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Govindjee: One of the Major Architects for the Conceptual Evolution of the Z-scheme of Photosynthesis[#]

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ABSTRACT

Govindjee stands out as the world's most recognised photosynthesis researcher driven by a single-minded fascination with the process of photosynthesis. Covering all fields of the 'light reactions' of photosynthesis, Govindjee's research contributions have led to the addition, correction and supplementation of concepts and information. Here we present the contributions of Govindjee and his coworkers to the Z-scheme of electron transport in oxygenic photosynthesis. We begin with the conceptual origin of the scheme and then cover its time-to-time advancement made with the research contributions by scientists worldwide. We focus here on the contribution of Govindjee and how he has updated the scheme by adding new information, some of it his own. We present a summary of the contributions of Govindjee in disseminating the knowledge of the 'light reactions of photosynthesis', through posters, symposium presentations and teaching through drama. We also recognise the teacher in him for his hallmark method of teaching with an aim to present such a complicated process of light reactions in a fun-filled manner. Our tribute to him complements that by Block (2022), Kumar *et al.* (2022) and Nonomura (2022), as well as the article by Yates (2022) on what is known as Govindjee's museum.

Keywords: Quantum yield, Primary photochemistry, Photosystem II, Bicarbonate, Z-scheme, Robert (Robin) Hill, Robert Emerson, Eugene Rabinowitch, L.N.M. Duysens, Bessel Kok

INTRODUCTION

Govindjee (known as Mister Photosynthesis in the circle of plant physiologists) stands as the great banyan tree in photosynthesis research contributing greatly through his knowledge and experience in all branches of plant biology including plant production and for nurturing hundreds of young researchers across the globe. Govindjee was born in India, on 24 October 1932, at Allahabad, Uttar Pradesh (U.P.), to Savitri Devi and Vishveshwar Prasad. He studied at the University of Allahabad, receiving his BSc in 1952 and MSc in Botany (Plant Physiology) in 1954, both in the first division. In 1956, he went to the USA and joined the University of Illinois at Urbana-Champaign (UIUC) for a PhD in Physico-Chemical Biology under Robert Emerson (1903–1959), the discoverer of the Red Drop phenomenon (Emerson and Lewis, 1943) and the Enhancement (two light) effect (Emerson *et al.*, 1957). However, after the

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[#] In recognition of 90th birthday of Govindjee, now known as Govindjee Govindjee; for an article in recognition of 88th birthday of his wife Rajni Govindjee, an authority on the photobiology of bacteriorhodopsin, see the article by Balashov *et al.* (2023).

tragic death of Emerson on 4 February 1959, he worked with Eugene Rabinowitch (1901–1973), the well-known chemist with several important discoveries in physical chemistry (e.g. the 'cage effect' in photochemistry; Franck and Rabinowitch, 1934). In 1960, Govindjee completed his PhD thesis, in Biophysics, titled 'Effect of combining two wavelengths of light on the photosynthesis of algae', which was an in-depth study of the Emerson enhancement effect, which he dedicated to the memory of Robert Emerson (Govindjee, 1960). See Govindjee (2004a, 2004b) and Govindjee (2018) for his respectful thoughts on Emerson. Thereafter, Govindjee taught at the UIUC from 1961 until his retirement in 1999 and many years thereafter around the World. During this period, he guided more than 25 graduate students and many post-doctoral researchers from several different countries. Additionally, Govindjee has been intensely involved in research activity in association with scientists from various laboratories in the USA as well as outside the USA (for his publications, see his website https://www.life.illinois.edu/govindjee/g/Publications.html). During the 23 years of post-retirement from active service, Govindjee has published many papers related to the history of photosynthesis (see e.g. Govindjee *et al.*, 2005; Stirbet *et al.*, 2020a) bringing the exciting stories of photosynthesis experiments to the knowledge of students and researchers around the World; he has regularly written reports on conferences highlighting contributions from young researchers entering the field. He has collaborated with hundreds of scientists from almost two dozen countries in almost every aspect of photosynthesis and has been active in bringing out publications on every aspect of oxygenic photosynthesis (see Govindjee, 2019a, 2019b). What is amazing is that he has co-authored with about 580 scientists, from 30 countries, but mostly from the USA, India and China (see the List of Names of Govindjee's Co-authors (1955–2022) at <https://www.life.illinois.edu/govindjee/g/Publications.html>): Australia (8), Azerbaijan (5), Belgium (2), Bulgaria (1), Canada (11), **China** (55), The Czech Republic (18), Egypt (2), Estonia (2), Finland (6), France (18), Germany (22), Greece (4), Hungary (9), **India** (63), Iran (4), Israel (5), Japan (13), Korea (1), Mexico (9), The Netherlands (17), New Zealand (1), Norway (1), Poland (3), Russia (24), Slovak Republic (3), Sweden (5), Switzerland (5), UK (9) and **USA** (238).

Over the years the research contributions of Govindjee have been highly significant in the areas of light absorption, excitation energy transfer, primary photochemistry and electron transport, especially as related to Photosystem II (PS II; the water-plastoquinone [PQ] oxidoreductase of photosynthesis) and on the regulation of excitation energy distribution between the two photosystems (PS) of the electron transport chain. In particular, Govindjee is best known for his novel, ingenious and thorough use of chlorophyll (Chl) *a* fluorescence as a powerful, quick and highly sensitive tool for monitoring various steps and processes in photosynthesis from the time of light absorption (femtoseconds) until carbohydrate formation (seconds to minutes). He is clearly recognised for the discovery that bicarbonate plays a critical role in PQ reduction on the so-called Q_B side of PS II. In addition, Govindjee and his outstanding collaborators were the first to measure the time of primary charge separation in both photosystems on a picosecond time scale and have provided the theory for the mechanism of thermoluminescence in photosynthetic systems. For earlier recognition of Govindjee's life and research, see for example, several articles by Block (2022), Eaton-Rye (2007a, 2007b, 2012, 2013, 2018, 2019), Kumar (2020), Kumar *et al.* (2022) and Prásil (2014), Sharma (2018).

Photosynthesis is a highly complex process carried out by all oxygen-producing organisms (plants, algae, cyanobacteria) and some anoxygenic bacteria (Blankenship, 2021; Blankenship *et al.*, 1995; Rabinowitch and Govindjee, 1969; Shevela *et al.*, 2013a, 2013b). Our understanding of photosynthesis in general and in light-dependent reaction, in particular, is based on the discoveries and research of many scientists (see e.g. Blankenship, 2021; Eaton-Rye, 2018, 2019; Govindjee and Björn, 2012; Govindjee *et al.*, 2005, 2018; Rabinowitch, 1945; Rabinowitch and Govindjee, 1969; Shevela *et al.*, 2021, 2023).

The Z-scheme of photosynthesis, which involves the participation of two light reactions and two-pigment systems, results in the transfer of electrons from water to nicotinamide dinucleotide phosphate ($NADP^+$). The chain includes more than 20 intermediates, systematically arranged as both intrinsic and extrinsic components in the thylakoid membrane with specific energy levels. Over the past 80 years, the concept of Z-scheme has evolved with the intellectual input of many research groups from all over the world, but for our understanding, highly significant contributions have been made by Govindjee and his co-workers to the modern Z-scheme as we see it today in every publication around the World. We present below our perspective on the contribution of Govindjee, directly or indirectly, to the conceptual evolution of the electron pathway (For earlier accounts, see Govindjee and Björn, 2012; Govindjee *et al.*, 2017). We present here the experimental, analytical and intellectual contribution of Govindjee on: (1) The two-light reaction and two-pigment system in oxygenic photosynthesis; (2) The issue of the minimum quantum yield of oxygen evolution; (3) The charge separation and the primary photochemistry; (4) The unique involvement of bicarbonate in the Z-scheme of electron transport; (5) The conceptual evolution of the Z-scheme from the early time of Eugene Rabinowitch (1945) to the present (we have included here schemes that are linked to Govindjee); and (6) His hallmark presentation of the Z-scheme to the students around the World. This article aims at presenting the contributions of Govindjee that led to the improvement in the Z-scheme of photosynthesis and in making a chronological upgradation of the scheme for the benefit of the readers.

