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On the Reactions in Oxygenic Photosynthesis as Related to the Z-scheme: Contributions by Govindjee

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ABSTRACT

We honor Govindjee, Professor Emeritus of Plant Biology and Biophysics at the University of Illinois at Urbana-Champaign, for his significant scientific contributions to the Z-scheme concept in oxygenic photosynthesis and studies on electron transport components. He is renowned for pioneering work in discovering the two-light reactions and two photosystems (Photosystem (PS) I and II) and for other ground breaking findings related to the function of different components of the Z-scheme. These include light harvesting and primary charge separation in PSI and PSII, the role of bicarbonate in the two-electron gate of PSII, water photooxidation, and nonphotochemical quenching of chlorophyll *a* fluorescence, which regulate the photosynthetic electron flow represented in the Z-scheme. We also discuss the application of chlorophyll *a* fluorescence, delayed fluorescence (delayed light emission), thermoluminescence, and nuclear magnetic resonance in these studies. Furthermore, we emphasize Govindjee's dissemination of fundamental scientific knowledge and the Z-scheme's principles throughout the world.

"**Few phenomena in natural science equal photosynthesis in sweep and grandeur**" – Martin Kamen (1963) Primary processes in photosynthesis, Academic Press, N.Y.

Keywords: Bicarbonate effect, Emerson enhancement effect, Excitation energy transfer and conversion in photosynthetic reaction centers, Govindjee's educational poster series, History of science, Nonphotochemical quenching of chlorophyll *a* fluorescence, Oxygen evolution, Z-scheme

Abbreviations: A_{1A}, A_{1B} – Phylloquinones, attached to the A (PsaA) and B (PsaB) protein branches of the A/B heterodimer of the Photosystem I reaction center; Cyt – Cytochrome; D1/D2 – Heterodimer with two protein branches D1 (PsbA) and D2 (PsbD) that provide ligands for the redox active cofactors in the Photosystem II reaction center; DCMU (or diuron) – 3-(3,4-dichlorophenyl)-1,1-dimethylurea; DLE – Delayed Light Emission; EEE – Emerson Enhancement Effect; E_m – Midpoint redox potential, measured at a given pH, temperature and 1 atm H_2, at

the midpoint of a redox titration; ESR – Electron Spin Resonance spectroscopy; Fd – Ferredoxin; FeS – Rieske protein (Fe_2S_2), redox component of cytochrome b_6f complex; FNR – Ferredoxin-$NADP^+$ oxidoreductase, a ubiquitous flavin adenine dinucleotide (FAD)-binding enzyme; F_X, F_A, F_B – Redox active iron-sulfur clusters on the (electron) acceptor side of Photosystem I; HCO_3^- – Bicarbonate ion (hydrogen carbonate); NMR – Nuclear Magnetic Resonance spectroscopy; Mn_4CaO_5 cluster – Mn-Ca containing water-splitting catalyst in the Oxygen-evolving center; NADP – Nicotinamide adenine dinucleotide phosphate; NHI – Non-heme iron; OEC – Oxygen-evolving complex (or Center) of Photosystem II; O,K,J,I,D,P,S,M,T – Steps of chlorophyll *a* fluorescence induction curve; P680, P700 – Photosystem II and Photosystem I primary electron donors, with maximum absorption red bands at 680 nm and 700 nm, respectively; P680*, P700* – Electronic excited states of P680 and P700; P_{D1}, P_{D2}, Chl_{D1}, Chl_{D2} – Redox active Chl *a* molecules in the Photosystem II reaction center; P_A, P_B, Chl_{0A}, Chl_{0B} – Redox active Chl *a* molecules in the Photosystem I reaction center; PC – Plastocyanin; $Pheo_{D1}$ – Pheophytin on D1 branch, primary electron acceptor of Photosystem II; PQ, PQH_2 – Plastoquinone and plastoquinol; PSI, PSII – Photosystem I and Photosystem II; Q_A, Q_B – Primary and secondary plastoquinone electron acceptors of the Photosystem II reaction center that are one-electron and two-electron acceptor, respectively; RC – Reaction center (of Photosystem I or Photosystem II); S_0, S_1, S_2, S_3, S_4 – Redox states of Mn_4CaO_5 cluster of the oxygen-evolving complex; TL – Thermoluminescence; Y_D – Redox active tyrosine 160 on the D2 branch (D2Tyr160), accessory electron donor to $P680^+$; Y_Z – Redox active tyrosine 161 on the D1 branch (D1Tyr161), secondary electron donor to $P680^+$.

INTRODUCTION

Govindjee was trained by Robert Emerson (1903-1959) (Govindjee and Govindjee 2021) and Eugene Rabinowitch (1898-1973) (Govindjee et al. 2019) on the basics of oxygenic photosynthesis. He then chose to collaborate with many others including William Arnold (1904-2001) (Choules and Govindjee 2014; Govindjee and Srivastava 2014), Louis N. M. Duysens (1921-2015) (Govindjee and Pulles 2016), C. Stacy French (1907-1995) (Govindjee and Fork 2006), Martin Kamen (1913-2002) (Govindjee and Blankenship 2021), and Bessel Kok (1918-1979) (Myers 1987). Thus, he was in the hearts of the major photosynthetikers, as Jack Myers would have said if he were with us. Whenever we talk with Govindjee, he tells us how Stacy French and Bessel Kok requested him not to put their names on his work by saying, essentially the same thing - 'you did all the planning, thinking, doing the experiments, and writing the paper, and thus, it is not fair to you at all.' In essence, Govindjee's contributions have been many and varied (see e.g., description of his research in his own words (Govindjee 2019). At his 90th birthday, much had been written on Govindjee and his research by many (see e.g., Stirbet et al. 2022; Naithani et al. 2022; Seibert et al. 2022; Lichtenthaler et al. 2022; Nonomura and Kumar 2022, as well as references to earlier articles, therein). Here, we focus on his contributions before, during, and after the "Z-scheme" of oxygenic photosynthesis, as well as how it became a part of textbooks in biology, biochemistry, and biophysics. A basic theoretical Z-scheme for the 'light reactions' of oxygenic photosynthesis was published by Hill and Bendall (1960). It was a two-light reaction scheme, where the redox potentials of the photosynthetic electron transfer components were represented on the Y-axis. Further, it was based on the redox potentials of two different cytochromes. However, it turned out later that the Cyt *b*, used in the system, was not involved as had been proposed. Furthermore, in this paper, the already existing concept of two light reactions and two pigment systems from the Emerson Enhancement Effect (Emerson et al. 1957) was not even mentioned. In relation to that, see a commentary by Govindjee (2022) on a presentation by Emerson and Chalmers (1958). Also, see Govindjee

(2023) for a recent historical minireview on the evolution of the concept of the Z-scheme. A Z-scheme made in 2017, for Govindjee's Educational Poster Series, is shown in Figure 1.

