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HISTORICAL CORNER

The controversy over the minimum quantum requirement for oxygen evolution

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Abstract During the early- to mid-twentieth century, a bitter controversy raged among researchers on photosynthesis regarding the minimum number of light quanta required for the evolution of one molecule of oxygen. From 1923 until his death in 1970, Otto Warburg insisted that this value was about three or four quanta. Beginning in the late 1930s, Robert Emerson and others on the opposing side consistently obtained a value of 8–12 quanta. Warburg changed the protocols of his experiments, sometimes in unexplained ways, yet he almost always arrived at a value of four or less, except eight in carbonate/bicarbonate buffer, which he dismissed as "unphysiological". This paper is largely an abbreviated form of the detailed story on the minimum quantum requirement of photosynthesis, as told by Nickelsen and Govindjee (*The maximum quantum yield controversy: Otto Warburg and the "Midwest-Gang"*, 2011); we provide here a scientific thread, leaving out the voluminous private correspondence among the principal players that Nickelsen and Govindjee (2011) examined in conjunction with their analysis of the principals' published papers. We explore the development and course of the controversy and the ultimate resolution in favor of Emerson's result as the phenomenon of the two-light-reaction, two-pigment-system scheme of photosynthesis came to be understood. In addition, we include a brief discussion of the discovery by Otto Warburg of the requirement for bicarbonate in the Hill reaction.

Keywords History of photosynthesis · Twentieth-century controversy in photosynthesis research · Maximum quantum yield of photosynthesis · Minimum quantum requirement of photosynthesis · Einstein's law of photochemical equivalency · Oxygen evolution · Robert Emerson · Otto Warburg · Eugene Rabinowitch · Dean Burk

Prologue

The minimum quantum requirement (or the maximum quantum efficiency) of photosynthesis is highly pertinent today because, to overcome the energy crisis facing us, attempts are being made to improve natural photosynthesis, as well as to convert solar energy by "artificial photosynthesis." We need to know the limits and to see what can or cannot be done (see, e.g., Bolton and Hall 1991; Blankenship et al. 2011; McGrath and Long 2014).

This Historical Corner perspective on the controversy over the minimum quantum requirement for photosynthesis was read and edited by two experts on the history of photosynthesis—Kärin Nickelsen and Ekkehard Höxtermann (both of Germany) and by John F. Allen (of UK), an authority on photosynthesis research. Nickelsen wrote "Thank you for the latest version. I will be happy to see it in print." Höxtermann's message read: "It is a wonderful, exciting and very instructive historical article. I learned a lot, especially about the disputes and situation in the 1960s. I've found nothing to improve this paper. You have my approval for the present version." Allen, who had made several suggestions to improve our paper, which we have

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incorporated in the present version, wrote: "I have now read this superb manuscript on the maximum quantum yield controversy. I enjoyed it and I admire that the authors have provided here a valuable historical perspective, after the publication of 100+ papers on various aspects of photosynthesis in "Discoveries in Photosynthesis", which I had co-edited with Govindjee, Tom Beatty, and the late Howard Gest (see Govindjee et al. 2005)."

Introduction

Oxygenic photosynthesis is the conversion of solar energy, by living organisms, into chemical energy that the organisms use to convert water and carbon dioxide into carbohydrates, which in turn are converted into fats, proteins, nucleic acids, and other molecules essential for life. The conversion of light energy into chemical energy releases molecular oxygen and produces organic matter (Rabinowitch and Govindjee 1969; Blankenship 2014).

At the dawn of the 20th century, Blackman (1905) postulated that there are separate light and dark phases in photosynthesis. This led to quantitative studies of the light phase, and in the early stages of that research a fundamental question arose: What is the maximum quantum yield, i.e., the maximum number of oxygen molecules evolved per quantum of light absorbed? This question is often posed inversely as: What is the minimum number of quanta required for each molecule of oxygen evolved? Researchers thought that this problem had to be solved in order for them to begin to decipher the physical and chemical pathways involved in the conversion of light energy into chemical energy and the production of carbohydrate from simple precursors (Rabinowitch 1945). The efficiency of the energy conversion process, as indicated by the minimum quantum requirement, would give some idea whether many intermediate steps were involved, because each step would consume energy. A finding of high efficiency would indicate fewer intermediates, whereas a finding of low efficiency would indicate a larger number of intermediates.

