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Photosystem II fluorescence: Slow changes – Scaling from the past ☆

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ABSTRACT

With the advent of photoelectric devices (photocells, photomultipliers) in the 1930s, fluorometry of chlorophyll (Chl) *a in vivo* emerged as a major method in the science of photosynthesis. Early researchers employed fluorometry primarily for two tasks: to elucidate the role in photosynthesis, if any, of other plant pigments, such as Chl *b*, Chl *c*, carotenoids and phycobilins; and to use it as a convenient inverse measure of photosynthetic activity. In pursuing the latter task, it became apparent that Chl *a* fluorescence emission is influenced (i) by redox active Chl *a* molecules in the reaction center of photosystem (PS) II (*photochemical quenching*); (ii) by an electrochemical imbalance across the thylakoid membrane (*high energy quenching*); and (iii) by the size of the peripheral antennae of weakly fluorescent PSI and strongly fluorescent PSII in response to changes in the ambient light (*state transitions*).

In this perspective we trace the historical evolution of our awareness of these concepts, particularly of the so-called 'State Transitions'.

"Every so often someone manages to remove another stone from the wall through which we all want to see, and the crowds tend to flock around the new peep-hole" (B. Kok and A. Jagendorf, 1963).

1. Introduction

Chlorophyll *a* (Chl *a*) is the chosen molecule for oxygenic photosynthesis, and is functionally the most versatile one [1]. Chls *a* are involved in photon harvesting, in the transfer of excitation energy (EE), in photochemical trapping, as well as in ground state electron transfers. Through its characteristic absorption and fluorescence properties in the 400–750 nm part of the electromagnetic spectrum, Chl *a* becomes "visible" in the protein complexes of Photosystem I (PSI) and of Photosystem II (PSII) as well as in its various functional roles.

The present *Historical Perspective* focuses primarily on the fluorescence which Chl *a in vivo* emits and traces the historical evolution of our awareness of its role in the molecular mechanism of oxygenic photosynthesis, with emphasis up to about the late 1970s. As soon as a solution of Chl *a*, a plant leaf, an alga, or a cyanobacterium is moved from darkness to light, they start emitting Chl *a* fluorescence. However, while the solution emits constant fluorescence under steady excitation, the intensity of fluorescence emitted by the photosynthetic organisms changes with time continuously (*variable fluorescence*), tracing characteristic time patterns that are typical of the major taxonomic groups of oxygenic photosynthesizers (e.g., cyanobacteria, green algae, red algae, vascular plants). These Chl *a* fluorescence time patterns, known also as *fluorescence induction*, consist of two transients (or waves), a fast one (μs to s; symbolized as OJIPS [2–9] and a slower one (seconds to tens of minutes); symbolized as SMT [10–13]). For background and explanation of these transients, see reviews [14–20]. Fig. 1 shows characteristic fast (OJIPS) and slow (SMT) fluorescence induction patterns recorded with a plant leaf (*Phaseolus vulgaris*), suspensions of a green alga (*Chlamydomonas reinhardtii*), a phycobilisome (PBS) – containing cyanoabacterium (*Synechocystis* sp.) and a PBS-minus cyanobacterium (*Acaryochloris marina*). Here, O stands for "*origine*" or initial fluorescence, J and I for intermediate levels, P for peak, S for semi-steady state, M for maximum, and T for terminal steady state; occasionally, there is an inflection denoted as D (for dip).

☆ We honor Louis Nicole Marie Duysens through this review, and we dedicate this historical perspective to the memory of several who studied chlorophyll fluorescence and with whom we have associated. They are (in alphabetical order): Jean-Marie Briantais (1936–2004); Steve Brody (1927–2010); Warren Butler (1925–1986); Ashish Ghosh (1937–2011); Elizabeth Gross (1940–2007); C. Stacy French (1907–1995); Jack Myers (1913–2006); Eugene Rabinowitch (1898–1973); Gauri Singhal (1933–2004); and Laszlo Szalay (1920–1997). Above all, we recognize and celebrate the 1931 discovery of the fluorescence transient by Hans Kautsky with his own eyes (see Govindjee, Sixty-three years since Kautsky: Chlorophyll *a* fluorescence, Aust. J. Plant Physiol. 22 (1995) 131–160.).

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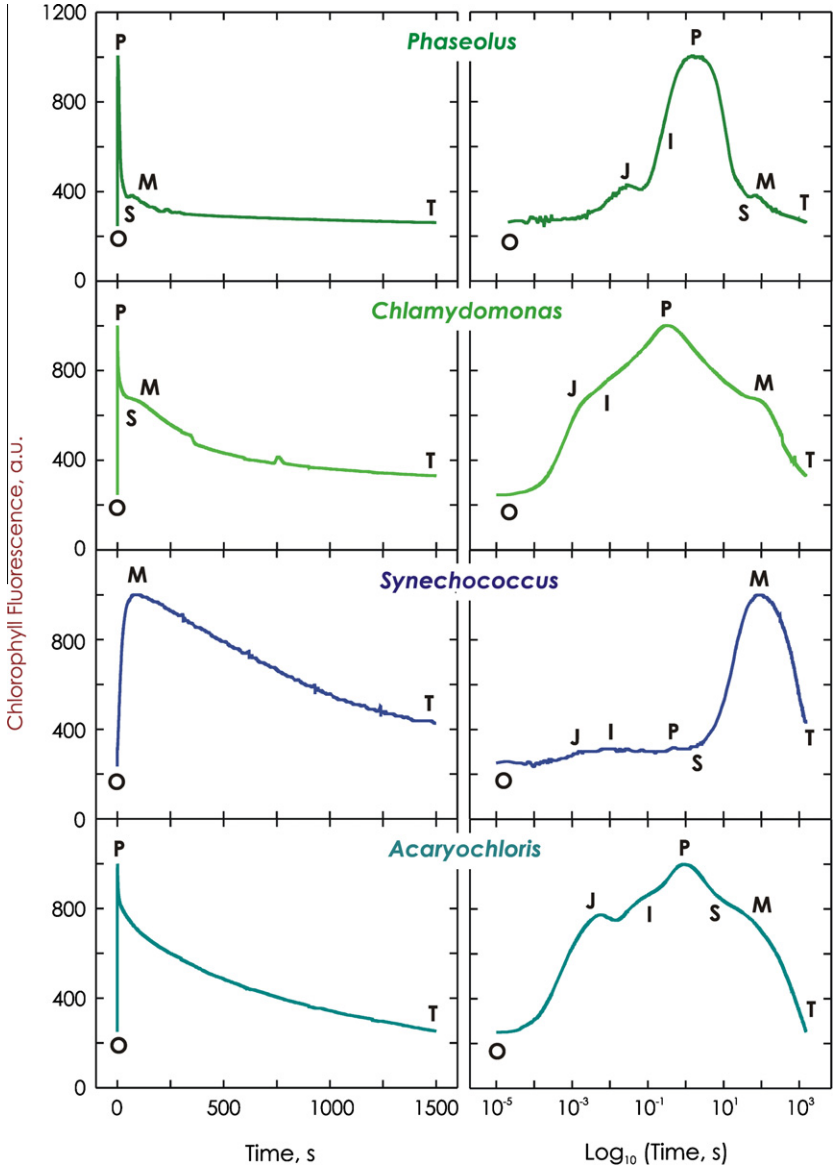

Fig. 1. Chlorophyll *a* fluorescence induction traces recorded with a higher plant (*Phaseolus vulgaris*) leaf, a green alga (*Chlamydomonas reinhardtii*), a phycobilisome (PBS)/Chl a-containing cyanobacterium (*Synechococcus* sp PCC 7942), and with a *phycobiliprotein*/Chl *d*/Chl *a* – containing cyanobacterium that has phycocyanin/allophycocyanin rods attached to the cytoplasmic side of the thylakoid membrane but no PBS (*Acaryochloris marina*). Fluorescence data on the left panels are plotted against linear time scales and on the right against logarithmic time scales. All curves were recorded with the Handy PEA fluorometer of Hansatech Instruments, Ltd. (UK). Samples were preadapted to darkness for 20 min before measurements. Fluorescence excitation, $\lambda = 650$ nm, $\Delta\lambda = 22$ nm; fluorescence detection through an RG9 long pass glass filter (transmittance: starting at ~690 nm; 50% at ~725 nm; and maximal at ~780 nm; Schott Glass Technologies, Inc, USA). Excitation intensities in μmol photons m^{-2} s^{-1}: *P. vulgaris*, 50; *C. reinhardtii*, *Synechococcus* sp. PCC 7942 and *A. marina*, 1500. See text for explanation of the symbols (OJIPSMT) used; a.u. stands for arbitrary units. Reproduced from Papageorgiou et al. (2007); the figure used here was produced by Dmitry Shevela.