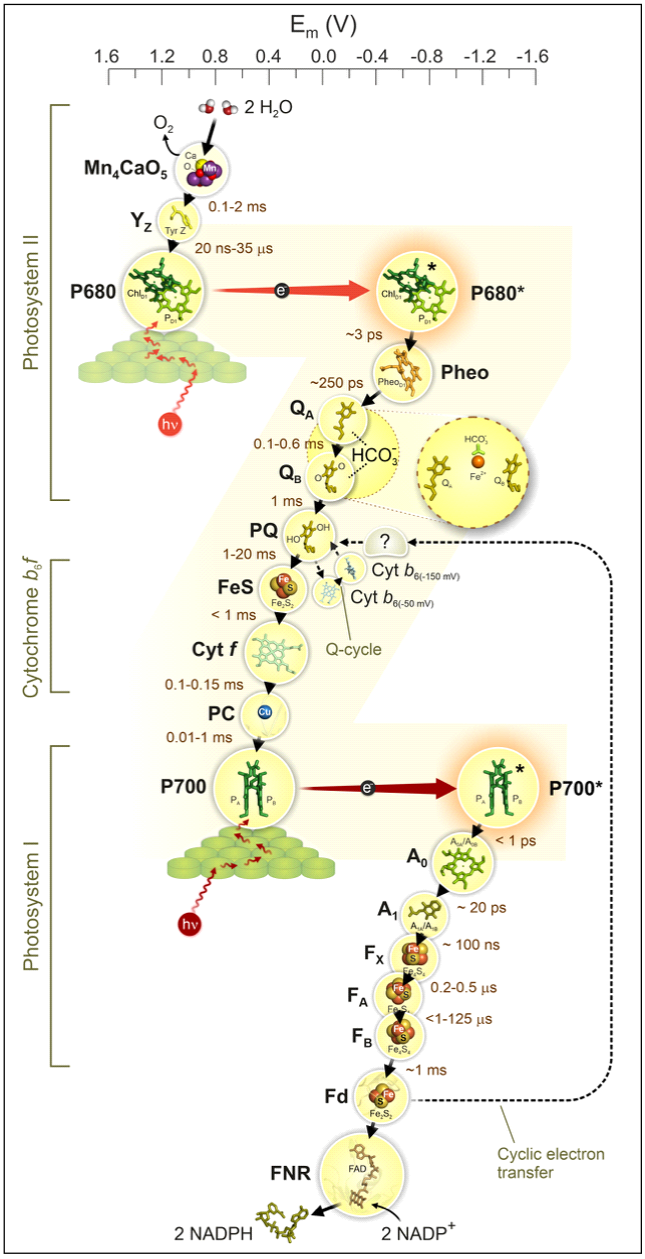

Figure 1. The Z-scheme of the linear electron transport from water to $NADP^+$ in oxygenic photosynthesis, initiated by the photochemical reactions in PSII and PSI reaction centers. The electron transport carriers are plotted horizontally according to their midpoint redox potentials at pH 7.0 (E_m, 7), and the half times ($t_{1/2}$, equal to 0.693/k) of the various electron transport reactions in the Z-scheme are also shown, except for the formation of P680* (in PSII) and P700* (in PSI) that occur in the femtosecond time scale. P680 and P700 refer to primary electron donors of Photosystem II (PSII) and Photosystem I (PSI), respectively, with 680 and 700 being the wavelength of absorption maxima, in nanometers. P680 includes the Chl *a* molecules P_{D1}, P_{D2}, Chl_{D1}, and Chl_{D2}, but only P_{D1} and Chl_{D1} are shown. P700 is a Chl *a*/Chl *a'* pair (labeled as P_A/P_B), where Chl *a'* is the C-10 epimer of Chl *a*; P680* and P700* are first singlet excited states; after excitation, charge separation takes place (i.e., photochemistry), when the excitonic energy is converted into chemical energy. The first radical pair of PSII is $P680^+Pheo_{D1}^-$, where $Pheo_{D1}$ is the primary electron acceptor of PSII (the pheophytin on the D1 polypeptide). The electron hole in $P680^+$ is filled by an electron from the redox-active tyrosine D1-Tyr161 (i.e., Y_Z) which obtains an electron *via* water oxidation performed by a cluster of four manganese ions and one calcium ion (Mn_4CaO_5), while the electron from $Pheo_{D1}^-$ is passed to the primary plastoquinone Q_A (tightly bound to PSII), which then reduces sequentially the secondary plastoquinone Q_B (loosely bound at the Q_B–site). The bicarbonate ion (HCO_3^-), located between Q_A and Q_B, is required for the efficient electron transfer to Q_B and for the protonation of Q_B^-. Thus, the HCO_3^- ion (bound to the non-heme iron, NHI) is essential for optimal function of PSII and, thereby, plays a key role in oxygenic photosynthesis. After Q_B accepts 2 electrons from the reduced Q_A and binds 2 protons, the plastoquinol (PQH_2) formed at the Q_B-site is released, and then replaced by a new plastoquinone (PQ) molecule from a mobile PQ-pool in the thylakoid membrane. The cytochrome (Cyt) b_6f complex accepts electrons from PQH_2; it contains several intersystem components: the iron-sulfur protein known as the Rieske FeS protein, one Cyt *f*, two cytochromes b_6 (Cyt b_p and Cyt b_n) and a heme *c* (which is not shown). The re-oxidation of PQH_2 is the slowest reaction in the photosynthetic electron transport pathway. A mobile copper protein plastocyanin (PC), from a PC-pool in the lumen, accepts one electron from Cyt b_6f (via Cyt *f*) and reduces the oxidized primary electron donor of PSI ($P700^+$). On the acceptor side of PSI, the electron is passed from A_0^-, the reduced primary electron acceptor of PSI (i.e., A_{0A} or A_{0B}) through a series of electron carriers including the phylloquinone A_1 (i.e., A_{1A} or A_{1B}, F_X, F_A, and F_B (bound iron-sulfur clusters of PSI), to reduce a mobile ferredoxin (Fd) molecule from a Fd-pool in the stroma, which participates in the reduction of $NADP^+$ to NADPH via FNR (ferredoxin-$NADP^+$ oxidoreductase), the ubiquitous flavin adenine dinucleotide (FAD)-binding enzyme. The dotted straight arrow shows the cyclic photo-phosphorylation pathway around PSI, where the electrons cycle from Fd to the Cyt b_6f complex, generating ATP. All shown cofactors were generated using coordinates from available PDB entries: 3ARC, 1VF5, 2GIM, 4Y28, 2MH7, and 1SM4. Phytyl tails of Chl and Pheo, and the isoprenyl chains of the quinones have been cut for clarity. This figure was modified from the Educational Poster "Z-scheme of Electron Transport in Photosynthesis" (Govindjee's Educational Poster Series) printed and distributed by Brandt iHammer (USA) in 2017.

In this paper, we focus on the pioneering work of Govindjee, often together with his life partner Rajni Govindjee, on the two-pigment system and two-light reaction concept before and after the Hill and Bendall (1960) paper on the Z-scheme. This work deals with:

(i) the pigment composition of the two photosystems (Govindjee and Rabinowitch 1960a,b), showing that, in contrast to Emerson's concept, a short wavelength form of chlorophyll *a* is in the same system where the accessory pigments are present (called Photosystem II, PSII);

(ii) the proof that the Emerson Enhancement Effect (EEE) is not in respiration, but in photosynthesis, through mass spectrometry (Govindjee et al. 1963) and through EEE in NADP reduction in chloroplasts (R. Govindjee et al. 1962, 1964);

(iii) the very first picosecond measurements on the primary photochemistry of both PS I and II (Fenton et al. 1979; Wasielewski et al. 1989 a,b);

(iv) the unique function of 'bicarbonate' (HCO_3^-) in the Q_A - Q_B region (the electron acceptor side of PSII) where a plastoquinone (PQ) is reduced to plastoquinol (PQH_2) – involving electron as well as proton transfer (Wydrzynski and Govindjee 1975; Govindjee et al. 1976); thus, without bicarbonate bound here – photosynthetic electron transfer will cease, and there will be no photosynthesis.

(v) the demonstration of the existence of the period four Joliot-Kok 'S' states in the 'Water Oxidation Clock" through not only NMR (Wydrzynski et al. 1976a,b), but through thermoluminescence (Rutherford et al. 1984a,b); here it is important to note that Ted Mar, a graduate student of Govindjee, had explored all the possible kinetic models for oxygen evolution – inventing in the process new models of their own (Mar and Govindjee 1972) – recognized later by both Pierre Joliot and Bessel Kok.

In addition to the above, Govindjee's research was heavily involved with innovation and application of chlorophyll *a* fluorescence as a tool in breakthrough studies on the nonphotochemical quenching process, with his postdoctoral associate Adam M. Gilmore, as well as on the regulation of excitation energy distribution and redistribution between the two pigment systems (the so-called "State Changes", discovered independently in Jack Myers' and Norio Murata's laboratories). We mention these aspects later, as related to the Z-scheme! An interesting historical note is that Govindjee was the first one to propose the existence of "P680", the reaction center of PSII (Krey and Govindjee 1964; Rabinowitch and Govindjee 1965) and to prove that it was not a fluorescence artifact (Döring et al. 1969).

The Concept of the Two Light Reactions and Two Pigment Systems and the Z-scheme

Much has been written about Govindjee's contributions to the "light reaction" aspect of oxygenic photosynthesis, including the Z-scheme by Hill and Bendall (1960) and its subsequent modifications (see, e.g., Govindjee et al. 2017; Govindjee, 2019). Govindjee's quest for a deeper understanding of photosynthesis began in 1953 while he was a student in plant physiology at the University of Allahabad in India. He was fascinated with the "Red Drop Effect" discovered by Emerson and Lewis (1943), which shows an abrupt decrease in the maximum quantum yield of photosynthesis under wavelengths of light exceeding 680 nm, even when Chl *a* still absorbs light (see Govindjee 2019, 2023).

Before long, in 1956, Govindjee was admitted as a graduate student at the University of Illinois in Urbana-Champaign (UIUC), under the guidance of Robert Emerson. In 1957, Rajni Varma joined him at UIUC, having also come from Allahabad to pursue her doctorate under Emerson's supervision (see Figure 2 for a photo of Govindjee and Rajni, circa 1960). After Emerson's untimely death in 1959 due to a plane accident, both Govindjee and Rajni completed their PhDs under the guidance of Eugene Rabinovitch.

The doctoral thesis of Govindjee (Govindjee 1960) centered on experiments of the Emerson Enhancement Effect in which the oxygen evolution measured with far-red light (720 nm), together with a supplementary

Figure 2. (**A**) A 1960 photograph of Govindjee with his lifelong partner Rajni, in Urbana, Illinois, when they were close to finishing their PhDs; **(B)** Botany Department, University of Allahabad; and **(C)** Natural History building, where they both had come to work, in the late 1950s, with Robert Emerson, UIUC. Photos from Govindjee's archive.

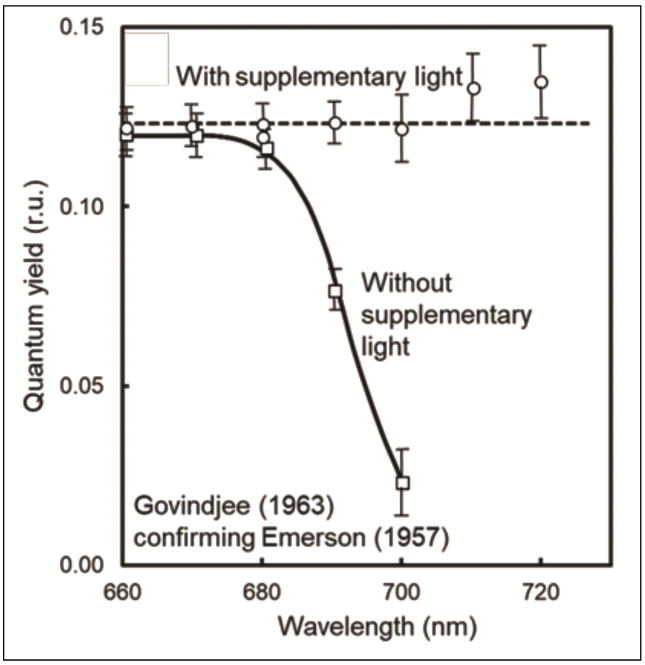

Figure 3. The 'red drop' and Emerson Enhancement Effect measured by Govindjee (1963) in the green alga *Chlorella* (for further details, see the text).

light of a shorter wavelength (absorbed primarily by accessory pigments), was found to be higher than the total sum of oxygen evolution measured when these two different wavelengths of light were given separately (see Figure 3). In his experiments, Govindjee found that light absorption by Chl *a* 670, a soon to be discovered spectral form of Chl *a* (Cederstrand et al. 1966), enhances the yield of photosynthesis measured under far-red light (from 685 to 720 nm) as effectively as does the light absorbed by the accessory photosynthetic pigments.

Govindjee's results (see Govindjee 2022 for a commentary) revealed that the two light reactions involved in the Emerson Enhancement Effect were not run by accessory pigments and Chl *a,* respectively, as Robert Emerson had implied (Emerson et al. 1957; Emerson and Chalmers 1958), but the accessory pigments must be transferring the excitation energy to a short-wavelength form of Chl *a* (see Figure 4 (A, B) and Govindjee and Rabinowitch 1960a, b).

In these measurements, Govindjee used as the source for the supplementary light a monochromator providing all wavelengths of light, instead of the Hg-Cd lines used by Emerson (Rabinowitch and Govindjee 1961). This was the very first observation showing that Chl *a* is in the antenna system of what is now called Photosystem II (PSII), but with a different absorption band than that in PSI, and it worked in synchrony with the auxiliary pigments (such as Chl *b* or phycobilins).

Later, Bedell and Govindjee (1966) confirmed, in deuterated *Chlorella* cells, that Chl *b* (peak at 650 nm)

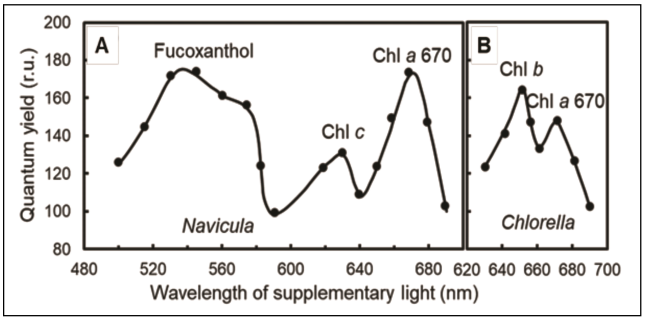

Figure 4. Action spectra of the Emerson Enhancement Effect: **(A)** in the diatom *Navicula*; and **(B)** in the green alga *Chlorella*. Figure modified from Govindjee (1960) and Govindjee and Rabinowitch (1960a, b).

and Chl *a* (peak at 670 nm) were in the same photosystem (now PSII) and Chl *a* (peak at 710 nm) was in another photosystem (now PSI).

Further, and quite importantly, Govindjee et al. (1960) discovered that the two-light reactions and two-pigment systems concept has a clear counterpart in the quenching of Chl *a* fluorescence – emitted after excitation with Light 2 (which is absorbed by the short-wavelength form of Chl *a*) – by far-red light (i.e., Light 1, absorbed by the long-wavelength form of Chl *a*) (Govindjee et al. 1960). This effect was investigated in depth and explained later by Duysens and Sweers (1963), who recognized Govindjee's findings. Their explanatory hypothesis was that the Light 2 reduces a quencher "Q" of Chl *a* fluorescence, now identified as the first plastoquinone acceptor of PSII (i.e., Q_A), while the Light 1 oxidizes the reduced "Q", and thus quenches the Chl *a* fluorescence (see reviews by Govindjee 1995, 2004; Stirbet and Govindjee 2011, 2012).

