment System Concept



1960

Govindjee and Rajni look back at
their experiments done 54 years
ago..



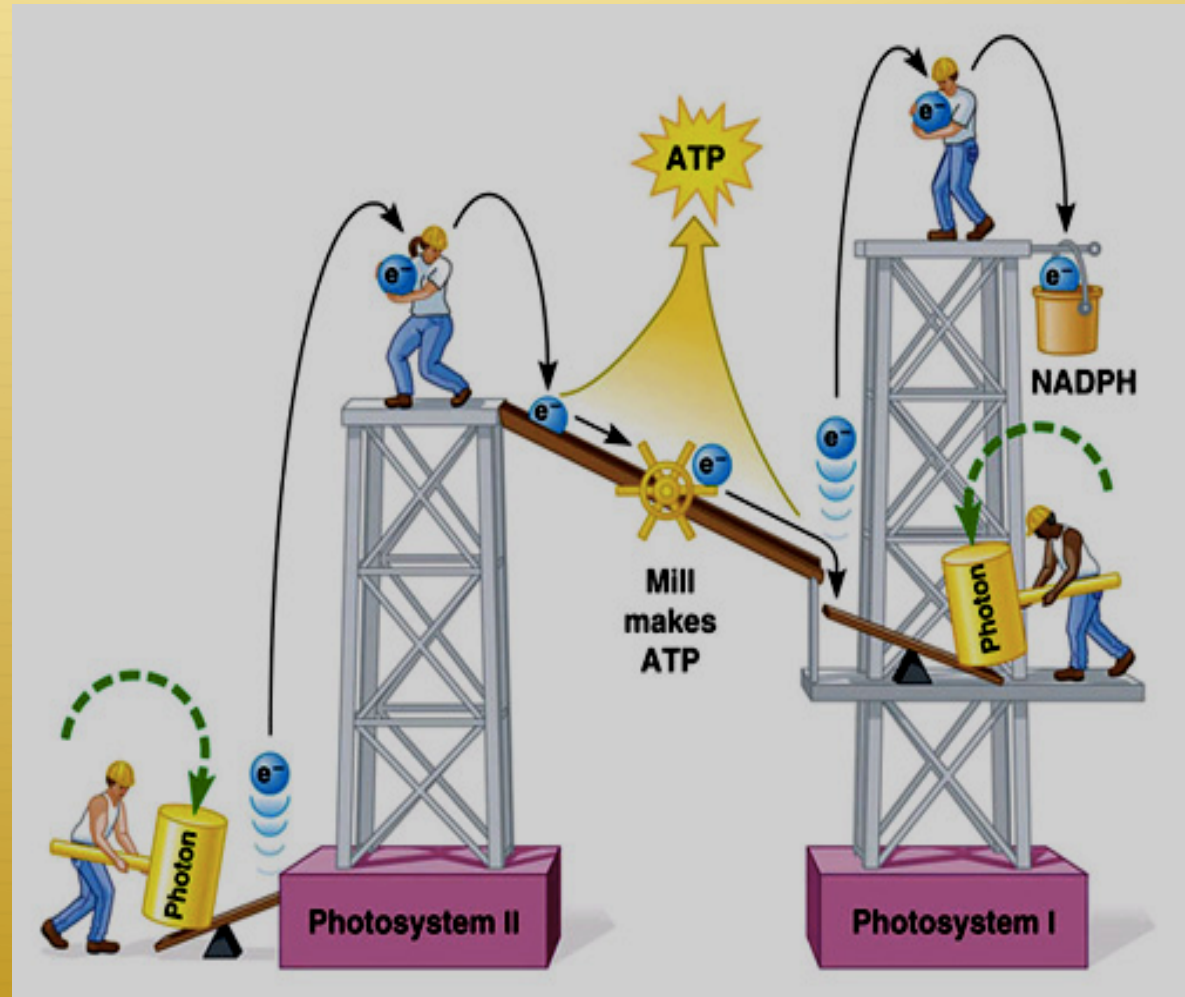
A short wavelength absorbing form of chlorophyll a (Chl a 670) is present in the system that has chlorophyll b.

And the effect is not on respiration as Larry Blinks had said!