SOLVING THE ISSUE OF THE MINIMUM QUANTUM REQUIREMENT FOR OXYGEN EVOLUTION

The maximum quantum yield of photosynthesis (or its inverse, the minimum quantum requirement), was in place since 1923 by the experiments of the great German biochemist and the Nobel laureate Otto Warburg, who argued for a minimum quantum requirement of 4, in accordance with the one-electron-one-photon principle (Warburg 1958; Warburg and Burk, 1950; Warburg and Negelein, 1923). He even eventually found a requirement of only three photons per oxygen evolved and elaborated a theory to explain this. His concept of quantum yield was based on the Stark-Einstein equivalence law (Einstein, 1905), which states that one photon 'reacts' with one molecule to move one electron. The oxidation of two water molecules to yield one oxygen molecule requires removal of four electrons and four protons and it is natural to assume that the movement of one electron (or proton) requires one photon and thus, four photons. This assumption was in place until the findings of Robert Emerson (Emerson and Lewis, 1941, 1943) contradicting Warburg's conclusion. Emerson and Lewis (1941, 1943) found a minimum quantum requirement of 10–12 photons per oxygen molecule evolved. Since these experiments were highly intricate, it was far from easy to resolve this disagreement. In a long series of experiments, Yuan *et al.* (1955) also obtained a requirement of 8.7 ± 1.0 photons per molecule of carbon dioxide assimilated and 9.1 ± 1.1 photons per molecule of oxygen evolved. However, while disagreeing with Emerson's finding, Warburg was of the opinion that there were experimental problems such as the age of the cells and the limitation of CO_2. Govindjee made a significant contribution to settling the quantum controversy (see below). After Emerson's death in 1959, Warburg started telling people that Emerson's values were high because he had not used young synchronous cultures and used low (5%) CO_2 (Warburg had used 10% CO_2) that, he stated, is needed for the low quantum requirement. Govindjee *et al.* (1968), by replicating Warburg's experimental conditions, demonstrated that the minimum quantum requirement for cultures of *Chlorella* was indeed 8–12, as Emerson had measured. Warburg *et al.* (1969) never accepted the findings of Robert Emerson and, thus, of R. Govindjee *et al.* (1968) (for this controversy, see Govindjee [1999] and a wonderful and thorough book by Nickelsen and Govindjee, 2011; also see Balashov *et al.*, 2023, for contributions of Rajni Govindjee). Emerson's values of minimum quantum requirement (and, thus maximum quantum yield) for oxygen evolution have been accepted by all subsequent researchers.

THE INITIATORS OF THE DISCOVERY OF TWO PHOTOSYSTEMS

The idea of two light reactions and two photosystems (PSs) could be traced to the 1943 experiments of Emerson and Lewis (1943) on the 'red drop' in the action spectrum of the quantum yield of photosynthesis, but, much more clearly, to the 'Emerson enhancement' effect in 1957 (Emerson and Chalmers, 1958; Emerson and Rabinowitch, 1960; Emerson *et al.*, 1957; also see Govindjee, 2004b). This discovery was the foundation of the concept of the 'Z'-scheme of photosynthesis (Hill and Bendall, 1960). Further, the two light reactions 'required' two reaction centres (RCs); P700, for Photosystem I (PSI), was discovered by Bessel Kok (Kok, 1957). However, the idea of P680 in PS II was first mentioned by Govindjee in the paper with Anna Krey and then, with Rabinowitch (see Krey and Govindjee, 1964; Rabinowitch and Govindjee, 1965). Emerson suggested that one of the light reactions was run by Chl *a* (his long-wave system), but the other by one of the auxiliary pigments (e.g. Chl *b* or phycobilins; Emerson and Chalmers, 1958). Govindjee knew this was in contradiction to the known fact from Duysens (1952) that excitation energy transfer from Chl *b* to Chl *a* is 100%; he used to tell this to Emerson, in 1958, when they would walk together after work, but Emerson seemed not to accept it (Govindjee, personal communication to one of us, PKM; also see Govindjee, 2018). This question was solved in Govindjee's PhD thesis, where he established that both the PSs were run by Chl *a*: a short-wavelength spectral form of Chl *a* was in the same system that had Chl *b* or other accessory pigments (Govindjee and Rabinowitch, 1960). By measuring the action spectra of the Emerson Enhancement effect in the green alga *Chlorella* and the diatom *Navicula,* Govindjee observed peaks at 670 nm, in addition to those at 650 nm (in *Chlorella* attributable to Chl *b*) or at 630 nm (in *Navicula* attributable to Chl *c*). This showed that the excitation of Chl *a* form (Chl *a* 670) can supplement 'Chl *a* 680–700', in these algae and the effect of the auxiliary pigments must be mediated by excitation energy transfer from these pigments to 'Chl *a* 670'. Thus, Govindjee concluded that the reason the excitation of the auxiliary pigments improves the efficiency of photosynthesis in the long-wave region is by resonance transfer of excitation preferentially to a short-wavelength absorbing form of Chl *a* that is not (or not strongly enough) excited by direct absorption of light >680 nm in green and brown algae and > 650 nm in red algae. Govindjee achieved this success by changing Emerson's experimental set-up, which had used a Hg-Cd lamp and did not have the possibility of giving the second beam of light at appropriate wavelengths in the red region.

French (1979; see Govindjee and Fork, 2006) and Cederstrand *et al.* (1966) had been able to see these spectral forms of Chl *a* through absorption spectroscopy (also see Krasnovsky, 1992, for work on *in vitro*). Further, Kautsky *et al.* (1960), by observing and analysing Chl *a* fluorescence transients, had also speculated that there may be two light reactions in photosynthesis but had failed to mention two pigment systems. Independently, Govindjee *et al.* (1960) discovered the two-light effect in Chl*a* fluorescence; they observed quenching of blue light-excited Chl fluorescence (activation of PS II) by far-red light (activation of PS I function). Such antagonistic effect of far-red light on blue light, an exact opposite of Emerson's enhancement could also explain (in today's terms) the existence of two pigment systems: PS II reducing a quencher (Q) of Chl *a* fluorescence, whereas PS I oxidising the reduced Q, now known as Q_A (see Duysens and Sweers, 1963, who clearly recognises the earlier discovery by Govindjee *et al.*, 1960). Further, to distinguish between light-induced changes in oxygen evolution (photosynthesis) and oxygen uptake (respiration), which Emerson's (and Govindjee's) experiments were lacking, it was important to prove that the effect was not in respiration. Rajni Govindjee *et al.* (1960) worked on this point; she inhibited respiration with parabenzoquinone and showed that the two-light effect was not in respiration, but in the Hill reaction (this term was already in use by that time); also see: Balashov *et al.* [2023]). This finding also put an end to the idea by Lawrence Blinks (1957, 1959) that the two light effects may be in respiration!

Additional proof of the two-light effect on photosynthesis was clearly obtained by mass spectroscopic results with Oxygen-18 in which Govindjee was deeply involved (see e.g. Govindjee *et al.*, 1963; also see Owens and Hoch, 1963). For most plant biochemists, the proof came when the existence of the Emerson enhancement effect was shown in NADP reduction in chloroplasts (R. Govindjee *et al.*, 1964; see Balashov *et al.*, 2023; Nickelsen, 2015). We note that the Emerson Enhancement Effect was shown to exist even in deuterated *Chlorella* cells (Bedell and Govindjee, 1966). In addition, throughout this period, Govindjee did extensive work in characterising the two light reactions and two pigment systems by other biophysical techniques (for references, see Govindjee and Björn, 2012). To our knowledge, such terms were used, for the first time, in the description of Z-scheme of photosynthesis (Govindjee *et al.*, 2005; for its relation to changes in various parameters of Chl *a* fluorescence, see Demmig-Adams *et al.*, 2014; Govindjee 2004a; Ostroumov *et al.*, 2014; Papageorgiou, 2004; Papageorgiou and Govindjee, 2004).