An important question was raised at that time since both Emerson, and, then Govindjee, had used manometry to measure the Emerson Enhancement Effect, with which it is not possible to distinguish between oxygen evolution (photosynthesis) and oxygen uptake (respiration). It was R. Govindjee et al. (1960) and R. Govindjee and Rabinowitch (1961) who had shown for the first time that the Emerson Enhancement Effect was not in respiration by using para-benzoquinone in the Hill reaction of whole algal cells (i.e., evolution of O_2 in presence of artificial electron acceptors; Hill 1937), since benzoquinone kills respiration; moreover, the presence of Chl *a* in both photosystems was confirmed in these papers. However, this was partly an "artificial" system, and the problem clearly was resolved when Govindjee et al. (1963) made mass spectroscopy measurements using $^{18}O_2$, and proved that there was indeed an enhancement effect in photosynthesis, although there are light-induced effects on respiration. Furthermore, R. Govindjee et al. (1962, 1964) showed a clear Emerson Enhancement Effect in $NADP^+$ reduction (Hill reaction) in experiments on isolated spinach chloroplasts done in collaboration with George Hoch in Bessel Kok's laboratory in Baltimore, Maryland. In addition, Govindjee and Bazzaz (1967) showed that even ferricyanide can pick up electrons from both PSII and PSI in their isolated chloroplast preparations, involving two light reactions. Based on all the above experiments, the Emerson Enhancement Effect was established by Govindjee and his coworkers to be clearly in photosynthesis.

At the end of Govindjee's research for his thesis, Robert (Robin) Hill and Fay Bendall published their famous theoretical paper on the Z-scheme of oxygenic photosynthesis (Hill and Bendall 1960), in which the electron transfer from water to oxidized nicotinamide adenine dinucleotide phosphate ($NADP^+$) was schematically represented with the redox components arranged conforming with their redox potential values, which highlights the idea that the two photosystems work in series. However, it is worth remembering that a similar scheme had been suggested even before by Franck and Herzfeld (1941) and Rabinowitch (1945), based on the fact that the minimum quantum requirement for the release of one molecule of oxygen was 8-10 (for the evolution of the Z-scheme, see Govindjee et al. 2012, 2017; Govindjee 2023). Only later this concept was proven experimentally in the laboratory of Louis N.M. Duysens, The Netherlands (Duysens et al. 1961; Duysens and Amesz 1962), through key observations of the antagonistic effect of Light 1 and Light 2 on the redox state of Cyt *f*; and by the experiments of Keith Boardman and Jan Anderson (in Australia) on the physical separation of the two photosystems (Boardman and Anderson 1964). It is interesting to note that, while the reaction center of PSII, P680, was discovered in Horst Witt's laboratory as Chl a_{II} (Döring et al. 1967, 1968), the idea of its existence was first suggested by Govindjee from the observation of a small new fluorescence band at 693–695 nm, when photosynthesis was saturated in the red alga *Porphyridium* (Krey and Govindjee 1964). This concept was included in the "light reaction part of oxygenic photosynthesis" in a popular article written for *Scientific American* by Rabinowitch and Govindjee (1965).

Energy Transfer and Primary Photochemistry in Oxygenic Photosynthesis

In photosynthesis, the light energy absorbed by the antenna pigments of PSII or PSI is transferred toward the respective reaction center (RC), where it is converted into chemical energy through a photochemical reaction (see Figure 1 and its legend). Govindjee had successfully used Chl *a* fluorescence as a powerful tool to measure the primary events in photosynthesis through excitation and the emission spectra in both the antenna and the reaction centers of PSI and PSII (cf. Das and Govindjee 1975). To study this process, Cederstrand et al. (1966), using a home-built innovative spectrophotometer (see Cederstrand and Govindjee 2022), provided the absorption and fluorescence characteristics of the two photosystems, showing the existence of different spectral forms of Chl *a*, both *in vivo* and in separated pigment systems. After that, the temperature dependence of excitation energy transfer by measuring Chl *a* fluorescence was examined, first down to 77K (using liquid nitrogen, Cho et al. 1966), and then down to 4 K (using liquid helium, Cho and Govindjee 1970a, b), which fully supported the concept of Förster's resonance energy transfer (FRET) theory (Förster 1946, 1948; also see Clegg et al. 2010) both in the antenna of cyanobacteria and in green algae during the excitation energy migration from the phycobilins to Chl *a* and from one group of Chl *a* to another, respectively. In addition, Govindjee and Yang (1966; also see Govindjee 1966) examined both the excitation and emission spectra of Chl *a* fluorescence as a function of temperature in isolated spinach chloroplasts and provided key information as to which pigment-protein complex gives which emission band. In the same way, Krey and Govindjee (1964, 1966) provided similar information on the fluorescence bands of the red alga *Porphyridium cruentum*. Further, Das and Govindjee (1967) showed that, at room temperature, a particular long wavelength absorbing form of Chl *a* (Chl *a* 693) was responsible for the "Red drop" in Chl *a* fluorescence, and for the F723 emission band at 77 K. Govindjee also examined a specific regulation mechanism of excitation energy distribution in the two photosystems observed in some cyanobacteria, now known as chromatic acclimation (CA; see e.g., Lazar et al. 2022). This phenomenon was investigated, e.g., by varying both the intensity and the color of light for growth; in this type of experiment, Ghosh and Govindjee (1966) obtained different ratios of phycocyanin and Chl *a* in *Anacystis nidulans*. All the above, and more on the light energy conversion process in oxygenic photosynthesis, was summarized in two major reviews by Govindjee (1967), and Govindjee et al. (1967a), mainly based on Chl fluorescence spectral data obtained both at room and low temperatures.

During the photochemical process in the reaction centers of the two photosystems (see Blankenship and Prince 1985): (**1**) the primary electron donors of both the photosystems become excited (P680 + Light 2 $\rightarrow$ P680*, and P700 + Light 1 $\rightarrow$ P700*), when one electron is promoted to an excited electronic level; (**2**) since the excited primary donors are strong reductants (see the difference in the midpoint redox potential (E_m) between P680 and P680*, and P700 and P700*, shown in Figure 1), they are able to transfer electrons to their respective primary acceptors ($Pheo_{D1}$ in PSII, and A_0 in PSI) during the primary 'charge separation reactions', producing radical pairs ($P680^+Pheo_{D1}^-$ and $P700^+A_0^-$) which initiate the photosynthetic electron transport. Govindjee's training in biophysics (that had included courses in optics and thermodynamics) enticed him to ask the most fundamental question in 1979, *How fast is the primary photochemistry in photosynthesis?* Fenton et al. (1979) provided the very first measurement of the time of charge separation reaction in PSI, which they found to be in the picosecond range. Several years later, work in collaboration with Mike Wasielewski, at the Argonne National laboratory, led to newer detailed measurements of the early steps of charge separation in PSI by using picosecond transient absorption spectroscopy which indicated that a special Chl *a* must be one of the early electron acceptors (Wasielewski et al. 1987). Soon, Michael Seibert (who had been preparing stable and highly active PSII particles) joined, and this 3-way collaboration resulted in the publication of the first data

on primary PSII photochemistry, in the picosecond time scale, by time-resolved pump-probe absorption spectrometry that used 500 femtosecond laser flashes of 610 nm (Wasielewski et al. 1989a). These authors inferred from their data that the formation of the radical pair $P680^{+}Pheo_{D1}^{-}$ (and the disappearance of P680* in the PSII RC) took place within ~3 ps at 4°C. Further, Wasielewski et al. (1989b) provided data on this reaction down to a temperature of 15 K with nuances which still need to be examined. Govindjee and Wasielewski (1989) reviewed all the research on PSII, from femtoseconds to milliseconds. Soon thereafter, Wasielewski et al. (1990) and then Seibert et al. (1992) summarized their results on the primary charge separation in isolated PSII reaction centers, which were all in the picosecond range.

By exploiting Chl *a* fluorescence of the PSII, Govindjee et al. (1990a) observed a clear difference in Chl *a* fluorescence lifetime distribution when the reaction center was open versus when it was closed; the 5-20 ns component was ascribed to the back reaction of $P680^{+}Pheo^{-}_{D1}$. However, the observed faster picosecond component was suggested to have originated during the excitation energy migration in the system. Later, by using multifrequency cross correlation phase fluorometry, Govindjee et al. (1993a) established (using both thylakoids and PSII preparations) that the rate of primary charge separation was dependent on the ratio of Q_A/Q_A^{-}, being higher when this ratio was high and lower when this ratio was low. This was shown also by using several oxidants and reductants, as well as inhibitors of the electron flow. These experiments were followed by femtosecond dichroism measurements on similar samples by Wiederrecht et al. (1994), who presented time-resolved pump-probe kinetic spectroscopy with ~100-femtosecond time resolution and with the pump laser polarized at the magic angle (54.7°) relative to the polarized probe beam. The formation of the charge separated state $P680^{+}Pheo_{D1}^{-}$ occurred within 3 ps and, as expected, this component disappeared if the electron acceptor $Pheo_{D1}$ was reduced prior to P680 excitation.

Govindjee continued his collaboration with Michael R. Wasielewski. Greenfield et al. (1996) reported on wavelength and intensity dependent results in PSII – observing several components in the range of ~100 fs; ~1-3 ps; ~8-20 ps; and ~50-100 ps – involving excitation energy transfer and primary charge separation steps. Then, Greenfield et al. (1997) provided direct measurements on ~ 8 ps and ~ 50 ps components, the latter being limited by excitation energy transfer time from long-wavelength absorbing Chl *a* to the reaction center. An uphill energy transfer was inferred, which, we are told, was enjoyed greatly by Govindjee.

Understanding the Role of Bicarbonate in Photosystem II Reactions

During 1973-1974, Govindjee became interested in the role of CO_2/HCO_3^{-} in the function of PSII. It all began when Govindjee was lecturing in his graduate-level course on "Bioenergetics of Photosynthesis" and had come across the 'unconventional' idea proposed by Otto Warburg, a Nobel laureate in 1931, suggesting that bicarbonate (HCO_3^{-}) was the source of oxygen evolution in photosynthesis (Warburg and Krippahl 1958). While this assertion generally was and still is not accepted (see, e.g., Clausen et al. 2005; Hillier et al. 2006; McConnell et al. 2007), there were indications that HCO_3^{-} (or CO_2) might have a role in the "electron transfer side" of photosynthesis, beyond the Calvin-Benson-Bassham cycle. Alan Stemler, a graduate student of Govindjee at the time, took on this topic and demonstrated the crucial role of HCO_3^{-} in photosynthesis. It became evident that without it, oxygen evolution in the Hill reaction was significantly inhibited (Stemler and Govindjee, 1973; Stemler and Govindjee, 1974a, b). However, it remained unclear whether this "bicarbonate effect" was related to the water (the electron donor) side of PSII, the plastoquinone (the electron acceptor) side, or both. In collaboration with Gerald Babcock (1946-2000), Stemler et al. (1974) published detailed and convincing data supporting the necessity of HCO_3^{-} for "oxygen evolution" in flashing light. This paper brought significant attention to the importance of 'bicarbonate' for PSII activity.

In the following year, Thomas Wydrzynski, another graduate student under Govindjee's supervision,

established the role of bicarbonate on the electron acceptor side of PSII (i.e., at the Q_A-NHI-Q_B side, see Wydrzynski and Govindjee, 1975; cf. Figure 1), using Chl *a* fluorescence as a tool. Subsequently, experiments by Govindjee et al. (1976) in the laboratory of Louis N. M. Duysens in The Netherlands, clearly demonstrated, through the use of single flashes of light, that HCO_3^- was required after the second flash, most likely functioning in the protonation reactions leading to the formation of Q_BH_2. Furthermore, Paul Jursinic, another graduate student, contributed additional insights, through the Electron Spin Resonance (ESR) Signal IIvf, fast Chl *a* fluorescence yield changes, and Delayed Light Emission (DLE), on the various components involved in this bicarbonate effect (see Jursinic et al. 1976).

