The Great Masters of the Past: Photochemists, Biochemists, and Biophysicists

October 10, 2013, Moscow, Russia

Dedicated to

Alexander Abramovitch Krasnovsky

(1913-1993)

He was always ahead of his time

by
Govindjee
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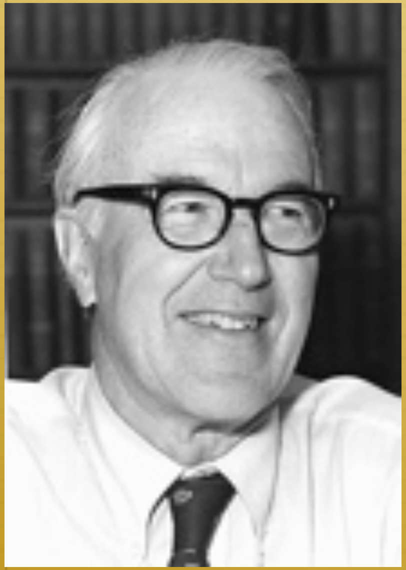
Others who would have been 100 in 2013 are : **Britton Chance** (1913-2010); **Martin D. Kamen** (1913-2002); **Jack Myers** (1913-2006); and **Sam Ruben** (1913-1943)



Chance

Kamen

Ruben

Myers

By Govindjee

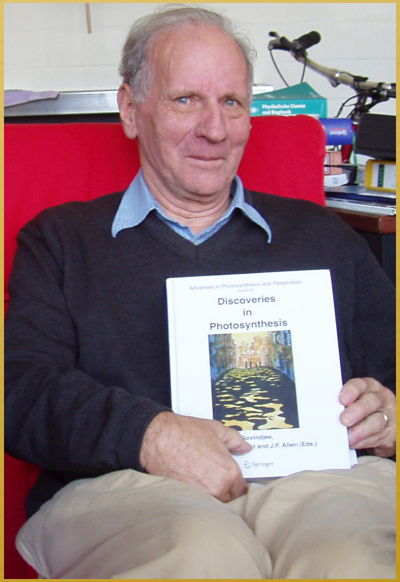
Major discoverers who are no longer with us include the following

Jan Amesz (1934-2001)
W.A. Arnold (1904-2001)
Daniel I. Arnon (1910-1994)
M. Avron (1931—1991)
G.T. Babcock (1946-2000)
L.R. Blinks (1900-1989)
Warren Butler (1925-1986)
Melvin Calvin (1911-1997)
Rod Clayton (1922-2011)
Don C. DeVault (1915-1990)
Robert Emerson (1903-1959)
V.B. Evstigneev (1909-1977)
James Franck (1882-1964)
C. Stacy French (1907-1995)

Hans Gaffron (1902-1979)
Howard Gest (1922-2012)
Norman Good (1917-1992)
Francis Haxo (1921-2010)
Robin Hill (1899-1991)
Joseph J. Katz (1912-2008)
Bessel Kok (1918-1979)
George Porter (1920-2002)
Gernot Renger (1937-2013)
A.A. Shlyk (1928-1984)
Hiroshi Tamiya (1903-1984)
C.B.Van Niel (1897-1985)
Horst T. Witt (1922-2007)
A. San Pietro (1922—2008)

There are many who are with us who need to be recognized ; I will mention only a few selected ones (leaving out the luminaries who are present here today):

Andrew Benson
Louis N.M. Duysens
André Jagendorf
Achim Trebst



By Govindjee

My first visit to Moscow was to attend ..
The 5th International Biochemistry Congress, in 1961

Left to Right (Last row)

A.A. Krasnovsky

E.C. Wassink

N.G. Doman

V.B. Evstigneev

Whose back is it??

Next row:

Whose back is it?

Daniel Arnon

Mary Belle Allen

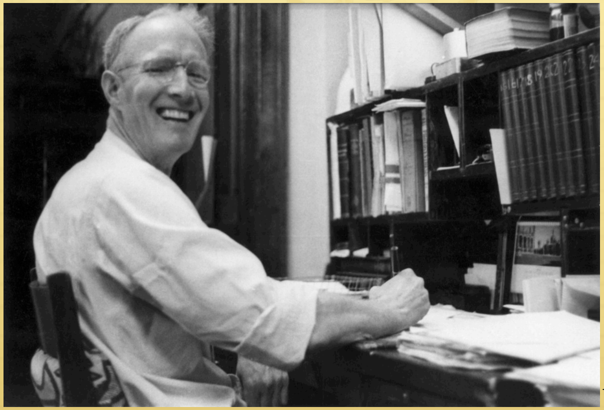
C. Stacy French

JHC Smith

By Govindjee

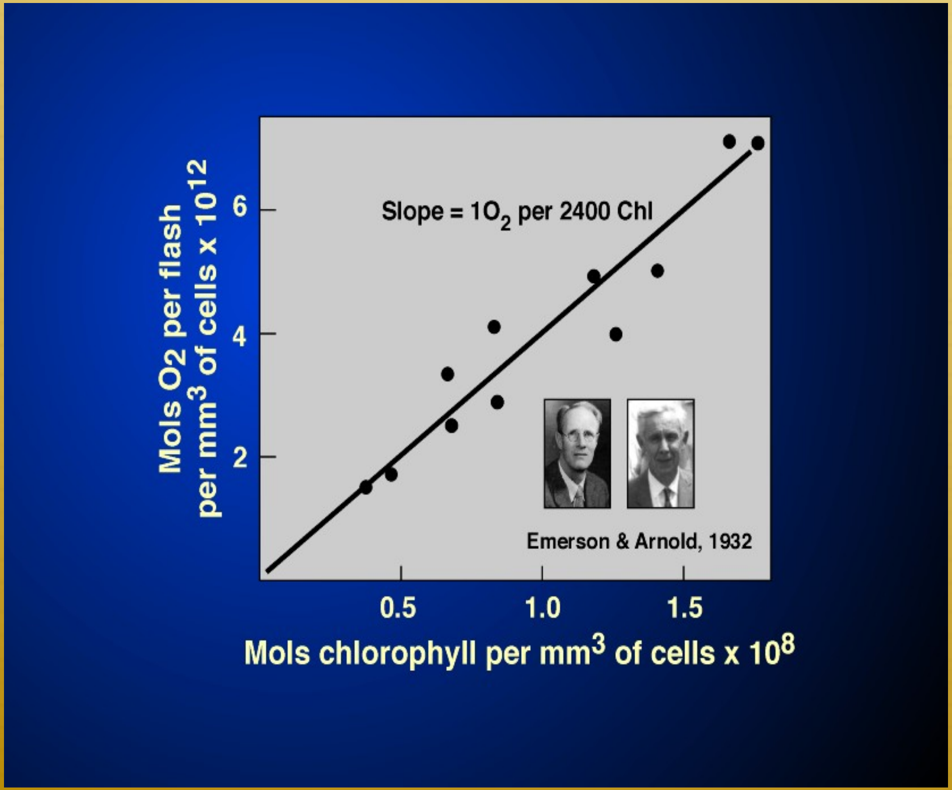
1932

Robert Emerson
Had, in1958,
Explained this
1932 Experiment
to me..Photo by
Govindjee



The 1932 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”



Presentation by Govindjee

1936

•Hans Gaffron (1902-1979)

The "Concept of Excitation Energy Transfer" and a "photoenzyme

Hans Gaffron

Provided by Late Bob Clegg

Presentation by Govindjee

1936,1937

Rabinowitch and Weiss (1936, 1937): See data in the next slide

- "**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.

Reversible oxidation of chlorophyllide by ferric chloridem (Rabinowitch-Weiss reaction)

1936

[From E. Rabinowitch, and J. Weis (1936) Nature 138: 1098-1099]

$$\mathrm{Chl} + \mathrm{Fe}^{+3} \longrightarrow \mathrm{Chl}_{\mathrm{ox}} + \mathrm{Fe}^{+2} \longrightarrow \mathrm{Chl}$$

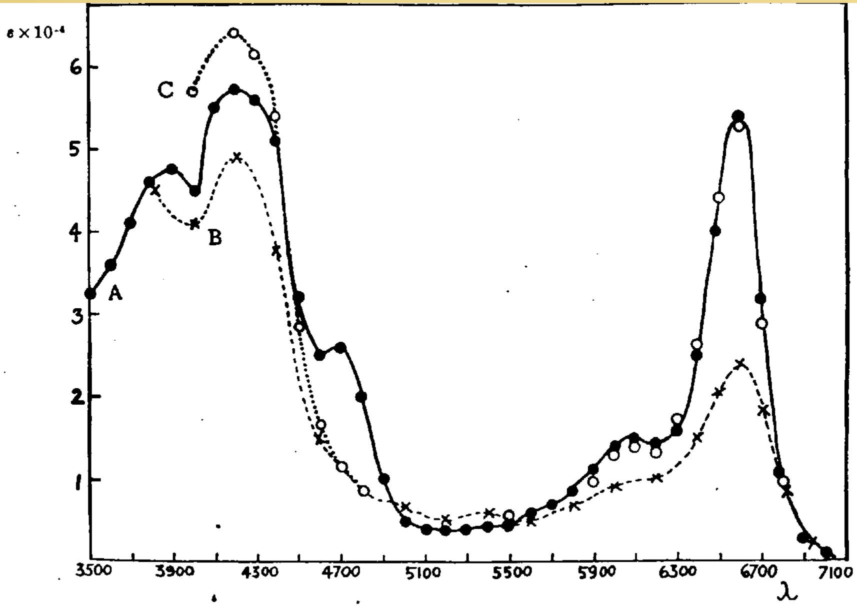


FIG. 1. Molecular extinction coefficient of ethyl chlorophyllide solutions: Curve *A*, original chlorophyllide; Curve *B*, oxidized chlorophyllide; Curve *C*, recovered chlorophyllide.

Of significance was their observation that the oxidation reaction was favored greatly by red light. Soon thereafter, D. Porret and E.I. Rabinowitch (1937; Nature 140: 321-322) discovered a light-induced reversible bleaching of chlorophyll in methanol under oxygen-free conditions; it was proportional to the square root of light intensity.

A – Absorption spectrum of chlorophyllide in methanol (had high red fluorescence)
B –The same after treatment with Fe$^{+3;}$ (fluorescence was decreased to 33%)
C –After further treatment with Fe^{+2} (fluorescence was restored) [Gov and AAK, Jr.]

1946,1947

Alexander Abramovitch Krasnovsky , and Galina Petrovna Brin made a major discovery **that pthalocyanins and ascorbate when exposed to light produced reduced pthalocyanin and oxidized ascorbate. This** was followed by their work that led to the discovery of what we all call the **Krasnovsky reaction**.

Photo from : Krasnovsky, Jr. (2003)
Photosynth Res 76: 389-403

A.A. Krasnovsky and G.P. Brin (1946) Catalytic and photosensitized oxidation of ascorbic acid by pthalocyanins. Dokl AN SSSR 53: 447-450 (done in water solutions)

A.A. Krasnovsky and G.P.Brin (1947) Photosensitizing action of magnesium pthalocyanin(e) and chlorophyll in solution. Dokl AN SSSR 58: 1087-1090 (done in organic solutions)

1948: Discovery of the reversible photochemical reduction of chlorophyll

A.A. Krasnovsky (1948) Reversible photochemical reduction of chlorophyll by ascorbic acid. Dokl AN SSSR 60:421-424; a red intermediate with an absorption maximum at 520 nm reacting reversibly in the dark was formed. It was the first reversible photochemical reaction of Chl (that will be known to others as the Krasnovsky reaction). This was further studied 10 years later by (a) Thomas Turpin Bannister under Rabinowitch (1958 PhD thesis" The Reversible Photoreduction of Chlorophyll", 134 pp.); 16 years later by (b) Gil Seely and Folkamanis (1964) ; and 26 years later by (c) Hugo Scheer and Joe Katz (1974).

T.T. Bannister (1959) Photoreduction of chlorophyll a in the presence of ascorbic acid in pyridine solutions. Plant Physiol 34: 246-254.