2. Chlorophyll *a* fluorescence *in vivo*

For detailed information on various aspects of Chl *a* fluorescence *in vivo*, including its practical applications on both land and marine organisms, see books edited by Govindjee et al. [21], Lichtenthaler [22], DeEll and Toivonen [23], Papageorgiou and Govindjee [24], and Suggett et al. [25]. For information on the details of Photosystem II (PSII) that gives rise to most of constant and variable Chl *a* fluorescence, see a book edited by Wydrzynski and Satoh [26], and a review [27]; for details on Photosystem I (PSI) that gives rise to a constant and a low fluorescence, see a book edited by Golbeck [28].

2.1. Why Chl a fluorescence in vivo is variable under steady excitation?

For Chl *a* in solution that becomes excited by absorbing light, the law of energy conservation can be expressed as follows (Parson [29]).

$$K_E[\text{Chl}\,a](I_{ABS}/I_0) = k_F[\text{Chl}\,a^*] + k_H[\text{Chl}\,a^*] \quad (1)$$

where I_{ABS} and I_0 are the absorbed and incident light intensities per unit time. The rate of absorption equals $k_E[\text{Chl}\,a][I_{ABS}/I_0]$, and when [Chl *a*] does not change, it can be made a part of the rate constant *k*. Specifically, the first order rate constants considered here are k_E for excitation, k_F for fluorescence emission, and k_H for the dissipation of

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EE as heat. Eq. (1) simply states that the rate of photon absorption (left side) equals the sum of the excitation energy (EE) dissipation rates of the excited molecules (right side), both radiatively and non-radiatively. It is important to note that (i) k_E operates on the entire ground state population of Chl *a* [Chl *a*] and k_F and k_H on the entire excited state population [Chl a^*]; and (ii) that the two EE dissipation processes operate independently of each other.

For Chl *a in vivo*, the energy conservation equation takes the form:

$$K_E[\text{Chl}\,a](I_{ABS}/I_0) = k_F[\text{Chl}\,a^*] + k_P[\text{Chl}\,a^*] + k_H[\text{Chl}\,a^*] + k_{NPQ}[\text{Chl}\,a^*] \quad (2)$$

Here, two additional dissipation routes are included, one corresponding to the photochemical use of the EE for photosynthetic electron transport (PSET; rate constant k_P) and one for PSET-regulated thermal dissipation of the EE (rate constant k_{NPQ}, where NPQ stands for non-photochemical quenching); in addition, we have spontaneous thermal dissipation (rate constant k_H) that is independent of PSET. For a background on the principles of fluorescence, see Lakowicz [30].

Eqs. (1) and (2), although formally similar, pertain to entirely different physical situations. In Eq. (2), the EE dissipative routes do not operate on the same Chl a^* population as they do in Eq. (1). For example, since the majority of PSII and PSI Chls *a* are engaged exclusively in light harvesting, they are not directly involved in the photochemical dissipation of the EE. Only 8 Chls *a* are photoactive, four in the reaction center of PSII ($PSII_{RC}$; Loll et al. [31]) and four in the reaction center of PSI (PSI_{RC}; Jordan et al. [32]), so k_P must strictly pertain to them only. Second, a rate constant in Eq. (2) may actually be a function of several rate constants, as for example in the case of k_{NPQ}. And a third, and most important, difference is that the EE dissipative routes (e.g., k_P and k_{NPQ}) *in vivo* are mutually inter-dependent.

The photochemical conversion of the EE of Chl *a in vivo*, and the ground state reactions it initiates, produce(s) chemical signals that affect either the excited population of Chl *a* [Chl a^*] or its ground state population ([Chl *a*]). These signals, which accumulate at different rates and are slower than the PSET rate, give rise to the fluctuations of Chl *a* fluorescence intensity, as is shown in the fluorescence induction patterns of Fig. 1.

2.2. Ground state chemical regulators of the intensity of Chl a fluorescence in vivo

The intensity of the emitted Chl *a* fluorescence (F) is directly related to the concentration of excited [Chl a^*]:

$$F = k_F[\text{Chl}\ a^*] \quad (3)$$

and in order for it to vary with time under constant monochromatic excitation, [Chl a^*] must vary. *In vivo*, [Chl a^*] is influenced by two kinds of processes (see e.g., [20]): (a) kinetic processes that reduce or restore both the quantum yield (φ) and the lifetime (τ) of the emitters by the same proportion (quenching and dequenching processes); and (b) processes that shift Chl *a* holochromes reversibly from the fluorescing PSII to non-fluorescing PSI, but have no effect on φ and τ (*fluorescence increase*, or *fluorescence lowering*). *In view of this concept, lifetime of fluorescence measurements are important in distinguishing between reversible processes that cause quenching/dequenching from processes that cause fluorescence lowering/increase.* Examples of the latter are the light/dark – adaptive processes that are known as *state transitions* (*vide infra*). We exclude photoinhibitory processes here; they are irreversible chemical conversions. (For a historical review, see Ref. [33].) (We also remark that the terms *nonphoto*-chemical and *photo*-inhibitory are contradictory.)

Three kinds of chemical signals, all generated by the ground state photosynthetic electron transport (PSET), and one external chemical signal, affect the ground state and excited state populations of Chl *a* (see Section 4, Table 1). They are: the redox state of the primary plastoquinone electron acceptor of PSII, Q_A; the redox state of the plastoquinone pool (and cytochrome (Cyt) b_6f complex); the high-energy state of the membrane, X_E, and the osmolarity of the external phase in the case of cyanobacterial cell suspensions. We discuss them below.

(1) *The redox state of Q_A.* Q_A is the first quinone electron acceptor of the reaction center (RC) of photosystem II ($PSII_{RC}$). It quenches Chl *a* fluorescence (i.e., it decreases [Chl a^*] $PSII_{RC}$, when it is oxidized but not when it is reduced (Duysens and Sweers [34]; also see Duysens and Talens [35]).

(2) *The plastoquinone pool (PQ_{POOL}) and the Cyt b_6f complex.* The redox states of these intersystem electron transport intermediates affect Chl *a* fluorescence physicochemically in two ways:

(i) They regulate the sizes of the peripheral antenna complexes (PAC) of PSII and PSI ($PSII_{PAC}$, PSI_{PAC}). In the reduced state, the PQ_{POOL} triggers reactions that cause the translocation of peripheral antenna complexes from PSII (the high fluorescing photosystem) to PSI (the weakly fluorescing photosystem), thereby decreasing Chl *a* fluorescence (*the state 1 to state 2 transition*). Conversely, in the oxidized state the PQ_{POOL} triggers reactions that cause the translocation of antenna complexes from PSI to PSII, thereby increasing Chl *a* fluorescence (*state 2 to state 1 transition*). For early research, see Bonaventura and Myers [36,37]; Bonaventura[38]; Murata [39–41]; and Duysens [42–44]; for reviews, see references [14,17,45–55]. In the case of state transitions (*state* 1 ⇆ *state* 2), the population of the excited Chls *a* is determined by the ground state population, and not kinetically by quenching interactions. Such changes in the optical cross section of the PSII light-harvesting antenna should not entail changes in fluorescence quantum yield (φ) and lifetime (τ), and should not be considered as quenching processes [see Papageorgiou et al., 20].