In their 2011 book, Nickelsen and Govindjee presented a detailed treatment of the attempts to measure the minimum quantum requirement during the early- to mid-20th century, and of the intense and bitter conflict that arose among some of the researchers during that period. The present paper is in large part a condensed version of that book. The period of intensive research on the minimum quantum requirement constitutes an important chapter in the overall history of research on photosynthesis. (For detailed treatment of the overall history of photosynthesis research, see Govindjee et al. 2005; for specific coverage of the early pioneers of the field, see Hill 2012; for history from ca. 1840 to 1960, see Nickelsen 2009a; and, for an especially comprehensive treatment of that period, see Nickelsen 2014.) Timelines of major discoveries in photosynthesis are provided in: Höxtermann (1992), Huzisige and Ke (1993), and Govindjee and Krogmann (2004).

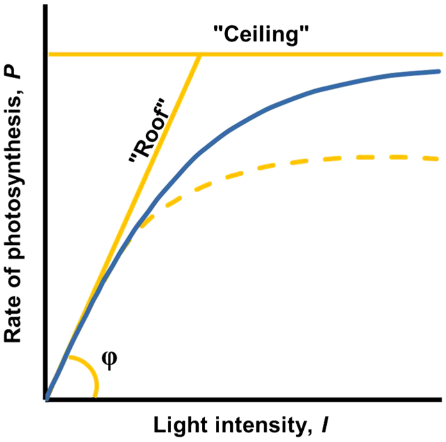

Fig. 1 A schematic drawing of rate of photosynthesis (P) as a function of light intensity (I), i.e., $P = f(I)$. At low intensity, photosynthesis increases linearly with light intensity, and the slope of this curve (φ) is the quantum yield of oxygen evolution when photosynthesis is measured as molecules of oxygen evolved and light intensity as number of photons (or quanta) of light absorbed. It is like a "roof." As the light intensity increases, the rate of photosynthesis decreases and the curve bends and then saturates, reaching a sort of "ceiling"; the latter being due to limitation in the "dark" reactions of photosynthesis. The *dashed curve* shows the effect of lowering the temperature. This figure was modified and redrawn by A. Stirbet and Govindjee from the original figure in Rabinowitch and Govindjee (1969; available free at http://www.life.illinois.edu/govindjee/g/Books.html; see Fig. 6.1, and its discussion on p. 61)

As Nickelsen and Govindjee (2011) emphasized, the experimental difficulties encountered in the search for the minimum quantum requirement were great. Limitations in methodology led to considerable uncertainty regarding all the results. A major problem was measuring the photosynthetic rate accurately, especially because of the difficulty of distinguishing clearly between the gas exchange that was due to photosynthesis and that due to respiration. This problem stemmed mainly from use of the manometric technique (measurement of changes in gas pressure; see Umbreit et al. 1957). In addition, the major test organism, the unicellular green alga *Chlorella pyrenoidosa*, was difficult to culture. Use of an acidic, phosphate-containing buffer solution led to much lower values for the minimum quantum requirement than did use of an alkaline, carbonate-bicarbonate buffer solution, because CO_2 release would be read as O_2 release (see section on "Emerson and Lewis's challenge").

Another problem was identifying the optimal light intensity at which to make the measurements and controlling the light source. Blackman (1905) had demonstrated

Fig. 2 Otto Warburg in 1931, when the Nobel Prize was awarded to him. *Source* Höxtermann and Sucker (1989; see cover picture). Photograph is courtesy of E. Höxtermann (personal collection); the original is in the Berlin State Library-Prussian Cultural Heritage

that the photosynthetic rate at first increases linearly with light intensity and then reaches saturation (Fig. 1). The law of photochemical equivalency (Einstein1912a, b) states that for each quantum of radiation that a substance absorbs, one molecule of the substance reacts; thus, conclusions about the number of photochemical steps required for one molecule of oxygen to be evolved in photosynthesis, and the amount of energy needed for the process to operate, could be drawn only from the minimum quantum requirement, which can be defined as the initial slope of the light curve. The initial slope is expected to be the limiting high value of ($\Delta P/\Delta I$) as I approaches zero (where P is photosynthesis, expressed as the number of molecules of oxygen evolved, and I is light intensity, expressed as the number of quanta (or photons) absorbed). This value is the one obtained as close to zero illumination as possible.