G.R. Seely and A. Folkamanis (1964) Photoreduction of ethylchlorophyllide by ascorbic acid in ethanol-pyridine solutions. J Amer Chem Soc 86: 2763-2770

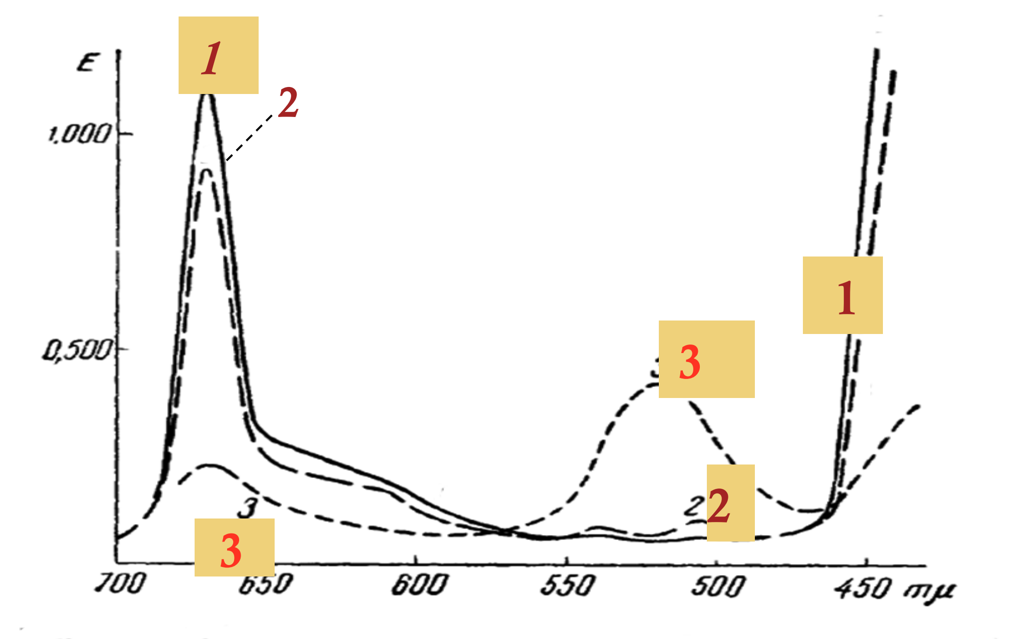
H. Scheer and J.J. Katz (1974) Structure of the Krasnovsky photoreduction product of chlorophyll a. Proc Natl Acad Sci USA 71: 1626-1629

Presentation by Govindjee

1948

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

$h\nu \longrightarrow$ Chl + ascorbic acid $\rightarrow \mathrm{Chl_{red}} \longrightarrow$ Chl



The reaction was reversible: order of experiment:
1 to 3 to 2, original number
was retained

1 – Absorption spectrum of a mixed solution of Chl (a+b) and ascorbic acid in water-free pyridine; it showed strong red fluorescence.

3 – Absorption spectrum of #1 after 1-2 min illumination by red light under anaerobic conditions. A new absorption band at 530 nm appeared; the sample had no detectable fluorescence

2 – Absorption spectrum of #3 after 2-3 hours in darkness; fluorescence restored to that of #1.

[This slide was made by A.A. Krasnovsky, Jr., and Govindjee]

1949: Photoreduction of NAD in a model system

A.A. Krasnovsky and G. Brin (1949) Hydrogen transfer from ascorbic acid to codehydrase I under action of light absorbed by chlorophyll. Dokl AN SSSR 67: 325-328

Here, they showed in the model system

Ascorbate-Chlorophyll-NAD

photoreduction of NAD, 2 years before NADP reduction was discovered in chloroplasts by **S. Ochoa and W. Vishniac** (Nature 167: 768-769, 1951), **L.J. Tolmach** (Nature 167: 946-948) and **Dan Arnon** (Nature 167:1008-1010)

1952

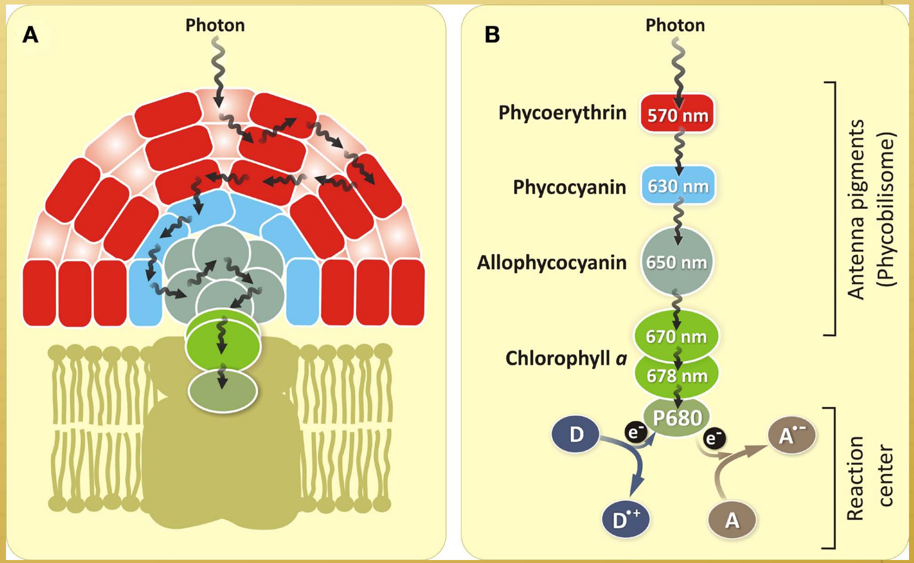
Energy transfer, the trap (P) and oxidation of Chl:

PhD thesis of L.N.M. Duysens

- Duysens’ 1952 thesis on excitation energy transfer is a classic of all times. However, the ” P870 “ concept for a few molecules, in vivo, doing the reaction: oxidation of BChl (Chl) was an important concept that was born here

1952: Phycobilins don't do chemistry as Chls do; they are light harvesters

A.A. Krasnovsky, V.B. Evstigneev, G.P. Brin and V.A Gavrilova (1952) , Dokl. AN SSSR (Biochemistry), 82: 947-950 showed that phycobilins are incapable of significant reduction and oxidation. In my opinion, it was an important new observation for that time.



It agrees with the1952 picture of Duysens and of C.S. French that phycobilins harvest light energy and then transfer the excitation energy to chlorophylls.

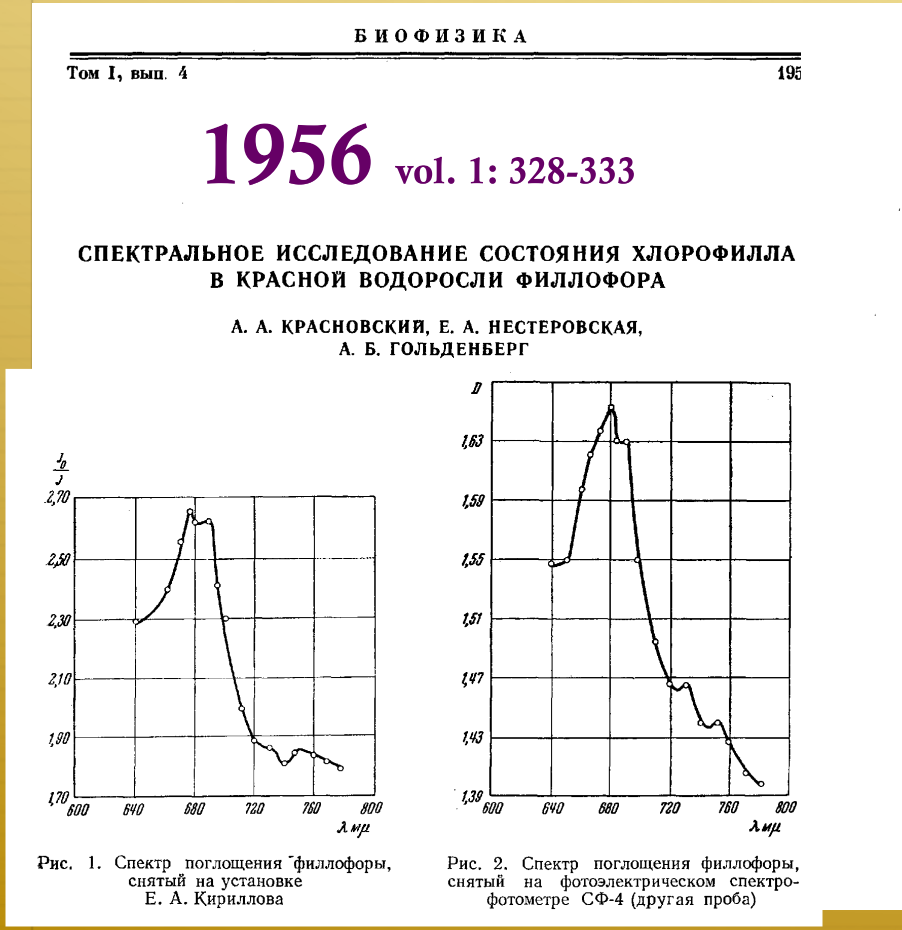
Figure from a review by Govindjee and D. Shevela (2011) Frontiers in Plant Science, vol. 2, article 28: 1-17.

Presentation by Govindjee

1956

Discovery of Different Spectral Forms of Chl a in vivo

Again ahead of his time



БИОФИЗИКА

Том I, вып. 4 195

1956 vol. 1: 328-333

СПЕКТРАЛЬНОЕ ИССЛЕДОВАНИЕ СОСТОЯНИЯ ХЛОРОФИЛЛА В КРАСНОЙ ВОДОРОСЛИ ФИЛЛОФОРА

А. А. КРАСНОВСКИЙ, Е. А. НЕСТЕРОВСКАЯ,
А. Б. ГОЛЬДЕНБЕРГ

Рис. 1. Спектр поглощения филлофоры, снятый на установке Е. А. Кириллова

Рис. 2. Спектр поглощения филлофоры, снятый на фотоэлектрическом спектрофотометре СФ-4 (другая проба)

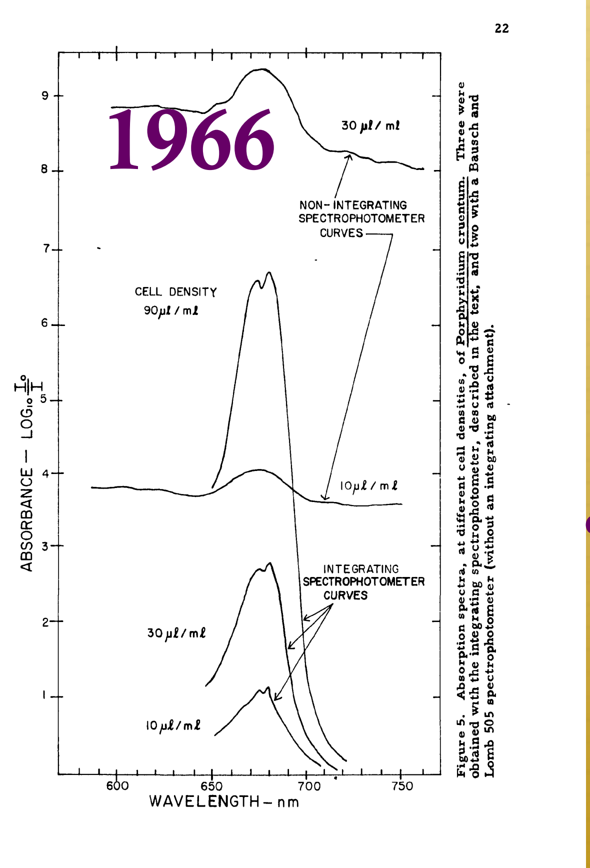


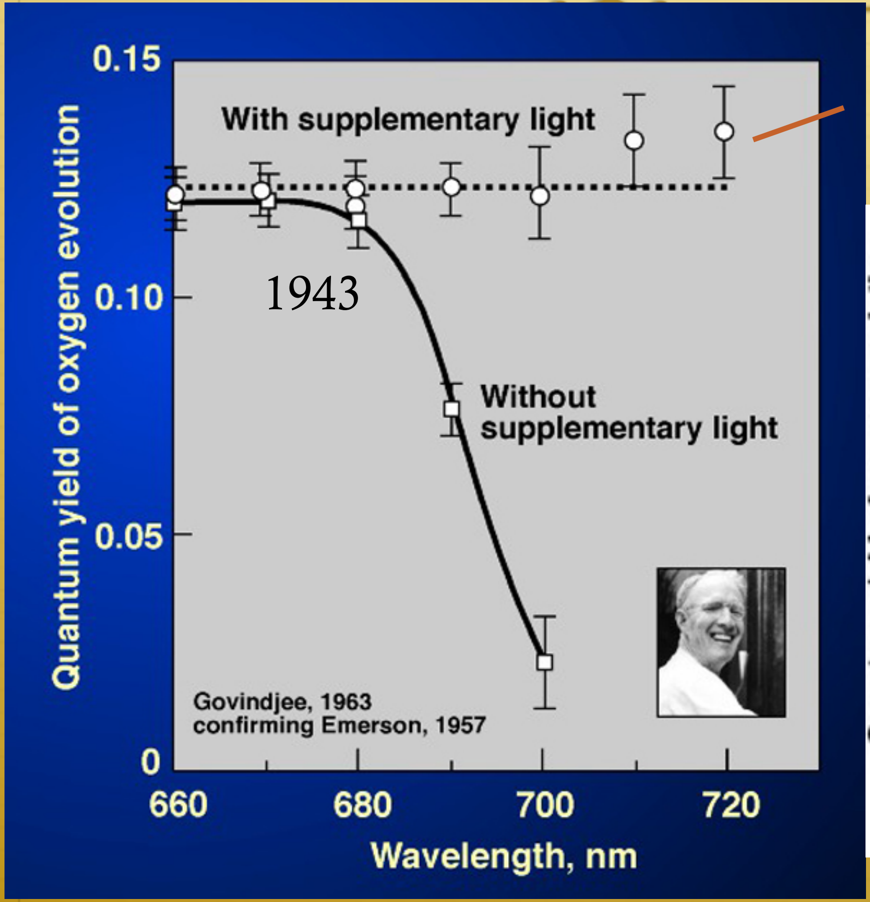
Figure 5. Absorption spectra, at different cell densities, of Porphyridium cruentum. Three were obtained with the integrating spectrophotometer, described in the text, and two with a Bausch and Lomb 505 spectrophotometer (without an integrating attachment).