(ii) When the PQ_{POOL} is oxidized, Chl *a* fluorescence is lower than when it is reduced [56–61]. Oxidized plastoquinones decrease Chl *a* fluorescence by a dynamic quenching mechanism since both its lifetime (τ) and its quantum yield (φ) are also decreased [see e.g., 62].

[In addition to the above short-term physicochemical processes, changes in the redox state of intersystem intermediates affect photosynthesis and metabolism at the level of gene expression [63,64]. We do not discuss these events here.]

(3) *The high energy state of the thylakoid membrane, X_E.* Non-cyclic and cyclic PSETs force the translocation of H^+s from the stroma space to the intrathylakoid space (lumen) and, thus, establish an electrochemical imbalance across the thylakoid membrane that includes transthylakoid $\Delta pH + \Delta\Psi$ (membrane potential; inside acidic, positive) that polarizes the membrane and quenches primarily the fluorescence of peripheral antenna complexes. A number of mechanisms have been proposed for X_E-quenching, including allosteric and protein conformation effects as well as the xanthophyll cycle mechanism (for different views, see reviews by various research groups [65–70]). Since cyanobacteria have no Chl *a*-containing peripheral antenna complexes, X_E-quenching is very limited in them, but nevertheless, it is present.

(4) *The hyperosmolarity of cyanobacterial cell suspensions.* A cell suspension is hyperosmolar when the external osmolarity exceeds that of the cytoplasm. Only non-penetrating osmo-

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lytes contribute to the external osmorality that the cell perceives. Hyperosmolar media prevent the light-adaptive *state 2* to *state 1* transition of phycobilisome (PBS)-containing cyanobacteria (i.e., cells are locked in a low fluorescence state) and force an instantaneous transition of *state* 1 cyanobacteria to *state* 2 (measured as fluorescence lowering). Conversely, in hypo-osmotic media the light-adaptive state transitions occur normally. The hyperosmolarity effects on cyanobacterial cells are fully reversible [71–76].

3. Historical evolution of our awareness of the direct and the indirect regulation of Chl *a* fluorescence by photosynthetic electron transport (PSET)

3.1. Direct regulators of Chl a fluorescence: The fast changes

Up to the early 1960s, Chl *a* fluorescence was assayed in order to answer questions mainly about the light harvesting roles of the accessory pigments in photosynthesis and about photosynthetic activities. Questions about the light harvesting roles of accessory pigments were handled by comparing action spectra of photosynthesis and of sensitized Chl *a* fluorescence (Duysens [77]). Thus, action spectra of Chl *a* fluorescence were used to prove EE transfer from various accessory pigments to Chl *a* (from carotenoids, see [78], and reviews [79,80]; from phycobilins, see [81,82]; and from Chl *b*, see [77]). For general reviews on Chl fluorescence and EE transfer, see [83–86]. In the early days, photosynthesis was measured in terms of O_2 evolution (manometrically), or in terms of CO_2 uptake (either spectrographically, or by ^{14}C incorporation). With the advent of photoelectric devices, photosynthesis could be also estimated indirectly, but more conveniently, using Chl *a* fluorescence as its inverse indicator.

The first compelling evidence for a complementarity relation between fluorescence and photosynthesis was obtained, in 1940, by McAlister and Myers [87,88]; they recorded mirror-image kinetics for CO_2 uptake and Chl *a* fluorescence (measured with a photocell) upon exposing dark-adapted wheat plants and suspensions of the green alga *Chlorella pyrenoidosa* to light. The complementarity relation is further supported by the fact that while photosynthetic cells emit less than 2–5% of the absorbed light quanta as Chl *a* fluorescence, for Chl *a* in solution this fraction rises to 20–30% [89–91].

The above information led to the reasonable assumption that Chl *a* disposes all quanta that cannot be used for photosynthesis as fluorescence, while the balance, namely the fraction of quanta lost by thermal de-excitation, was constant and independent of photosynthesis. Despite the accumulating evidence to the contrary, the photosynthesis-Chl *a* fluorescence complementarity was a dominant dogma until about the middle of 1970s.

As late as 1971, two of us [14] wrote:

"...both Chl a fluorescence and photosynthesis draw on the excited Chl a population, and thus a change in the photosynthetic rate is reflected as a change in the yield of fluorescence;"

And Myers [92], in 1974, stated:

"a Chl a molecule cannot use the same quantum of energy for both fluorescence and photochemistry."

These statements were, in all likelihood, attempts to simplify the relationship, but they are historical curiosities considering that five years before, the same authors had obtained strong evidence against the absolute dominance of the complementarity dogma (see [10–13,37,92]).

Nineteen sixty was, in a way, the demarcation year between the *old* photosynthesis and the *new* photosynthesis (see Myers [92]). By that time, the concept of two pigment systems and two light reactions was established (see e.g., Emerson and Rabinowitch [93]) and the photosynthetic electron transfer from water to $NADP^+$ was fit into the framework of a Z-scheme by Hill and Bendall [94]; see also Fig. 2 in Stirbet and Govindjee [9], this issue. For the evolution of the current model, and a historical perspective, see [95] and [96]. (Also see Delosme et al. [97].) After these developments, the relation of photosynthesis to Chl *a* fluorescence could not be viewed simply as a direct competition between a photochemical act and a photoemissive act, as in the days of McAlister and Myers [87,88]. The questions asked, the design of the experiments, and the interpretations of results were now guided by a new frame of thought, one that involved two pigment systems with partially overlapping action spectra, and two photoreactions, one reducing and the other oxidizing an intersystem set of electron carriers. In this spirit, Duysens and Sweers [34] interpreted their own measurements with algae, cyanobacteria and chloroplasts, and the earlier results of Govindjee et al. [98] and Butler [99] on the quenching of PSII fluorescence by PSI light, by postulating that $PSII_{RC}$ (which they designated as Q for quencher, not for quinone) is a regulator of Chl *a* fluorescence. Fluorescence was maximal when all Q was reduced (to QH) by PSII, and minimal when it was all oxidized (to Q) by PSI. Their kinetic scheme explained the fast OP fluorescence rise both in chloroplasts and in algae by invoking a PSII against PSI competition for the photoactive and redox-active quencher Q.

In the 1960s, evidence started piling up suggesting a more complex relation of Chl *a* fluorescence to photosynthesis. To explain the P to S fluorescence decline (see Fig. 1), which was observed in algae but not in isolated chloroplasts, Duysens and Sweers [34] invoked the conversion of QH to another quencher Q' by means of "*a side reaction*," meaning not directly related to the main PSET. Thus, these authors viewed Q/QH as a direct (that we can also call an *on-line*) quencher while the QH/Q' as an indirect (that we can call an *off-line*) quencher, a first attack on the complementarity dogma.

The strongest argument, however, against the complementary relation between fluorescence and photosynthesis, was based on observations of parallel rise or decay kinetics of Chl *a* fluorescence and of O_2 evolution. Using actinic light of very high intensity, with or without PSET inhibitors, and fast recording of fluorescence kinetics, Morin [100], and Joliot [101] in the green alga *Chlorella* and Delosme [102] in chloroplasts succeeded in resolving the initial OP fluorescence rise in two phases: a first photochemical phase (corresponding to the OI phase; see Fig. 1), and a second thermal phase (corresponding to the IP phase). The first phase was assigned to the destruction of a quencher Q, a primary photoactive and redox-active reactant of $PSII_{RC}$, and the second phase to a redox-active intermediate R located between PSII and PSI. (Discovery of this "R" has remained elusive until today.) During the photochemical phase O_2 evolution and Chl *a* fluorescence rise in parallel, but during the thermal phase O_2 evolution declines while fluorescence continues to rise.

3.2. Indirect regulation of chlorophyll a fluorescence: high energy state, protein/membrane conformation, state transitions, quenching

The concept of those early landmark studies was that the regulator of Chl *a* fluorescence is a photoactive and redox-active molecule or group of molecules, a link in the noncyclic PSET, which was identified either as the $PSII_{RC}$, or part of it. Inherent was also the assumption that, at room temperature, Chl *a* fluorescence originates *mostly* from PSII, the O_2-evolving photosystem. This assumption was confirmed, in 1966, after the biochemical separation of the PSII and PSI supercomplexes [103–105; also see 106].