Duysens *et al.* (1961), with their two light experiments on the red alga *Porphyridium cruentum*, showed, for the first time, the sequential oxidation and reduction of cytochrome f (Cyt f) confirming that Cyt f has its place between PS II and PS I; this was the key experiment proving the ‘basics’ of the ‘Z’ scheme. In these experiments, light absorbed by PS I was ~680 nm (named after light 1—which was given first) and that absorbed by PS II was ~562 nm (named after light 2, which was given next). These experiments coupled with the contributions of a large number of researchers from different groups, around the World, established the positions and the sequence of all other intermediates in the Z-scheme and the details of the electron transport components involved in the electron transport pathway (for further information, see Blankenship, 2021; Shevela *et al.*, 2018).

CONTRIBUTIONS ON MEASUREMENTS OF PRIMARY CHARGE SEPARATION

The very first step that starts the photochemistry in oxygenic photosynthesis is the primary charge separation at the RCs (P700 and P680) and these charge separation events occur within picoseconds (Mamedov *et al.*, 2015; Milanovsky *et al.*, 2014; Nadtochenko *et al.*, 2014; Wasielewski *et al.*, 1989). The concept of charge separation emerged long ago. First, there were the experimental findings and theoretical insight of Förster (1948), which led to the concept that efficient energy transfer cannot take place by (re) absorption of fluorescence, but rather by resonance excitation energy transfer (Förster resonance energy transfer [FRET]). Among many others in the field of photosynthesis, Govindjee and his coworkers also took the challenge to study the absorption of light, excitation energy transfer, primary photochemistry and electron transport contributing immensely to the concept we now have in the literature; in particular, we mention his work on temperature dependence down to liquid helium temperature (4K), where Förster theory was supported for energy transfer from phycobilins (and Chl *b*) to Chl *a* (see e.g. Cho and Govindjee, 1970a, 1970b, for background and summary of the primary events of the overall process, see the Scientific American article by Govindjee and Govindjee, 1974).

During 1970–2000, research in Govindjee’s laboratory led to the development of knowledge on both the primary charge separation, as well as electron transfer in the Z-scheme, which was hitherto not fully understood. After his retirement in 1999, Govindjee, in collaboration with his many coworkers, from other labs across the globe (see https://www.life.illinois.edu/govindjee/recent_papers.html), has summed up this field in a number of informative book chapters and reviews (for historical development on charge separation and excitation energy transfer, see Clegg *et al.*, 2010; Ostroumov *et al.*, 2014).

Govindjee's experimental findings, as well as those of many others, have shown that the primary photosynthetic processes must be extremely fast since the excitation energy transfer must be faster than the rate at which the excited state of Chl decays via fluorescence or non-radioactive decay, in order for the excitation energy to reach the RC, rather than be lost. Govindjee and his group and those of others he actively collaborates with, through their experiments, have explained the photophysical principles by which excitation energy is absorbed by photopigments and have described mechanisms of electronic excitation energy transfer, as well as optical properties of the various light-harvesting antenna complexes (Clegg *et al.*, 2010; Govindjee and Govindjee, 1974; Kiang *et al.*, 2007; Mirkovic *et al.*, 2017). The energy transfer occurs through pigment-pigment/pigment–protein interactions. Along with other aspects of light absorption and energy transfer, publications by Govindjee provide an overview of the excitation energy pathways in the light-harvesting antennas of different photosynthetic organisms (Cho and Govindjee, 1970a, 1970b; Ghosh and Govindjee, 1966; Govindjee and Govindjee, 1974; also see Mirkovic *et al.*, 2017). Such findings were the basis of incorporating a well-coordinated antenna complex that Govindjee made in their scheme of 1975 (Govindjee and Govindjee, 1975).

The late George Papageorgiou (see Prásil *et al.*, 2022), while working for PhD in Govindjee's Lab, contributed much in the early stages of Chl fluorescence induction research (Papageorgiou and Govindjee, 1967, 1968a, 1968b). The phenomenon of Chl *a fluorescence induction*, also called *fluorescence transient*, begins with a fast (~0.3 s) fluorescence rise (OJIP) followed by a slow (~300 s) decrease (PSMT) and is based on the basic early observation by Kautsky and Hirsch (1931; see Govindjee, 1995). Many subsequent research publications by Govindjee and his group provided detailed explanations for the polyphasic fluorescence rise and could couple this with the mechanism of charge separation and electron transport. It is generally accepted that the variable Chl fluorescence (the difference between F_0, the fluorescence minimum and F_M, the fluorescence maximum) is mostly from Chl *a* in PS II, whereas the contribution from Chls of PS I is rather negligible (see e.g. Wientjes and Croce, 2012).

THE PIONEERING RESEARCH ON THE ROLE OF BICARBONATE IN PS II

Since 1973, Govindjee and his co-workers have been heavily involved in the study of the effect of bicarbonate on the function of PS II and on the transfer of electrons beyond Q_A (Blubaugh and Govindjee, 1986; Eaton-Rye and Govindjee, 1984, 1988a, 1988b; Govindjee and van Rensen, 1978, 1993; Govindjee *et al.*, 1997; Stemler and Govindjee, 1973; Stemler *et al.*, 1974; Xiong *et al.*, 1998). Wydrzynski and Govindjee (1975; also see Shevela *et al.*, 2012) showed that in the absence of bicarbonate, the PS II behaved like being inhibited by the herbicide dichlorophenyl dimethyl urea (DCMU), that is, more or less complete blockage of electron flow beyond Q_A. In many subsequent papers, Govindjee (with his research team) has substantiated the role of HCO_3^- in regulating electron transfer in PS II, particularly on its electron acceptor side (Eaton-Rye and Govindjee, 1988a, 1988b; Govindjee *et al.*, 1976; Khanna *et al.*, 1977, 1980, 1981). In addition, Govindjee exploited thermoluminescence measurements on leaves, obtaining firm evidence that HCO_3^- (*in vivo*) facilitates Q_A^- to Q_B electron transfer (Garab *et al.*, 1988). Known for his insight into the mechanism of delayed light emission (or delayed fluorescence) and thermoluminescence, Govindjee's thought of using thermoluminescence, based on the early afterglow experimental findings of William Arnold (Arnold and Sherwood, 1957). Here, we mention a finding of Govindjee, with his student Ted Mar (Mar and Govindjee, 1971), where they discovered that pre-illuminated spinach chloroplasts and *Chlorella pyrenoidosa*, when given a quick temperature jump of about 15 °C, emitted light on treatment with the herbicide 'diuron', as well as by other means (including the absence of bicarbonate) that blocked PS II – PS I electron transfer, and that this effect was absent on treatment with hydroxylamine, that blocked electron transport on the (electron) donor side of PS II. All of the above showed that 'bicarbonate' functions on the electron acceptor side of PS II. Further, subsequent theoretical research by Govindjee and coworkers (DeVault and Govindjee, 1990; DeVault *et al.*, 1983) corrected the then basic theory of thermoluminiscence since the experimental results of Tatake *et al.* (1981) did not fit with the available theory. Govindjee's passion for understanding and application of thermoluminescence became evident when he approached Don DeVault (co-discoverer of electron tunnelling in biology) to help him write the appropriate equations and theory, using the detailed scheme of PS II reactions that he presented to him. By postulating temperature dependent equilibria between two or more electron carriers in PS II, that act as traps for electrons (or holes), they modified and extended the existing theory and explained not only the abnormally large activation energies that Tatake *et al.* (1981) had found, but the abnormal frequency factors involved. This led to the correct theory of thermoluminescence from plants (see DeVault and Govindjee, 1990; DeVault *et al.,* 1983).