In 1960-- “the Z” Scheme was invented by Robin Hill and Fay Bendall



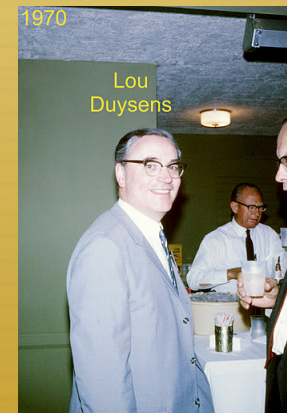
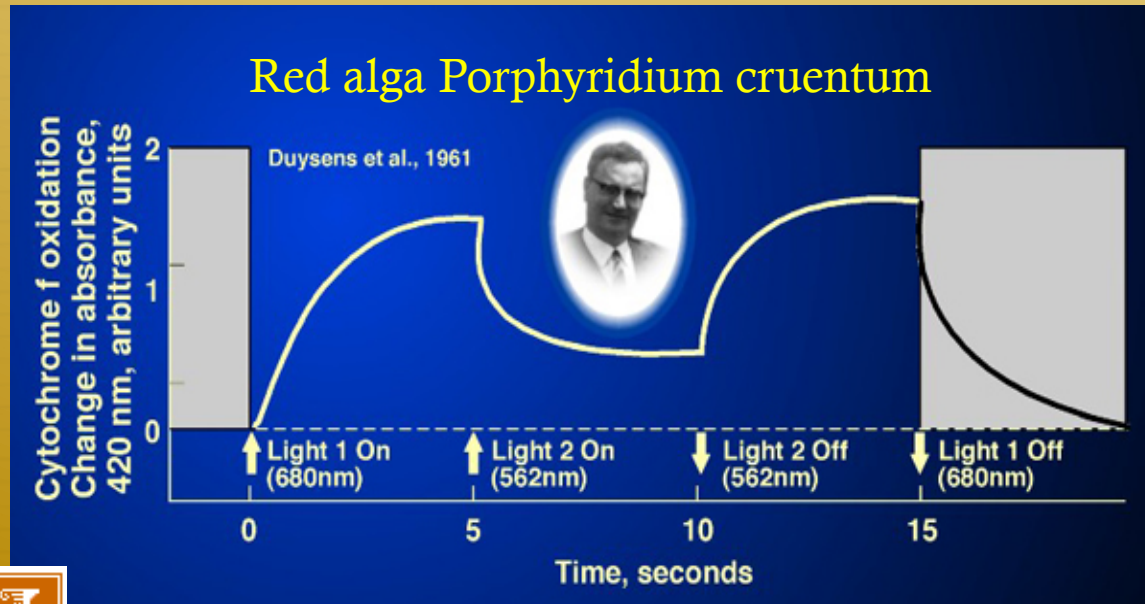
R.C. Prince (1992)
“Robert Hill, FRS;
his published work”.
Photosynth Res 34:
329-332



Louis N. M. Duysens et al. (1961) and Duysens and Ames (1962) were responsible for the names of the photosystems we use today

Light 1 (red light) oxidizes cytochrome f (called Light Reaction 1 and its Photosystem, PS 1) ; whereas, Light 2 (green light) reduces it (called Light Reaction 2, and its photosystem, PS 2).

This push-pull antagonistic effect on a redox intermediate is the crux of the Z-Scheme.



1964: Guessing Existence of P680

570

BOTANY: KREY AND GOVINDJEE

PROC. N. A. S.

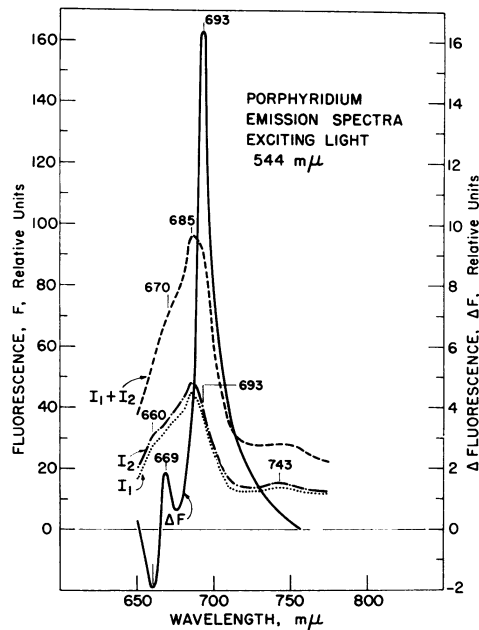


FIG. 2.—Emission spectra obtained in low intensities [I_1 (dotted), and I_2 (dashes and dots)] and in high intensity [$I_1 + I_2$ (dashes)] of green (544 $m\mu$) light in *Porphyridium cruentum*. The solid line (ΔF) is the “difference emission spectrum” (see text).