Ten years later, Cederstrand, Rabinowitch and Govindjee (BBA 126: 1-12; 1966) rediscovered what Krasnovsky had seen already in 1956: direct evidence of the presence of Chl a 670 and Chl a 680 in the absorption spectrum of algal cells.

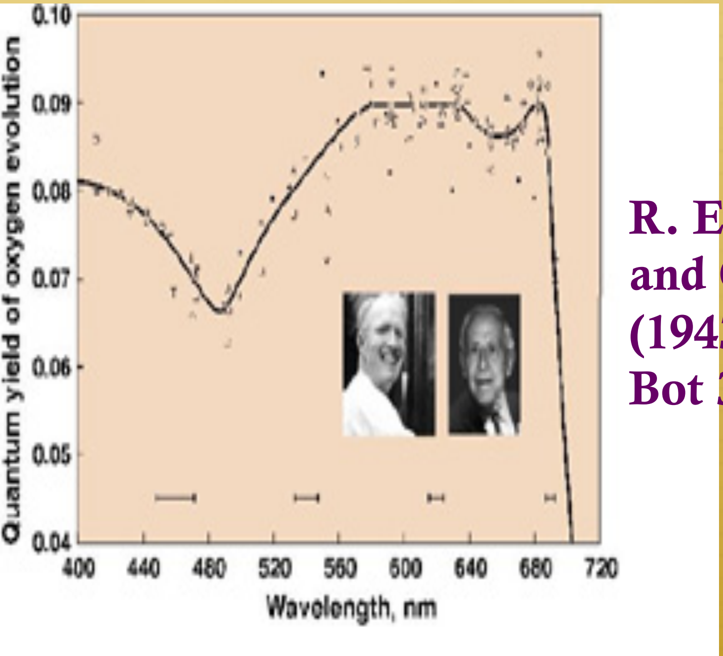
Presentation by Govindjee

1957

The Emerson Enhancement Effect : Existence of two light reactions and two photsystems; this had followed the discovery of the red drop by Emerson and Lewis in 1943



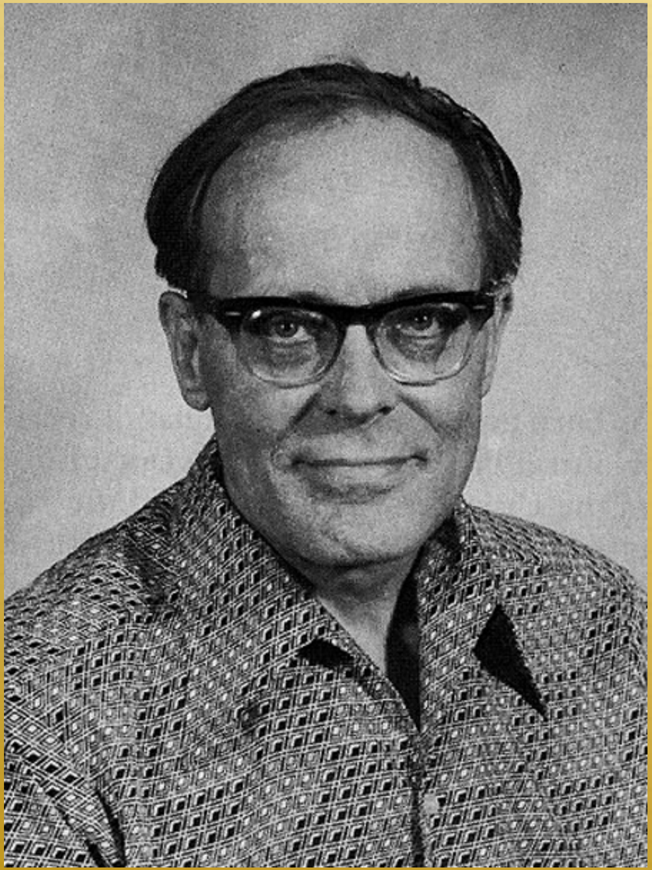
R. Emerson, R. V. Chalmers and C. Cederstrand (1957) Proc Natl Acad Sci USA 43: 133-143

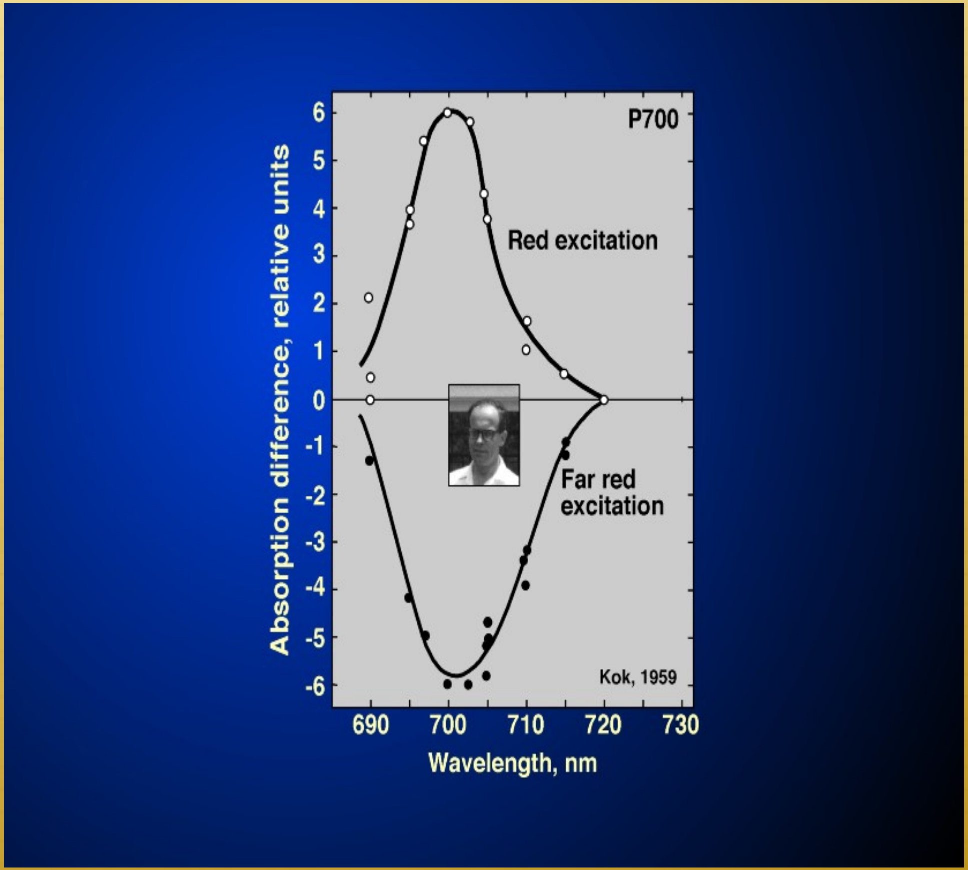


R. Emerson and C.M. Lewis (1943) Amer J Bot 30: 165-178

1956-1957, 1959: Discovery of P700 and 2 light effect on it

Bessel Kok (1918-1979) discovered P700 in 1956-1957 in Wageningen, The Netherlands; in 1959, he also showed the two-light effect on it. (see BBA 22: 399, 1956)

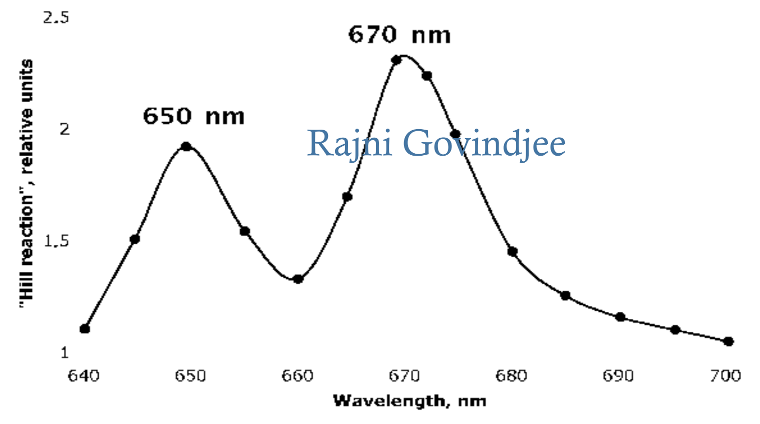


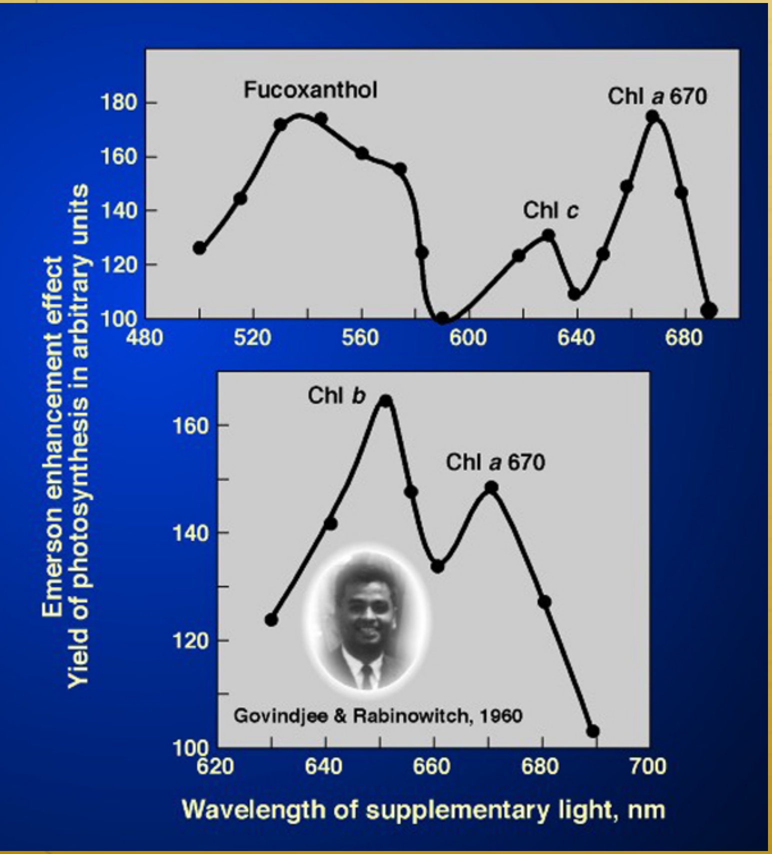


Must not forget experiments of Duysens, Amesz and Kamp (1961) on antagonistic effect of light 1 and 2 on cytochrome f..That is where the terminology of Photosystem I and Photoystem II, and Light reaction I and II arose. [Presentation by Govindjee]

1960

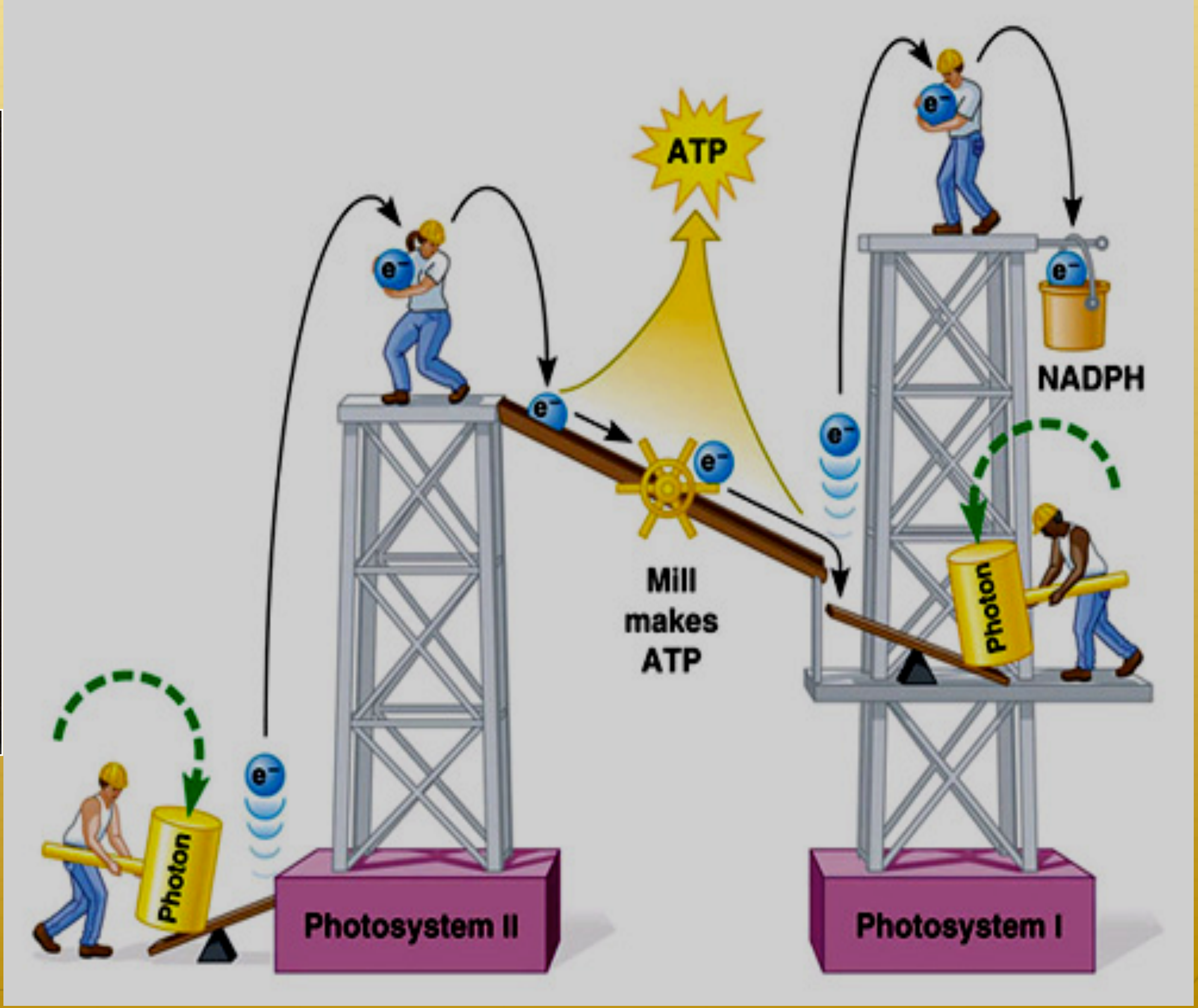
Govindjee and Rajni look back at their experiments done 53 years ago..