The early 1960s saw the formulation of the chemiosmotic theory by Mitchell [107] and the dramatic demonstration by Hind and Jagendorf [108] that photophosphorylation can be split into a light

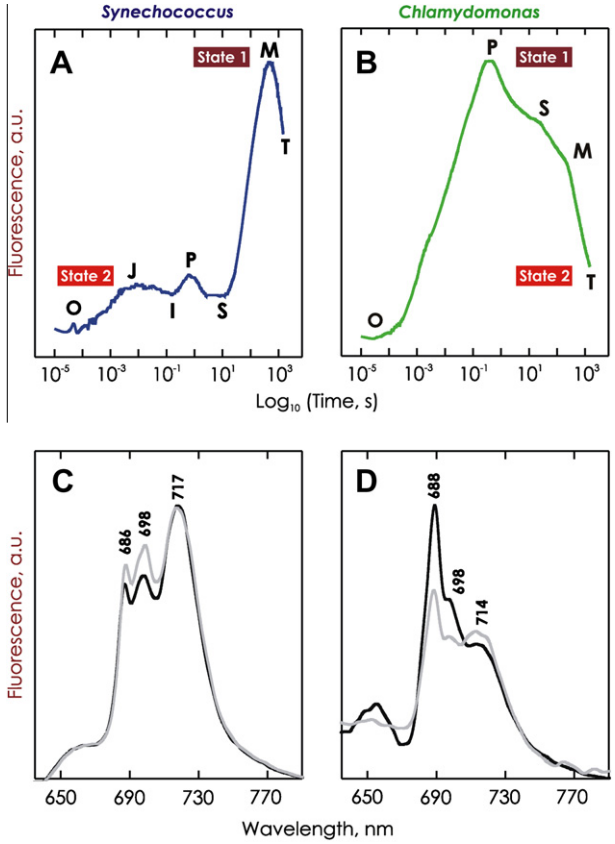

Fig. 2. State transitions in the phycobilisome (PBS)-containing cyanobacterium *Synechococcus* (A and C) and in the green alga *Chlamydomonas reinhardtii* (B and D) as detected by room temperature fluorometry (A and B) and by 77 K fluorescence spectroscopy (C and D). After dark adaptation, *Synechococcus* (A) exists essentially in state 2 (see P level in panel A) and upon intense (red) actinic light illumination (3000 μmol photons m^{-2} s^{-1}) it shifts essentially to state 1 (levels M, T). In contrast, after dark adaptation, *Chlamydomonas* is in state 1 (see P level in B) and after actinic light illumination, it shifts to state 2 (see the T level). Panel C shows the 77 K fluorescence spectra of state 2 *Synechococcus* (dark adaptation; black line) and of state 1 *Synechococcus* (actinic light $\lambda > 690$ nm; gray line). Panel D shows the 77 K fluorescence spectra of state 1 *Chlamydomonas* (dark adaptation, plus 3-(3,4-dichlorophenyl)-l,1-dimethylurea, DCMU; black line) and of state 2 *Chlamydomonas* (broad blue band actinic light; gray line). *Original data*, courtesy of Kostas Stamatakis; the figure used here was produced by Dmitry Shevela. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stage in which a *high energy intermediate*, X_E, is formed, and a subsequent dark stage in which X_E drives the esterification of a phosphate group to ADP (see a historical review [109]). X_E was viewed as either the transthylakoid ΔpH difference established by PSET, or as a hypothetical high-energy compound. At about the same time, Packer [110,111], using 546 nm light, reported light-induced light scattering increase at 546 nm (ΔLS_{546}) in chloroplast suspensions. ΔLS_{546} was correlated with phosphorylating PSET because it was reversed by darkness, and abolished by 3-(3,4-dichlorophenyl)-1,1-dimethylurea, DCMU (a PSET inhibitor) and by NH_4^+ ions (protonophoric ion). Soon thereafter, Dilley and Vernon [112,113] reported that an efflux of Mg^{2+} and K^+ ions into the stroma space compensates for the PSET-induced influx of protons into thylakoids, and that this ionic traffic is related to chloroplast shrinkage through the high energy intermediate X_E. In 1965, Hind and Jagendorf [114] proposed X_E to reflect not a chemical entity, but "*some strained conformation of the chloroplasts.*"

The efflux of Mg^{2+} and K^+ as counterions to the light-induced influx of H^+ was confirmed about 10 years later [115,116]. By that time, the X_E concept evolved to imply a strained state of the thylakoid membrane which was characterized by an outward pointing proton gradient, an inward pointing metal cation gradient, and by electrical polarization of the membrane (*positive inside*). This X_E was implicated as a direct as well as an indirect regulator of Chl *a* fluorescence *in vivo*. The following mutually interactive events have been considered to explain changes in Chl *a* fluorescence: (i) *effects on the rate of non-cyclic PSET*: accumulation of "X_E" delays reoxidation of reduced Q_A by PSI, leading to chlorophyll *fluorescence rise*, while its destruction, by uncouplers of photophosphorylation, accelerates oxidation of reduced Q_A, leading to chlorophyll *fluorescence decline*; (ii) *changes in the ionic environment:* this is due to the efflux of Mg^{2+} ions from the intra-thylakoid space to the stroma space; (iii) *direct quenching of excited Chl a molecules*; and (iv) *effects on protein and membrane conformation.*

3.2.1. Effects of the high-energy state on the rate of the noncyclic electron transport

In 1965, Arnon et al. [117] attributed the rise of Chl *a* fluorescence they had observed, upon illumination of chloroplast suspensions that lacked ADP and/or inorganic phosphate, to the back-pressure that X_E exerts on the rate of the noncyclic PSET. This explanation was consistent with the regulation of Chl *a* fluorescence by a direct photochemical quencher [34,100; cf. 118]. However, Arnon et al. [117] observed a decrease in Chl *a* fluorescence intensity, when they accelerated the cyclic PSET by adding catalysts, such as menadione or phenazine methosulfate (known also as *N*-methyl phenazonium methosulfate) to chloroplast suspensions. (For personal history, we mention that Louisa Yang-Ni, working with one of us (Govindjee) had obtained similar results in 1964, which remain unpublished; see Ref. [15].) Since the cyclic PSET does not affect the redox state of quencher Q_A, this new phenomenon could not be explained by invoking a direct photochemical quencher, as in the noncyclic PSET.

Disregarding the fact that PSI Chls *a* fluoresce weakly at room temperature, Arnon and coworkers [117] proposed another regulator, a photoactive and redox-active Chl *a* in the cyclic electron transport. This example illustrates how strong was the conviction, at that time, that only a direct competition between PSET and fluorescence emission could affect the fluorescence of photosynthetically active samples. The proof that PSET across PSI quenches excited Chls *a*, not *via* an on-line redox-active Chl *a*, but by energizing the thylakoid membrane, was obtained in 1969, by Murata and Sugahara [119] on the basis of cyclic-PSET, and in 1970 by Wraight and Crofts [120] on the basis of noncyclic PSET.

3.2.2. Changes in the protein and membrane conformation

During the 1960s, several reports appeared that pointed strongly to an indirect regulation of Chl *a* fluorescence by PSET mediated by slowly accumulating chemical signals (see Section 4, Table 1). In 1966, Govindjee et al. [3] showed that continuous actinic light (AL), either PSII light (590 nm; AL_{590}), or PSI light (436 nm; AL_{436}), given to a cyanobacterium *Anacystis nidulans* caused reversible changes in the emitted fluorescence intensity and in the fluorescence spectrum. These changes were too slow (s to min) to be directly related to PSET and too fast to be related to processes, such as chromatic adaptation. Furthermore, in the case of AL_{590}, they did occur also after the noncyclic PSET was blocked by the addition of DCMU. In our own words:

> *"preillumination modifies the emission spectrum, and that the direction of the changes depends on the quality of the light to which the cells have been exposed. The changes in spectra occur around 685 nm (the usual peak) and around 695 nm (a new difference fluorescence peak)."*

The F695 peak[1] had been studied independently in several laboratories including our own at the University of Illinois at Urbana-Champaign by fluorescence spectroscopy at 77 K (see e.g., [121–125]). The general consensus was (and is) that F685 and F695 originates in PSII while F715–735 originates in PSI (see 1963 papers[1] in Kok and Jagendorf [125]; for F720, see Brody [126]).