First, the half-band width of the 688- and 693-nm peaks is 10-15

Krey and Govindjee (1964)
Proc Natl Acad
Sci USA 52: 1568-1572 :
“We believe
that the small 693-nm
fluorescence band
emanates
from “photochemically
frustrated”
trap II (P680) under
high light and DCMU
conditions”



1965--1970

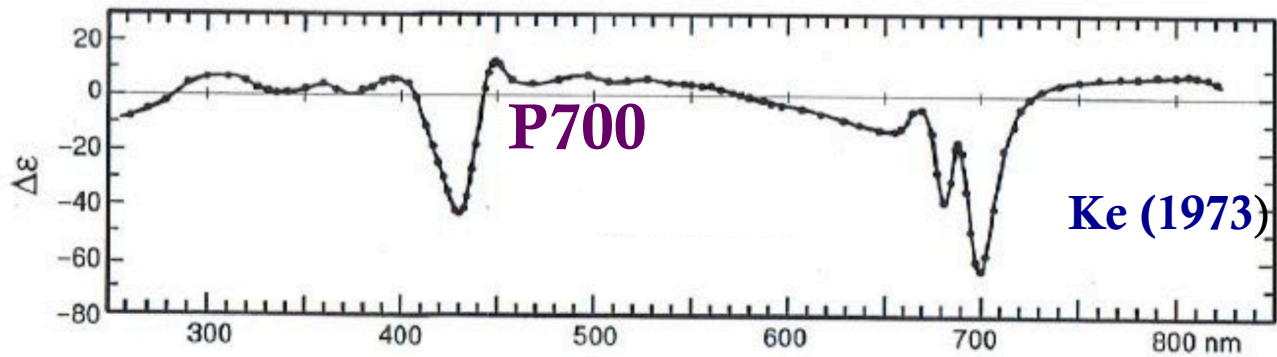
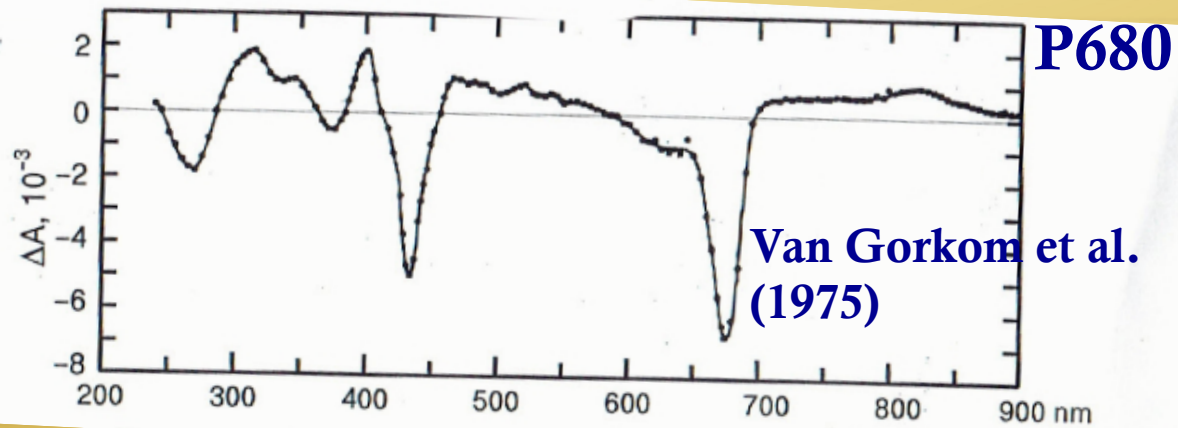


Horst T. Witt (1922-2007)

- ✦ Rabinowitch and Govindjee (1965, Sci Am 213: 74) proposed that a “P680” must exist as a reaction center of Photosystem II, just as “P700” exists for Photosystem I.
- ✦ In H.T.Witt’s lab, Döring, Bailey, Kreutz, and Witt (1968, Naturwiss 55: 220), and Döring, Renger, Vater and Witt (1969, Z Naturforschg 24b: 1139) discovered its existence.