The hypothesis is that bicarbonate, which is bound on the non-heme iron between Q_A and Q_B, plays an essential role in providing protons to stabilise the reduced Q_B (see: Shevela *et al.*, 2012; Umena *et al.*, 2011). Govindjee has continued his research in this field even after his retirement although he was (and is) unable to perform wet lab experiments in his own laboratory. We emphasise that Govindjee has always been active in motivating many research groups to continue investigations on the role of bicarbonate in PS II. His constant reminder *'do not forget about bicarbonate'* has been heard by many and, thus, active research on this topic has continued in other labs around the world (Ananyev *et al.*, 2018; Banerjee *et al.*, 2019; Brinkert *et al.*, 2016; Forsman and Eaton-Rye, 2020; Forsman *et al.*, 2019, 2020; Koroidov *et al.*, 2014; Rose *et al.*, 2008; Shevela *et al.*, 2007, 2012; van Rensen and Klimov, 2005). On the other hand, Govindjee has continued his own contributions to the bicarbonate field with historical reviews, which contain his current thoughts about the key regulatory role of bicarbonate in oxygenic photosynthesis and in the evolutionary development of O_2-evolving PS II (Govindjee and Shevela, 2011; Shevela *et al.*, 2012, 2021). Interestingly, Govindjee saw to it that the HCO_3^- ion on the electron-acceptor side on PS II became a firm part of all the latest Z-Scheme versions. This HCO_3^- has been shown to be the instant H^+ donor for the protonation of the reduced Q_B and to accelerate the electron transfer from the reduced Q_A to Q_B (Shevela *et al.*, 2012). Brinkert *et al.* (2016) reported that the light-induced formation of reduced Q_A results in a significant weakening of HCO_3^- binding, thus creating a higher chance to lose HCO_3^-, more specifically at low ambient HCO_3^-concentration. This finding confirmed the earlier observations of Shevela *et al.* (2012) suggesting that the absence of bicarbonate might down-regulate the electron transfer between Q_A and Q_B and the Q_BH_2 exchange with the PQ pool.

The other important contribution, which was hitherto not known to the researchers working on the light reaction of photosynthesis is the importance and involvement of HCO_3^- on the electron donor side of PS II, as studied by Alan Stemler, one of Govindjee's former graduate students (Stemler, 1979, 2002; Stemler and Radmer, 1975). Further, we refer to papers, by many others, on the role of bicarbonate on the electron donor (water) side of PS II (Ananyev *et al.*, 2018; Koroidov *et al.*, 2014; Shevela *et al.*, 2013a, 2013b, 2016; Shutova *et al.*, 2008). Govindjee and his research group (and many others) have suggested that easily exchangeable HCO_3^- ions may stimulate water oxidation by mediating the shuttle of protons, produced during water-splitting, into the thylakoid lumen (van Rensen *et al.*, 1999; also see: Banerjee *et al.*, 2019; Koroidov *et al.*, 2014; Shevela *et al.*, 2012, 2021; Shutova *et al.*, 2008; Villarejo *et al.*, 2002). However, none of these implies that bicarbonate acts as a substrate for oxygen evolution (see e.g. Clausen *et al.*, 2005; Hillier *et al.*, 2006). However, it has a crucial—still to be discovered role—on the water oxidation side of PS II. Research on the role of Govindjee's favourite ion, HCO_3^-, continues in many labs, with the full intellectual participation of Govindjee.

Even today, he is discussing the possible mechanism for the role of bicarbonate on the electron donor side of PS II with Alan Stemler—and this via e-mail (Govindjee, personal communication).

EVOLUTION OF THE OF THE Z-SCHEME (ONLY GOVINDJEE'S VERSIONS ARE COVERED)

Through many of his publications and presentations, Govindjee has made a detailed historical account of the Z-scheme citing his own research contributions as well as those of others (Govindjee *et al.*, 2017). He has stated (and told us personally) that his PhD advisor, Eugene Rabinowitch, is the real pioneer in bringing out the concept of the Z-scheme (Rabinowitch, 1945; Figure 1), although not in the form that Hill and Bendall (1960) made it (Figure 2). There have been bits and pieces of key ideas for a simple two-light reaction 'Z-scheme' in Rabinowitch's writings. Rabinowitch (1956) wrote (as pointed to us by Govindjee):

> The quantum requirement of the hydrogen transfer reaction as a whole would be (at least) 8, since two quanta will be needed to transfer each of the four required H atoms (or electrons), first from water to the cytochrome, and then from the cytochrome to the final acceptor.

In the scheme in Rabinowitch (1945), oxidation of an unknown intermediate HZ to Z corresponds to today's oxidation of an electron donor(s) of PS II and of HY to Y would correspond to today's oxidation of electron donor(s) of PS I. In 1956, however, Rabinowitch implied, as pointed to us by Govindjee, that a Cyt might be the Y, the electron carrier, mentioned above (Rabinowitch, 1956). Many key experiments that followed, in which Govindjee was involved (e.g. the two light effects and the maximum quantum yield) must have contributed, without being specifically stated, to the conceptual origin of the Z-scheme of Hill and Bendall (e.g. discussions at the early 1960 'Light and Life' symposium, where Robert (Robin) Hill was present and did not present the Hill and Bendall scheme, but Govindjee's work (Govindjee and Rabinowitch, 1960)was presented by Rabinowitch (Rabinowitch and Govindjee 1961; for further discussion, see Govindjee *et al.*, 2003). Hill (1965) himself acknowledged that the concept of two PSs was known to him from the findings of Robert Emerson (see Rabinowitch, 1961 for Emerson's contributions). The theoretical Z-scheme was based on two thermodynamic arguments: (1) The two cytochromes (Cyt*b* and Cyt*f*) must be located between H_2O and CO_2 (we now know that Cyt b is not involved)

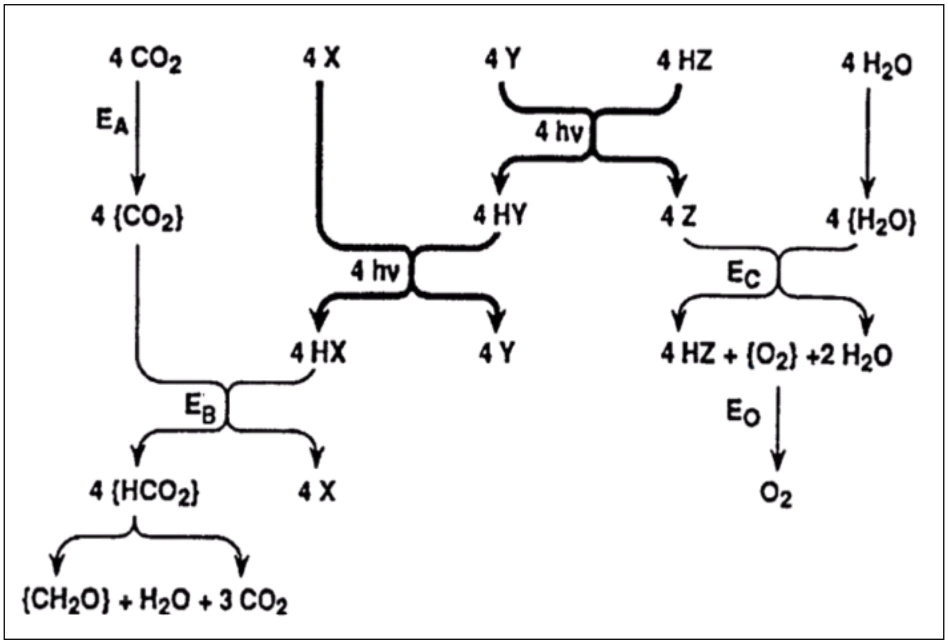


Figure 1: The Pioneering Two-photoact Scheme of Photosynthesis Published by Eugene Rabinowitch (Rabinowitch, 1945; also see Govindjee and Björn, 2012). This scheme explains the quantum requirement of the hydrogen (electron) transfer reaction, with two light reactions, but does not demonstrate the existence of two PSs

and (2) Energy for ATP synthesis could be available from the downhill transfer of electrons from Cyt*b* to Cyt*f*. Though there were errors with regard to the position of some of the components in the Hill and Bendall scheme, it was no doubt the first of its kind to explain the oxidation of water by PS II and the reduction of NADP$^+$ by PSI. The Z-scheme also could satisfactorily explain the quantum requirement of 8–12 for O_2 evolution (see above for discussion).