Rita Khanna, yet another graduate student of Govindjee, conducted further biochemical experiments, skillfully employing artificial electron acceptors and donors as well as inhibitors. Her work provided strong biochemical evidence that a major bicarbonate site existed between Q_A and Q_B on the electron acceptor side of PSII (Khanna et al. 1977; see the HCO_3^- location in Figure 5), providing substantial support for the earlier findings by Wydrzynski and Govindjee (1975).

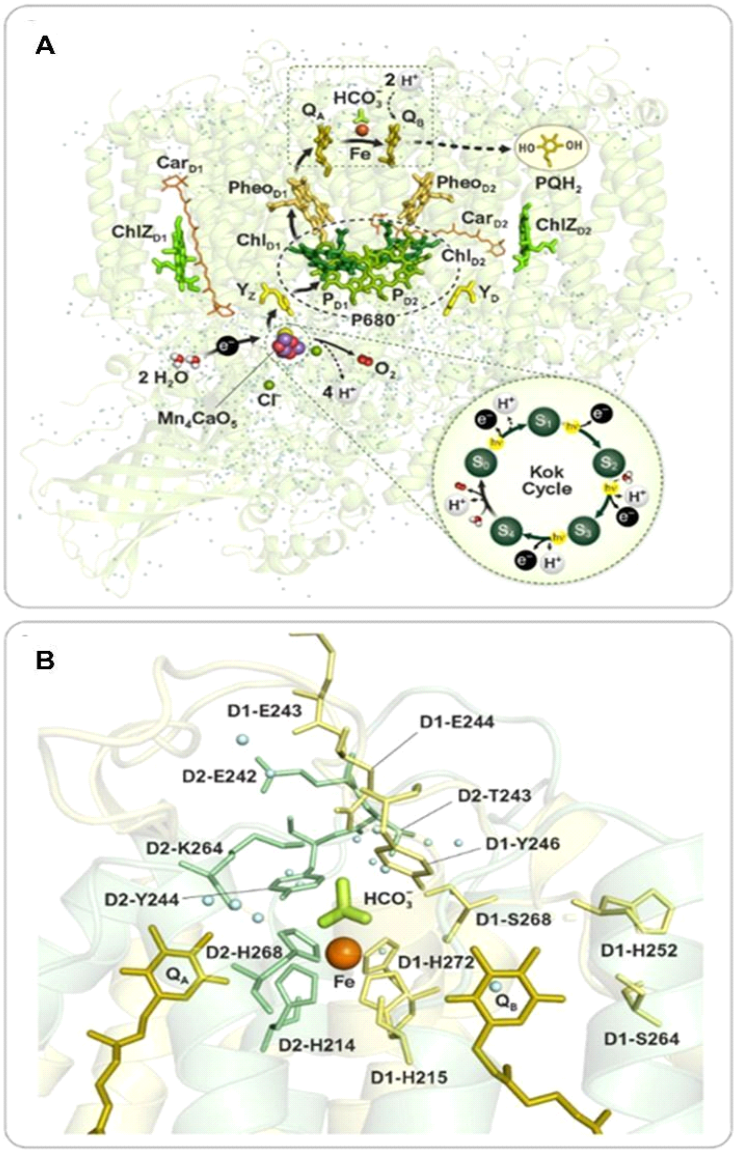

Figure 5. The Photosystem II structure with its central redox cofactors as seen along the thylakoid membrane. **(A)** Arrangement of the electron transfer cofactors of the PSII reaction center. The sequential electron transfer from Q_A^- to the plastoquinone Q_B and Q_B^- is facilitated by the HCO_3^- ion bound to NHI (Fe), which also enables proton transfer to the reduced Q_B (Wydrzynski and Govindjee 1975; Govindjee and Van Rensen 1993). A view on the bottom left shows the stepwise process of water oxidation by the Mn_4CaO_5 cluster (the Kok cycle, also known as the Kok-Joliot cycle). **(B)** A zoomed view of the electron acceptor side of PSII with HCO_3^- bound to iron (Non-Heme Iron), in the middle of the plastoquinones Q_A and Q_B, and their protein environment. Some of the residues shown here (e.g., D1-H215, D1-S264, D2-H214, and D2-H268) were predicted to be in close vicinity to the bound HCO_3^- by the 3-dimentional model of the D1/D2 protein cofactors of PSII published by Xiong et al. in (1996). For further details, see the text and legend of Figure 1. The PSII structure was generated using the coordinates deposited at PDB with ID 6W1O (Ibrahim et al. 2020). The figure shown in panel (A) is adopted and modified from Agrisera Educational Poster 5 (Shevela et al. 2021) and reproduced with permission of Agrisera AB (Sweden).

A summary of how Chl *a* fluorescence measurement had helped to pinpoint the site of the action of HCO_3^- in PSII was published by Govindjee (1977), followed by another on how HCO_3^- functions on the electron acceptor side of PSII (Govindjee and Van Rensen 1978). Furthermore, Khanna et al. (1980) provided the first clear result on the effect of HCO_3^- on protonation reactions on the electron acceptor side of PSII; this was possible because of a collaboration with Wolfgang Junge in Berlin (Germany). Soon thereafter, Khanna et al. (1981a) showed, from biochemical measurements, the close relationship of HCO_3^- binding and those of many herbicides on the electron acceptor side of PSII. In addition, experiments by Vermaas and Govindjee (1982) provided an analysis of the effects of various herbicides as compared to that by depletion of HCO_3^- in PSII.

We note that one of us (Julian Eaton-Rye, also a former graduate student of Govindjee), discovered (see Eaton-Rye and Govindjee 1984) the influence that HCO_3^- has on the electron flow from water to methyl-viologen (a PSI electron acceptor), involving only non-cyclic electron flow (see the Z-scheme in Figure 1), and Vermaas et al. (1982) provided a new insight on the binding region of HCO_3^- to the electron acceptor side by modifying the nearby amino-acids, and by using ioxynil, a different herbicide than those used before. Further, using still newer measurements, Robinson et al. (1984) confirmed and extended the conclusions on the effect of HCO_3^- on the plastoquinone side of PSII, by removing it through the addition of formate; here, a competition between formate and bicarbonate binding near the Q_A and Q_B binding sites was supported. Additionally, Govindjee et al. (1984) obtained clear evidence from thermoluminescence (TL) experiments about the role of HCO_3^-, involving its function at the Q_B level for the back reaction that leads to TL. Also, Sane et al. (1984b) provided information on the effects of HCO_3^- depletion on the TL Peak I (which is due to the back reaction from the plastoquinol to the S-states of the oxygen-evolving complex (OEC), namely by the Mn_4CaO_5 cluster, the water-splitting catalyst (see Figure 1 and Figure 5A), and Peak II (involving electron transfer from Q_A^- to the oxidized 'S' state). Sane et al. (1984b) showed that the intensity of Peak I decreased, while that of Peak II increased – this is in agreement with the role of HCO_3^- in the formation of plastoquinol.

To gain further insight on the function of HCO_3^-, Eaton-Rye and Govindjee (1988a, b) presented detailed observations on its effect after one light flash (electron transfer from Q_A^- to Q_B), and after two light flashes (electron transfer from Q_A^- to Q_B^-); these results provided detailed information on the kinetics of the second electron transfer that was hindered in the absence of HCO_3^-. Using kinetic data on the rates of electron transport as a function of HCO_3^- concentration, Blubaugh and Govindjee (1988) found that there are two essential binding sites of HCO_3^-, showing cooperativity. Also, it was necessary to know if this HCO_3^- effect could be observed in the leaves of higher plants and cyanobacteria. Garab et al. (1988) showed clearly that this phenomenon exists in the leaves, by using TL measurements, and Jiancheng Cao, also a graduate student of Govindjee, discovered (see Cao and Govindjee 1988) this effect in unicellular cyanobacterium *Synechocystis* sp PCC 6803. However, Shopes et al. (1989) showed that this effect was absent in anoxygenic photosynthetic bacteria, and this information later helped Jin Xiong, a graduate student of Govindjee, to find the precise site of HCO_3^- binding on the electron-acceptor side of PSII (see e.g., Xiong et al. 1996).

Earlier, Govindjee's group had mostly used algal cells, isolated chloroplasts, and PSII particles in bicarbonate studies, but it was important to check the existence of this phenomenon in leaf tissues from plants. El-Shintinawy and Govindjee (1990) showed the requirement of HCO_3^- in PSII reactions in leaf discs, and soon-thereafter El-Shintinawy et al. (1990) showed that the bicarbonate effect was on both sides of PSII, i.e., on the water oxidation (electron-donor side), as well as on the plastoquinone reduction (electron-acceptor side). Further, in collaboration with Claudie Vernotte and Ann-Lise Etienne in France, Govindjee et al. (1990b) showed that there was a clear interaction of herbicides with HCO_3^- in cyanobacteria, confirming its role on the

electron acceptor side of PSII in these organisms. This was soon followed by the paper of Cao et al. (1991) using *Synechocystis* mutants to detail the possible involvement of a specific arginine in the D2 polypeptide in the bicarbonate effect. Additionally, Cao et al. (1992) showed a closer interaction of herbicide and HCO_3^- binding in a herbicide-resistant mutant of *Synechocystis*. Further, in collaboration with B. Schwarz, J.-D. Rochaix and R. J. Strasser, Govindjee et al. (1991) observed that a *Chlamydomonas* mutant of D1 polypeptide (L275F) failed to show the bicarbonate reversible formate effect (see also Strasser and Govindjee 1992). This implied that the residue number 275 has an important influence on the binding of HCO_3^-.

To understand the binding of formate, ChunHe Xu, another graduate student of Govindjee, in collaboration with the research group of Antony (Tony) R. Crofts (at UIUC), provided kinetic characteristics of the binding of formate, which displaces the HCO_3^- needed for the formation of Q_BH_2 (see Xu et al. 1991). Also, Strasser et al. (1992) proposed kinetic models for these and other effects, and Govindjee et al. (1993b) enhanced the ways of checking on the effect by including measurements on both PSII and PSI, not only in algal cells, but also in cyanobacteria.

Govindjee and Van Rensen (1993) have summarized different aspects of all the accumulated results as well as all the ideas on the role of HCO_3^- in electron transport in oxygenic photosynthesis. Finally, the question was posed: "Why is it that anoxygenic bacteria do not show the HCO_3^- effect on the electron-acceptor side of their reaction center?" In collaboration with the research groups of Colin Wraight (UIUC) and Dieter Oesterhelt (Germany), Wang et al. (1992) correctly asked, "Is HCO_3^- in PSII the equivalent of the glutamate ligand to the iron atom in bacterial reaction centers?" Which was pursued later in Govindjee's laboratory. The answer was and is: "Yes!".