The P680 and P700



1977: Discovery of pheophytin as PSII acceptor

V.V. Klimov, A.V. Klevanik, **V.A. Shuvalov** and A.A. Krasnovsky (1977) Reduction of pheophytin in the primary light reaction of Photosystem II. FEBS Lett 82: 183-186 ; they discovered that membrane fragments enriched in PSII showed photoreduction of pheophytin coupled to photooxidation of Chl.

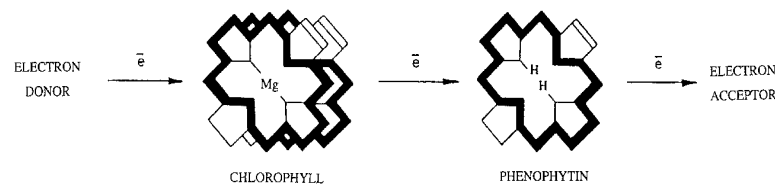


Fig. 4. Photoinduced electron transfer between chlorophyll and pheophytin.



I.Fujita, M. S. Davis, J. Fajer (1978) Anion Radicals of Pheophytin and Chlorophyll a: Their Role in the Primary Charge Separations of Plant Photosynthesis. J Am Chem Soc 100: 6280- 6282



Figure 4. A photograph of Jack Fajer in 1977.

.....the first reduced chemical products of green plant photosynthesis are the anions of pheophytin in PSII and chlorophyll in PS I. Such a mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both photosystems I and II.



1979: Primary Photochemistry of Reaction Center of Photosystem I

Fenton in 1999

Volume 100, number 1

FEBS LETTERS

April 1979



PRIMARY PHOTOCHEMISTRY OF THE REACTION CENTER OF PHOTOSYSTEM I

J. M. FENTON, M. J. PELLIN^{†,*}, GOVINDJEE and K. J. KAUFMANN[†]

Division of Biophysics, Department of Physiology and Biophysics and [†]Department of Chemistry, University of Illinois, Urbana, IL 61801 USA

Received 22 January 1979

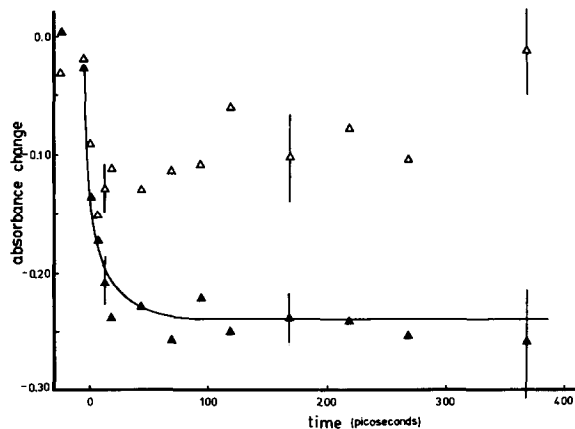


Fig.4. Kinetics at 700 nm for dark-adapted samples (\blacktriangle) and samples illuminated as in fig.2 (\triangle); Chl:P700 ratio \approx 38; Chl \approx 1.1 mM.