Because of complications due to respiration, however, measurements must be made near the "compensation point," where gas exchange due to photosynthesis just balances that due to respiration. At this light intensity, photosynthesis operates at only one-tenth to one-fifth of the maximum rate of which the cells are capable (Rabinowitch and Govindjee 1969, pp. 148–149). Because many different quantum requirements can be measured, researchers' claims that a measured value was in fact the minimum quantum value had to be based on solid criteria.

In the attempt to determine the minimum quantum requirement for photosynthesis, a conflict developed between, on the one hand, German chemist and cell physiologist Otto Heinrich Warburg (1883–1970; Fig. 2; see Krebs (1972, 1981) and Höxtermann and Sucker (1989) for biographical information about Warburg); and, on the other hand, Warburg's erstwhile graduate student, the American plant physiologist and biophysicist Robert Emerson (1903–1959; Fig. 3; see Rabinowitch (1959, 1961) and Govindjee (2001, 2004) for biographical information about Emerson). Warburg was a member of a wealthy European banking family; had distinguished himself in military service in World War I; and was a prominent cancer researcher who had received the 1931 Nobel Prize in Physiology or Medicine "for his discovery of the nature and mode of action of the respiratory enzyme" (The Nobel Prize in Physiology or Medicine 1931). Warburg was thus much better known than, and overshadowed, the younger Emerson.

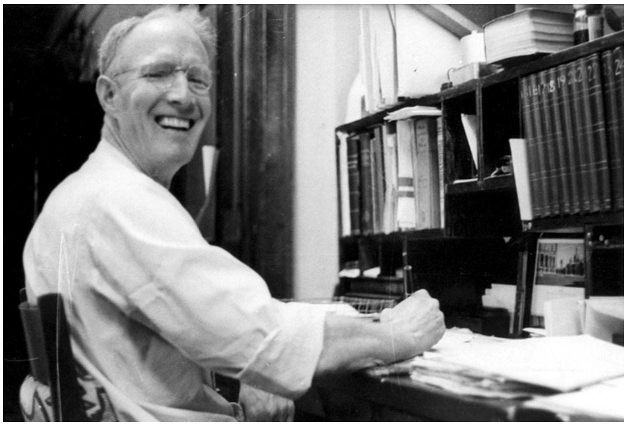

Fig. 3 A 1957 photograph of Robert Emerson in 157 Natural History Building at the University of Illinois at Urbana-Champaign. Emerson is sitting at his desk with all his numbered record books on top right shelf. *Source* Govindjee (2004, p. 186). Photo by Govindjee

Otto Warburg's father, Emil Warburg, was an experimental physicist who had confirmed Einstein's law of photochemical equivalency in many inorganic, photochemical reactions (Warburg 1917). Otto, influenced by his father, firmly believed that this law also applied to photosynthetic reactions in plants. Otto Warburg's initial work on photosynthesis was pioneering. He introduced new research methods that soon became standard practice (Warburg 1919, 1920, 1921; see discussion by Nickelsen 2007, 2009b). One of these was the use of manometry for measuring photosynthetic rates (Fig. 4). Another innovation was the use of optically simpler suspensions of the unicellular green alga *Chlorella pyrenoidosa* in place of leaves or whole plants. In his 1920 paper, Warburg reported that the rate of photosynthesis in *Chlorella* decreased substantially with increasing oxygen concentration. This phenomenon came to be known as the "Warburg Effect" (see Mohr and Schopfer 1995, pp. 236–237). (This effect is different from the "Warburg Effect" in cancer; see Vander Heiden et al. (2009) for a recent discussion of the Warburg effect in cancer.)