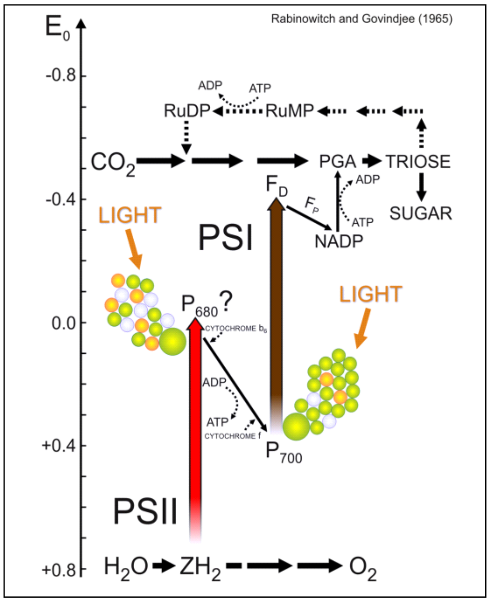


Figure 3: A 1965 Scheme of Two Light Reactions and Two PSs of Rabinowitch and Govindjee. This scheme, for the first time, included the light harvesting pigments (though at a 'Wrong' place for PS II). It also integrated water splitting with CO_2 fixation (Calvin–Benson) cycle. This Scheme Removed the Conceptual 'Flaw' of Hill and Bendall (1960) scheme (Figure 2) (water/oxygen system at the top, rather than the other way around) (reproduced without modification from Rabinowitch and Govindjee, 1965)

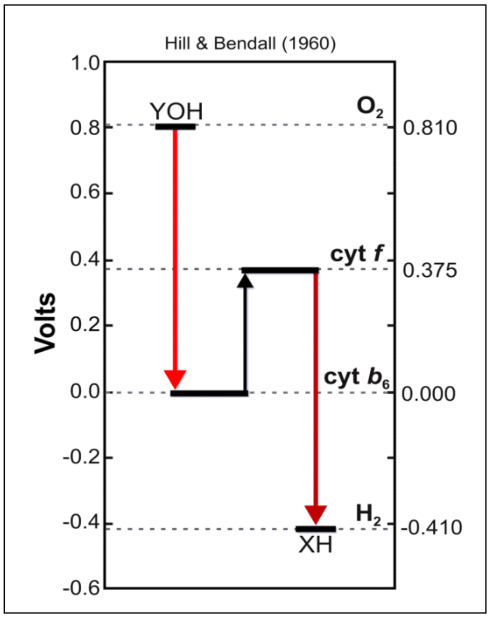


Figure 2: The Z-scheme (with Two Light Reactions) of Hill and Bendall (1960) (Original Source: Hill and Bendall, 1960). Y is Equivalent to the Y of Figure 1 (PS II); X is Equivalent to the X of Figure 1 (PS I). (Reprinted from Govindjee *et al.*, 2017)

The original two-light reaction scheme of Hill and Bendall (1960) placed the water/oxygen system at the top, rather than the other way around. In the light reaction related to the current PS II, a reductant 'Y' reduces oxidised Cytb_6 becoming YOH and in the other, Cyt*f* reduces an intermediate 'X' to 'XH' (Figure 2). The apparent conceptual 'flaw' of the top as the 'low energy' was removed in the scheme of Rabinowitch and Govindjee (1965) (Figure 3), in which water/oxygen was placed at the lowest energy level and electron flow was presented as an uphill reaction, using light energy. However, these authors placed the pigment complex of PS II closer to Cytb_6, which was energetically at the same level as the excited P680. Later, Govindjee and Govindjee (1975) made a horizontal presentation of the Z-scheme. The terms 'cyclic and non-cyclic' were introduced to the scheme by the authors, as it was known to exist from the research of the others. In this scheme, the flow of electrons from H_2O to NADP$^+$ was designated as 'non-cyclic'; from the PS I to PQ or plastocyanin (PC) intersystem intermediates as 'cyclic I'; and a similar PS II limited electron flow as 'cyclic II' (Figure 4). Here, the PS II light-harvesting pigment complex was placed in the right place. Although P700 and P680 were appropriately placed in the scheme, there was no mention of P680* and pheophytin, but a quencher of PS II fluorescence 'Q' (based on the ideas of Louis N.M. Duysens) was taken as the first electron acceptor (Govindjee, Personal Communication). Govindjee also included the ferredoxin-reducing substance (FRS) considering the data of various investigators but did not elaborate further as there were too many to mention, he

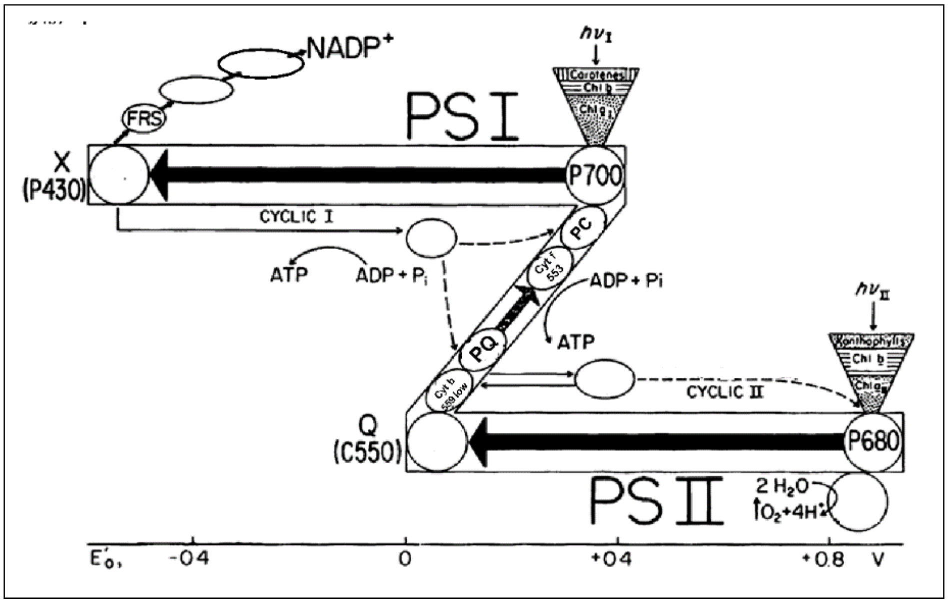


Figure 4: The First Ever Horizontal Z-scheme of Govindjee and Govindjee (1975). In this scheme, antenna pigment complexes are placed in the right positions and they included a large number of known intersystem components. FRS was not elaborated on as they were too many (as told by Govindjee). (Reproduced without modification, except type setting of some intersystem components, from Govindjee and Govindjee, 1975)

told us. This scheme subsequently was the skeleton for later improvement with the inclusion of research findings of Govindjee and many other researchers.

In 1978, Govindjee and Jack van Rensen published the bicarbonate effect on the electron flow in isolated broken chloroplasts and in this publication, they modified the 1975 Z-scheme by including CO_2 (HCO_3^-) (Govindjee and van Rensen, 1978; Figure 5). They also separated the antenna and RC Chls to present the idea that energy in all the antenna pigments, after light absorption, is ultimately transferred to the few RCs. However, in this scheme, there was still no mention of pheophytin as an intersystem intermediate even though the discovery of pheophytin function as one of the 'primary' electron acceptors of PS II was known (Klimov *et al.*, 1997; see a review by Mamedov *et al.*, 2015). Later, Govindjee (2018) mentioned that the scheme by Blankenship and Prince (1985) had correctly included P680, P680*, P700 and P700* as participants in the electron flow and had discussed why excited singlet state potentials of the Chls should be included. Thus, Demeter and Govindjee (1989) presented a detailed scheme in the form of 'Z', which was based partly on the horizontal scheme of Govindjee and Govindjee (1975) (Figure 6). Here, the electron carriers were placed horizontally according to their midpoint redox potentials at pH 7.0 (E_m 7). To read this scheme, we begin by initiating the electron flow when a photon (or exciton) reaches the RC P680 (in PS II) and P700 (in PS I) to form P680* and