PSI prep (Chl/P700=38), modified D144 prep. Wavelength, 528 nm; 10 mJ; 8 ps pulse:

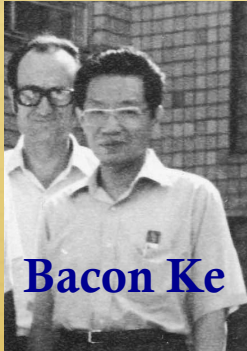
Result: Increase in absorption at 800 nm region and decrease in

absorption in 700 nm region:

charge separation was within 10 ps; and a 40 ps component was due to antenna



1979: Kinetic and Spectral Properties of A_1 in Photosystem I



Volume 100, number 1

FEBS LETTERS

April 1979

KINETIC AND SPECTRAL PROPERTIES OF THE INTERMEDIARY ELECTRON ACCEPTOR A_1 IN PHOTOSYSTEM I

Subnanosecond spectroscopy

V. A. SHUVALOV⁺, Bacon KE* and Ed DOLAN
Charles F. Kettering Research Laboratory, Yellow Springs, OH 4538

Received 26 January 1979

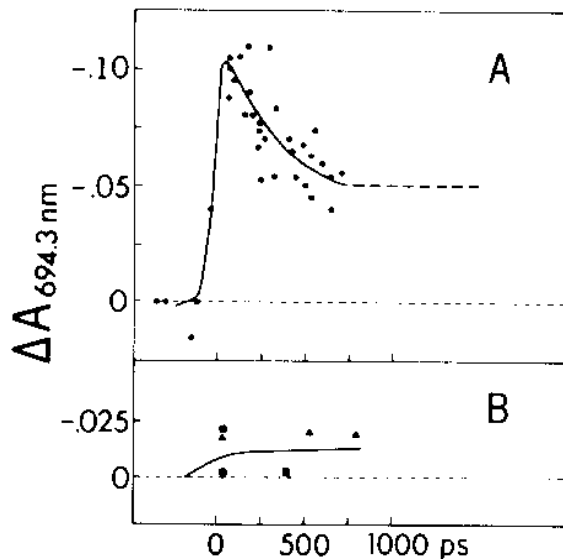
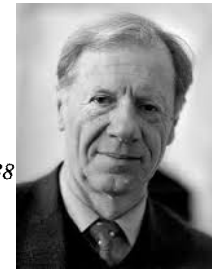


Fig.2. Kinetics of $\Delta A_{694.3}$ in TSP
694.3 nm pulses (50–60 ps dur
of 1 mJ/cm²) at 20°C. Each poi
average of 10–20 measurements

PSI prep (Chl/P700=26), TSF1(Triton)
prep. Wavelength, 694 nm; 1mJ;
50-60 ps pulse

Result: Decrease in absorption at ~ 700 nm : A_1 was reduced in <60 ps; next step 200ps

1986: Picosecond Spectroscopy of PSI RCs: With Leiden group



310

BBA 42055

chimica et Biophysica Acta 850 (1986) 310–318
Elsevier

Picosecond absorbance difference spectroscopy on the primary reactions and the antenna-excited states in Photosystem I particles

Antonius M. Nuijs, Vladimir A. Shuvalov *, Hans J. van Gorkom,
Johan J. Plijter and Louis N.M. Duysens

Department of Biophysics, Huygens Laboratory of the State University, P.O. Box 9504, 2300 RA Leiden (The Netherlands)

(Received February 3rd, 1986)

(Revised manuscript received April 14th, 1986)

**Calculated spectra of
reduced acceptor: a Chl⁻**

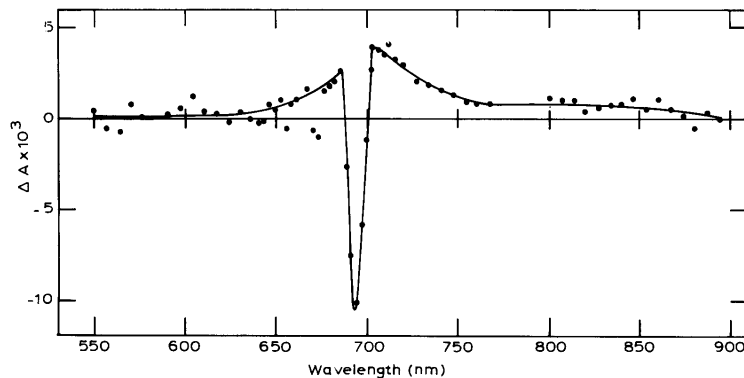


Fig. 9. Absorbance difference spectrum calculated for the reduction of the primary electron acceptor. See text for details.