Interestingly, a study in Finland by Maenpaa et al. (1995), with Govindjee's collaboration, was highly useful because it showed that a mutation in the D-E loop of the D1 polypeptide changes the stability of $S_2Q_A^-$ and $S_2Q_B^-$ states, as it was related to the region of the HCO_3^- binding-site. Similarly, studies on the effects of various extrinsic quinones and herbicide resistant mutants – involved in the site in the suggested HCO_3^- region – provided further information on the physico-chemical nature of this site (see Srivastava et al. 1995a, b; a work done in Switzerland by Govindjee, with collaboration with Reto J. Strasser and his research group). Another collaborative study of Govindjee with Claudie Vernotte (in France) showed differential effects of formate and HCO_3^- in specific double mutants of D1 in *Synechocystis* sp. PCC 6714 (see Vernotte et al. 1995),

Of note, Govindjee's collaborators in China made enormous efforts to see the effects of chloroacetates, instead of formate, in removing HCO_3^-. These acetates seem to affect not only the electron acceptor side of PSII (i.e., Q_A-NHI-Q_B), but also the electron donor side (i.e., the reactions on the oxygen-evolving side, see Figure 5A). For example, Xu et al. (1995) showed the release of many polypeptides involved in both the electron donor and acceptor sides of PSII after treatment with chloroacetates, while Yu et al. (1997) compared the effects of these acetates in oxygenic and anoxygenic photosynthesis. On the other hand, Li et al. (1997), also from China, reported that trichloroacetate affects the redox active tyrosine 160 on the D2 polypeptide (i.e., Y_D), which serves only a regulatory and protective function in photosynthesis, whereas the redox-active tyrosine 161 on the D1 polypeptide, Y_Z, is the immediate oxidant of the oxygen-evolving Mn_4CaO_5 cluster, and reduces $P680^+$ (see Figure 5A).

About this time, a major progress in the understanding of the binding site of HCO_3^- on the electron acceptor side was made by Jin Xiong, a graduate student of Govindjee. Xiong et al. (1995), in collaboration with Richard Sayre, showed the importance of D1-arginine-269 for the HCO_3^- effect by using a mutant where this arginine was replaced by glycine (see also Hutchison et al. 1996). Further, Xiong et al. (1996), in collaboration with Shankar Subramaniam, modeled the entire molecular structure of D1/D2 polypeptides, including the binding

sites of HCO_3^- and the key herbicides. In addition, Xiong et al. (1997) modified the PSII acceptor side for bicarbonate binding – D1 arginine 269 to glycine – as mentioned above, this brought Govindjee closer to an understanding of the bicarbonate binding niche. The possible role of D1-R 257 related to HCO_3^- binding was further elucidated by Xiong et al. (1998a), and the almost penultimate 3-D model of PSII reaction center, including where HCO_3^- may be binding (i.e., the NHI between Q_A and Q_B binding sites) was published by Xiong et al. (1998b). We have been told that this gave Govindjee great satisfaction. Then, Van Rensen et al. (1999) presented an important review on the role of HCO_3^- in the function of the electron-acceptor side of PSII as was known until then. Govindjee retired in 1999, and closed his laboratory in 2002, but returned after several years to the role of HCO_3^- on the electron acceptor side of PSII, and used not only Chl *a* fluorescence, but also thermoluminescence. He did this by collaborating with the research group of Antony R. Crofts, also at UIUC. They showed that D1 arginine mutants (i.e., R257E, K and Q) had a lowered redox potential of Q_B (Rose et al. 2008), reflecting on the involvement of R257 in the bicarbonate effect.

Thus, in summary today, we know that HCO_3^- is a ligand to the NHI and is known to facilitate electron transport and the protonation of Q_B, and thus, plays a protective and essential role in oxygenic photosynthesis. Based on current knowledge, there are mobile HCO_3^- ions on the electron donor-side of PSII, but HCO_3^- on the electron-acceptor side of PSII is strongly bound under normal conditions. Therefore, CO_2/HCO_3^--depleted conditions would initially have a minimal effect on the functioning of the electron-acceptor side. However, limitation of carbon fixation under CO_2-depleted conditions would lead to the reduction of the PQ-pool. Consequently, upon reduction of the PSII electron-acceptor side, the binding affinity for HCO_3^- could decrease, resulting in its release from PSII. The release of HCO_3^- would slow the formation of PQH_2 and, according to Brinkert et al. (2016), would lead to a positive shift in the E_m of the $Q_A/Q_A^{\bullet-}$ couple. This would increase the energy gap between Q_A and $Pheo_{D1}$ (see Figure 1), thus-minimizing a possibility for back-reaction which may give rise to photodamage (*via* formation of triplet Chls and singlet O_2 molecules).

As mentioned above, the role of HCO_3^- on the electron-donor side of PSII has been intensively discussed since the original studies in Govindjee's laboratory (Stemler and Govindjee 1973; Stemler et al. 1974b) and many various roles of this unique anion have been proposed (Stemler 2002; Van Rensen and Klimov 2005; Klimov and Baranov 2001; see a historical perspective by Shevela et al. 2012). Later, the absence of any (tightly) bound HCO_3^- on the electron-donor side has been clearly supported by several research groups (Ulas et al. 2008; Shevela et al. 2008; Aoyama et al. 2008). These results are in line with all the available recent X-ray crystallographic and cryo-EM studies that have revealed only one HCO_3^- firmly bound as a bidentate ligand to the NHI (between Q_A and Q_B) on the electron-acceptor side of PSII (Umena et al. 2011; Ago et al. 2016; Hussein et al. 2021) (see also Figure 1 and 4). Despite the currently known absence of tightly bound HCO_3^- on the water-splitting (donor) side, available data show that mobile (non-bound) HCO_3^- ions may act on the electron donor side of PSII (**i**) as easily exchangeable acceptor of protons (Ananyev et al. 2005; Shutova et al. 2008; Koroidov et al. 2014; Banerjee et al. 2019; Ulas and Brudvig 2010); (**ii**) as a native cofactor in the photoassembly of the Mn_4CaO_5 cluster (Baranov et al. 2004; Dasgupta et al. 2008); and (**iii**) as a stabilizing agent for the OEC (Van Rensen and Klimov 2005). On the other hand, based on new experimental data, a more important role of HCO_3^- during the photosynthetic oxygen evolution has been recently suggested by Stemler and Castelfranco (2023), which however, needs further consideration and research. There is a need to reexamine if there is or is not any bound bicarbonate on the electron donor side of PSII.

Oxygen-Evolving Complex: Electron Transport on the Donor Side of PSII

Another important area of research in the Govindjee laboratory was to investigate the steps on the electron

donor side of PSII (see the Z-scheme in Figure 1), where the water-splitting reactions take place. Ted Mar, a graduate student of Govindjee, explored all the possible kinetic models for oxygen evolution – even inventing new models in the process (Mar and Govindjee 1972) – which were recognized by both Pierre Joliot and Bessel Kok; however, ultimately the 'oxygen clock' model by Bessel Kok won. Later, Thomas Wydrzynski, a very ingenious graduate student of Govindjee, collaborated with Paul Schmidt, in the Chemistry Department at UIUC, to use proton Nuclear Magnetic Resonance (NMR) to monitor (although indirectly) chemical changes of the Mn_4CaO_5 cluster in the OEC (Wydrzynski et al. 1975). This was followed, by a collaboration with Herbert Gutowsky (1919–2000), the father of NMR, which led to novel observations that proton NMR changes – after excitation of thylakoids by single light flashes – showing its potential to monitor the steps during flash-induced transitions of the S-states ($S_n + h\nu \rightarrow S_{n+1}$, where n = 0, 1, 2 and 3) in the "oxygen clock" of the OEC (see Figure 5A; Kok et al. 1970; Wydrzynski et al. 1976a, b). Govindjee also hoped to have more measurements, with Herb Gutowsky's research group, to 'chisel-out' information on changes in Mn. Govindjee et al. (1978) summarized all that was known on this topic until then, including the role of chloride on water oxidation. However, on the experimental side, there was a major investigation by Wydrzynski et al. (1978); also see Marks et al. (1978). During this investigation, data was obtained on both proton and oxygen-17 NMR relaxation rates (transverse as well as longitudinal) on chloroplast suspensions. Frequency and temperature dependence of NMR results showed that what was being measured was mostly loosely bound Mn (II) in the membranes, which amounted to 1/3rd to 1/4th of Mn (II), with the rest being at higher Mn oxidation states, most probably as Mn (III). Based on the analysis of the frequency dependence of the data on the samples before and after detergent treatment, it was obvious that the examined Mn was all in the thylakoid membrane! Further, an analysis of proton relaxation rates showed that the average lifetime of a water molecule inside a thylakoid was >1 ms, in agreement with its role in water oxidation. Govindjee and Wydrzynski (1981) summarized their results on the proton NMR and the changes in Mn. For the important role of Thomas John Wydrzynski (1947-2018) in the study of water splitting process, see Conlan et al. (2019).

Rita Khanna, who had become fascinated with this application of NMR in photosynthesis, examined different pools of Mn in the chloroplast, by including Electron Spin Resonance (ESR), and neutron activation methods for this study. Khanna et al. (1981b) found that free Mn (i.e., not used in photosynthesis) is replaced by Mg ions, and that even isolated 'light harvesting complexes' contain bound Mn. Afterwards, Khanna et al. (1983) looked at the water proton relaxation rates (PRR), and the ESR spectrum of free Mn (II), reflecting the status of Mn, under many conditions: aging; heat treatment; high and low pH; treatment with H_2O_2; hydroxylamine; and tetraphenyl boron (TPB). In addition, a highly interesting phenomenon was revealed by ^{1}H NMR of plant leaves by McCain et al. (1984). Besides revealing that there are two water compartments in leaves, Govindjee's coauthors showed that in some plant leaves the NMR signals are orientation dependent. It was suggested that chloroplasts of these plants are preferentially aligned with respect to the leaf surface. This novel and exciting study needs to be further pursued, to seek its possible relationship to the productivity of plants.

On the other hand, while visiting Japan, working with Bill Rutherford in Y. Inoue's laboratory, he observed a period four oscillation in both TL and delayed light emission, DLE (Rutherford et al. 1984a, b; see the next section for more on these phenomena), with maxima on flashes 2 and 6, establishing a clear relationship with the charge accumulation process in the OEC. Furthermore, these data showed that the time of deactivation of the "O_2-evolving centers" in leaves is in the 20 to 30 s range, and that in darkness, the ratio of Q_B and Q_B^- in leaves is 1:1; these results proved the importance of TL and DLE measurements in studies on the redox reactions in PSII. We also mention that key information on the structure and the function of the OEC was published by Inoue et al. (1983), and in addition, Kambara and Govindjee (1985) presented several

different theoretical new schemes of water oxidation, based on the functioning of Mn in the OEC, under two different chemical environments. At about the same time, Govindjee et al. (1985), using TL measurements, studied oxygen evolution in thermophilic cyanobacteria, and correlated the back reactions of PSII to the oxygen clock mechanism of the OEC (see Govindjee 1986). Further, in collaboration with D.N. Hendrickson, Padhye et al. (1986) explored the chemistry of the Mn-histidine cluster, an essential part of water-chemistry in photosynthesis. Further, on a visit to the laboratory of Jack Van Rensen in The Netherlands, Govindjee measured flash-induced transitions of the S-states of the OEC in thylakoids and showed that there were always higher "misses" after odd (1, 3, 5), than after even (2, 4, 6) flashes (see Naber et al. 1993). This observation seems to be related to the complexity of the effects of the amounts of $P680^+$ and Q_A present in the samples.