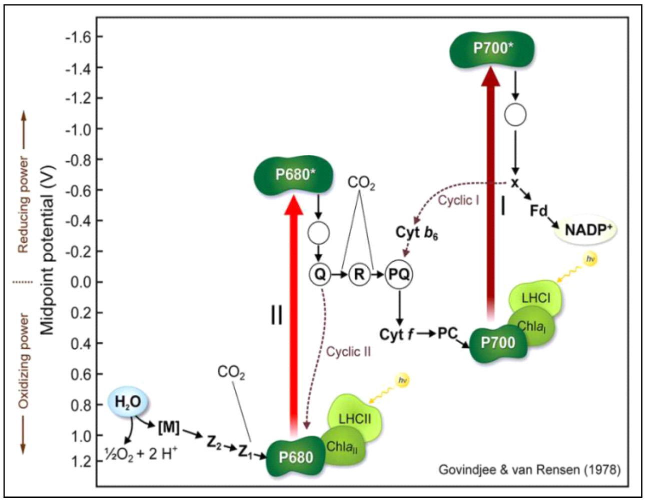
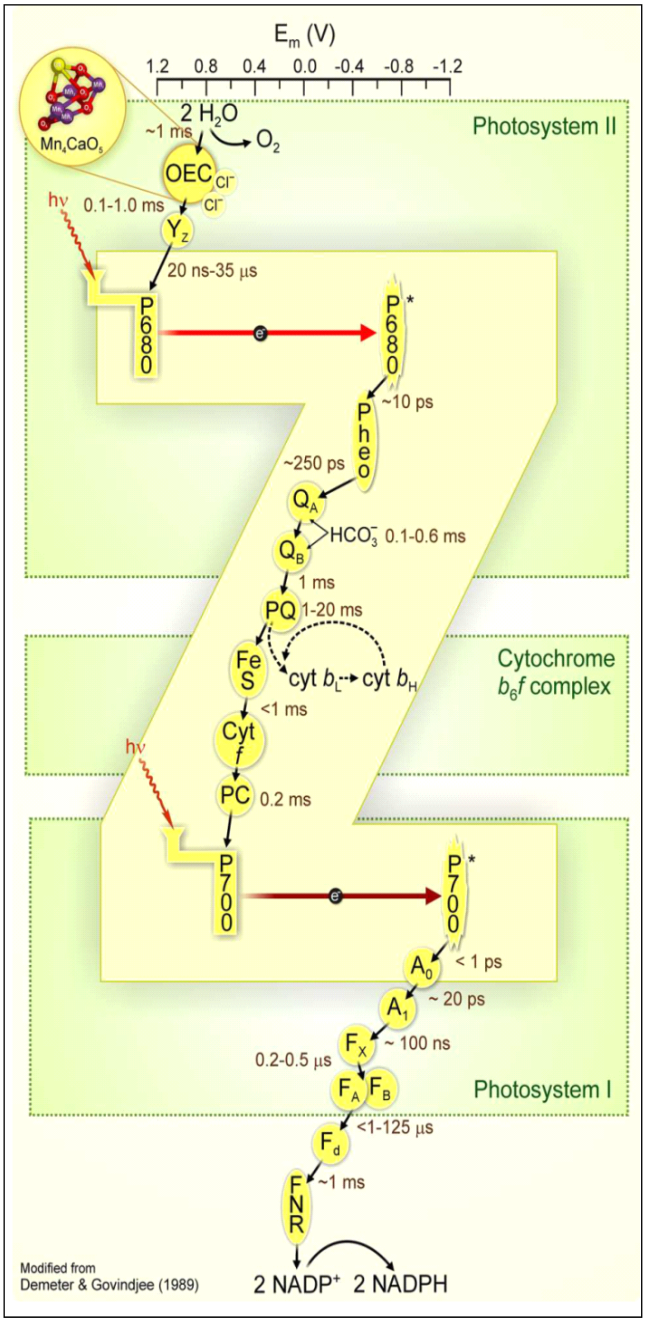


Figure 5: A Simplified and Coloured Version of Z-scheme from Govindjee and van Rensen (1978). This scheme shows the position of the RC Chl *a* of both systems (P680 and P700) between the antenna complexes and the photoreactions; it also includes the excited states of the RC Chls (P680* and P700*). The colours of the arrow in the uphill direction correspond to the wavelength of the absorbed light (red for P680 and deep red for P700). This scheme also, for the first time, included CO_2 (bicarbonate) between the quinones indicating its role on the electron acceptor side of PS II- the PQ side (reproduced from Govindjee and van Rensen, 1978; for details, see the discussion in the text, as well as the legend of Figure 1 in Govindjee and van Rensen, 1978)

P700*, respectively. The first reaction is the charge separation from (or 'in') P680* (formation of the cation $P680^+$ and the anion $Pheo^-$ within ~10 ps and from (or in) P700* (formation of $P700^+$ and A_0^- in <1 ps). The $P680^+$ recovers an electron from Y_Z, tyrosine-161, of the D1 polypeptide of PS II. The positive charge on Y_Z (thus, formed) is then transferred to the charge accumulator Mn_4CaO_5 cluster or the oxygen-evolving complex (OEC). Four positive charges must accumulate sequentially before an O_2 molecule is evolved (see e.g. Govindjee and Coleman, 1990). The $Pheo^-$ delivers the 'extra' electron to a primary (PQ) electron acceptor, Q_A; then, the Q_A^- transfers its electron to a secondary (PQ) electron acceptor Q_B-located on the D1 polypeptide of PS II. After two light reactions, there is a reduction to Q_B (H_2), a plastoquinol, which then exchanges with a mobile PQ molecule. Bicarbonate ions (HCO_3^-) are now known to be involved here (mainly because of the work of Govindjee and many others) and to function in the Q_A-Fe-Q_B region, where Fe is a non-heme iron atom between the two bound PQs (Q_A and Q_B), It is this function of bicarbonate that Govindjee and his many PhD students are known for (Govindjee *et al.*, 1997). Plastoquinol (PQH_2) delivers one electron to the Rieske iron-sulfur protein (FeS) and the other to a Cytb_L. The electron on reduced FeS reduces Cyt*f* and the one on Cyt$b_L$is transferred to Cytb_H, returning back in a cyclic process (called the Q-cycle). Reduced Cyt*f* delivers its extra electron to a copper protein, PC, which delivers the electron to $P700^+$ (produced in the primary PSI reaction). On the other hand, A_0 passes its electron to A_1 (a phylloquinone molecule).

This scheme of Govindjee is highly elaborate and included much new information as well as a much more detailed representation of the intersystem intermediates. There is a mention of the oxygen-evolving complex (OEC; Mn_4CaO_5) and chloride (Cl^-) on the (electron) donor side of PS II. Govindjee has explained the function of chloride ions on the electron donor side of PS II in other publications (Coleman and Govindjee, 1987; Critchley *et al.*, 1982). We know that bicarbonate is also known to have effects on the water-oxidising



Modified from Demeter & Govindjee (1989)

Figure 6: A Horizontal Z-scheme with Electron Carriers placed according to their Mid-point Redox Potentials at pH 7.0 (E_m 7). Compared to all the previously published models, this scheme is probably the most elaborate and descriptive one with (a) demarcation of the three complexes—PS II, Cyt b_6f and PS I; (b) inclusion of measured or estimated times of electron transfer between any two intersystem components; and (c) presentation of Cl^- alongside OEC. For full form of abbreviations used, see the description in the text. (Reproduced with modification from Demeter and Govindjee, 1989)

side of PS II (see e.g. Stemler *et al.*, 1974); unbound bicarbonate ions, on this side, may act as proton acceptors (Ananyev *et al.*, 2018; Koroidov *et al.*, 2014; Shevela *et al.*, 2013a, 2013b, 2016; Shutova *et al.*, 2008) or participate in the photoassembly of the OEC (Allakhverdiev *et al.*, 1997, Baranov *et al.*, 2004; Dasgupta *et al.*, 2008) or stabilise the water-oxidising complex (Klimov, 2003; Klimov *et al.*, 1997), but not to act as a substrate for oxygen evolution (see e.g. Clausen *et al.*, 2005; Hillier *et al.*, 2006). However, currently, the mechanism of bicarbonate function on the electron donor side of PS II is being extensively debated by many investigators. We shall refrain from discussing it here.