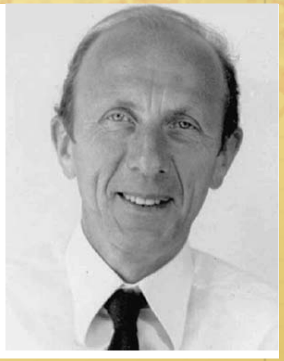
Govindjee and Rabinowitch (1960) and R. Govindjee et al. (1960) showed that a short wavelength absorbing form of chlorophyll a (Chl a 670) was present in the same system that used chlorophyll *b* (or other accessory pigments) . This agreed with Duysens (1952) that all energy absorbed by chlorophyll *b* is transferred to chlorophyll *a*. The longwavelength form of Chl a was in the other system!

Going Back to 1960-- A Cartoon of "Z" Scheme of Hill and Bendall



1956--1970

The Early Story of P680, as Govindjee has watched it



Horst T. Witt (1922-2007)

- Coleman, Holt and Rabinowitch (1956, Science, 123: 745) discovered two absorbance decreases in the 680-685 and 700 nm range in the green alga Chlorella; they considered the former to be due to Chl a oxidation.
- Rubinstein and Rabinowitch (1963, Science 682: 141) and Karapetyan, Livin and Krasnovsky (1963, Biofysika 8: 191) showed it to be caused by fluorescence artifact .
- 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.
- It was challenged by Warren Butler to be a fluorescence artifact, but it has stood to be a true change (see e.g., Govindjee, Döring, Govindjee, 1970, BBA 205: 303), and the current literature.

1963

The role of Chl in oxidation and reduction was already born in 1948; however, the validity that Chl molecule, in model systems, serves as an uphill electron carrier was firm by 1963.

A.A. Krasnovsky and N.N. Drozdova (1963) showed reversible photochemical interaction of Chl , BChl and bacterioviridin with quinone and oxygen in ethylalcohol-glycerol media [photooxidation was done at -70C and reversal was shown after thawing.

Reviews are:

- A.A. Krasnovsky (1972) The fragments of the photosynthetic electron transfer chain in model systems. Biophys J 12: 749-763
- A.A. Krasnovsky (1992) Excited chlorophyll and related problems. Photosynth Res 33: 177-193
- A.A. Krasnovsky (1997) A lifetime journey with photosynthesis. Comprehensive Biochemistry 40: 205-252

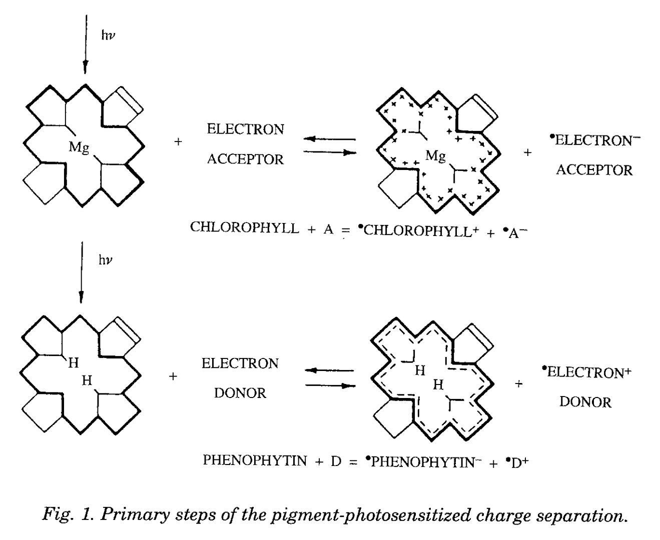

A LIFETIME JOURNEY WITH PHOTOSYNTHESIS 225

Fig. 1. Primary steps of the pigment-photosensitized charge separation.

1956--1963

The early story of “P680”: “Yes”, and then “No”

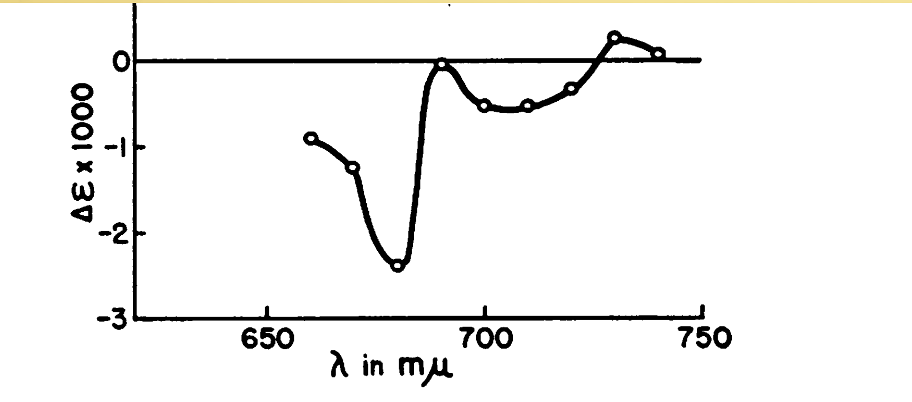


Fig. 1. Reversible bleaching of chlorophyll

J.W. Coleman, A.S. Holt and E.I. Rabinowitch (1956)Science 124: 795-796

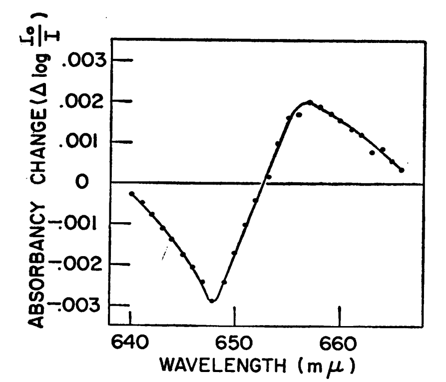


Fig. 1. The change in the absorption spectrum of a *Chlorella* suspension upon irradiation with blue light of high intensity (corrected for fluorescence).

J.W. Coleman And E.I. Rabinowitch (1959) J Phys Chem 63: 30-34 had discovered other changes that must not be forgotten

Jan., 1959 EVIDENCE OF PHOTOREDUCTION OF CHLOROPHYLL *in Vivo* 31

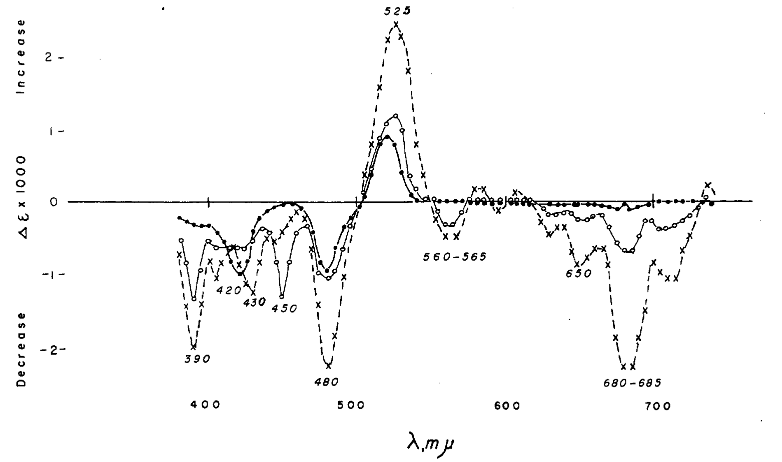
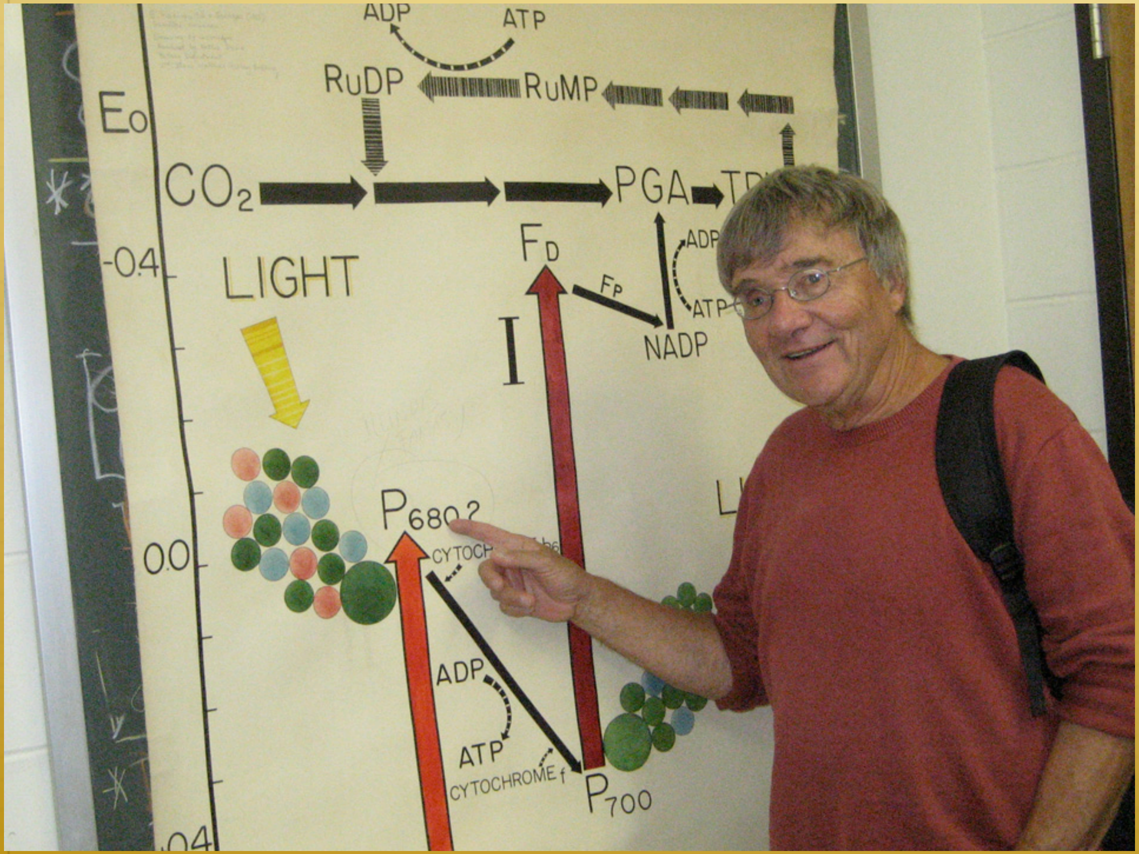


Fig. 1.—Difference spectra of *Chlorella pyrenoidosa* (“thin” suspension in carbonate buffer, no. 9) in white light (λ_{max} = 555 mμ) of different intensities: dots, incident light intensity, 3.4 × $10^{14}h\nu$/(sec. × cm.^{2}); circles, incident light intensity, 12.0 × $10^{14}h\nu$/(sec. × cm.^{2}); crosses: incident light intensity, 31.4 × $10^{14}h\nu$/(sec. × cm.^{2}).

D. Rubinstein and E.I. Rabinowitch (1963) Science 142: 681-682; And, N.V. Karapetyan, F.F. Litvin and A.A. Krasnovsky (1963) Biofizika 8: 191-200 proved this “P680” to be an artifact of fluorescence!