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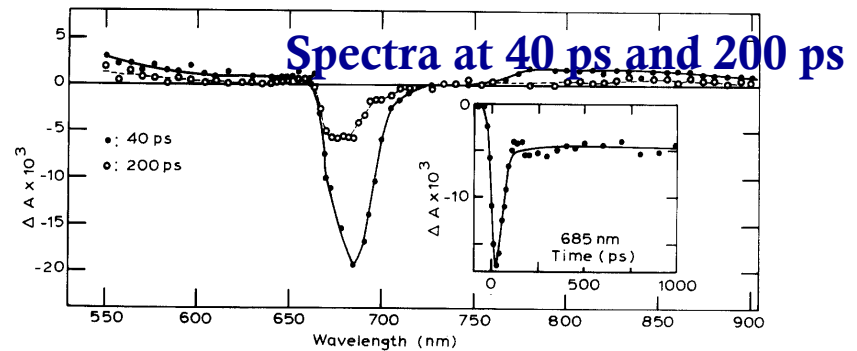


Fig. 1. Absorbance difference spectra of PS I particles from spinach at 40 ps (●) and 200 ps (○) after the 532 nm excitation pulse, in the presence of 3 mM ferricyanide and under continuous background illumination. The inset shows the kinetics at 685 nm. The extinction of the sample was 1.4 at 675 nm in a 2 mm cell. The excitation energy density was about 0.9 mJ/cm².

**PSI (intact) (Chl/P700=70),
Wavelength of excitation, 532nm;
2.5 mJ;
35ps pulse
Chl a 693 nm must be the electron
acceptor, being oxidized within
50ps**



1987 :Picosecond Spectroscopy of PSI: Illinois

Photosynthesis Research 12, 181–190 (1987)
© Martinus Nijhoff Publishers, Dordrecht—Printed in the Netherlands

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Regular paper

The rate of formation of $P700^+ - A_0^-$ in photosystem I particles from spinach as measured by picosecond transient absorption spectroscopy

M.R. WASIELEWSKI,¹ J.M. FENTON² & GOVINDJEE^{2,3}

¹ Chemistry Division, Argonne National Laboratory,* Argonne, IL 60439, USA; ² Department of Physiology and Biophysics, University of Illinois, Urbana, IL 61801, USA; ³ Department of Plant Biology, University of Illinois, 289 Morrill Hall, 505 S. Goodwin Ave., Urbana, IL 61801, USA (for correspondence and/or reprints)

Received 1 December 1986; accepted in revised form 18 December 1986

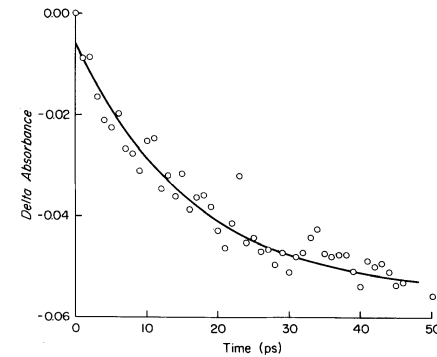


Fig. 4. Time dependence of absorbance change at 690 nm of PS-I particles (with antenna changes subtracted) following a 1.5 ps, 610 nm laser pulse.

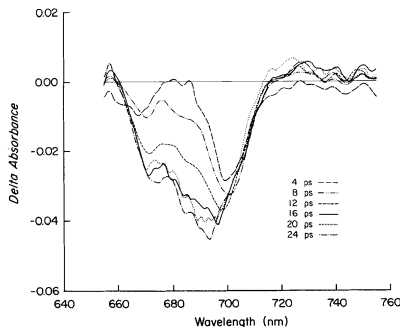


Fig. 2. Wavelength and time dependences of transient absorbance changes of PS-I particles (with antenna changes subtracted) following excitation with 1.5 ps, 610 nm laser pulse.

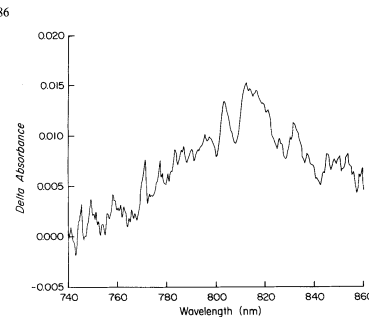


Fig. 5. Wavelength dependence of transient absorbance change of PS-I particles (with antenna changes subtracted) at 0 ps following a 1.5 ps, 610 nm laser pulse.