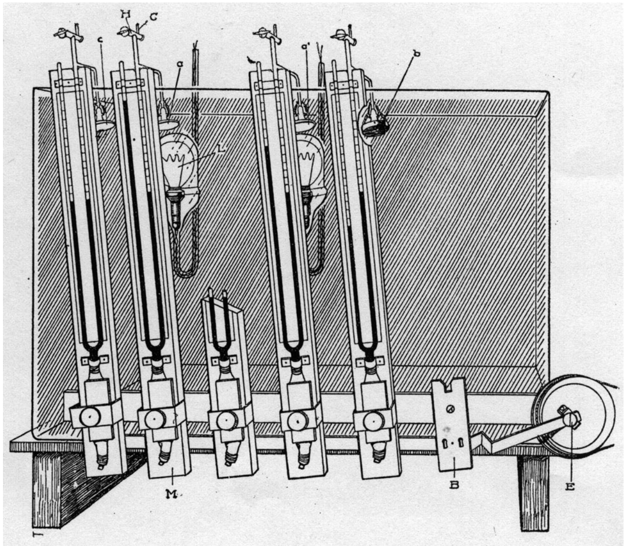

Fig. 4 Manometers used by Otto Warburg in his early photosynthesis measurements. Source: Warburg (1919, p. 245). *a*, *a*′, *b*, and *c* are for manometer vessels; *B* is for the base plate on which manometer is mounted; *C* and *H* are parts of a stop cock that is used to open the manometer before experiments are done; *E* is for the shaft of a motor that is used to shake the manometers during the experiments; and *M* is for the entire manometer unit. See discussion in Nickelsen (2007) and in Höxtermann (2007)

Although considered of lesser stature than Warburg in the quantum-yield debate, Emerson had made a significant contribution to the understanding of photosynthesis before he turned his attention to the quantum-yield question. Together with William Arnold (for biographical background on Arnold, see Govindjee et al. 1996; Govindjee and Srivastava 2014), he had discovered that about 2,400 chlorophyll molecules deliver light quanta to a functional unit for the evolution of one oxygen molecule (Emerson and Arnold 1932). Soon thereafter, Gaffron and Wohl (1936) provided the concept of the *photosynthetic unit* and a photoenzyme, which was an early term for the reaction center. We now know that there are two such units: Photosystem II, which is called water-plastoquinone oxido-reductase (Wydrzynski and Satoh 2005); and Photosystem I, which is plastocyanin-ferredoxin oxido-reductase (Golbeck 2006). For a discussion of the evolution of the concept of two photosystems, see Govindjee and Bjorn (2012).

Warburg and Negelein make the first measurement of the maximum quantum yield

Brown and Escombe (1905) were among the first to study energy efficiency in photosynthesis. They investigated the energetics of the process, but not the quantum yield. They measured light absorption by the weakening of light as it passed through a leaf and evidently misinterpreted light scattering by the leaf as absorption. Therefore, they greatly underestimated photosynthetic efficiency, with their estimates being as low as 6 %. In contrast, Warburg and his research partner Erwin Negelein (Fig. 5) exposed thick suspensions of the alga *Chlorella*, which absorbed nearly all the incident light, to 570 nm (yellow–green) and 645 nm (red) light, and, using manometry, made the first measurement of the minimum quantum requirement (Warburg and Negelein 1922, 1923). Warburg and Negelein (1922) reported a minimum requirement of 4–5 quanta of light absorbed for each molecule of oxygen liberated, indicating that a high proportion—60 to 70 %—of the absorbed radiation energy was transformed into chemical energy. Warburg and Negelein (1923) reported similar, although slightly lower, figures (see Nickelsen and Govindjee 2011, pp. 12–13).

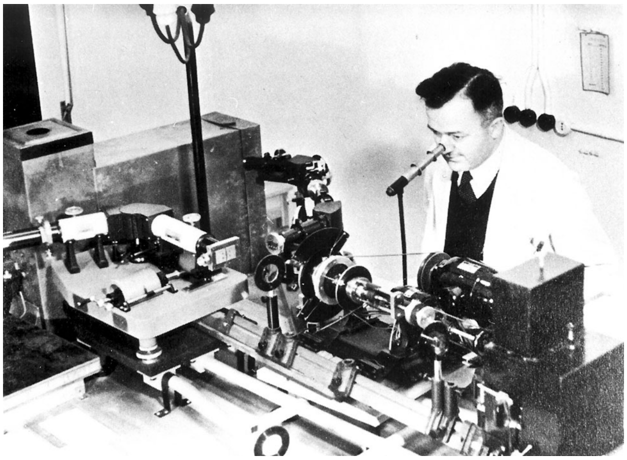

Fig. 5 Erwin Negelein (1897–1979) at an instrument (a spectrophotometer) in Warburg's lab, 1929. *Source* Bücher (1983, see p. 19). Photograph is courtesy of E. Höxtermann (personal collection)

Since oxidation of two water molecules would provide one oxygen molecule and four hydrogen atoms (or four electrons plus four protons), a value of 4 quanta per O_2 released seemed plausible at the time. It corresponded to the four hydrogen atoms (or, alternatively, four electrons) needed to reduce one molecule of carbon dioxide (CO_2) into the basic unit of carbohydrate (see Eqs. 1a, 1b).