1964--1965

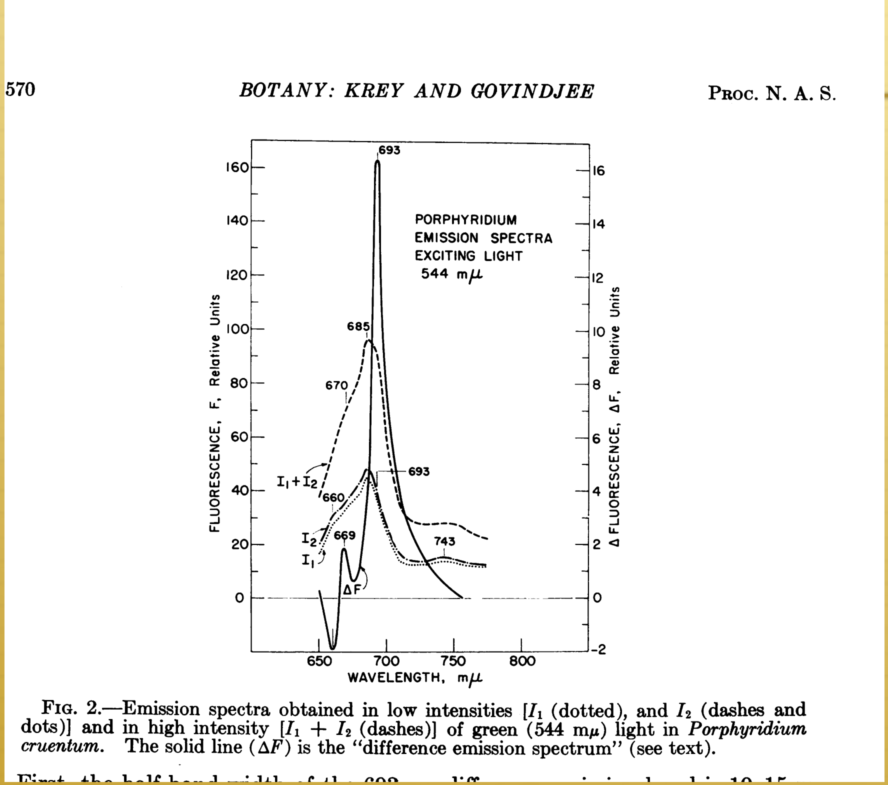
There must be a real P680, we said



In the summer of 1964, I made a scheme for teaching a course in Urbana, and convinced Rabinowitch that a real "P680" must exist in Photosystem II, and he agreed to include it in our popular article (Rabinowitch and Govindjee (1965) Sci Amer 213: 74-83) . Here Wolfgang Junge is looking at it on Sep.27, 2013

1964-1965

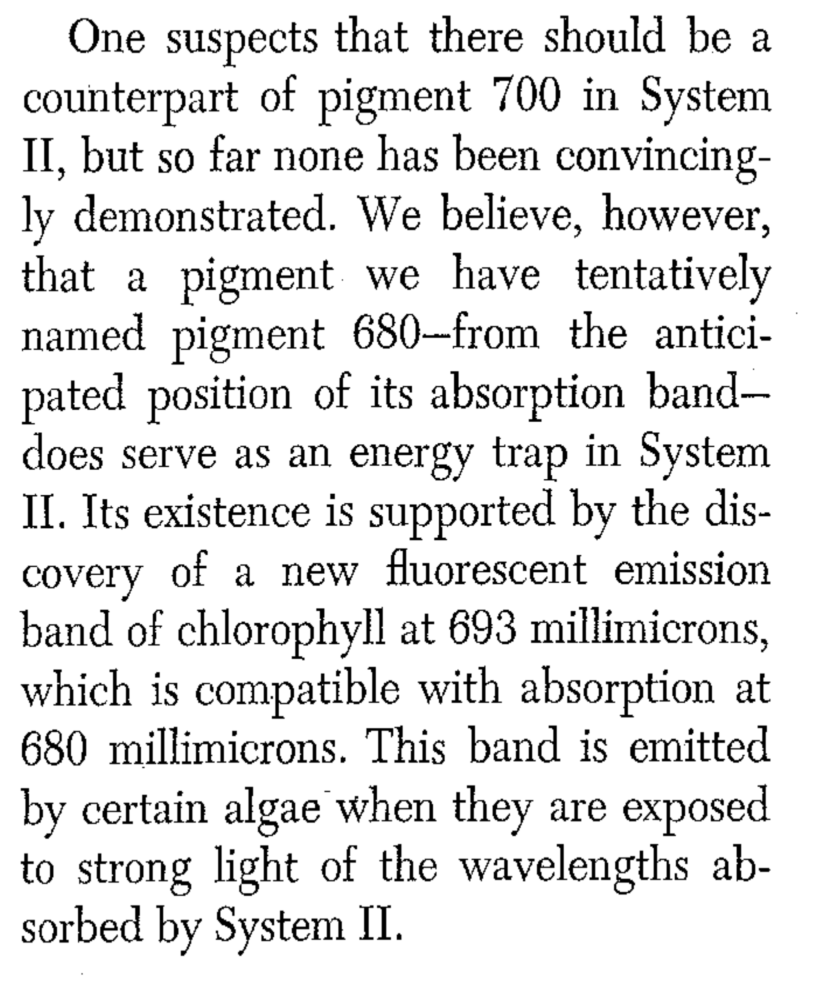
How did I convince Rabinowitch to my point of view of "P680"?



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 mμ) light in *Porphyridium cruentum*. The solid line (ΔF) is the "difference emission spectrum" (see text).

Krey and Govindjee (1964) in Proc Natl Acad Sci USA 52: 1568-1572 wrote : "We believe that the small 693-nm fluorescence band emana from "photochemically frustrated" trap II under these [high light and DCMU] conditions"

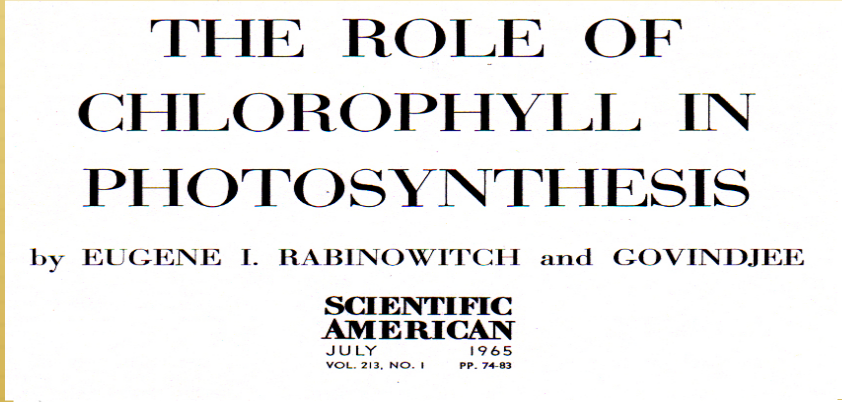


One suspects that there should be a counterpart of pigment 700 in System II, but so far none has been convincingly demonstrated. We believe, however, that a pigment we have tentatively named pigment 680—from the anticipated position of its absorption band—does serve as an energy trap in System II. Its existence is supported by the discovery of a new fluorescent emission band of chlorophyll at 693 millimicrons, which is compatible with absorption at 680 millimicrons. This band is emitted by certain algae when they are exposed to strong light of the wavelengths absorbed by System II.

Sci Amer 213: 74-83 (1965)

1969

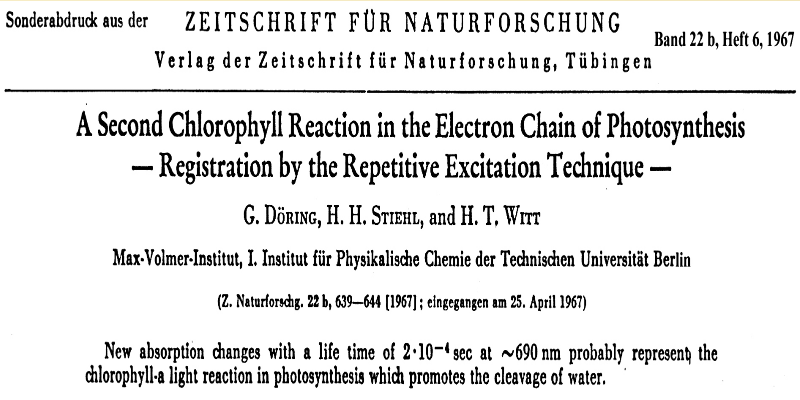
Discovery of Reaction Center of PSII, P680, in Berlin in Witt's lab



THE ROLE OF CHLOROPHYLL IN PHOTOSYNTHESIS

by EUGENE I. RABINOWITCH and GOVINDJEE

SCIENTIFIC AMERICAN
JULY 1965
VOL. 213, NO. 1 PP. 74-83



Sonderabdruck aus der ZEITSCHRIFT FÜR NATURFORSCHUNG Band 22 b, Heft 6, 1967
Verlag der Zeitschrift für Naturforschung, Tübingen

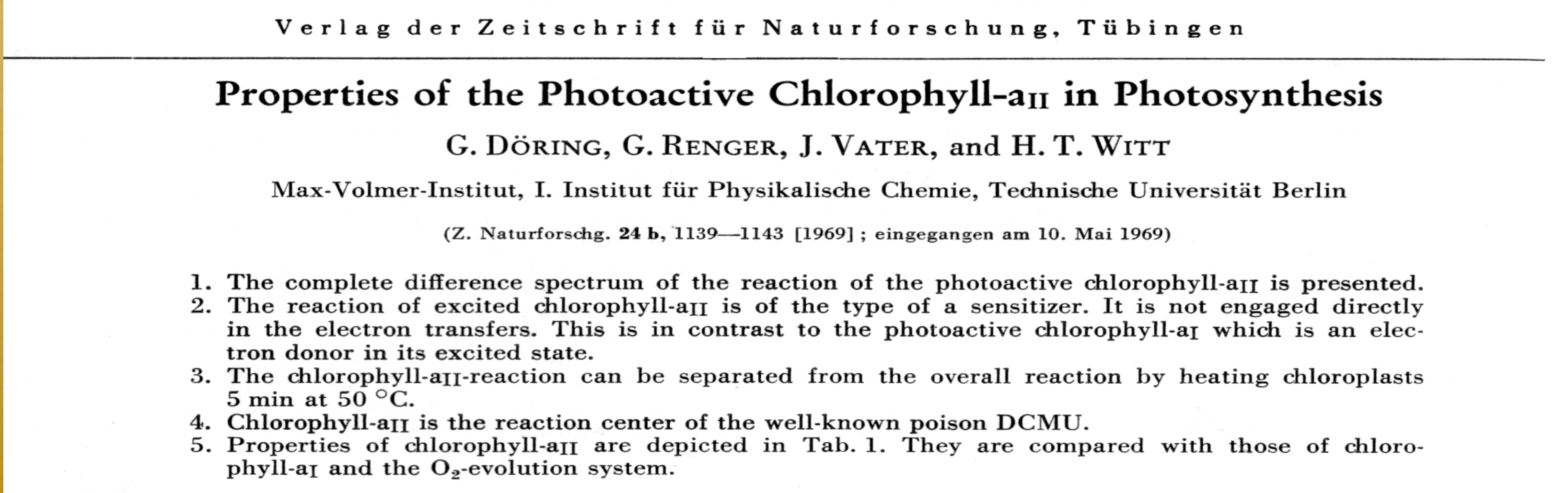
A Second Chlorophyll Reaction in the Electron Chain of Photosynthesis
— Registration by the Repetitive Excitation Technique —

G. Döring, H. H. Stiehl, and H. T. Witt

Max-Volmer-Institut, I. Institut für Physikalische Chemie der Technischen Universität Berlin

(Z. Naturforschg. **22 b,** 639—644 [1967]; eingegangen am 25. April 1967)

New absorption changes with a life time of $2 \cdot 10^{-4}$ sec at ~690 nm probably represent the chlorophyll-a light reaction in photosynthesis which promotes the cleavage of water.



Sonderdruck aus der ZEITSCHRIFT FÜR NATURFORSCHUNG Band 24 b, Heft 9, 1969
Verlag der Zeitschrift für Naturforschung, Tübingen

