Ann. Phys. (Berlin) 524, No. 11, A157–A160 (2012) / DOI 10.1002/andp.201200748

THEN & NOW

From the Red Drop to the Z-scheme of photosynthesis

Kärin Nickelsen

In 1943, the US-American biophysicist Robert Emerson (see Fig. 1) and his collaborator, the physicist C. Charlton M. Lewis, were investigating the efficiency of photosynthesis, determined as its quantum yield, i.e., the number of light quanta required for the release of one molecule of oxygen, and its relationship to the wavelength of light.[1] In the course of this work, they observed, at low light intensities, an unexpected sharp decline of photosynthetic efficiency in the far red, that is, from 685 nm towards the infrared region of the spectrum [5, p. 166]. This was the phenomenon that later became known as the "Red Drop" of photosynthesis efficiency (see Fig. 2). The puzzling fact was that at wavelengths even above 685 nm chlorophyll absorption was still rather high, and no pigments were known to compete with chlorophyll in this region, which might have caused the drop in efficiency. Emerson and Lewis were completely at a loss as to how to explain this finding. And as in the years afterwards, Emerson became involved in an atrocious controversy on the maximum quantum yield of photosynthesis with the eminent – and extremely stubborn – cell physiologist Otto Warburg, over the next ten years he did not investigate this curious phenomenon any further.[2]

It was only in 1955 that Emerson came back to his former line of enquiry, and he hit upon an even stranger effect. It turned out that the Red Drop of photosynthetic efficiency disappeared if a supplementary light beam of shorter wavelengths was provided (see [7]). As a possible explanation, Emerson and his co-workers, Ruth Chalmers and Carl Cederstrand, suggested that "the significance of the supple-

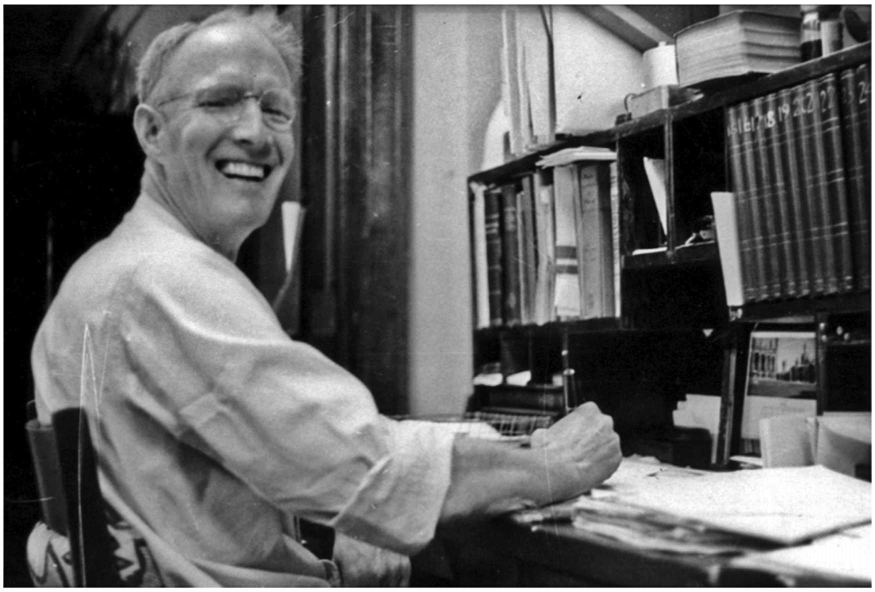

Figure 1 Robert Emerson at his desk in the Natural History Building at the University of Illinois at Urbana. (Photograph taken by Govindjee in 1957.)

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[1] The development of the Z-scheme of photosynthesis already was the subject of earlier accounts, e.g., [1], and recently [2] as well as [3]. See also [4], Chapter VI. I am grateful to Govindjee for comments on this text and for the permission to print the photograph of Robert Emerson, Fig. 1.

[2] See, e.g., the recent book [6]. While Warburg insisted on a value of 4–5 light quanta per oxygen, Emerson established a value of 8–12 quanta per oxygen (which is still believed to be correct today).