Besides looking at Mn, Govindjee utilized Cl-NMR to study the role of chloride in photosynthesis. Together with Christa Critchley (from Australia), Critchley et al. (1982), and Baianu et al. (1984) provided the first clear evidence for the role of chloride in oxygen evolution. [Christa Critchley had come from Australia to work with Govindjee.] Cl-NMR was then used by Coleman et al. (1984) to look at changes in chloride during thermal inactivation of chloroplasts (see also Govindjee et al. 1983). Govindjee also published thorough reviews on the roles of chloride and Mn ions in oxygen evolution (see Govindjee et al. 1985b; Renger and Govindjee 1985). Soon thereafter, Coleman and Govindjee (1987a) presented a new model for the function of chloride during oxygen evolution. This was followed by direct measurements of changes in chloride by Cl-NMR (Coleman and Govindjee 1987b) which clearly supported the role of chloride on the electron donor side of PSII. In addition, these data revealed the importance of Ca^{2+} (along with the role of chloride) in oxygen evolution. The function of chloride in the OEC was reviewed by Govindjee and Homann (1989). In summary: (**i**) there are many chloride ions bound on the electron donor side of PSII and they cannot be replaced by bicarbonate; (**ii**) chloride ions are bound somewhere between the OEC and Y_Z, the electron donor to $P680^+$ (see Figure 1); (**iii**) without Cl^- (or Br^-), the OEC cannot go beyond the S_2 state; (**iv**) 17 and 23 kDa proteins protect its binding; and (**v**) Cl^- functions in the H^+ abstraction process from the OEC. Related to these, it is interesting to note that recent research on the role of chloride ions in the OEC have confirmed the above points, by showing that Cl^- ions are necessary for the $S_1 \rightarrow S_2$ transition, as they maintain a protonated internal water network near the Mn_4CaO_5 cluster (Brahmachari et al. 2017).

Overviews of the process of oxygen evolution in photosynthesis, including the main findings obtained in Govindjee's laboratory until then, were published by Govindjee and Coleman (1993) and Renger and Govindjee Eds. (1993), Also, Govindjee and his coauthors used Chl *a* fluorescence to study the kinetics of the oxygen evolution steps in plants. For example, Shinkarev et al. (1997) developed a new approach for the analysis of the flash-induced Chl *a* fluorescence in plants, which is based on the use of the generalized Stern–Volmer equation for multiple quenchers. This analysis revealed the presence of a new quencher of fluorescence (a non-identified product of the reaction leading to oxygen evolution in PSII) whose amplitude is characterized by a periodicity of four, with maxima after the third and the seventh flashes, in phase with oxygen release. The quencher appears with a delay of 0.5 ms followed by a rise time of 1.2–2 ms at pH 7, also in agreement with the expected time for oxygen evolution. The question that we ask is: What is this quencher? Further, in collaboration with R. J. Strasser, Govindjee studied how the greening pea leaves acquire the period 4 "oxygen clock" (Govindjee et al. 1998; Strivastava et al. 1999).

Probing photosynthesis: More on Chl *a* Fluorescence Induction, Lifetime of Fluorescence, Delayed Light Emission and Thermoluminescence Measurements

Chl *a fluorescence induction measurement*

Govindjee has had a particular interest in exploiting Chl *a* fluorescence induction (i.e., the Kautsky effect;

Kautsky and Hirsch 1931), also known as the O(K)JI(D)PS(M)T transient (see highly cited reviews by Govindjee 1995, 2004; Stirbet and Govindjee 2011), which is measured *in vivo* and shows characteristic Chl *a* fluorescence variations during several minutes of illumination with constant light on the photosynthetic sample (see Figure 6 for examples of Chl *a* fluorescence transients measured in different organisms). [Note that "O" is for the first Chl *a* fluorescence point in a dark-adapted sample; K is visible under conditions when OEC is inactivated (e.g., by heat stress); J & I are intermediate inflections observed between O and P; D is for a dip observed in plants and green algae maintained under anaerobic conditions; P is for the peak; S is for an intermediary 'steady-state'; M is for a maximum that in many cyanobacteria, as well as in *Chlamydomonas reinhardtii* cells, is maintained under anoxic conditions during darkness, appears after more than 100 s of illumination, and is higher than the P level – see Figure 6), which has been associated with a regulatory process called '*state transition*' (see discussion below); and 'T' is for the final (terminal) steady-state.]

While the Chl *a* fluorescence transient rise from the origin O to the peak P is fast (100–1000 ms), the P to T decrease is much slower (several minutes) (see Figure 6). As mentioned earlier, the oxidized plastoquinone electron acceptor Q_A is a quencher of Chl *a* fluorescence, but not its reduced form Q_A^- (Duysens and Sweers 1963); however, later, several other types of quenching processes were also found to modulate the Chl *a* fluorescence induction, especially during the slow PSMT phase.

The very first results obtained on Chl *a* fluorescence induction curves in his laboratory, were presented at a conference by Govindjee et al. (1967b). Soon thereafter, detailed novel studies were published on the "slow" PSMT fluorescence transient from the cyanobacterium *Anacystis nidulans*, and the green alga *Chlorella pyrenoidosa* (Papageorgiou and Govindjee 1968a, b). For *Anacystis*, the data showed a large Chl *a* fluorescence rise from S to M in 1-2 minutes, which requires Light 2, and is abolished by an uncoupler of phosphorylation,

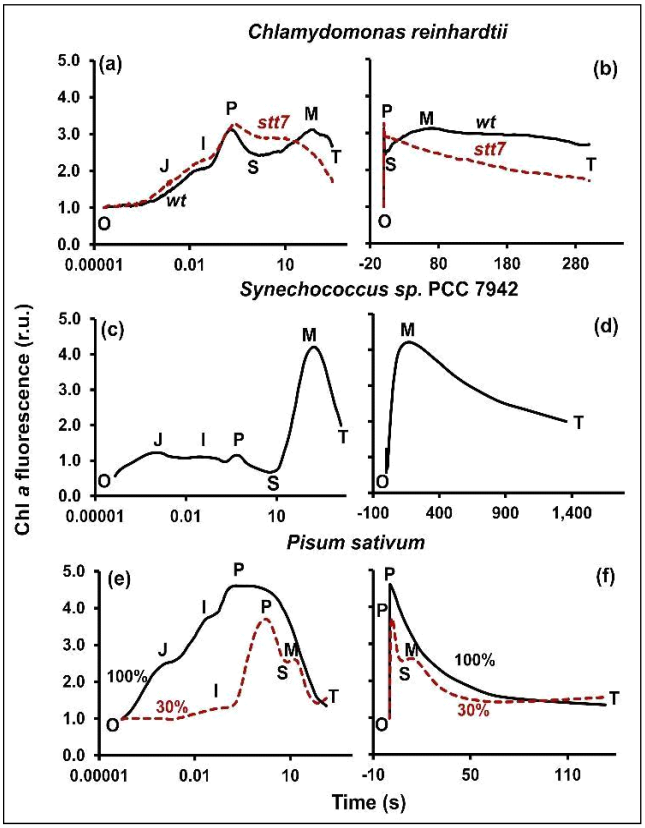

Figure 6. Chlorophyll *a* fluorescence induction (ChlF) curves of different photosynthetic organisms; the curves at left are on logarithmic time scale, and at right, on linear time scale. ***(a & b)*:** ChlF curves of *Chlamydomonas reinhardtii* cells, dark adapted for 45 min in anoxic conditions; *wt* is for wild type, and *stt7* for *stt7* mutant cells. ***(c & d)***: ChlF curves of *Synechococcus* sp. PCC 7942 cells. ***(e & f)***: ChlF curves of leaves of *Pisum sativum*, measured under light intensities of 3,000 (100%) and 333 (30%) µmol photons $m^{-2}s^{-1}$. The O, J, I, P, S, M, and T notations marked in the figures indicate respectively: **O,** the origin (the minimum fluorescence level), usually the first measured fluorescence level; **J** (at ~2 ms) and **I** (at ~30 ms), two fluorescence inflections; **P**, the peak; **S**, a semi-steady-state level; **M**, a maximum; and **T**, the terminal steady state. The curves were measured with PEA (Photosynthetic Efficiency Analyser, Hansatech, UK) instrument under continuous red light, and "r.u." stands for relative units. Figure modified from Stirbet and Govindjee (2019).

and then there is a slow decrease to a steady-state level T (see Figure 6); however, the fluorescence of phycocyanin remained constant throughout the light illumination. For *Chlorella*, there was a faster (40 s) S to M rise that coincided with an increase in the rate of O_2 evolution, then a decay to the T level in ~10 minutes;

uncouplers of photophosphorylation were shown to affect the fluorescence time course only when they were functioning at an earlier stage. These observations were followed by theoretical and experimental research on the initial OPS part of the fluorescence transient (see e.g., Munday and Govindjee 1969a, b, c) on cell suspensions of *Chlorella*. John Munday, one of the first students of Govindjee, observed an "inflection" (I) and a "dip" (D) in-between the "O" and the "P" levels, with the dip D present only under anaerobic conditions. These data, particularly because of the observed effects of methyl viologen – an electron acceptor from PSI – firmly established that PSI activity influences the "OP" fluorescence rise (even when it originates almost only from PSII), reflecting the transient bottleneck in the electron flow on the electron acceptor side of PSI (i.e., after P700), and showing that the O to P fluorescence rise is related to the entire linear electron transport flow, from water to ferredoxin, Fd (see the Z-scheme in Figure 1, and a review by Stirbet et al. 2014).

In the late 1960s, Prasanna Mohanty, from India, joined Govindjee's laboratory as his graduate student and discovered the time-dependent quenching of PSII fluorescence by PSI light (Mohanty et al. 1970). This gave a hint on the phenomenon of state transitions that regulates the distribution of light energy between PSI and PSII, which was first established by Bonaventura and Myers (1969) and Murata (1969) (see also a review by Papageorgiou and Govindjee 2011). This was followed by detailed '*attacks*' on light-induced fast O-P rise (up to a second) and on the slow PSMT (minute range) changes in Chl *a* fluorescence yield, as related to the electron transport and other connected processes (see Mohanty and Govindjee 1973a, b; Mohanty and Govindjee 1975). Also, Govindjee, together with another of his graduate students, Barbara Zilinskas, established that silicomolybdate and silicotungstate are electron acceptors in the presence of (DCMU) (Zilinskas and Govindjee 1975).

More than a decade later, another graduate student, Jin Cao, used OJIP Chl *a* fluorescence transients to examine PSII heterogeneity, in terms of active and inactive PSIIs (Cao and Govindjee 1990). The inactive center had a faster initial fluorescence rise and stress (e.g., light and heat) led to the conversion of active PSIIs to inactive PSIIs. Also, Shinkarev and Govindjee (1993), using Chl *a* fluorescence in spinach thylakoids, confirmed that $P680^+$ is indeed a quencher of Chl *a* fluorescence, but showed, using single flashes of light, that its quenching efficiency is dependent upon the amount of oxidized Q_A present. Around this period, Govindjee visited Reto Strasser in Geneva (Switzerland), and Strasser and Govindjee (1991, 1992) presented their very first measurements on the fast (< 1 s) Chl *a* fluorescence transient in continuous light – showing what we all know now as the OJIP fluorescence rise (presented on a logarithmic time scale) – in different species and conditions. Strasser et al. (1995) surveyed this, not only in plants, but also in algae and cyanobacteria, noting the differences and explaining it all in terms of their photosynthetic reactions.