In 1967, Papageorgiou and Govindjee [10] considered two possible explanations for the slow fluorescence changes. The first, consistent with the direct regulation, was the accumulation of reduced Q_A (or QH) because of (i) *the imbalance in the primary photoreactions in* $PSII_{RC}$ *and* PSI_{RC} *in the case of – DCMU cells, with PSII predominating*, and *(ii) the inability of PSI to reoxidize* reduced Q_A (*QH) in the + DCMU cells.* The second was a novel idea of "*conformational changes in the membrane*" as the cause of the light-induced slow changes of Chl *a* fluorescence. It was inspired by the work of Packer [110,111], Dilley and Vernon [112,113] and of Hind and Jagendorf [114] on light-induced light scattering changes by chloroplast suspensions, mentioned earlier. This was the first time that light-induced changes in Chl *a* fluorescence were not linked to PSET directly, but to PSET-related indirect causes. In 1971, Myers [127] wrote about our work:

> *"A common explanation has been reached in terms of almost naked speculation: that small conformational changes alter distances [between] pigment molecules and thereby provide partial carburetor control in transfer of excitation to the reaction centers. The idea is not novel. It was reached previously by Papageorgiou and Govindjee (102) from fluorescence time course studies."*

If the membrane conformational changes, a byproduct of photophosphorylating PSET, are indeed behind the slow S to M fluorescence rise in *Anacystis*, then photophosphorylation inhibitors ought to block it out. The question was: which one of the two stages that Hind and Jagendorf [114] had described was responsible for it? Was it the photochemical formation of X_E, or the dark phosphorylation of ADP? The dilemma was resolved by our observation in 1968 [12,13] that the SM fluorescence rise was blocked (although not quantitatively) by the protonophore carbonyl cyanide p-trifluoromethoxy phenylhyhydrazone (FCCP), while it was insensitive to phlorizin that allows ΔpH formation across the thylakoid membrane but inhibits phosphorylation.

Another striking result, which could not be rationalized in terms of the 'direct' quenching, was the demonstration that O_2 evolution rises in parallel with fluorescence during the SM phase in both algae and cyanobacteria ([11, 12; also see papers by Bannister [128] and Bannister and Rice [129]). The two of us [13] attributed it to "*a conversion of a nonphotoactive and nonfluorescent portion of Chl a to the photoactive and fluorescent form*", whereas Bannister and Rice [129] attributed it to the conceptually equivalent "*slow activation* |that| *converts inactive PSII units* (II_i) *to active ones* (II_a)." Implicit in the above explanations is the idea that only the Chls *a* of PSII were involved, so these proposed activations were *intra-PSII* events. The same phenomenology, namely the parallel kinetics of O_2 evolution and of Chl *a* fluorescence were interpreted one year later by Bonaventura and Myers [36–38] and by Murata [39–41] by a mechanism that involves the Chls *a* of both photosystems, namely by an *intersystem regulation*, the *state transition* mechanism (see Section 3.2.3).

[1] The F695 band, at 77 K, had been discovered independently, in 1963, by B. Kok (Fluorescence Studies, pp. 45–55), Govindjee (Emerson Enhancement and Two Light Reactions in Photosynthesis, pp 318–334), S. S. Brody and M. Brody (Aggregated chlorophylls *in vivo*, pp. 455–478) and J.A, Bergeron (Studies of the Localization, Physicochemical Properties, and Action of Phycocyanin in *Anacystis nidulans*, pp. 527–536) (see Kok and Jagendorf (Eds.), 1963, Photosynthetic Mechanisms of green Plants, Publication #1145, National Academy of Sciences—National Research Council, Washington, DC [125]. The F720 band, at 77 K, was discovered even earlier by Brody (1958) [126].

3.2.3. State transitions

The term *state transitions* describes a reversible physiological mechanism that enables plants, algae, and cyanobacteria to optimize PSET at rapidly fluctuating light conditions, and additionally to enable cyanobacteria to dissipate excess EE as heat. In state *1*, the PSII light harvesting antenna is larger and the PSI antenna smaller than in *state 2*. Conversely, in state 2, the PSII antenna is smaller and the PSI antenna larger than in state 1. The light state of photosynthetic cells can be recognized by kinetic fluorometry at room temperature and by spectrofluorometry at very low temperatures. At room temperature, the conversion of photosynthetic cells from state 2 to state 1 is observed by a kinetic rise of Chl *a* fluorescence, whereas the state 1 to 2 conversion by a decline. At 77 K, and in state 1, the PSII emission bands, F684 and F696, are stronger and the PSI emission band F720 is weaker than when the cells are in state 2 (see examples in Fig. 2).

In the early 1960s, one could have intuitively postulated the necessity of a valve that would adjust the timing of photoreactions I and II in changing light conditions by regulating the amount of EE they receive from peripheral antennae. As mentioned above, such a mechanism, that of the state transitions of today, was indeed postulated at the end of the decade, independently by Bonaventura and Myers [36–38], and by Murata [39–41]. This discovery was not based on theoretical reasoning but it was deduced from specifically designed experiments.

Going after the events in chronological order, we recognize that, by 1969, at least four groups had independently reported simultaneous slow rises in Chl *a* fluorescence and in O_2 evolution rate: Duysens and Talens [35] in cyanobacteria, Bonaventura and Myers [36–38], Bannister and Rice [129], and the two of us [11–13] in both cyanobacteria and green algae. (See also the 1970 paper by Mohanty et al. [130] in green algae, and our 1971 review [14].) These parallel rise kinetics of O_2 evolution and Chl *a* fluorescence, which were totally different from the mirror-image kinetics reported by McAlister and Myers in 1940 [87,88], constituted the first demonstration of what we would call today a *state* 2 to *state* 1 transition. However, as mentioned above, our research group [12,13] and that of Bannister [128,129] had invoked an *intra-PSII activation* of Chl *a* while the core of the *state transition* concept focuses on *intersystem* EE exchanges and their regulation by light absorbed in PSII and PSI, and by darkness.

The latter idea matured independently in 1968 in two research groups, one in the USA and the other in Japan, which, at the time, were unaware of each others' experiments. At the University of Texas, at Austin, Texas, Celia Bonaventura and Jack Myers [36] used the green alga *Chlorella pyrenoidosa* for their experiments while at the University of Tokyo, Norio Murata [39] experimented with the red alga *Porphyridium cruentum*. Their results were published the following year: by Murata [40] in the January 1969 issue of *Biochimica et Biophysica Acta*, by Bonaventura [38] also in January 1969 in her Ph.D. Thesis at the University of Texas, at Austin, and by Bonaventura and Myers [37] in the August 1969 issue of *Biochimica et Biophysica Acta*.

By preilluminating the red alga *Porphyridium cruentum*, at room temperature, with either actinic light 2 (AL_{PSII}) or with actinic light 1 (AL_{PSI}) and by comparing their effects by measuring the 77 K Chl *a* fluorescence emission bands of PSII (F684, F695) and PSI (F712), Murata [40] concluded:

> *"Upon illumination of pigment system II, a greater amount of absorbed light energy is transferred to chlorophyll a in pigment system I and a lesser amount of light energy is transferred to chlorophyll a in pigment system II than occurs upon illumination of pigment system I. Such a change of excitation transfer reduces the difference between the amounts of excitation energy available for photoreactions I and II."*

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In her experiments, Bonaventura examined the effects on O_2 evolution and Chl *a* fluorescence emission by *Chlorella pyrenoidosa* suspensions upon switching from light 1 to light 2, and back. Her findings were summarized as follows by Bonaventura and Myers [37; see Fig. 3]:

> *"Slow changes following rapid chromatic transients indicate differences in the physiological states assumed by cells adapted to light 1 or light 2 illumination. The light 1 state is characterized by most efficient use of light 1 and least efficient use of light 2. Conversely, the light 2 state shows most efficient use of light 2 and least efficient use of light 1."*

Thus, Bonaventura was the first to use the terms *light 1 state* and *light 2 state* for the two light–adaptive physiological states of an oxygenic photosynthetic organism. In a first page footnote in Ref. [37], Bonaventura and Myers recognized the published work of Murata without discussing it further. They wrote, "*A report, published during preparation of this manuscript, by N. Murata (Biochim. Biophys. Acta, 172 (1969) 242) contains some information similar to that presented here*."