By measuring thermoluminescence (see above), Critchley *et al.* (1982) concluded that Cl^- depletion inhibited S2–S3 transition (of the Oxygen Evolving Complex, OEC) and the addition of Cl^- restored the function of the electron donor side of PS II. Replacement of chloride by various anions (Br^-, NO_3^-, I^-) had a significant negative effect on O_2 evolution. Thus, Cl^- has been suggested to stabilise the oxygen-evolving complex, adjusting its redox properties and/or participating in the deprotonation of water. Govindjee, in collaboration with William Rutherford, used thermoluminiscence to investigate the deactivation of the S states for the analysis of the positive charge accumulation by OEC (Rutherford *et al.*, 1984a, 1984b). Govindjee *et al.* (1985) continued this research with thermophilic cyanobacterium *Synechocystis vulcanus* and rightfully, suggested that the stability of S states is much more in the thermophilic organisms than in the chloroplasts of other plants and algae.

As mentioned above, the scheme of Demeter and Govindjee (1989) had much more detailed information, than included earlier; here, we have the estimated times of electron transport except for that needed for the formation of P680* and P700* that occur in femtosecond time scale. The electron carriers on the electron acceptor side of PS I, that is, F_X, F_A and F_B (iron-sulfur clusters), Fd (ferredoxin) and FNR (Ferredoxin-NADP+ Reductase), are all included in this scheme. The bottleneck reaction was noted to be of the order of 5 ms, which is for the total time involved in the exchange of $Q_B(H_2)$ with PQ and the diffusion of PQH_2 to the Cyt*b6f* complex, as well as the reoxidation time of PQH_2. Of course, these are general estimates and need not be taken too literally.

For a general reader, a simpler scheme was needed. Thus, Govindjee and Veit (2010) developed the most explanatory simplest Z-scheme of photosynthesis that made the best presentation of the antenna and the FQR-PQ cyclic electron flow (Figure 7). [We note that Dr Wilbert Veit, Govindjee's coauthor, is a dentist by profession.] Furthermore, in 2016, Shevela and Govindjee (2016) produced a detailed poster on oxygenic photosynthesis (available free: at http://www.life.illinois.edu/govindjee/Electronic%20Publications/2016_Postershevela_Govindjee.pdf; for a collage of posters developed by Govindjee and his coworkers (see Stirbet *et al.*, 2020a, 2020b). This poster includes the oxygen-evolving manganese clock; the ATP synthesis clock; the two-electron gate for PQ reduction; and the carbon reduction cycle (the Calvin–Benson–Bassham cycle; see Benson, 2002). However, further development of the scheme by Govindjee and his coworkers (his team of friends; see Shevela *et al.*, 2018) is now available with the structures of all the components (the RC Chl, the OEC and the intersystem intermediates of the electron transport chain; Figure 8). In this scheme, Govindjee

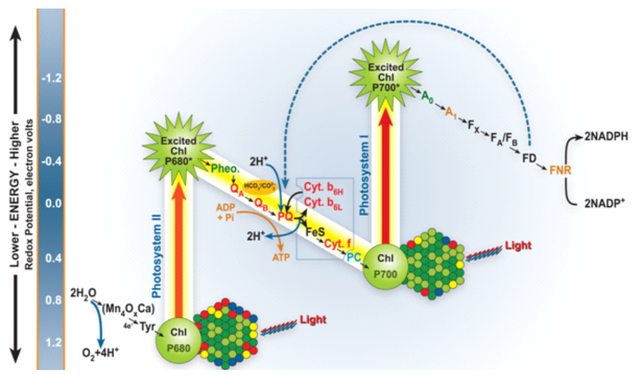


Figure 7: The Most Popular and Simplified Z-scheme of Photosynthesis (Reproduced from Govindjee and Veit, 2010; also Available at http://www.life.illinois.edu/govindjee/page3.html; http://www.life.illinois.edu/govindjee/textzsch.htm; http://www.moleculardventures.net/)

and coworkers have integrated the electron transport pathways with the location of the photosynthetic thylakoid membrane in higher plants, algae and cyanobacteria; further, here, the schematic view of photosynthetic protein complexes are embedded in the thylakoid membrane (see Figure 1 in Shevela *et al.*, 2021).

TEACHING THE Z-SCHEME

In addition to Govindjee's extensive research achievements, he has whole-heartedly dedicated himself to teaching the students and researchers about photosynthesis through his own unique styles, such as the use of analogies (students acting as molecules; Jaiswal *et al.*, 2017; Mohapatra and Singh, 2015); use of the internet (Orr and Govindjee, 2013); and use of well-written reviews published in journals, books and encyclopedias. He has also spread the knowledge of the Z-scheme through his own (as well as by others) educational articles (Govindjee and Björn, 2012; Govindjee *et al.*, 2017; Mohapatra and Singh, 2015) and posters (Figure 9). He discusses, in his lectures, each and every aspect of the historical controversy on oxygenic photosynthesis (Shevela *et al.*, 2013a, 2013b), a minimum quantum requirement for oxygen evolution (Hill and Govindjee, 2014; Nickelsen and Govindjee, 2011), natural and artificial water oxidation (Najafpour and Govindjee, 2011; Najafpour *et al.*, 2012, 2013a, 2013b) and even on why Emerson said what he said; recently, he has even re-published, with a detailed prologue, the lecture of Emerson and Chalmers (1958); see Govindjee (2022).

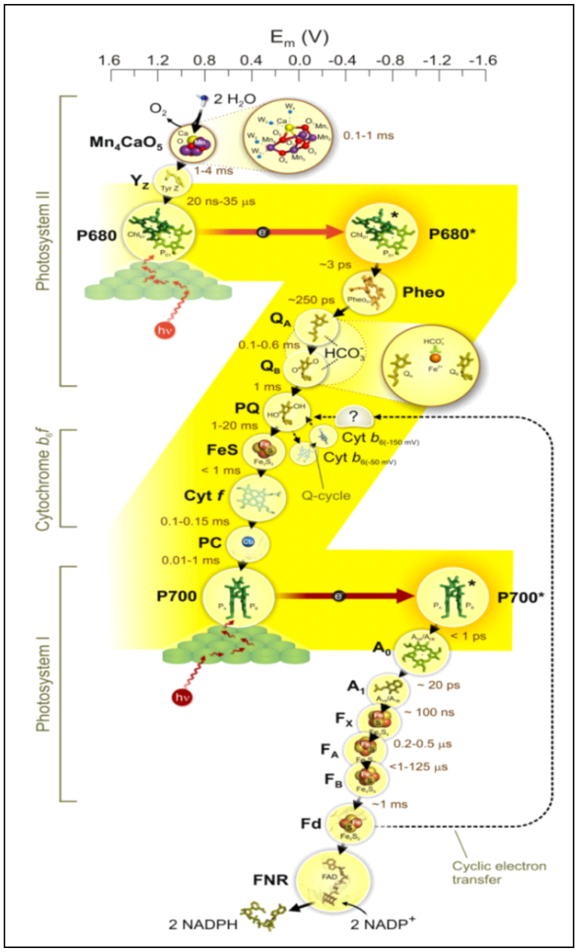


Figure 8: The Horizontal Z-scheme of Photosynthesis of Shevela *et al.* (2018). The scheme includes the cartoon structures of the PSs and all the intersystem components. The colours of arrows of uphill reactions correspond to the wavelength of light absorbed. Also seen is the position of bicarbonate between Q_A and Q_B (Reproduced from Shevela *et al.*, 2021)