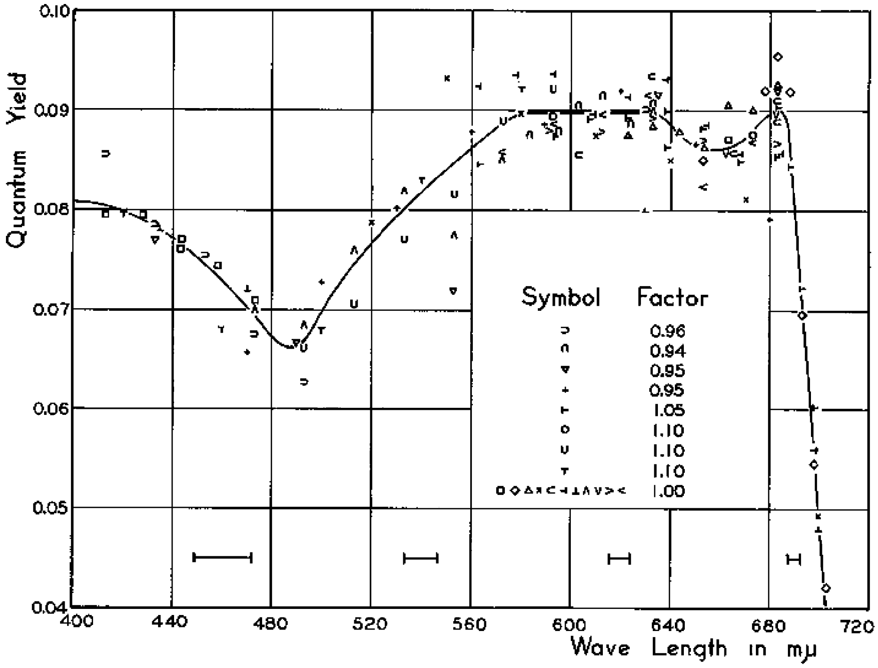

Figure 2 The quantum yield of photosynthesis as a function of wave length for *Chlorella*. The points obtained on each of nineteen separate runs are indicated by a distinct symbol. For eight of these runs arbitrary adjustments have been made by multiplying all the values obtained in each run by a factor close to unity. The factors used are given in the figure. The band half widths that were commonly used in the various parts of the spectrum are indicated by horizontal lines of corresponding lengths. Reproduced from Emerson and Lewis (1943), p. 171.

mentary light may be that it adds excitation of other pigments besides chlorophyll *a*"; in the green algae, with which they were working, the authors speculated, this pigment might be chlorophyll *b*.[3] Tragically, Emerson's untimely death on 4 February 1959 in an airplane crash (at age 56) prevented his further research into these issues.

In 1960, Emerson's longstanding friend and colleague, Eugene Rabinowitch, published some of the work that Emerson had left behind [11]. It was in this publication that the phenomenon in question was called, for the first time, the "Emerson Effect" (in later years, it became the "Emerson Enhancement Effect"). Rabinowitch duly presented Emerson's data, although he argued against the assumption that the effect was due to a direct contribution of chlorophyll *b* in photosynthesis: the Dutch biophysicist Louis N. M. Duysens had firmly established, in his dissertation of 1952, that almost 100 per cent of the light energy absorbed by chlorophyll *b* (and other accessory pigments) was transferred to chlorophyll *a* [12]. Rabinowitch rather suggested that two types of chlorophyll *a* were present in the living cell. In fact, one of Emerson's former doctoral students, Govindjee (no first name), was able, together with Rabinowitch, to experimentally establish the existence of these two species of chlorophyll *a*, which had distinct functions in the photosynthetic process.[4]

The important idea that emerged from Emerson's findings (and subsequent work) was that photosynthesis might involve two different light reactions, prompted by light of different wavelengths.[5] Further evidence for this fact was amassed over the next years, with a number of photosynthesis researchers arriving at very similar conclusions around the same time (while only some of them can be mentioned in the following).

Among these researchers was the aforementioned biophysicist Duysens, who decided, strongly inspired by Emerson's findings, to examine the action spectra for the redox reactions of photosynthetic cytochromes. It had been known for some time that chloroplasts contain specific cytochromes, that is, hemoproteins that were known to be involved in the electron transport chain of respiration (see [20–22]). Duysens found that cytochrome was

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[3] [8], p. 142.; cf. also [9, 10].

[4] See [13] and [14]. French [15], presented in March 1960, had independently come to the same conclusion. [16] established the presence of a short wavelength absorbing chlorophyll *a* also in systems that used chlorophyll *b* as an accessory pigment.

[5] It has to be noted that already in [17], p. 1862, the assumption was formulated that there may be two photochemical reactions that involved electron transport via cytochromes; this has independently been drawn attention to by, e.g., [18], p. 74, and [19].