Further, Stirbet et al. (1995) presented one of the earliest mathematical models of the OJIP transient, based on PSII electron transport reactions, which was perfected by Stirbet et al. (1998). Compared with other similar models at that time, these authors had considered for the first time the initial Q_B/Q_B^- ratio, the S states of the OEC, the excitonic connectivity between PSIIs (see Stirbet 2013), as well as a hypothetical quenching effect on Chl *a* fluorescence, which was assumed to be dependent on the redox state of the PQ-pool.

Several years after his retirement, Govindjee collaborated with Stephen (Steve) Long's group at UIUC on a paper presenting another model of the OJIP Chl *a* fluorescence transient, which was also based on PSII reactions (see Zhu et al. 2005). In addition, Govindjee, in collaboration with Reto Strasser, used Chl *a* fluorescence induction in pea leaves to look at changes in PSII in parallel with P700 transmission changes in PSI (see Strasser et al. 2001; Schansker et al. 2003), all of this to get an in-depth understanding of the complex and intricate relation between Chl *a* fluorescence and the various steps of the process of photosynthesis.

In 2009, Govindjee, in collaboration with the research group of Ondrej Prášil (in Trebon, The Czech Republic), worked on state transitions in cyanobacteria (Kaňa et al. 2009). We emphasize that state transitions are short-time light-adaptive phenomena that optimize the electron transport flow by synchronizing the turnover rates of PSII and PSI when there is an excitation imbalance between them. These transitions are initiated in all oxygenic photosynthetic organisms by redox changes in the PQ pool, with the transition from State 1 to State 2 being triggered by PQ pool reduction, and the transition from State 2 to State 1 by PQ pool oxidation (Allen and Mullineaux 2004; Papageorgiou and Govindjee 2011; Stirbet et al. 2019). Kaňa et al. (2009) measured Chl *a* fluorescence induction curves and fluorescence spectra at different times of illumination and found that the maximum M of the slow PSMT part of the fluorescence transient, measured with 622 nm excitation light, appeared ~30 s later than for illumination with 464 nm light. These data were explained considering the steps involved in the regulation of excitation energy distribution in the light-harvesting antenna of cyanobacteria during a dark to light transition. Further, Kaňa et al. (2012) showed that the S-M rise in the Chl *a* fluorescence transient is correlated with a transition from State 2 (low fluorescence; larger PSI antenna than that of PSII) to State 1 (high fluorescence; larger PSII antenna than that of PSI) in several cyanobacteria. Later, in collaboration with the research group of Rajagopal Subramaniam (in Hyderabad, India), a similar result was obtained in the green alga *Chlamydomonas reinhardtii* maintained in anoxic conditions during darkness (Kodru et al. 2015). Moreover, in both these studies, the fluorescence increase from S to M was absent or reduced in mutants that had no state transitions. However, the origin of M to T decay remained unclear for cyanobacteria (see Bernát et al. 2017). On the other hand, Stirbet and Govindjee (2016) validated the results on *Chlamydomonas* obtained by Kodru et al. (2015) by using a mathematical model of photosynthesis (see also Stirbet et al. 2020). Further, Govindjee has collaborated with Kumud B. Mishra on non-acclimated and cold-acclimated leaves of the cold-sensitive *Arabidopsis thaliana* (see Mishra et al. 2019), observing the slow PSMT phase of the fluorescence transient, as well as fluorescence emission spectra (from 650 nm to 780 nm), at selected temperatures during the controlled cooling of the plants from 22°C to –1.5°C. These results were explained by biochemical and photochemical changes by low temperature that modulate Chl *a* fluorescence induction and point to the importance of cold acclimation in the regulation of photosynthetic processes at low temperatures.

Lifetime fluorescence measurements

Govindjee knew that Chl *a* fluorescence intensity is not a measure of the quantum yield of Chl *a* fluorescence, since it depends on the concentration of the fluorophore and, therefore, he decided to measure the fluorescence lifetime (i.e., the time a fluorophore spends in the excited state before emitting a photon and returning to the ground state), which is linearly related to the quantum yield of fluorescence. Thus, in collaboration with the group of Henri Merkelo (a faculty in Electrical Engineering, at UIUC), Ted Mar (Govindjee's PhD student) constructed a new mode-locked laser instrument (see Merkelo et al. 1969). Then, Briantais et al. (1972) established the almost linear relationship between the lifetime of Chl *a* fluorescence and fluorescence intensity during the O to P fluorescence rise in green algae. Later, by measuring the lifetime of Chl *a* fluorescence, Moya et al. (1977) concluded that monovalent (Na^+) and divalent (Mg^{2+}) cations affect the "absorption cross sections" of PSI and PSII differently, while regulating excitation energy distribution between the two systems. However, by measuring the degree of polarization of Chl *a* fluorescence, Daniel Wong, a graduate student of Govindjee, concluded that Na^+ effects can be interpreted by increased excitation energy transfer from PSII to PSI, decreasing PSII fluorescence, with Mg^{2+} reversing this effect (Wong and Govindjee 1979). Gasanov et al. (1979) extended this concept to the pigment systems in grana and stroma and provided the identification of specific emission bands with specific pigment-protein complexes. For a review of this area, see Govindjee et al. (1979). Soon thereafter,

Malkin et al. (1980) measured in parallel both the intensity and the lifetime of Chl *a* fluorescence during the decreasing P to S phase of the fluorescence induction curve in leaves of various higher plants, and under different conditions. The results showed that the correlation between the Chl *a* fluorescence yield and lifetime during the P to S transition is not necessarily a linear one, and the so-called "lake" model of excitation energy exchange between the PSII units (known as PSII connectivity) is questionable in leaves. Then, Wong et al. (1981) provided quantitative information on the distribution and redistribution of excitation energy in the two pigment systems by using Chl *a* fluorescence lifetime measurements. Information on the effects of temperature (by heating the samples) on these processes was also provided, for use in further understanding of the regulatory events involved (see e.g., Sane et al. 1984a).

Gilmore et al. (1995a), based on simultaneous measurements of Chl *a* fluorescence intensity and lifetime on plants exposed to high light, discovered that an increased xanthophyll (zeaxanthin, Z, and antheraxanthin, A) concentration, in the presence of a pH gradient, decreases the fractional intensity of a fluorescence lifetime component with 2 ns, and increases the one with 0.4 ns. Based on many experiments and detailed analysis of the data, Gilmore et al. (1995b) concluded that both pH gradient and increased xanthophyll result in the formation of a "quenching complex" with a short (0.4 ns) fluorescence lifetime, leading to the protection of plants exposed to high light. By extending this research to chlorina mutants in barley, Gilmore et al. (1996) showed independence of this phenomenon from the size of the light harvesting antenna. This area of research was reviewed and summarized wonderfully by Gilmore and Govindjee (1999). Also, Gilmore et al. (2000) used time-resolved room temperature Chl *a* fluorescence emission spectra from the leaves of wild-type barley and Chl *b* deficient mutants and provided global spectral analysis of Chl *a* fluorescence from the light-harvesting complexes of both PSI and PSII.

Further, Govindjee and Nedbal (2000), in an editorial to a special issue of *Photosynthetica*, emphasized the concept of "*Seeing is Believing*" summarizing the history of Chl *a* fluorescence imaging in photosynthesis research. At that time, Govindjee started new Chl fluorescence lifetime measurements in collaboration with Robert M. Clegg at UIUC, and published papers on the use of a new technique called Fluorescence Lifetime Imaging Microscopy (FLIM), working with Oliver Holub, a graduate student from Germany (see: Holub et al. 2000). With this technique, Holub et al. (2007) obtained images during Chl *a* fluorescence induction in the wild type and in the NPQ mutants of *Chlamydomonas reinhardtii*, demonstrating clearly that zeaxanthin plays a photoprotective role in this alga. Finally, with Sizue Matsubara, also from Germany, the FLIM method was used to study the energy dependent component of NPQ (qE) in *Avocado*, which uses both lutein and violaxanthin cycles (see Matsubara et al. 2011). For a discussion of different xanthophyll cycles, see Papageorgiou and Govindjee (2014). Furthermore, Matsubara et al. (2011) found two major PSII fluorescence lifetime components, 1.5 ns (unquenched) and 0.5 ns (quenched). However, this line of research was interrupted after the premature death of Robert M. Clegg (1945–2012). Further research is needed to exploit this area of research.

Delayed light emission and Thermo-luminescence measurements

In the early 1970s, the idea of looking at the back reactions of photosynthesis through delayed light emission (DLE; also called delayed fluorescence) and thermoluminescence (TL) was exploited in Govindjee's laboratory, along with the prompt fluorescence, discussed above. DLE was discovered by Strehler and Arnold (1951). It is a weak light emission by intact photosynthetic samples after the termination of illumination, which was shown to be mostly emitted by excited Chl *a* molecules in the PSII antenna (see a review by Kalaji et al. 2012). The DLE intensity is a decreasing polyphasic function of the time after illumination, which depends on the kinetics of the reverse electron transport reactions involving the redox components on both the electron donor and the electron

acceptor sides of PSII (see the Z-scheme, Figure 1). On the other hand, the TL is a thermally stimulated luminescence, in which a sample emits a weak light (glow) while being heated following excitation, e.g., with light or ionizing/non-ionizing radiation. As the vibrational energy increases, with temperature, charge recombination occurs by overcoming the activation energy barriers. To understand this process of TL in photosynthetic samples, in molecular terms, see the original papers of Govindjee with Don DeVault (DeVault et al. 1983; DeVault and Govindjee 1990).

DLE measurement

Mohanty et al. (1971) presented their observations on DLE from the red alga *Porphyridium*, which revealed that DLE in the microsecond time range involves the back reaction between Q_A^- and Y_Z^+ in PSII—the data had included observations on cell suspensions treated with hydroxylamine, which not only acted as an inhibitor of normal electron flow, but also as an electron donor to PSII. Further, working on isolated chloroplasts and *Chlorella pyrenoidosa* cells, Mar and Govindjee (1971) introduced the temperature (jump) delayed light emission (TDLE) technique. Both the DLE as well as TDLE were chosen for exploitation also by Paul Jursinic, a graduate student of Govindjee (see Figure 7 for a few examples of DLE curves; Jursinic and Govindjee 1972), who found that, in addition to the back reaction from Q_A^- to Y_Z^+, there must be another reductant involved in giving DLE.