Properties of the Photoactive Chlorophyll-a_{II} in Photosynthesis

G. Döring, G. Renger, J. Vater, and H. T. Witt

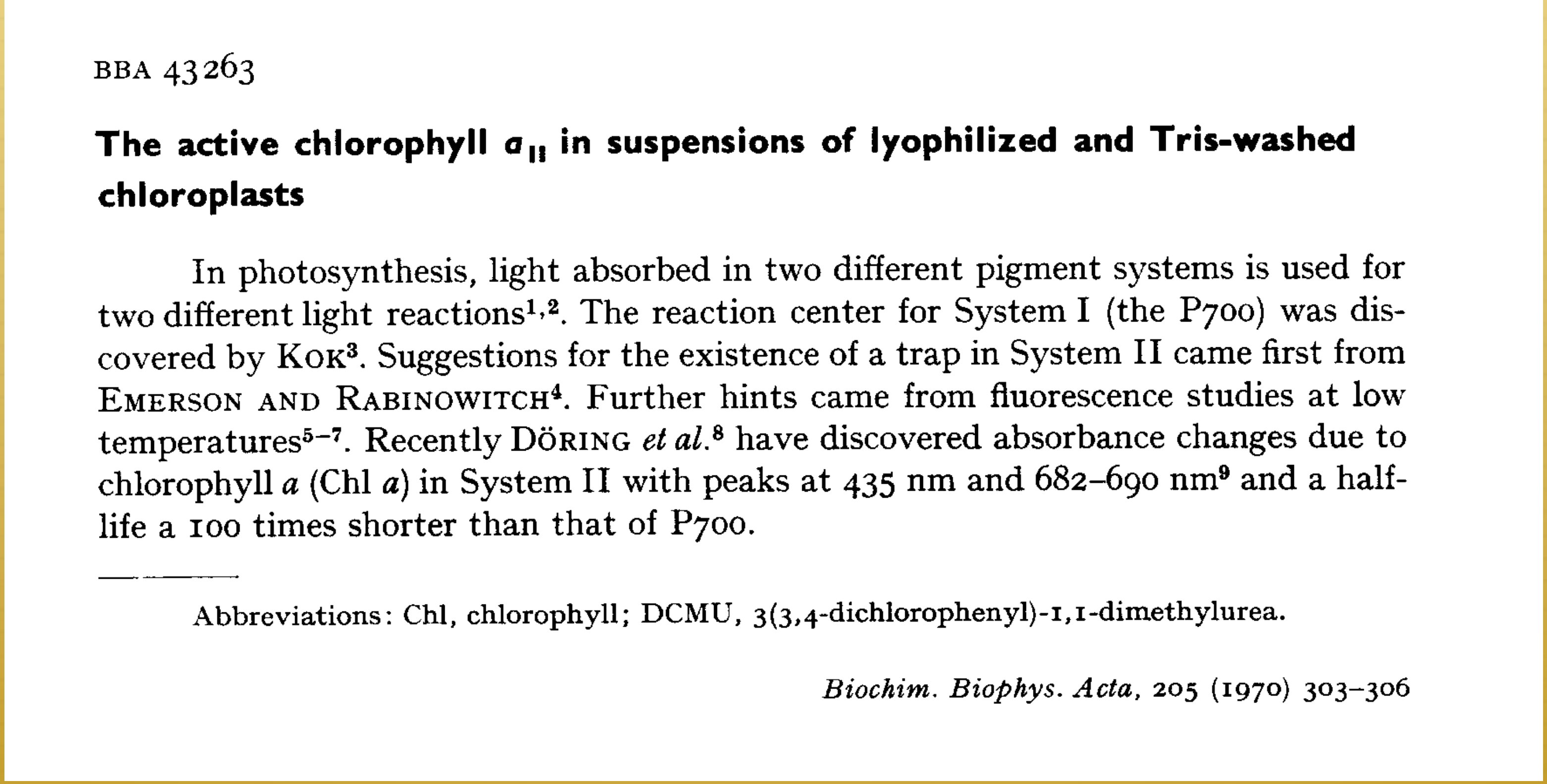
Max-Volmer-Institut, I. Institut für Physikalische Chemie, Technische Universität Berlin

(Z. Naturforschg. **24 b,** 1139—1143 [1969]; eingegangen am 10. Mai 1969)

1. The complete difference spectrum of the reaction of the photoactive chlorophyll-a_{II} is presented.
2. The reaction of excited chlorophyll-a_{II} is of the type of a sensitizer. It is not engaged directly in the electron transfers. This is in contrast to the photoactive chlorophyll-a_{I} which is an electron donor in its excited state.
3. The chlorophyll-a_{II}-reaction can be separated from the overall reaction by heating chloroplasts 5 min at 50 °C.
4. Chlorophyll-a_{II} is the reaction center of the well-known poison DCMU.
5. Properties of chlorophyll-a_{II} are depicted in Tab. 1. They are compared with those of chlorophyll-a_{I} and the O_2-evolution system.

1970 The Berlin P680 was not a fluorescence artifact

Govindjee, G. DÖring and R. Govindjee (1970) showed that P680 was present in wet-heptane extracted chloroplasts and in Tris-extracted chloroplasts and it was not due to fluorescence artifact.



BBA 43263

The active chlorophyll a_{II} in suspensions of lyophilized and Tris-washed chloroplasts

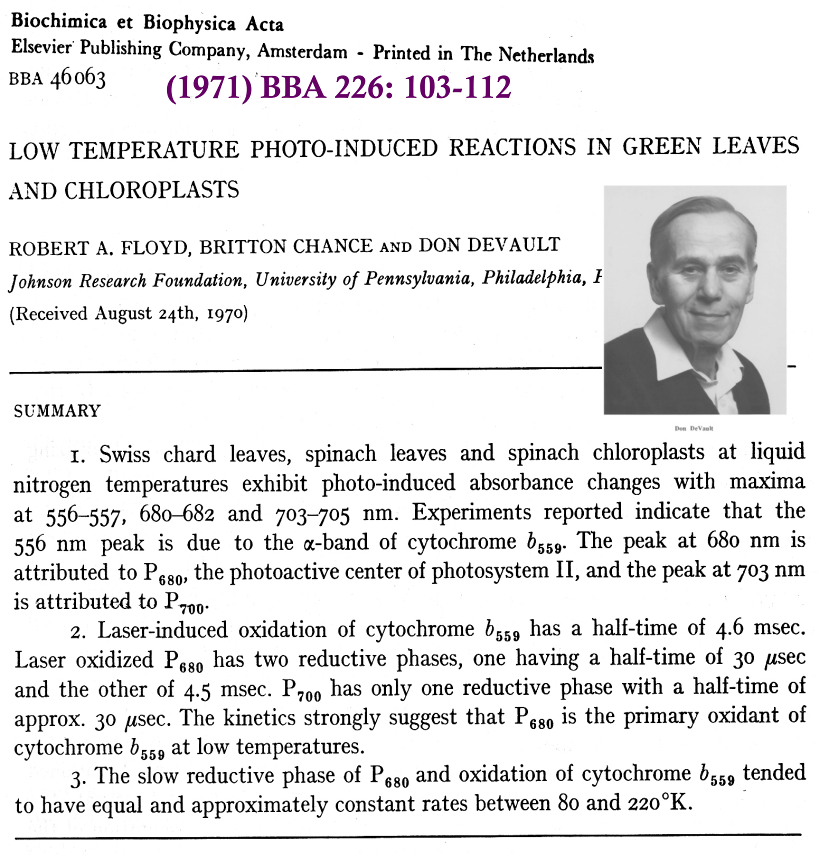
In photosynthesis, light absorbed in two different pigment systems is used for two different light reactions[1,2]. The reaction center for System I (the P700) was discovered by Kok[3]. Suggestions for the existence of a trap in System II came first from Emerson and Rabinowitch[4]. Further hints came from fluorescence studies at low temperatures[5-7]. Recently Döring *et al.*[8] have discovered absorbance changes due to chlorophyll *a* (Chl *a*) in System II with peaks at 435 nm and 682–690 nm[9] and a half-life a 100 times shorter than that of P700.

Abbreviations: Chl, chlorophyll; DCMU, 3(3,4-dichlorophenyl)-1,1-dimethylurea.

Biochim. Biophys. Acta, 205 (1970) 303–306

1971-1972

“P680” participates as electron carrier, not just as a sensitizer



Biochimica et Biophysica Acta
Elsevier Publishing Company, Amsterdam - Printed in The Netherlands
BBA 46063

(1971) BBA 226: 103-112

LOW TEMPERATURE PHOTO-INDUCED REACTIONS IN GREEN LEAVES AND CHLOROPLASTS

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Johnson Research Foundation, University of Pennsylvania, Philadelphia, P

(Received August 24th, 1970)

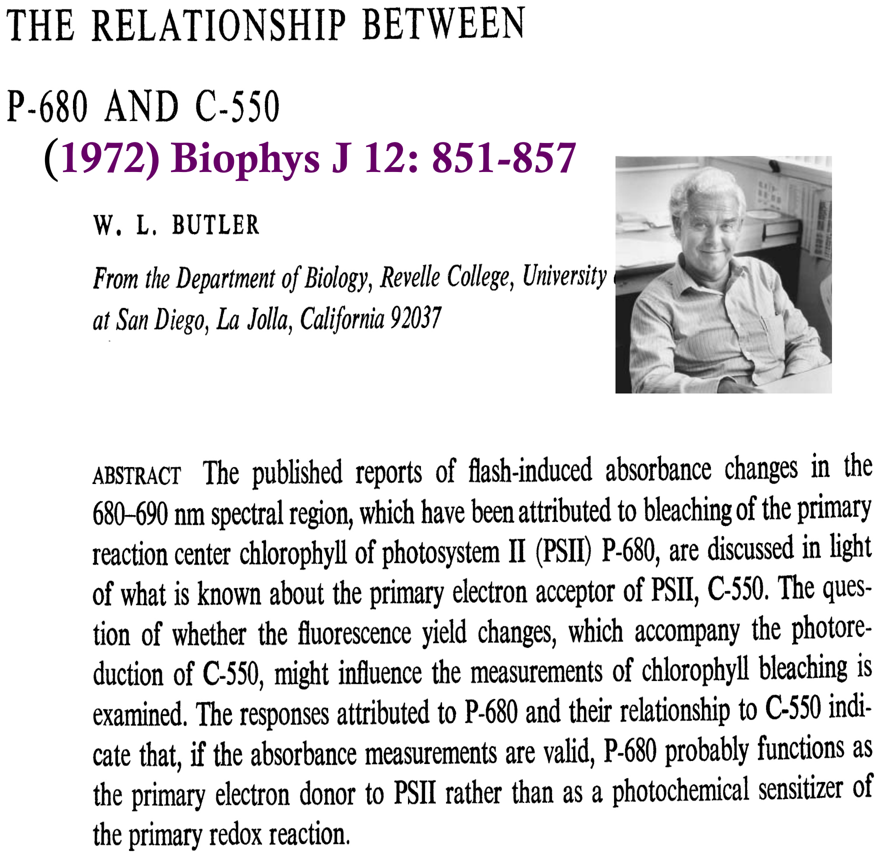
Don DeVault

SUMMARY

1. Swiss chard leaves, spinach leaves and spinach chloroplasts at liquid nitrogen temperatures exhibit photo-induced absorbance changes with maxima at 556–557, 680–682 and 703–705 nm. Experiments reported indicate that the 556 nm peak is due to the α-band of cytochrome b_{559}. The peak at 680 nm is attributed to P_{680}, the photoactive center of photosystem II, and the peak at 703 nm is attributed to P_{700}.

2. Laser-induced oxidation of cytochrome b_{559} has a half-time of 4.6 msec. Laser oxidized P_{680} has two reductive phases, one having a half-time of 30 μsec and the other of 4.5 msec. P_{700} has only one reductive phase with a half-time of approx. 30 μsec. The kinetics strongly suggest that P_{680} is the primary oxidant of cytochrome b_{559} at low temperatures.

3. The slow reductive phase of P_{680} and oxidation of cytochrome b_{559} tended to have equal and approximately constant rates between 80 and 220°K.



THE RELATIONSHIP BETWEEN P-680 AND C-550

(1972) Biophys J 12: 851-857

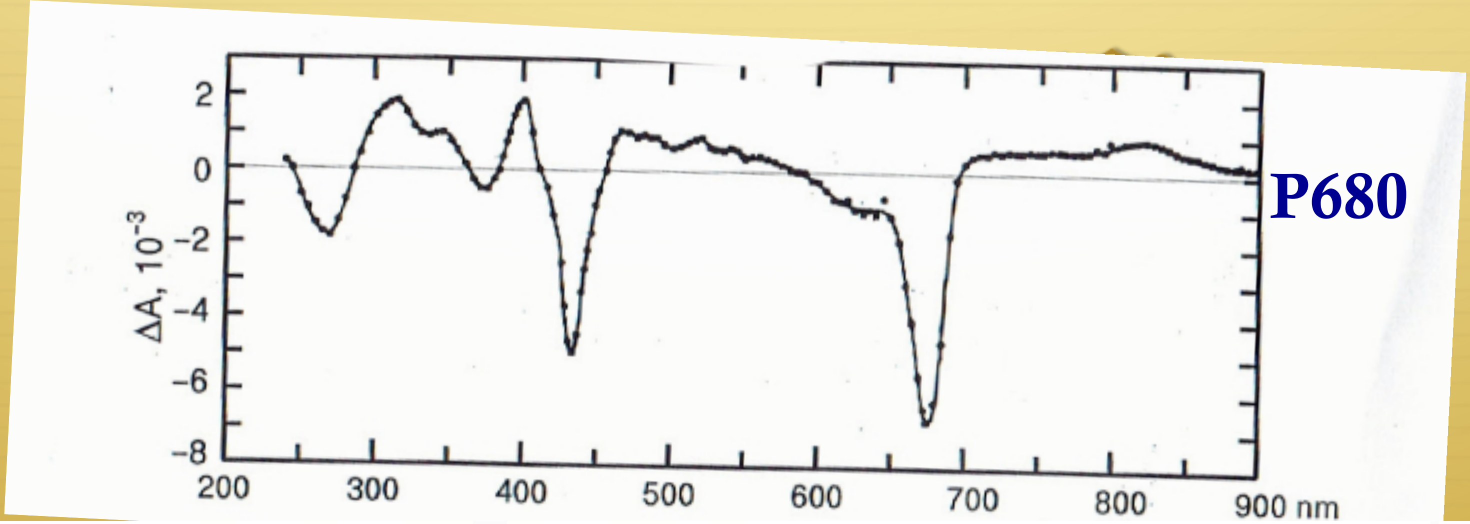
W. L. BUTLER

From the Department of Biology, Revelle College, University
at San Diego, La Jolla, California 92037