Ten months later, Murata published [41] in June 1970 issue of *Biochimica Biophysica Acta* the clearest description of these phenomena and for the first time he used the terms *state 1*, *state 2* and *state transitions* to describe the light adaptive states of photosynthetic organisms and their interconversions. He wrote:

> *"Terms, "State I" and "State II" are used to describe the state of excitation transfer. In the State I a lesser amount of excitation energy is delivered in Pigment System I and greater to Pigment System II than in the State II. The conversion of the states is achieved by the selective illumination of pigment systems."*

We must emphasize here that Bonaventura and Myers and Murata viewed the light-adaptive regulation of PSII and PSI in not quite the same way. For Bonaventura and Myers [36,37] light states 1 and 2 primarily pertained to changes in the photochemical efficiencies of the reaction centers, and not to intersystem EE transfers. On the other hand, Murata [40,41] clearly invoked interystem EE exchanges.

In 1972, Duysens [42,43] proposed pigment state 1[2] and pigment *state* 2 as more appropriate terms, arguing that *Chlorella* cells adapt to state 1 also in darkness, while in cyanobacteria a light-induced rise of Chl *a* fluorescence (a state 2 to state1 transition) occurs also in the presence of DCMU, as reported in 1969 by Duysens and Talens [35] and as reported earlier, in 1967 and 1968, by the two of us [10,12]. However, because Murata's terms *state* 1 and *state* 2 also apply both to dark and to light adaptation of PSII and PSI, and because they are simpler than the terminologies of Bonaventura and Myers and Duysens, they are now universally used.

In the late 1960s and early 1970s, the *state transition* phenomenology was rationalized within the X_E conceptual framework. There was no consensus on whether the light-adaptive changes in Chl *a* fluorescence pertained to the "bulk" or to the reaction center pigments and, of course, no one suspected that changes in the optical cross sections of PSII and PSI, in response to shifts in the redox state of the PQ pool, were involved, as we know today. Further, the state transitions were related to the X_E state of the thylakoid membrane and to the structural or conformational changes that this state entails. Murata [41] suggested that " *some conformational change of the lamella structure . . . which must modify the distances between and the mutual orientations of the chlorophyll a molecules, might cause alterations of the rate of excitation energy transfer*". On the other hand, Bonaventura and Myers [37] aptly stated: "*conformational changes may control the distribution of quanta to the two systems by altering the proximity of pigments to reaction centers*". Finally, Duysens [42,43] remarked that, ". . . *the pigment state I to 2 transition is caused by a change in the thylakoid membrane by which the pigments of the two reaction centers are moved closer towards each other*."

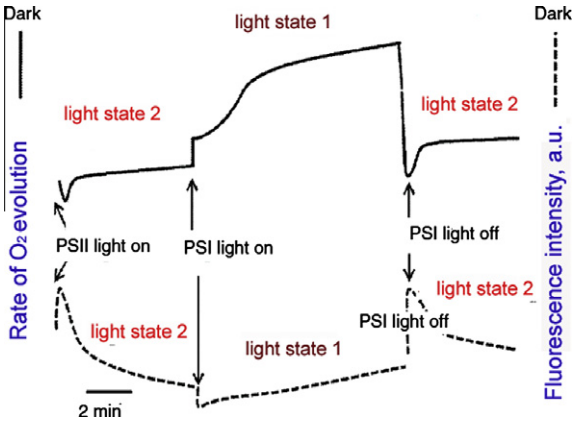

Fig. 3. Simultaneously-recorded kinetic traces of photosynthetic O_2 evolution (upper traces) and Chl *a* fluorescence (lower traces) that illustrate a state transition cycle (*light state* 2 → *light state* 1 → *light state* 2) in the green alga *Chlorella pyrenoidosa*. From left to right: (Left): state 2 is achieved gradually when cells are illuminated with modulated 650 nm light, which is absorbed preferentially by Photosystem II. At the end of this phase, the O_2 evolution rate is approximately the same as at the start, while Chl *a* fluorescence is lowered. (Middle) Upon switching on additional continuous light (710 nm), preferentially absorbed by PSI, *Chlorella* cells transit gradually to state 1. At the end of this phase, both the rate of O_2 evolution and Chl *a* fluorescence are higher than at the start. (Right) Upon switching the 710 nm light off, cells revert back to state 2. At the end of this phase, both the rate of O_2 evolution and Chl *a* fluorescence are lower than when PSI light was turned off. Qualitatively, these kinetic traces show that each state transition phase requires several minutes for completion, and that in State 1 the distribution of excitation energy between PSII and PSI is better balanced (higher O_2 evolution rate) than in state 2. This figure is based on the original data of Bonaventura and Myers [36] and its discussion by Allen and Mullineaux [47] (see text for further discussion).

Today, we know that the *state transition* phenomenology is caused by shifts of peripheral antenna elements from one photosystem core complex to the other. In higher plants and algae, these antenna elements are intramembranous light harvesting complexes of PSII (LHCII) which move to associate with PSI_{CC} after being phosphorylated by a kinase which is activated by the attachment of a plastoquinol to the Q_0 site of Cyt b_6f (see e.g., Bennett et al. [131]; Allen et al. [132]; and reviews [50,52–54]). In the PBS-containing cyanobacteria the shifting peripheral antenna is the extramembranous PBS. McConnell et al. [133] presented a model that includes not only large scale changes in the redistribution of PBS between PSII and PSI, but "spill-over" of EE from CP-47 of PSII to PSI, and small movement of PSI with respect to PBS/PSII complex, to explain state transitions in cyanobacteria. Bruce and Vasil'ev [134] have reviewed such inclusive models. On the basis of a detailed investigation of fluorescence transients in cyanobacteria, Tsimilli-Michael et al. [135] provided evidence favoring the mobile antenna model. Further studies are needed to fully understand the mechanism of 'state changes' in cyanobacteria.The state transition mechanisms in PBS-minus cyanobacteria (*Prochlorophytes*, *Acaryochloris*) are largely unknown.

Schematically, a simple state 1 ⇆ state 2 transition mechanism is illustrated in Fig. 4.

[2] The terms *pigment state* 1 and *pigment state* 2 imply that pigments (or the two pigment systems) are involved and it is, thus, indeed appropriate because in the actual mechanisms 'light-harvesting pigment complexes' have been shown to move from PSII to PSI and vice versa. However, the usage of the simpler terms state 1 and state 2 takes precedence. Further, for the novice, we point out here that these terms should not be confused with the S-states (S_0, S_1, S_2, S_3 and S_4) of the oxygen-evolving Mn_4O_5 Ca complex of the electron donor side of PSII) and with S_1 and S_2 used for the first and the second excited singlet states of pigment molecules.

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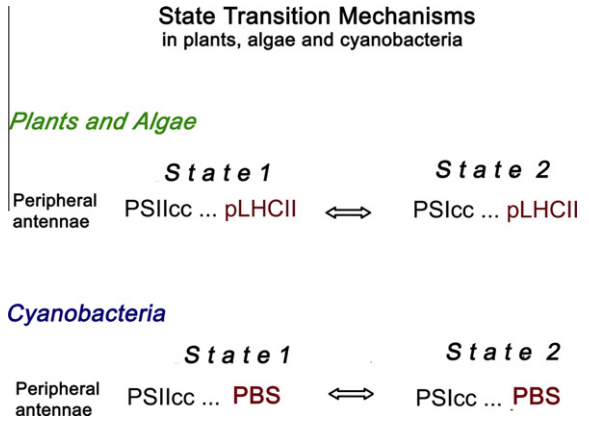

Fig. 4. A simple view of the state transition mechanism in plants and algae (upper part) and in PBS-containing cyanobacteria (lower part).The mechanism involves reversible shifts of peripheral antenna complexes (LHCII in plants and algae [50,54], PBS in cyanobacteria [47,49]) from an association with the core complex of PSII ($PSII_{CC}$) to an association with the core complex of PSI (PSI_{CC}).