Jursinic and Govindjee (1977a) measured Chl *a* fluorescence, as well as DLE changes using 10 ns light flashes, in Tris-washed chloroplasts in the presence of various artificial electron donors. They concluded: (**i**) $P680^+$ (the oxidized primary donor in the PSII reaction center) is indeed a quencher of Chl *a* fluorescence; (**ii**) DLE, in the microsecond time range, is due to a back reaction between Q_A^- and $P680^+$; (**iii**) there exist two electron donors between the Tris block and P680; and (**iv**) Mn^{2+} donates electrons to $P680^+$ via Y_Z (see these components in the Z-scheme, Figure 1). Based on the temperature and the light intensity dependence of DLE,

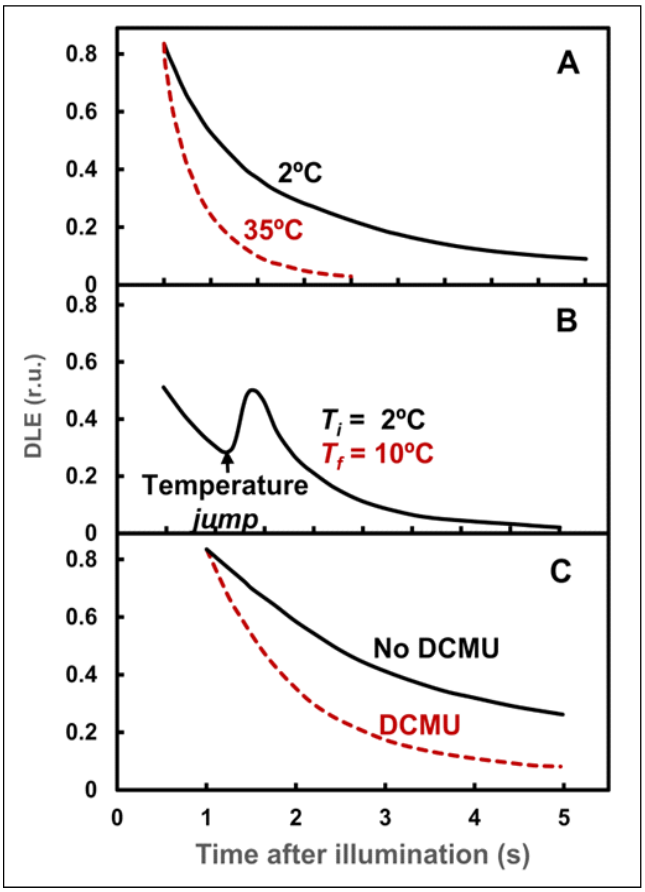

Figure 7. Examples of DLE and TDLE measurements (modified from Jursinic and Govindjee 1972). In all the experiments, samples were illuminated for 5 s with the same saturating light intensity, and the measurement of DLE decay started 1 s after illumination. **(A)** The DLE decay at two different temperatures (2ºC and 35ºC), measured on *Chlorella* cells. **(B)** Trace of DLE and TDLE: A temperature jump from 2ºC to 10°C was applied to a sample of DCMU treated *Chlorella* cells, at about 2 s after the end of illumination. **(C)** DLE curves of *Chlorella* cells with and without DCMU, measured at 10°C. DLE intensities at 1 s after illumination were normalized to an arbitrary value in both panels **(A)** and **(C)**.

Jursinic and Govindjee (1977b) provided an additional insight on the origin of DLE – being different in the 3-30 µs range than in the 100-350 µs range, but both taking place by recombination of primary charges – and, interestingly, showing that one involves a lipid environment. Further, based on all the data put together, they could even predict that the redox potential of P680/$P680^+$ must be in the range of +1.0 - +1.3 eV. By comparing light-induced (after a single 10 ns excitation

light flash) and salt-jump induced µs and ms DLE, Jursinic et al. (1978) showed that the faster DLE is independent of the membrane potential. However, the slower DLE is dependent on it, provided a proton gradient is already present. The light-induced potential calculated from this work was ~130 mV, in agreement with measurements by other independent methods. On the other hand, experiments on µs to ~ a ms range DLE, by Jursinic and Govindjee (1982) with single 10 ns excitation light flashes given to thylakoids from peas – with and without silicomolybdate and hydroxylamine – led to a detailed understanding of the DLE, which is mainly due to the back reactions in PSII.

TL measurement

TL measurements were initiated by Govindjee working with the research group of P. V. (Raj) Sane and the late V. G. Tatake (1926-2004; see Sane and Phondke 2006) at BARC (Bhabha Atomic Research Centre) in Bombay (Mumbai), India. Govindjee et al. (1977) discovered a new "glow peak" at 120 K in the anoxygenic photosynthetic bacterium, *Rhodopseudomonas sphaeroides*. As expected, it had counterparts in DLE, as well as in prompt fluorescence. Further, these authors showed that this newly discovered light emission was from Mg protoporhyrin, not bacteriochlorophyll. It had excitation peaks at 410 nm and at 545 nm, and emission peaks at 530 nm, 610 nm, and 660 nm. This was soon followed by TL measurements by Sane et al. (1977) on oxygenic photosynthesizers, which provided new information on the origin of glow peaks in isolated spinach chloroplasts, *Euglena* cells, and samples enriched in PSI or PSII that had been pretreated with different concentrations of the herbicide DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea), different light intensities, and that too, after mild heating at various temperatures. These results led to an understanding of the origin of all the glow peaks, except for what was then called Peak III: (**i**) The Z peak (appearing at the lowest temperature) originates in states unrelated to photosynthesis when other peaks are saturated; (**ii**) Peak I involves the back reaction of PSII from the reduced forms of Q_B to the oxidized 'S' states of the OEC; (**iii**) Peak II is due to the back reaction of electrons from Q_A^- to the oxidized 'S' states; and (**iv**) Peak IV is from both pigment systems of PSI and PSII, but its exact origin could not be deciphered; and (**v**) Peak V is from PSI.

In collaboration with V. G. Tatake, and P. V. Sane, Govindjee analyzed the theoretical TL curves, obtained earlier, with the existing theories (Tatake et al. 1981), and observed highly unusual activation energies! It was this result that led Govindjee to interact with Don Charles DeVault (1915-1990; see Seibert (1991), who had earlier discovered with Britton Chance the quantum mechanical tunnelling processes in biology. These TL results were explained by invoking back reactions of PSII and of PSI, as well as some other processes. However, William (Bill) Arnold, the discoverer of TL in photosynthetic systems, had a different theory (Arnold and Sherwood 1957): a solid state "electron-hole" recombination theory, which did not explain the results of Tatake et al. (1981). Thus, Govindjee privately submitted the manuscript with DeVault to Arnold for publication in PNAS (Proceedings of the National Academy of Sciences, USA), requesting him to edit and coauthor it. Within 7 days, a reply came: "*Yes, but condense the size of the paper*". Both Govindjee and DeVault were pleased that Arnold did not insist on his earlier hypothesis! This paper has the correct theory of TL – it is totally different from the solid state "Electron-hole" recombination theory of Arnold (see DeVault et al. 1983). Later, DeVault and Govindjee (1990) refined the earlier theory of DeVault et al. (1983) for TL, to relate TL peak shifts more accurately with the redox potential changes in the components involved in the back reactions leading to TL.

An important breakthrough in the field of TL was made when Richard T. Sayre brought *Chlamydomonas* mutants to Urbana to check on the involvement of amino-acid histidine in the reactions leading to TL. Roffey et al. (1994) showed that luminal side histidine residues (in the D1 polypeptide) affect electron transfer on the electron donor side of PSII. Using a specific histidine mutant, Kramer et al. (1994) showed that a particular TL band (labelled as A_T, with a peak at –16° C), present in samples in which

the Mn cluster of PSII is destroyed (e.g., by washing with high concentrations of Tris), may involve histidine-195 only in an indirect manner, since only its intensity, but not its position was affected in H195N, H195Y, and H195D mutants of *Chlamydomonas*. One conclusion was that Y_Z was not a 'trap' involved in the A_T band. Govindjee's interest in understanding the meaning of TL data continued with the research group of Eva-Mari Aro in Finland. The very first observations were by Maenpaa et al. (1995), but later, Keranen et al. (1998) showed that the "B" and "Q" TL bands, normally at different temperatures (see a representation of the main photosynthetic TL bands in Figure 8), come together in a D1 mutant, indicating the involvement of the D1 polypeptide in these back reactions. Finally, Vass and Govindjee (1996) provided a wonderful educational review on TL in photosynthetic systems, in which this method was presented as a powerful tool in probing a wide range of PSII redox reactions.

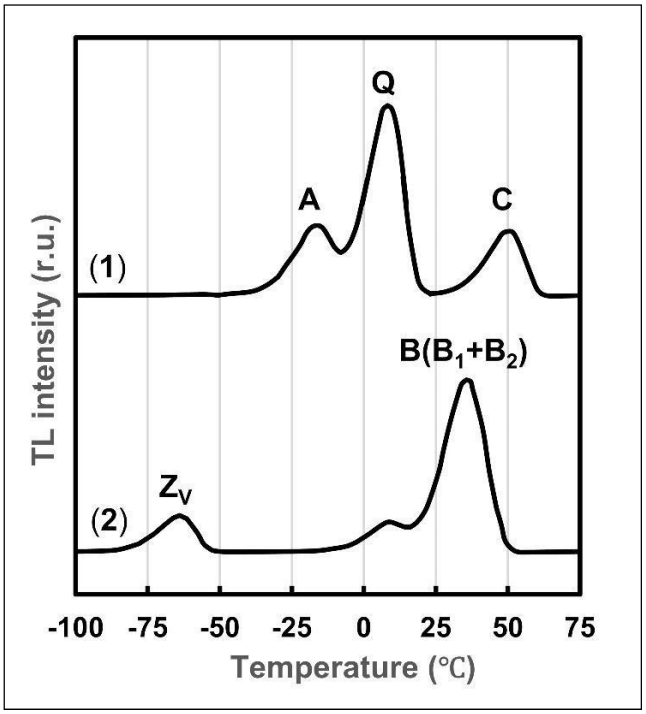

Figure 8. The main photosynthetic thermoluminescence (TL) bands (see Vass and Govindjee 1996). Top curve **(1)**: A-band (~-15°C; $S_3Q_A^-$); Q-band (~+5°C; $S_2Q_A^-$); and C-band (~+50°C; $Tyr_D^+Q_A^-$). Bottom curve **(2)**: Zv-band (-80 to -30°C; $P680^+(Chl^+?)Q_A^-$); B_1-band (+30 to +40°C; $S_2Q_B^-$); B_2-band (~+30°C; $S_3Q_B^-$).

Conclusions on Govindjee's key Contributions on the Light Reactions in Oxygenic Photosynthesis and on the Z-scheme

In this minireview we have attempted to show that much of the research conducted by Govindjee and his collaborators, spanning more than six decades, has led to the characterization of several components of the Z-scheme, their elucidation, and their function, such as light energy absorption and energy transfer in PSI and PSII antenna, primary photochemistry, water oxidation, electron flow from water to $NADP^+$, and short-time regulatory processes, such as nonphotochemical quenching of Chl *a* fluorescence, and state transitions. Moreover, Govindjee's exploitation of biophysical techniques, such as Chl *a* fluorescence, NMR, delayed light emission and thermoluminescence, to understand and reveal these processes has been one of the main themes of research spanning his entire career. When Govindjee left India in 1956, to start his PhD studies in the United States at UIUC, he was looking forward to work on solving the mystery of the "Red Drop Effect" and his passion to invest his efforts in deciphering important unknown areas of photosynthesis never left him from that moment. Here we have shown that, together with his collaborators, he has succeeded in making not one, but several important discoveries on the "light reactions of photosynthesis". In particular, we mention: the discovery of Chl *a* in what we now call PSII; the earliest picosecond measurements on the primary photochemistry of both PS I and PSII; the site and the function of bicarbonate on the electron acceptor side of PSII; and above all, highly efficient exploitation of all the light emission processes (prompt as well as delayed Chl *a* fluorescence; and thermoluminescence) for the understanding the details of many steps in the Z-scheme, as well as regulatory processes that control the overall yield of photosynthesis, and thereby, of plant productivity.

At the same time, Govindjee has excelled all his life in teaching younger generations about photosynthesis. For example, he not only taught the Z-scheme through

educational articles (see e.g., Govindjee and Björn 2012; Govindjee et al. 2017; Govindjee 2023), but he also distributed excellent posters by mail and personally by hand at photosynthesis conferences. On various occasions, Govindjee has organized special classes in which he has used students to act as molecules representing the entire electron transport chain, from water to NADP (see e.g., Mohapatra and Singh 2015).

DECLARATIONS

Conflict of interest. The authors declare no conflict of interest.

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