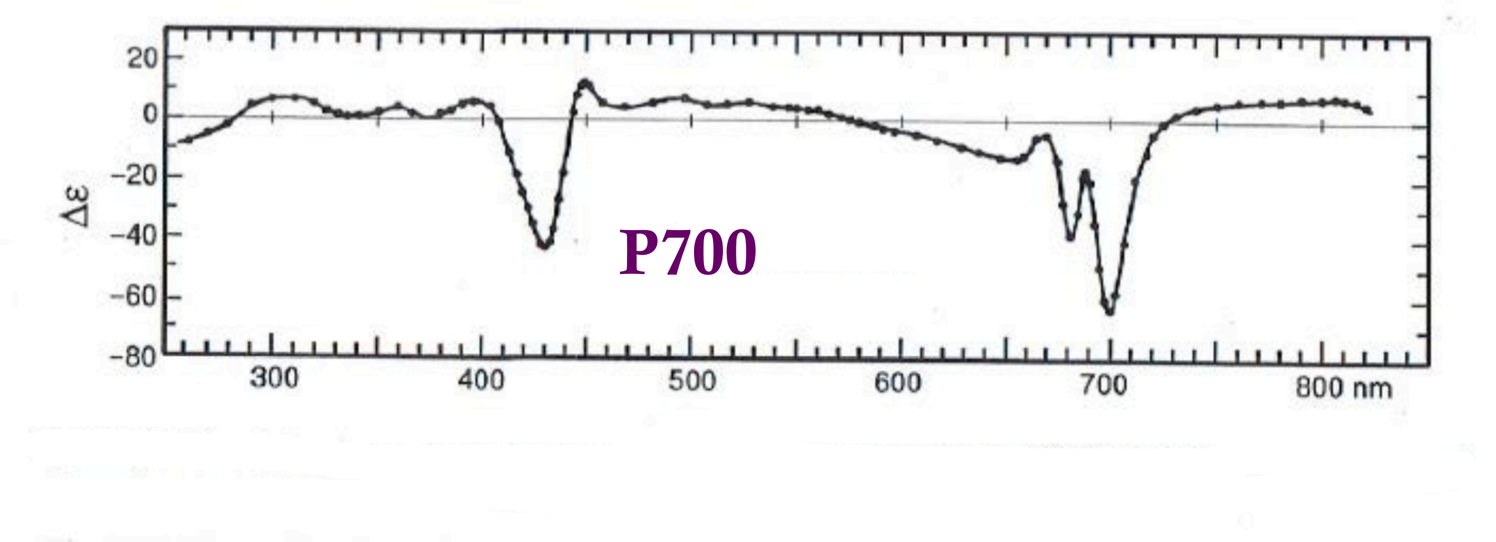
ABSTRACT The published reports of flash-induced absorbance changes in the 680–690 nm spectral region, which have been attributed to bleaching of the primary reaction center chlorophyll of photosystem II (PSII) P-680, are discussed in light of what is known about the primary electron acceptor of PSII, C-550. The question of whether the fluorescence yield changes, which accompany the photoreduction of C-550, might influence the measurements of chlorophyll bleaching is examined. The responses attributed to P-680 and their relationship to C-550 indicate that, if the absorbance measurements are valid, P-680 probably functions as the primary electron donor to PSII rather than as a photochemical sensitizer of the primary redox reaction.

There is no doubt now that P680 and P700 are real things

P680 and **P700** absorption changes (after **Ke, 1973**; after **Van Gorkom et al., 1975**)



P680



P700

1975; 1976: Krasnovsky goes for Hydrogen Evolution in TiO_2 and ZnO particles

Again ahead of his time

A.A. Krasnovsky, G.P. Brin and V.V. Nikandrov (1976) Photoreduction of oxygen and photoproduction of hydrogen on inorganic photocatalysts. Dokl AN SSSR 229: 990-993; see figure.

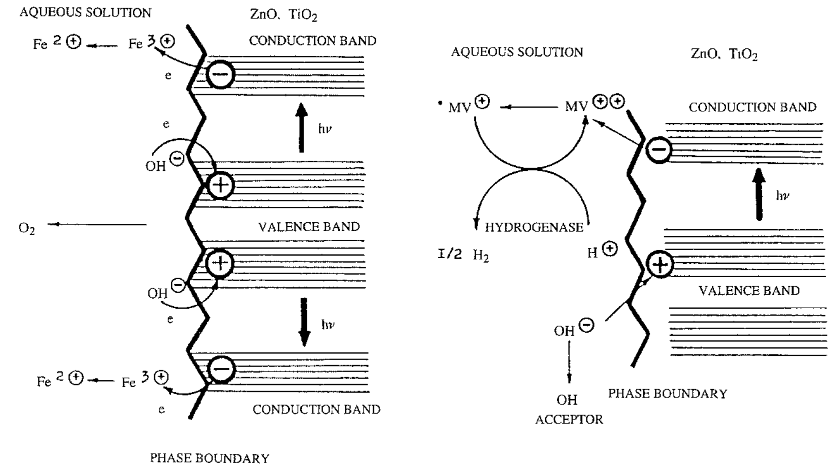


Fig. 5. Hypothetical scheme of photosensitized oxygen and hydrogen evolution on the particles of TiO_2 and ZnO.

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.

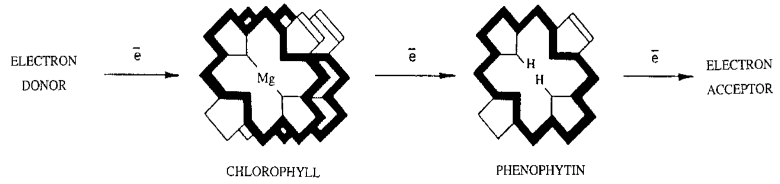


Fig. 4. Photoinduced electron transfer between chlorophyll and pheophytin.

1982; 1987: Reduction of methyl viologen in liposomal Systems; and hydrogen evolution, with hydrogenase present

Krasnovsky's group moved from solution systems to (anaerobic) liposomal systems where they used ascorbic acid inside the liposomes and succeeded in using methyl viologen as electron acceptors (A.A. Krasnovsky, A.N. Semenova and V.V. Nikandrov (1982) Chlorophyll-containing liposomes, photoreduction of methylviologen, and photoproduction of hydrogen. Dokl AN SSSR 262 :469-472); **and they were able to show hydrogen evolution, in the presence of bacterial hydrogenase** (A.N.Semenova, Ya V. Barannikova, V.V. Nikandrov and A.A. Krasnovsky (1987) Conditions for the efficient photoinduced transmembrane electron transfer in chlorophyll- and pheophytin-containing liposomes. Biolog Membr (in Russian) 4: 448-557.

Again Ahead of his Time

A LIFETIME JOURNEY WITH PHOTOSYNTHESIS 229

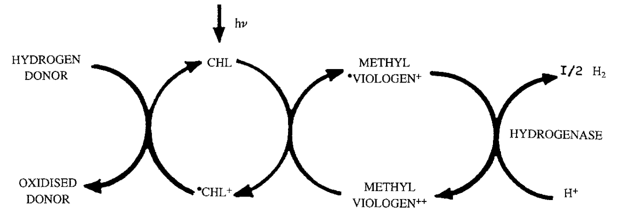


Fig. 2. Scheme of the photosensitized reduction of methyl viologen coupled to hydrogenase.

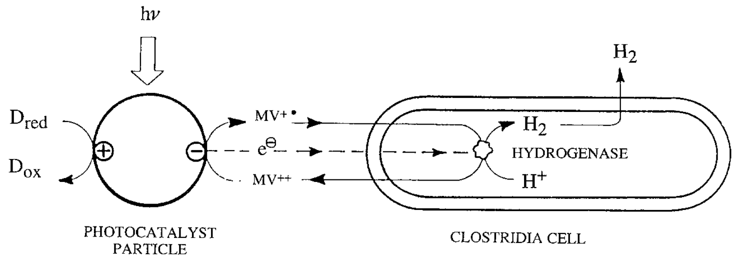


Fig. 6. Scheme for hydrogen photoproduction in the coupling of mineral photocatalyst to Clostridium *cells. MV, methyl viologen;* D_{red} *and* D_{ox}*, reduced and oxidized electron donor, respectively.*

1989

Primary Photochemistry: Conversion of light energy into chemical energy occurs in picoseconds in PSII: Our First measurements on P680 in PSII

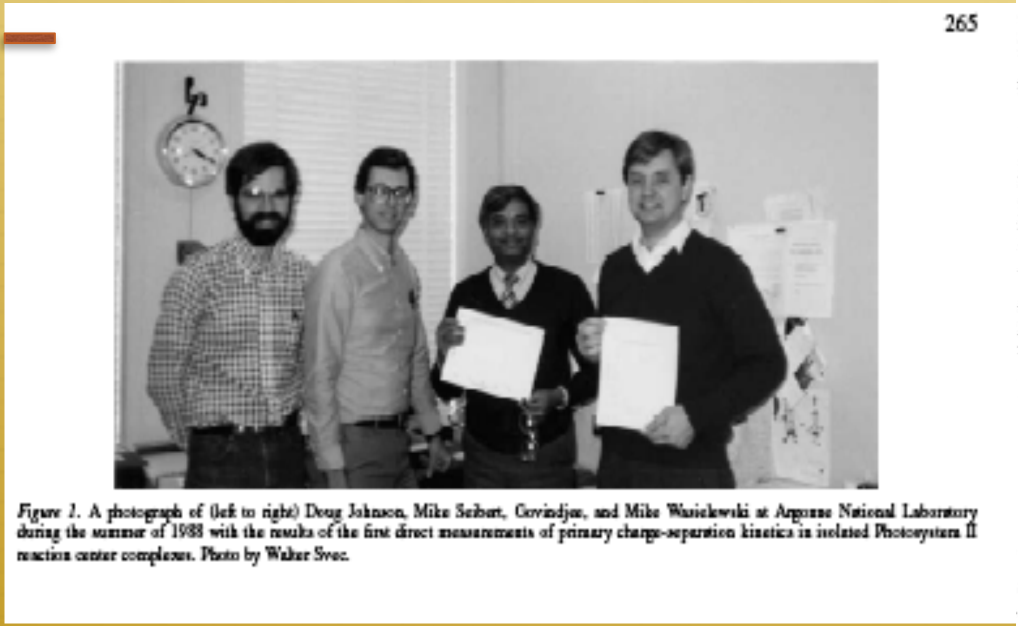


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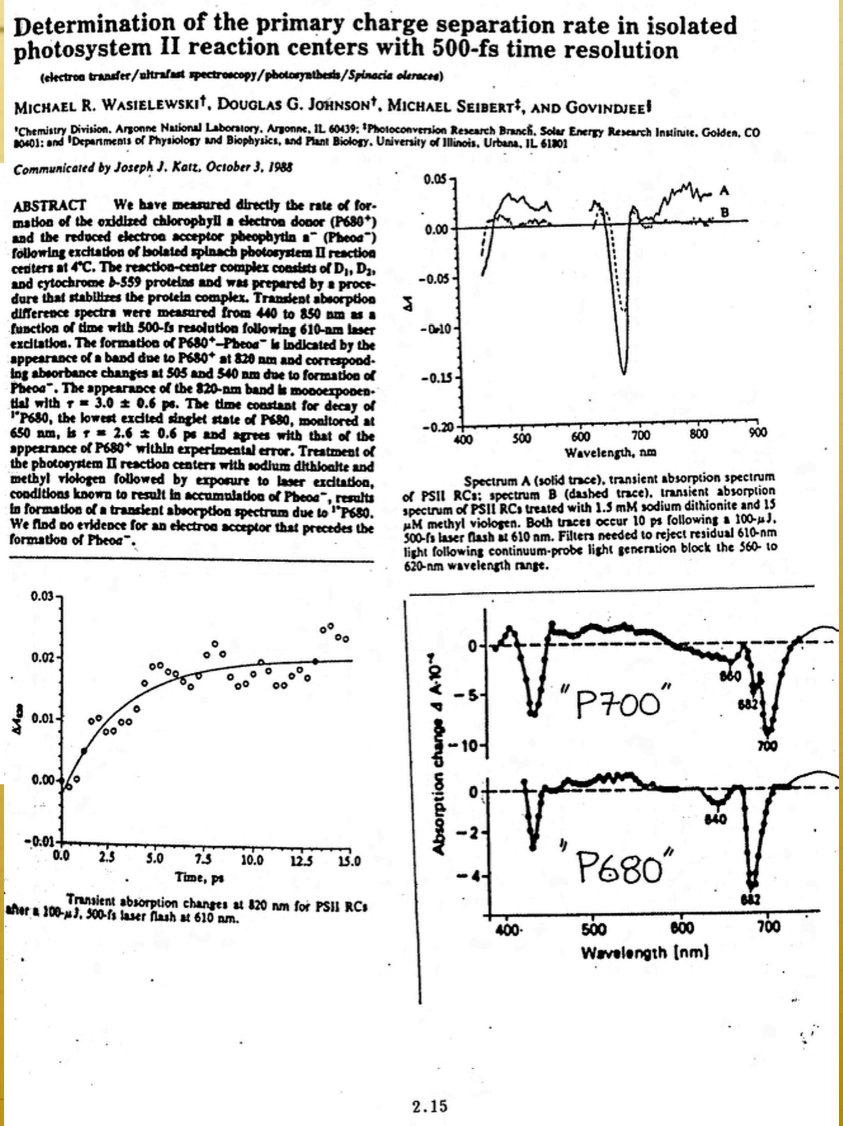
Figure 1. A photograph of (left to right) Doug Johnson, Mike Seibert, Govindjee, and Mike Wasielewski at Argonne National Laboratory during the summer of 1988 with the results of the first direct measurements of primary charge-separation kinetics in isolated Photosystem II reaction center complexes. Photo by Walter Svec.