$$2H_2O = 4H\,(\text{or}\,4H^+ + 4e^-) + O_2 \tag{1a}$$

$$\begin{aligned} &CO_2\,(\text{gas}) + H_2O\,(\text{liquid}) + n\,\text{photons} \\ &\quad = 1/6\{C_6H_{12}O_6\}\,(\text{solid}) + O_2\,(\text{gas}) \end{aligned} \tag{1b}$$

It also seemed reasonable energetically, with *n* being 4. The reduction of one molecule of CO_2 to the level of carbohydrate required at least 112 kcal of energy (Rabinowitch and Govindjee 1969, p. 15; also pp. 22–28). Four quanta, each at 660 nm, carry 172 kcal. This leaves 60 kcal for stabilization of intermediates. Since $112/172 \cong 70\ \%$, the calculated efficiency was close to the very high efficiency value obtained by Warburg and Negelein (see

Rabinowitch and Govindjee 1969, p. 149; Myers 1974). Warburg and Negelein (1922, 1923) stated: if photosynthesis were 100 % efficient, 2.8 light quanta per oxygen molecule would be required. Because no process is 100 % efficient, the minimum quantum value was to be expected to be a little higher.

The finding of high efficiencies led Warburg and Negelein to speculate that there were few or no intermediate, energy-requiring reactions in the photosynthetic reduction of CO_2 (Nickelsen and Govindjee 2011, pp. 14–15). Warburg and Negelein believed, as had Willstätter and Stoll (1918), that chlorophyll and carbonic acid existed in a complex within the cell (see Myers 1974) and that photodecomposition of this complex was the source of the oxygen liberated in photosynthesis. The idea that CO_2 was the source of the O_2 dated back to the early pioneers of photosynthesis research, in the late 18th century (see Hill 2012).

Nickelsen and Govindjee (2011, p. 15) noted, "The reception of these papers by Warburg and Negelein was highly favorable; and the requirement of 4–5 light quanta per molecule of oxygen was regarded as the authoritative answer to the question of photosynthetic efficiency for the next fifteen years."

The initial challenges to Warburg's view

Beginning in the mid-1930s, some researchers, using different techniques, reported higher values for the minimum quantum requirement of photosynthesis. The first to do so was William Arnold in his (1935) doctoral thesis at Harvard University (Cambridge, MA, USA). Using microcalorimetric techniques, which monitor the photosynthetic process by measuring the heat produced (not by measuring pressure changes, as in manometry), Arnold, who published his results much later, in 1949, reported that the minimum number of light quanta required to produce one molecule of oxygen was never less than nine (see Arnold 1949, Table 13.1 on p. 275).

The first published value that differed from Warburg-Negelein's was obtained by Manning et al. (1938), at the University of Wisconsin (Madison, USA). Using chemical gas analysis, they found a minimum requirement of 16–20 quanta. The Madison group next used microcalorimetric techniques and reported a minimum requirement of 12 quanta (Magee et al. 1939); however, in many of their experiments, they found a value of only about 10.

Foster Rieke, at Johns Hopkins University (Baltimore, MD, USA), used manometric techniques and found an average of about 5 quanta (Rieke 1939), which was close to the Warburg-Negelein value. Rieke obtained his lowest figures in a slightly acidic, phosphate-containing buffer solution, following the recipe of his colleague, the biochemist Dean Burk, who was later to become a close collaborator of Warburg's. In a single experiment using a carbonate-bicarbonate buffer solution, however, Rieke's value was about 8 quanta. Follow-up research, published by Rieke (1949), showed a minimum quantum requirement of 9–12, not 5 (see Nickelsen and Govindjee 2011, pp. 18–20).