PSI prep (Chl/P700=30),. Wavelength of excitation , 610 nm (into antenna)

1.5 ps pulse

Lifetime

of $P700^+ - Chl (A_0^-)$ formation was **14ps**;
in retrospect, could it include both
energy transfer and charge separation
time although we had thought that we
had separated the two?



1989

Primary Photochemistry: Conversion of light energy into chemical energy occurs in picoseconds: Our very first measurements(Proc Natl Acad Sci, 86: 524-528)

P680⁺ (oxidized form of reaction center chlorophyll) is formed within 3 picoseconds and excited state of chlorophyll disappears simultaneously with a half-time of 3 picoseconds (Wasielewski et al., 1989)



82 / Govindjee and Wasielewski

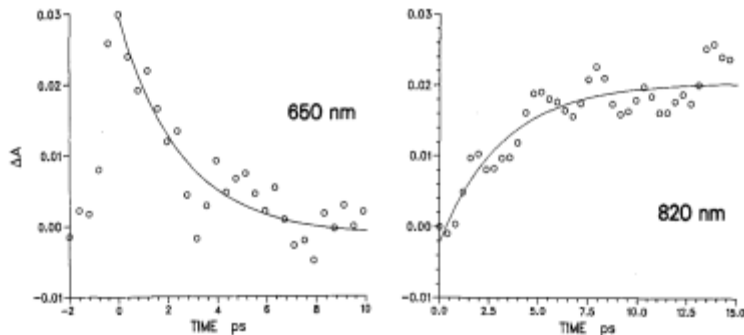


Figure 5. Transient absorption changes at 820nm (due to formation of P680⁺) and at 650nm (due to decay of ¹Chl_a^{*}) for photosystem II reaction centers following a 100 μJ, 500 fs laser flash at 610nm. Left: 650nm change; right: 820nm change. (After Wasielewski et al., 1989.)



Mike Wasielewski's 60th birthday



Primary light-energy conversion in tetrameric chlorophyll structure of photosystem II and bacterial reaction centers: II. Femto- and picosecond charge separation in PSII D1/D2/Cyt b559 complex

I. V. Shelaev · F. E. Gostev · V. A. Nadtochenko ·
A. Ya. Shkuropatov · A. A. Zabelin · M. D. Mamedov ·
A. Yu. Semenov · O. M. Sarkisov · V. A. Shuvalov

Biochimica et Biophysica Acta 1797 (2010) 1410–1420



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Biochimica et Biophysica Acta

journal homepage: www.elsevier.com/locate/bbabio



Shelaev et al. (2008,2010)

PSII (2008)

20 fs flashes

In 0.9 ps

P680⁺ Chl⁻_{D1}

is formed, and in 14 ps,

P680⁺ Pheo⁻_{D1}

is formed

PSI (2010)

20 fs flashes

< 100fs

P700⁺ Ao⁻

**is formed; in 5 ps, Chl^{*}
transfers its energy to**

P700, and in 25 ps,

P700⁺ Ao A₁⁻ is formed

Femtosecond primary charge separation in *Synechocystis* sp. PCC 6803 photosystem I

Ivan V. Shelaev^{a,c}, Fedor E. Gostev^a, Mahir D. Mamedov^b, Oleg M. Sarkisov^a, Victor A. Nadtochenko^{a,c,*},
Vladimir A. Shuvalov^{b,*}, Alexey Yu. Semenov^{b,*}