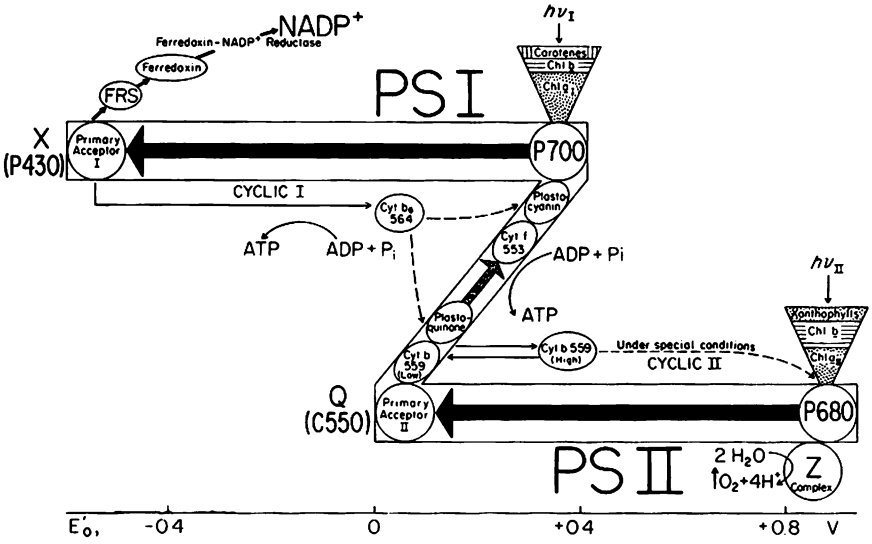

Figure 3 The "Z-scheme" of photosynthesis, in a version by Govindjee and R. Govindjee 1975, p. 27.

oxidised upon illumination at longer wavelengths, while it was reduced by superimposing light of shorter wavelengths.[6] In order to explain this switching of the oxidation state of a cytochrome, Duysens postulated the existence of two light reactions localised in two different pigment systems.

These findings were reported in 1960 at the Third International Congress of Photobiology held in Copenhagen, Denmark, and caused considerable excitement in the audience. Duysens later recalled that in the discussion following his Copenhagen talk a British colleague, Charles Whittingham, asked him whether these findings "supported the scheme proposed by Hill and Bendall in *Nature*". Duysens said he did not know, since he had not seen the paper; but he rushed back to his laboratory to finish the final experiments. He was able to establish that photooxidation and reduction of the cytochrome occurred with a reasonable quantum yield, which was strong evidence for the existence of two photosystems that acted in series to complete the photosynthetic light reactions.[7]

The paper that Whittingham had alluded to was a publication of 1960 by the British biochemist Robin Hill together with his co-worker Fay Bendall [25]. Therein, the problem was treated from the point of view of thermodynamics. Hill and Bendall had also postulated the existence of two photosystems, while they suggested, as a novel idea, that these might be linked by (plant specific) cytochromes of different redox potentials, and that oxidation of some of these provided the energy for the formation of ATP – which, of course, is one of the key purposes of the photosynthetic light reactions. Owing to a widespread representation of the conceptualised reaction sequence, the idea of photosynthesis as comprising two light reactions prompted by two different pigment systems became known as the "Z-scheme" of photosynthesis (see Fig. 3 for an example published in 1975).

Although the conceptual scheme of Hill and Bendall was ingenious, it lacked the experimental counterpart (complementing Duysens's work), which shortly thereafter was provided by the German biophysicist Horst Tobias Witt and his group. Witt succeeded in detecting absorption changes with his repetitive flash spectroscopy, which greatly increased the sensitivity and the time resolution of photosynthesis studies. The latter was crucial, since almost all the pertinent reactions were faster than 10 milliseconds – in fact, many were suspected to be in the range of micro- and nanoseconds.[8] With the help of this technique, in 1961 Witt and his collaborators found that (1) upon excitation with λ_1 = 710 nm one of the plant specific cytochromes was oxidised and stayed in this state for seconds; (2) after excitation with λ_2 = 670 nm an unidentified component X was oxidised to XO. From these findings, the group concluded, in line with Hill, Duysens, Rabinowitch and others, that photosynthesis was triggered by two different photochemical reac-

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[6] Cf. [18], p. 73, see [23] for the paper.

[7] Quoted [18], pp. 72–73; the experimental work was published in [24].

[8] A survey of Witt's methods and findings up to 1959 is provided by [26].

tions: one of these was the oxidation of cytochrome by the first species of chlorophyll *a* that had been identified, the other was the reduction of an unknown compound XO by the second species of chlorophyll *a*.[9]

In the light of this conclusion, arrived at from a range of different directions, the surprising Enhancement Effect that Emerson had hit upon in 1957 was rendered perfectly explicable.

Kärin Nickelsen
History of Science Ludwig Maximilians University, Munich, Germany
E-mail: K.Nickelsen@lmu.de

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[9] See [27, 28]; a retrospective, personal account is given in [29].