Determination of the primary charge separation rate in isolated photosystem II reaction centers with 500-fs time resolution

(electron transfer/ultrafast spectroscopy/photosynthesis/*Spinacia oleracea*)

MICHAEL R. WASIELEWSKI†, DOUGLAS G. JOHNSON†, MICHAEL SEIBERT‡, AND GOVINDJEE§

†Chemistry Division, Argonne National Laboratory, Argonne, IL 60439; ‡Photoconversion Research Branch, Solar Energy Research Institute, Golden, CO 80401; and §Departments of Physiology and Biophysics, and Plant Biology, University of Illinois, Urbana, IL 61801

Communicated by Joseph J. Katz, October 3, 1988

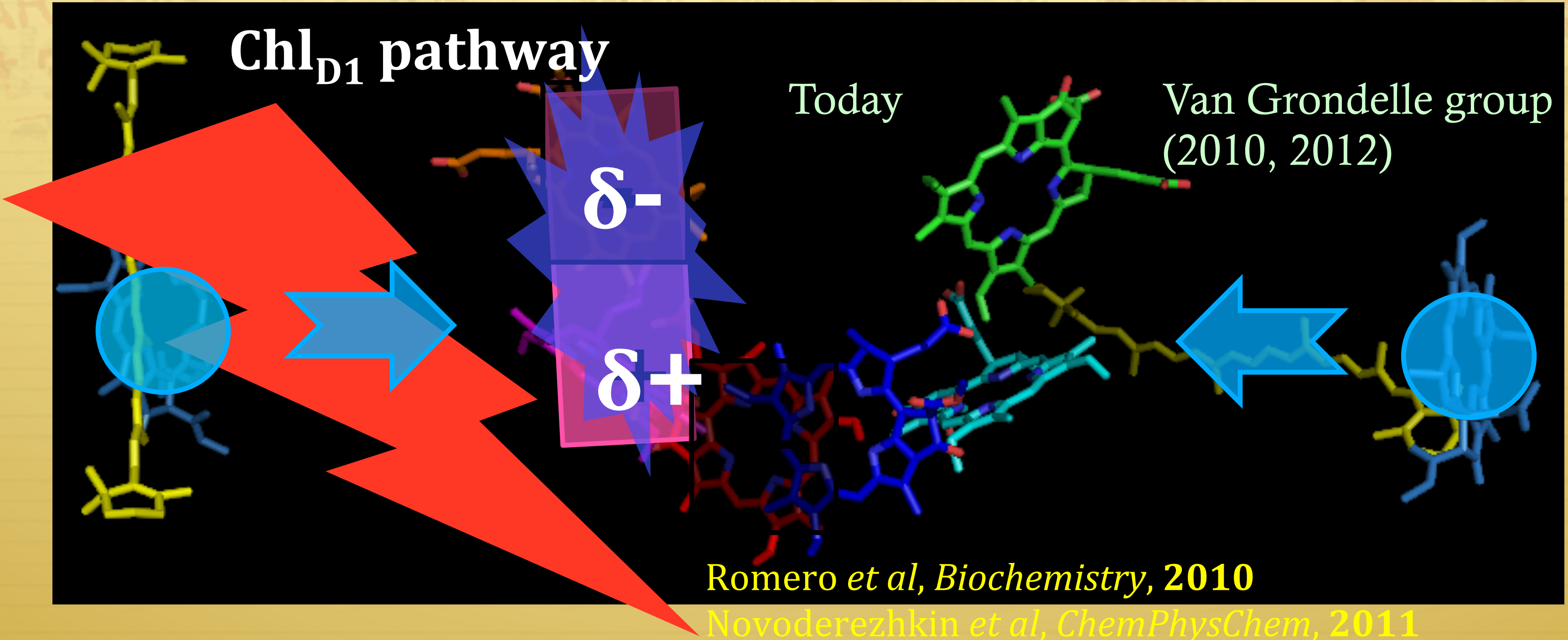
ABSTRACT We have measured directly the rate of formation of the oxidized chlorophyll a electron donor ($P680^+$) and the reduced electron acceptor pheophytin a^- ($Pheo a^-$) following excitation of isolated spinach photosystem II reaction centers at 4°C. The reaction-center complex consists of D_1, D_2, and cytochrome *b*-559 proteins and was prepared by a procedure that stabilizes the protein complex. Transient absorption difference spectra were measured from 440 to 850 nm as a function of time with 500-fs resolution following 610-nm laser excitation. The formation of $P680^+$–$Pheo a^-$ is indicated by the appearance of a band due to $P680^+$ at 820 nm and corresponding absorbance changes at 505 and 540 nm due to formation of $Pheo a^-$. The appearance of the 820-nm band is monoexponential with $\tau = 3.0 \pm 0.6$ ps. The time constant for decay of $^{1*}P680$, the lowest excited singlet state of P680, monitored at 650 nm, is $\tau = 2.6 \pm 0.6$ ps and agrees with that of the appearance of $P680^+$ within experimental error. Treatment of the photosystem II reaction centers with sodium dithionite and methyl viologen followed by exposure to laser excitation, conditions known to result in accumulation of $Pheo a^-$, results in formation of a transient absorption spectrum due to $^{1*}P680$. We find no evidence for an electron acceptor that precedes the formation of $Pheo a^-$.

Spectrum A (solid trace), transient absorption spectrum of PSII RCs; spectrum B (dashed trace), transient absorption spectrum of PSII RCs treated with 1.5 mM sodium dithionite and 15 μM methyl viologen. Both traces occur 10 ps following a 100-μJ, 500-fs laser flash at 610 nm. Filters needed to reject residual 610-nm light following continuum-probe light generation block the 560- to 620-nm wavelength range.

Transient absorption changes at 820 nm for PSII RCs after a 100-μJ, 500-fs laser flash at 610 nm.

2.15

Presentation by Govindjee



Chl$_{D1}$ pathway

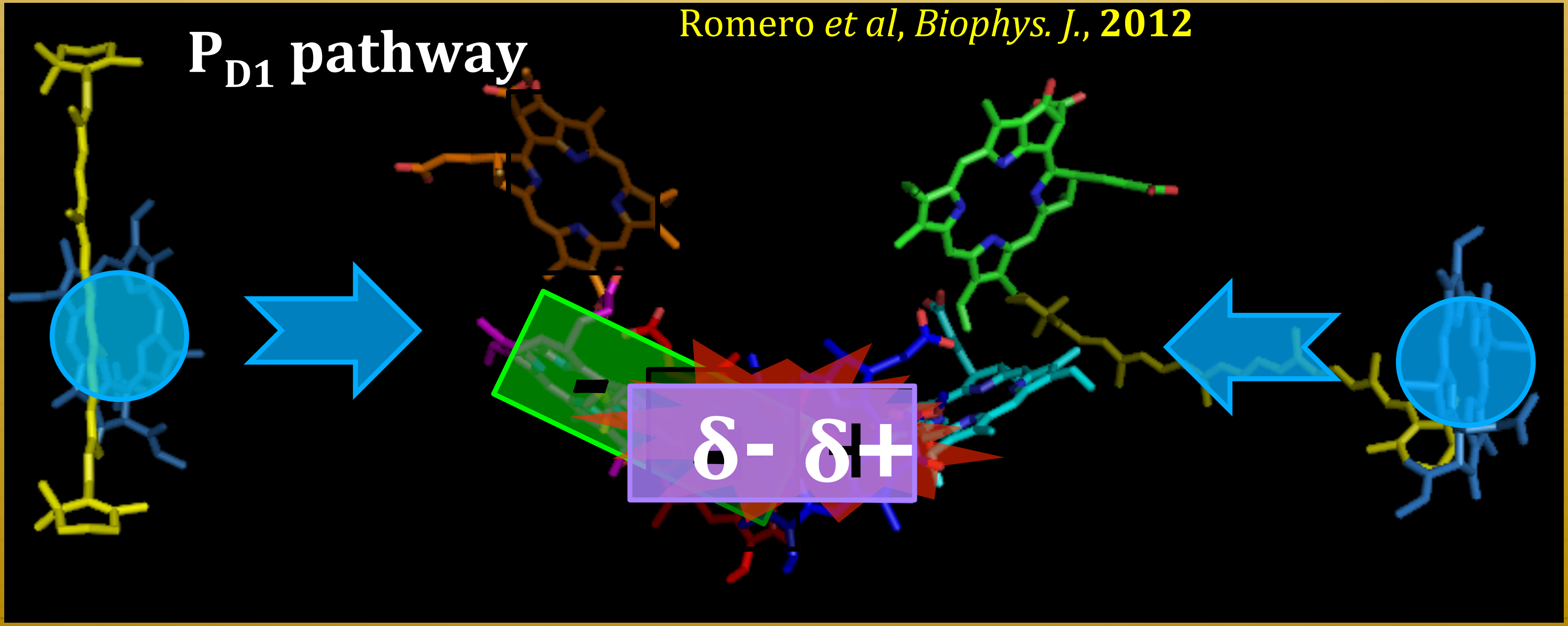
Today

Van Grondelle group (2010, 2012)

Romero *et al*, *Biochemistry*, **2010**

Novoderezhkin *et al*, *ChemPhysChem*, **2011**

Romero *et al*, *Biophys. J.*, **2012**



P$_{D1}$ pathway

Jan Amesz

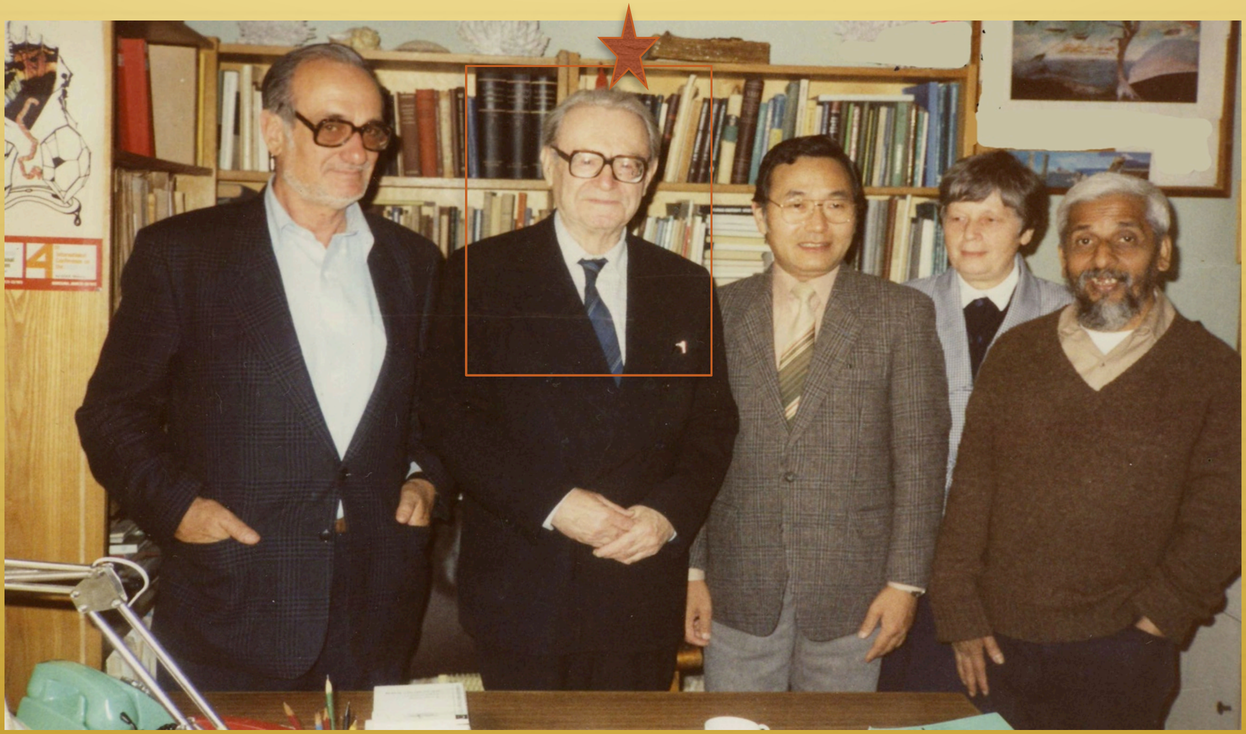
Navik Karapetyan

Figure 2. Alexander Krasnovsky (second from left) with scientists visiting Moscow: the late Jan Amesz (first on the left), Govindjee (third from the left), H. Metzner (fifth from the left) and N. Karapetyan (extreme right) (1970s). Courtesy of Govindjee.

I have several other photographs of Academicien Krasnovsky that had been provided to me by Armin Meister, of Germany (Email: armin.meister@t-online.de) some time ago, but I decided to provide them to you separately (they are with Navik Karapetyan and with A.A. Krasnivsky, Jr.) to celebrate Acad. Krasnovsky's 100th birth anniversary.

Presentation by Govindjee

Left to right: George C. Papageorgiou (Greece) , Acad. A.A. Krasnovsky, Norio Murata (Japan) , Esther Dujardin (Belgium) and Prasanna Mohanty (India); Photo, ~ 1991
(presented on behalf of George, my very first PhD student)



My thanks go to Navik Karapetyan for inviting me to share my thoughts with you, especially because of my deep appreciation for Acad. Krasnovsky.

Presentation by Govindjee