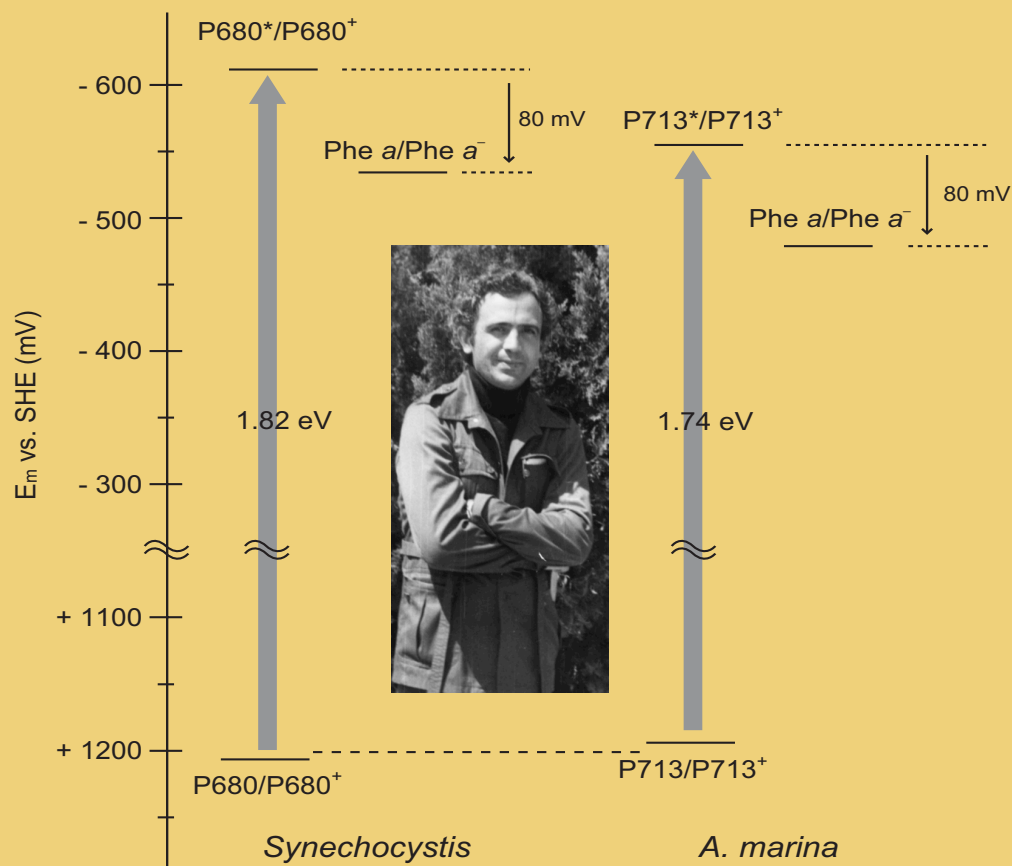
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Redox potential of pheophytin *a* in photosystem II of two cyanobacteria having the different special pair chlorophylls

Suleyman I. Allakhverdiev^{a,b}, Tatsuya Tomo^c, Yuichiro Shimada^b, Hayato Kindo^c, Ryo Nagao^d, Vyacheslav V. Klimov^a, and Mamoru Mimuro^{b,1}

2010



2011

77K : 0.9 ps for charge separation in PSII

[Shelaev et al.: The title tells the story]

Journal of Photochemistry and Photobiology B: Biology 104 (2011) 44–50



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P_{680} ($P_{D1}P_{D2}$) and Chl_{D1} as alternative electron donors in photosystem II core complexes and isolated reaction centers

I.V. Shelaev^a, F.E. Gostev^a, M.I. Vishnev^b, A.Ya. Shkuropatov^b, V.V. Ptushenko^c, M.D. Mamedov^c, O.M. Sarkisov^a, V.A. Nadtochenko^a, A.Yu. Semenov^c, V.A. Shuvalov^{b,*}

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A Global Scale Challenge for Science

“...if our black and nervous civilization, based on coal and oil, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.”

“...to fix the solar energy through suitable photochemical reactions with new compounds that master the photochemical processes that hitherto have been the guarded secret of the plants”

1912
Ciamician, *Science*

100 years later: Najafpour, M. M.;
Shen, J-R.; Barber, J.; Moore, G. F.;
Govindjee Running on Sun. *Chemistry
World* **2012**, November, 43.



The Sun, the tree, the flower and the birds by my granddaughter Sunita Christiansen; she is now an undergraduate student at Cornell University



The End
Thank you Vlad for all
your discoveries and
contributions
And for teaching us how
to live and dance!

Thank you Suleyman for being
a wonderful friend and for
inviting me here even though I
am retired and do really
nothing except e-mail



הללויה
halləlûyāh
ἀλληλοῦῖα