Emerson and Lewis's challenge

Robert Emerson, working with physicist Charlton Lewis in the late 1930s at the Plant Biology Laboratory of the Carnegie Institution of Washington (at Stanford University), demonstrated that values obtained for the minimum quantum requirement depended on many factors, including the kind of water used, the addition of certain heavy metals, light conditions during algal growth, and the age of the culture (Emerson and Lewis 1939). They also found that lower temperatures tended to increase photosynthetic efficiency (see Nickelsen and Govindjee 2011, p. 22). Largely following Warburg's experimental protocol, they obtained an apparent minimum quantum requirement of no more than 3—a value they dismissed as resulting from changes in the CO_2/O_2 ratio when the light source was turned on or off. When the light was turned on, there was a sudden peak in photosynthetic efficiency, which they attributed mostly to evolution of CO_2. All these experiments were done with *Chlorella* cells that were suspended in acid phosphate buffer, and changes in O_2 and CO_2 were recorded by a manometric technique that does not distinguish between these two gases. Previous measurements had been based on the assumption that the ratio $-CO_2/O_2$, or γ ("gamma"), during photosynthesis did not deviate from -1 (i.e., $\Delta O_2 = -\Delta CO_2$). Warburg and Negelein (1923) had found a ratio very close to -1, but had arrived at this value at high light intensities, with a light duration of more than one hour. Emerson and Lewis (1939) suspected that that value of γ was not valid for the low light intensities and shorter duration of illumination that Warburg and Negelein had used in their quantum-yield measurements (see Nickelsen and Govindjee 2011, pp. 22–23).

To investigate this matter further, Emerson and Lewis (1941) introduced a "two-vessel method" of manometry, which allowed ΔCO_2 and ΔO_2 to be calculated separately. This "differential manometry" did not require postulating $-\Delta CO_2 = \Delta O_2$, as did the original, single-vessel method. Each of the two manometer vessels contained the same amount of algal suspension, but the vessels differed in size and had different gas-to-liquid ratios. Using this technique, Emerson and Lewis (1941) found that the value of γ was quite variable, due mainly to changes in CO_2 pressure, while the O_2 pressure remained relatively constant. They found that γ was most variable during the first 10 minutes of light or darkness. Its variability at the beginning of a light period was due to variations in the extent of the *carbon dioxide burst*. Warburg and Negelein (1922, 1923) had measured the photosynthetic rate during the first 5 minutes of a light period, i.e., just when there was a sudden increase in pressure that was due not to photosynthetic O_2 but to CO_2. This CO_2 burst, when included as O_2 release, evidently led to Warburg and Negelein's finding of a low (~ 4) minimum quantum requirement (or high (0.25) maximum quantum yield). Further, to measure the photosynthetic rate (that is, O_2 evolution in the light), the rate of O_2 uptake in the dark had to be subtracted from the rate in the light (on the assumption that respiration was the same in the dark as in the light—an assumption that turned out to be erroneous) (see Eq. 2). Warburg and Negelein had measured oxygen uptake during the first 5 minutes of a dark period—i.e., the time when O_2 uptake was decreasing. Making his measurements during these two time periods evidently led Warburg to overestimate photosynthetic efficiency greatly (see Nickelsen and Govindjee 2011, pp. 23–24).

$$\begin{aligned}&\text{Rate of photosynthesis}(\mathrm{O_2}\ \text{evolution})\ \text{per unit time,}\\ &\quad t = \ \text{the measured rate of net}\ \mathrm{O_2}\ \text{release per unit time,}\\ &\quad t,\ \text{in light} - \text{the measured rate of net}\ \mathrm{O_2}\\ &\quad\ \text{uptake per unit time,}\ t,\ \text{in dark} \end{aligned} \tag{2}$$

When Emerson and Lewis (1941) calculated the rate of photosynthesis and its quantum yield from oxygen changes alone, they obtained a minimum requirement of about 10 quanta per oxygen molecule—i.e., close to the values of Magee et al. (1939), who had used very different methods. "Emerson and Lewis (1941) were convinced that this was a fair approximation of the actual value, and considered the issue to be settled" (Nickelsen and Govindjee 2011, p. 25).

The Red Drop

Subsequently, Emerson and Lewis (1943) discovered that, although the quantum yield remained relatively constant in the 580-685 nm region (i.e., yellow to red), it showed a sudden drop in the far-red region, that is, from 685 nm towards the infrared region. This *Red Drop* was not explained until the late 1950s, when it became clear that photosynthesis requires two light reactions and two photosystems rather than one light reaction and one photosystem (see Emerson and Chalmers 1958; Emerson and Rabinowitch 1960; Nickelsen and Govindjee 2011, pp. 25–27; Nickelsen 2012).

The photosynthesis project at the University of Illinois at Urbana-Champaign, and Warburg's visit

In 1946, the University of Illinois at Urbana-Champaign (UIUC) appointed Robert Emerson, a plant biologist and plant biophysicist, and soon thereafter physical chemist Eugene Rabinowitch (who had just published the first volume of an important work on photosynthesis (Rabinowitch 1945)), as co-directors of the newly founded "Photosynthesis Project," directly under the Graduate College of the UIUC (Rabinowitch 1959, 1961; Bannister 1972). This project was to develop into an important research center.