Here, PBS refers to (mobile) phycobilisome, pLHCII to phosphorylated mobile peripheral light harvesting complex of PSII, and PSI_{CC} and $PSII_{CC}$ to core complexes of PSII and PSI, respectively. In cyanobacteria, no membrane protein phosphorylation is involved [136], although the high energy state of the membrane is important for the state 2 to state1 transition [12].

During a long dark period, cyanobacteria adapt to *state* 2 (reduced PQ_{POOL}, low fluorescence; the O level) and after continuous illumination *state* 1 (oxidized PQ_{POOL}, high fluorescence, the M level) is formed, tracing the fluorescence induction pattern (Fig. 1); we note that on this slow change phenomenon, the fast fluorescence transient related to changes in Q_A, Q_B and PQ is superimposed (reviewed in Ref. [20]). Conversely, plants and algae adapt to *state* 1 (PQ-pool oxidized, high fluorescence) after darkness, and after continuous illumination, *state* 2 is formed, tracing the fluorescence induction pattern (reduced PQ-pool; low fluorescence, the T level). Here again, the fast transient related to changes in Q_A, Q_B and PQ are superimposed; in fact, here fluorescence is high when Q_A, Q_B and PQ are all reduced. Further, parallel measurements on fluorescence intensity and lifetime of fluorescence are necessary to separate '*state change*' effects (that should not lead to changes in lifetime of fluorescence) and PSII-related quenching changes (that would change both the lifetime and the quantum yield of fluorescence changes [20,59,137,138]). The entire OJIPSMT fluorescence induction pattern in cyanobacteria is dominated by an initial *state* 2 to a final *state* 1 transition (T level is above the P level), while in plants and algae, it is dominated by a state 1 to state 2 transition (T level is below the P level; see Fig. 1; and the review by Papageorgiou et al. [20]).

3.2.4. Effects of Mg^{2+} ions

Although Dilley and Vernon did show already in 1965 [112] that Mg^{2+} is the major exchange cation for the light-induced proton influx into the intrathylakoid space (and the only one according to Barber et al. [116]), its role as a specific Chl *a* fluorescence modifier was not suspected until 1969. In 1969, Homann [139] and Murata [140] reported, independently, that Mg^{2+} ions, added to chloroplast suspensions, at concentrations below 10 mM, elicit a rise in Chl *a* fluorescence from an initial F_o level to a limiting F_M level, and that the increment in fluorescence, $\Delta F_{CHLa} = F_M - F_o$, equals approximately what could be obtained upon the full reduction of the quencher Q of PSII. Additionally, Murata et al. [141] reported that Mg^{2+} ions accelerate PSII electron transport and slow down PSI electron transport, while the PSII 77 K emission bands (F684 and F695) are stimulated and that of PSI (F735) is suppressed. These effects, which could be observed in grana [139–142] but not in isolated PSII particles (Mohanty et al. [142]), were attributed by Homann [139] to cation-induced structural changes, while Murata [143] provided a more elaborate interpretation, according to which a Mg^{2+}-induced conformational change suppresses the *spillover* of excitation energy (EE) from the "bulk" Chls *a* of PSII to those of PSI. Soon thereafter, Briantais et al. [144] discussed in depth this intersystem exciton transfer.

These trend-setting publications were truly the peep-holes in *"the wall"*. The physicochemical mechanism by which Mg^{2+} ions act on the thylakoid membrane and the physiological role of Mg^{2+} as a Chl *a* fluorescence modifier became a highly popular research topic during the 1970s, even in our own separate labs. With Isaakidou, one of us (GP) studied Mg-induced membrane structure dependent changes [145,146] by comparing emission of non-chlorophyll fluorophores [tryptophyl residues and anilinonaphthalene sulfonate, ANS], whereas the other (Gov), partly inspired by the work of Gross and Hess [147], focused, with his collaborators, in looking at whole cells [148], and on the antagonistic effect of Na^+ and Mg^{2+} ions on the regulation of EE distribution between the two photosystems [149–151]. Gross and Hess [147] had reported that below 10 mM, monovalent cations act antagonistically to Mg^{2+} and stimulate the PSII to PSI spillover of EE (see Wydrzynski et al. [150]).

There were many others who studied this phenomenon, but the tendency was to implicate Mg^{2+} ions in all types of modifications of Chl *a* fluorescence, including quenching of excited Chls *a in vivo* by the high energy state of the thylakoid membrane and state transitions, irrespective of their timing. Specific questions asked pertained to the membrane sites to which Mg^{2+} must bind in order to exert its effects, whether Mg^{2+} is specific, or whether other metal cations could do the same, and whether the fluorescence of the PSII Chls *a* is suppressed by quenching or because they transfer their excitation to the non-fluorescing Chls *a* of PSI, or by both. Evidence obtained in several laboratories indicated that when Mg^{2+} is inside (presumably bound to negative sites of the inner thylakoid surface) chloroplasts exist in a high fluorescence state. This could be the result either of a *state transition effect* (e.g., due to the blocking of the PSII to PSI excitation energy spillover ([140,141,152,153]; see a review by Butler [154]) or of a local dequenching effect (reversal of the high energy quenching of the excited Chls *a* of $PSII_{CC}$; see e.g., Krause [155], and Barber and Mills [156]). Upon illumination of chloroplasts, protons (H^+ ions) are imported from the stroma into the lumen, and these were suggested to displace the bound Mg^{2+} ions (perhaps because carboxylic salts dissociate more easily than carboxylic acids); as a consequence, Mg^{2+} ions were exported to the stroma space. The resulting strained thylakoid membrane was characterized by a relatively higher concentration of Mg^{2+} ions outside and a relatively higher concentration of H^+s inside (see [147,155–158]). Both the state transitions and the local dequenching effects were suggested to be caused by local protein or membrane conformational changes. In broken chloroplasts, these conformational changes could be elicited by the addition of divalent metal cations at 10 mM, or lower concentrations, or of monovalent metal cations at 10 mM or higher concentrations (see e.g., [139,141,143]).

The lack of cation specificity, the higher sensitivity to divalent relative to monovalent metal cations, the monovalent – divalent cation antagonism and their roles in membrane stacking and destacking, led Barber and coworkers ([156,157]; see review [158]) to turn to the Gouy–Chapman theory for an explanation. In this theory, biological membranes carry fixed negative charges on their surfaces which attract cations that form a diffuse positively charged layer near the surface; the effects of Mg^{2+} and of other metal cations are not due to their binding to discreet negatively charged sites, but to their interactions with, and the

modification thereby, of the diffuse double electrical layers near the membrane surfaces. This purely electrostatic approach, however, disregards the possibility that the properties of cations with physiological functions (e.g., Mg^{2+}, Ca^{2+}) are not likely to be determined by their ionic charge only (P. Mohanty, personal communication, 2011).