Govindjee has a unique style of teaching the Z-scheme to students by presenting this complex process in a dramatised way. He has taught the Z-Scheme to his undergraduate students at the UIUC, at the University of Indore, Madhya Pradesh (where the students had enacted a drama on a stage inside an auditorium, with music and dances); in Finland at a workshop, in the Department of Botany, Ravenshaw University, Cuttack, Odisha (Mohapatra and Singh, 2015; Figure 10), at Jawaharlal Nehru University (JNU), New Delhi (Jaiswal *et al.*, 2017) and at several other places across the globe through the active participation of students and faculty. His unique style of dramatising the Z-scheme and representing each component that is directly and indirectly involved in the photon-driven electron transport has created a strong (and deep) impression in the minds of young graduate students around the World and has increased their interest in 'Photosynthesis' and what we can do to enhance plant productivity. The various versions of his Z-scheme drama have been performed, for example, in the lab (at the UIUC), under open-air tents (University of Indore, Indore), in a classroom (JNU, New Delhi) and in an outdoor garden (Ravenshaw

Figure 9: (A) Govindjee Presented with a Z-scheme Cake on the Occasion of His 60 Years at the UIUC; from Left to Right Fan Zhu, Govindjee, Rayme Ackerman and Mike Urban. (B) Govindjee Signing the Z-scheme Posters in India. (C) Govindjee with the Poster of the Z-scheme; From Left: Samantha B. Primer, Govindjee and Robert V. Buren with the 2010 Z-scheme Poster, in His Office at the UIUC. (D) Govindjee (Right) and Rajni Govindjee (Left) with Students Holding 2018 Z-Scheme Posters, in India. (Compiled from Govindjee's personal communication and from Eaton-Rye, 2013; for research of Rajni Govindjee in photobiology, see Balashov *et al.*, 2023)

University, Cuttack). Students have always enthusiastically volunteered to become the intermediates and played in the dramatised presentation of the mechanisms of the Z-scheme demonstrating the entire scheme from water oxidation (oxygen evolution) to NADPH and ATP production and sometimes to CO_2 fixation. On all occasions, Govindjee has personally prepared the script and monitored the presentation by the component (the student) before it is shown to the academic audience.

While organising the dramatised presentation, Govindjee has also been very meticulous in going through the script, acts of the component members of the scheme and the presentation of the processes during the drama. For example, two students, as a unit, perform the role of RC P680 symbolising that it is a dimer. Similarly, two students move as protons (H^+) to signify that two protons are needed by Q_B^{2-}during electron transport, to form Q_BH_2. These protons come from the stroma side and are ultimately transported into the thylakoid lumen, together with the so-called Q-cycle. Govindjee's drama has also included the associated processes for electron transport such as the Q-cycle, ATP synthesis and the role of bicarbonate in PS II. We recall the way Govindjee directed the herbicide DCMU to enter into the stage to inhibit the PS II activity (during demonstrations in Figure 10). Govindjee made sure that the voice and dress of the herbicide must look furious to inculcate in the minds of the students about the intensity of the inhibitory effect of DCMU on electron transport. With such an innovative approach, Govindjee ensures that the students do not easily forget this complicated pathway and understand the intricacies and complexity of electron transport as well as how herbicides inhibit this process.

We emphasise here that it is not only the Z-scheme he

Figure 10: Dramatisation of the Z-scheme of Photosynthesis by Govindjee. (A) Students and faculty engaged in the Z-scheme drama in the garden of the Department of Botany, Ravenshaw University, Cuttack, India; Govindjee (middle right) is seen explaining the topic; (B) Participants of the Z scheme drama from panel 'A'; Govindjee and Baishnab Tripathy are in the center of the group; (C) Govindjee, wearing Robert Emerson's lab apron (now in the Archives of the University of Illinois at Urbana-Champaign), participating in the Z scheme drama at School of Life Sciences (SLS), JNU, New Delhi, India; (D) Govindjee, wearing a red tie and acting as HCO_3^-, releasing a proton to a semiquinone (Q_B^-) in the Z scheme drama at SLS in JNU. (Compiled from Jaiswal *et al.*, 2017; Mohapatra and Singh, 2015)

Figure 11: (A) Govindjee demonstrates the splitting of two water molecules and release of one oxygen molecule. The red balloons represent two oxygen atoms and the white balloons represent four hydrogen atoms of two water molecules. (B) Govindjee with a volunteer Prakash Prasad in search of getting tonic water from a local store. (C) Govindjee demonstrated blue fluorescence from tonic water upon exposure to UV light; the 'show' was for higher secondary students (reproduced with modification from Mohapatra and Singh, 2015)

has taught, but he also shows the exciting power of Chl *a* fluorescence as a signature of photosynthesis; this was shown by Govindjee to the higher secondary school level students in a special lecture he was invited to give at Ravenshaw University (see Appendix I of Mohapatra and Singh, 2015; Figure 11). There was not only the lecture but also the practical demonstration of fluorescence to nearly 160 student participants and many teachers from different colleges in the state of Odisha, India. Most importantly, Govindjee made it possible for the students to see beautiful 'blue' fluorescence coming from tonic water and 'red' fluorescence from leaves and Chl solution under UV light without taking the help of any sophisticated equipment. Students were fascinated to see, through their naked eyes, the brilliant red colour of herbicide-treated *Chlorella* cells (the red Chl*a* fluorescence) under a UV lamp (shown before what he showed in Figure 11C).

While lecturing on fluorescence Govindjee mentions the origin of the concept of fluorescence and shows the 'celestial blue' light, from tonic water, under UV light. As expected from his committed approach he searched the city of Cuttack (India) to get the tonic water as a rider on the back seat of a motorbike, run by a student of our University (see Figure 11B). It was indeed a pleasure for all the students and the teachers of our University to have Govindjee with us once to give a course on 'Basics and Applications of Photosynthesis' for the benefit of all of us.

CONCLUSION

In this tribute to Govindjee's love for research and teaching, we have also mentioned scientific discoveries in the area of light absorption, excitation energy transfer, primary photochemistry, electron transport and related processes. We have presented our perspective as well as a perspective with regard to the conceptual evolution of the light reaction of photosynthesis from 1960 until recent times. With supporting experimental findings, we suggest that the early unique experiments on Emerson enhancement (in photosynthesis) and quenching of Chl a fluorescence of PS II by PS I light, as well as other two light effects studied, especially by Govindjee, were important parts of the basis for the evolution of the Z-scheme of Hill and Bendall (1960), as we know it now. Govindjee's research, as well as of others, showed that primary photochemical processes are very fast and excitation energy transfer occurs faster than the decay of Chl excited states. Experimental findings by Govindjee clearly strengthened Emerson's results and added that Chl *a* was in both PSs. Further, he proved that the Nobel laureate Otto Warburg was wrong not only on the minimum quantum requirement for oxygen evolution under his own stated experimental conditions, but on how bicarbonate (CO_2) functions in the 'light reactions' of photosynthesis; his work, with several graduate students, was the first of its kind to show that bicarbonate plays a vital role on the electron acceptor side of PS II involving electron transport and protonation.

The inclusion of the antenna pigment complex, the introduction of the 'cyclic' and 'non-cyclic' pathways, a greater number of intersystem intermediates, the position of the bicarbonate, chloride and other supporting components (ions) and the time kinetics of electron transport were added by him (and his colleagues) over the years to the Z-schemes he has been publishing-and distributing around the World. These were based on his original research as well as from the discoveries of many others. We also note that a really simple but reader-friendly Z-scheme of Govindjee (Govindjee and Veit, 2010) finds its place in many basic books, especially in teaching scenarios.

Govindjee's unique style of teaching Z-scheme to students through art and drama with active participation of students, researchers and teachers has created a strong impression in the minds of the students and seems to us that it is the best mode of teaching a complex process in a simpler way. Additionally, his demonstration of Chl fluorescence to students under UV light without using any sophisticated equipment shows that such methods need to be followed by others to teach complex subjects to students. We end this tribute to Govindjee, one of the major figures in teaching the basics and applications of oxygenic photosynthesis to the World at large, by extending our heartfelt congratulations for (1) receiving, together with Eva-Mari Aro (of Finland), the most prestigious Lifetime Achievement Award of the International Society of Photosynthesis Research at their 18th meeting, held in August 2022, in Dundein, New Zealand; and (2) being honoured at his 90th birthday at an International Conference in Plant Biology, held at the University of Calicut. Kerala, India, 26 October – 4 November 2022. We wish Govindjee Govindjee continued participation in teaching and research in Photosynthesis.

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