During 1979–1981, Wong and Govindjee [159,160] and Wong et al. [161–163] reinvestigated the effects of addition of low concentration of monovalent cation (Na^+) to cation-depleted thylakoids, and then the effect of divalent cation Mg^{2+} to Na^+-containing samples. They measured *simultaneously* the intensity, the lifetime (τ) and the quantum yield (φ) of Chl *a* fluorescence, as well as its depolarization. Some of these experiments included measurements at wavelengths selected to monitor preferentially PSII or PSI emission as a function of different wavelengths of excitation, as well as PSII and PSI electron transfer rates and pH dependence of some of these phenomena. Taken together, these experiments led Wong and co-workers to conclude that there are *multiple effects* of cations that include changes in: (a) coupling between Chl *b* (in LHCP) and Chl *a* in PSII reaction center; in other words, energy transfer within PSII: from Chl *b* – to $[\text{Chl } a]_{\text{LHCII}}$ – and then to $[\text{Chl } a]_{\text{PSIIcc}}$; (b) excitation energy redistribution between PSI and PSII; and (c) relative absorption cross section (*state changes*). Further, Wong et al. [163] using parallel fluorescence lifetimes and transients at 77 K, in a single sample, provided quantitative information on changes in absorption cross section of PSI, in excitation energy transfer from PSII to PSI and in radiationless losses: addition of 10 mM Mg^{2+} to a thylakoid suspension that had 10 mM Na^+ *led to three concomitant changes*: 50% decrease in energy transfer from PSII to PSI, a 20% increase in radiationless loss, and a 10% decrease in absorption cross section of PSI.

Finally, we mention that in the case of the Mg^{2+} ion effects what was the more solid gain out of all the research ado of the 1970s-early 1980s was the recorded phenomenology and the membrane surface electrostatics and the realization that externally added Mg^{2+} to chloroplast suspensions causes a number of effects, including excitonic coupling of chromophores, intra-system and intersystem EE transfers, and even changes in the relative absorption cross sections of PSI and PSII.

4. Concluding remarks

During the 1960s and 1970s, therefore, several "peep-holes" – in the sense of the Bessel Kok and André Jagendorf dictum – were discovered in the wall around photosynthesis that attracted "crowds" of researchers, who, naturally of course, discovered more peep-holes. Those discoveries became the question marks of future research, in as much as that the actual physical mechanisms behind the light-induced conformational changes of membranes and proteins, the high energy quenching and the state transitions were unknown.

It is now well-established that in all oxygenic photosynthetic plants, the electronic EE that resides at any moment in PSI and in PSII is subject to two general modulation mechanisms that do not depend directly on Q_A: (a) The dissipation of the EE of Chl *a* upon the establishment of an electrochemical gradient across thylakoid membranes (X_E quenching); and (b) the state 1 $\leftrightarrows$ state 2 processes that shift EE from one photosystem to the other and are triggered by the oxidoreduction state of the PQ-pool. The mechanisms of these two processes are similar but not identical in the evolutionary distant (by approx. 1 billion years) cyanobacterial cells and eukaryotic cells.

Table 1 summarizes four types of signals that modify the fluorescence of chlorophyll *a in vivo* (see text for details). They are (i) Q_A; (ii) PQ (pool) and Cyt b_6f; (iii) X_E; and (iv) Hyperosmolarity.

In plants and algae, the major part of X_E quenching/dequenching relates to the Chls *a* of peripheral antenna complexes (LHC proteins) and is mediated by the xanthophyll cycle mechanism. This type of quenching, which is the main contributor to the fluorescence decay along the P to S phase of the OJIPSMT fluorescence induction kinetics, is indeed quite prominent in the xanthophyll containing plants (*Phaseolus*) and algae (*Chlamydomonas*) (see Fig. 2 and Ref. [10]). Can we, however, view the presence of xanthophylls as *a sine qua non* condition for X_E-related quenching? This premise is not sustainable in view of the smaller, but non-negligible P to S decays detected in the xanthophyll-lacking and LHC-protein lacking cyanobacteria (*Synechococcus*, *Acaryochloris*). The early interpretation that such phenomena may relate to membrane structural changes and thereby to alterations in the distances and/or the orientations of chromophores may actually be correct, as far as EE generated directly in the core complexes, $PSII_{CC}$ and PSI_{CC} is concerned (see Fig. 4).

Another lingering question has been: do inorganic anions too have a role in the regulation of the EE distribution, as cations do? In 1998, Jajoo et al. [164] showed that indeed they do, and in fact in the presence of Cl^-, SO_4^{2-}, and HPO_4^{2-} (but characteristically not of F^-; Ref. [165]); PSI is favored as a recipient of EE, as is the case in state 2 transition. This effect was larger with higher valence anions, while organic anions were ineffective. In addition, "heat" – induced state changes were discovered in algae and leaves (see e.g., Sane et al. [166]). Mohanty et al. [167] showed involvement of pLHCII

Table 1
Ground state chemical signals that modify the fluorescence of chlorophyll *a in vivo*.

Chemical signal	Effects on [*Chl *a*]	References
Q_A – primary quinone electron acceptor of $PSII_{RC}$ (*photochemical quenching*)	Oxidized form (Q_A) quenches the EE of $PSII_{RC}$; the reduced form (Q_A^-) does not	[34,35,100–102]; reviews [8,9]
PQ_{POOL} & Cyt b_6f – intersystem electron carriers (*nonphotochemical quenching*) (*fluorescence lowering/increase*)	(a) Quencher of $(^*\text{Chl } a)_{ANT}$ when oxidized (b) Trigger of the state 2-to-1 transition when oxidized (*fluorescence increase*); trigger of the state 1-to-2 when reduced (*fluorescence lowering*)	[60,61] [36–44]; reviews [14,17,45–55]
X_E, high energy state of the thylakoid membrane (i.e., transmembrane ΔpH and $\Delta[Mg^{2+}]$ (*nonphotochemical quenching*)	(a) Cyanobacteria –quencher of $^*\text{Chl } a$ in $PSII_{CC}$ (b) Algae, plants – quencher of $^*\text{Chl } a$ in $PSII_{PAC}$ • Allosteric effects • Xanthophyll cycle • PsbS protonation	[65–70,119,120,143]; reviews [154,158]
Hyperosmolarity – Cyanobacteria cell suspensions (*fluorescence lowering*)	Hyperosmolar state 2 cells – Suppression of state 2-to-1 transition Hyperosmolar state 1 cells – Forced state 1-to-2 transition	[71–74,76]; review [75]

Abbreviations: EE – Excitation Energy; $PSII_{CC}$ – PSII core complex; $PSII_{PAC}$ – PSII peripheral antenna complex; $PSII_{RC}$ – PSII reaction center complex.

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in this process in peas; the results were different in cyanobacteria [168]. On the other hand, Pastenesz and Horton [169] observed the existence of heat-induced state changes in beans. The relationship of these phenomena to that discussed in this perspective is one of the open questions.

We end our historical perspective here with the remark, that both the fast phase (OJIPS) and the slow phase (SMT) of the Chl *a* fluorescence induction are very rich sources of information about the highly complex and unique process of oxygenic photosynthesis (also see Refs. [170,171]). (For a new conceptual link of nonphotochemical quenching and state transitions in plants, that came to our attention at the time of correcting the proofs, we refer the readers to Tikkanen et al. [172].) Above, we have briefly listed few open questions, but what is actually needed to exploit the potential of Chl *a* fluorescence is fresh ideas, new and unanticipated questions and imaginative use of new technology. Finally, the question of how state changes evolved in cyanobacteria, algae and plants needs to explored and understood. These are some of is the challenges we leave our readers with.

5. Abbreviations

Chl	chlorophyll
CC	core complex
DCMU	3-(3,4-dichlorophenyl)-l,1-dimethylurea
EE	excitation energy
F	fluorescence
FCCP	p-trifluoromethoxy-phenylhyhydrazone
k_E, k_F, k_H, k_{NPQ},	rate constant for excitation, fluorescence, heat loss and nonphotochemical quenching, respectively
OJIPSMT transient	chlorophyll *a* fluorescence transient starting with the minimum (initial) level (O) followed by inflections J and I, peak (P), semi steady state (S), maximum (M) and terminal steady state (T)
PBS	phycobilisome
pLHC	phosphorylated light-harvesting complex
PSI	photosystem I
PSI_{CC}	PSI core complex
PSI_{RC}	PSI reaction center complex
PSII	photosystem II
$PSII_{CC}$	PSII core complex
$PSII_{RC}$	PSII reaction center complex
PSET	photosynthetic electron transfer
RC	reaction center
ΔLS_λ	light scattering change at wavelength λ, in nm.

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