At about the time the *Photosynthesis Project* was initiated at UIUC, Warburg (1945, in German; 1948 English translation) was questioning Emerson and Lewis' value of ~ 10 quanta per molecule of oxygen. Warburg also criticized Emerson's bicarbonate solutions (Warburg's buffer #9), used in this research, as "unphysiological." Warburg (1948) reported that, by using a "new" method of determining the assimilatory quotient (γ) manometrically, he had found values close to -1 in an acidic, phosphate-containing buffer solution, even for intervals of only five minutes. He maintained that he had thereby refuted Emerson's claim that, at the onset of illumination, there is a burst of CO_2 that is immediately photochemically reduced. As in 1923, Warburg reported a minimum requirement of 4–5 quanta per O_2 molecule evolved. Warburg thus had not answered the objections to his experimental protocol directly, but had instead changed his methods and still obtained the same results.

In June 1948, at Emerson's invitation, Warburg came to UIUC so that he and Emerson could work together, comparing their experimental protocols and thereby resolve their differences. Warburg proved to be a difficult guest. On his orders, the laboratories were not heated in the winter and *Chlorella* cells were grown according to his recipe, except that, much to Warburg's disappointment, there was no north-facing window in which to grow them. Warburg ignored Emerson, except to make a refinement in Emerson's new, two-vessel manometric technique. Warburg also worked on constructing an actinometer, a device to measure radiation intensity by monitoring a chemical reaction (Warburg 1948, pp. 208–209; see Nickelsen and Govindjee 2011, pp. 49–50). Previously, he had used a bolometer, which measures incident radiation by the amount the radiation heats a material and is highly accurate. In December 1948, near the end of his Urbana visit, Warburg finally allowed outside observers to monitor experiments that he conducted in Emerson's laboratory. The results were inconsistent, which Warburg attributed to differences in the *Chlorella* cultures that were used (see Nickelsen and Govindjee 2011, p. 52).

At the conclusion of Warburg's visit, he and Emerson signed a protocol acknowledging that each other's data were obtained under their own specific conditions, but they did not agree about interpretation of these data; thus, the standoff persisted between Warburg's 4–5 quanta per oxygen molecule and Emerson's 8–12 (which was in agreement with the values obtained by Rieke (1949) and Magee et al. (1939); see Nickelsen and Govindjee 2011, p. 54). The visit ended with bitterness on both sides (Rabinowitch 1961). Warburg increasingly portrayed himself as the victim of a conspiracy among some Americans whom he later dubbed the "Midwest gang"; this label was given by Warburg to Robert Emerson and Eugene Rabinowitch (at Urbana, Illinois) and to James Franck and Hans Gaffron (of the University of Chicago, Chicago, Illinois) since the latter three were supporters of Emerson. A.A. Benson (personal communication, in July 2001, in La Jolla, California; and a phone call in Urbana, Illinois, in August 2011) told Govindjee that he and Warburg were walking together in 1952 in Helsinger, Germany, and as they looked through an iron gate into a dark expanse below a castle, Warburg remarked, "Ach, it's a perfect place for that 'Midwest Gang'" (Benson 2002; quoted in Govindjee 2004; as also cited in Nickelsen and Govindjee 2011, p. 57).

The controversy continues

After leaving Urbana, Warburg joined Dean Burk at the National Cancer Institute, Bethesda, Maryland, for four months. Upon completion of his trip to the United States, Warburg published three papers with U.S. collaborators. Emerson was not among the co-authors.

In the first paper, published as Burk et al. (1949), the authors stated that they had "rediscovered" the measurements by Warburg and Negelein (1923), using a slightly acidic, phosphate-containing buffer solution. By illuminating the vessels from above with white light, they assumed that they were ensuring that the photosynthetic rate always far exceeded the respiration rate and that they therefore did not need to correct for respiration effects. Addition of a red-light beam produced an increase in the photosynthetic rate, which they recorded using a two-vessel manometric set-up. The authors concluded that, in the spectral region 630–660 nm, no more than 4 quanta are required to produce one molecule of O_2, and that the requirement might be as low as 3. In a carbonate buffer solution, however, they measured values of 10.5, 9.8, and 11.3—consistent with the measurements made by most of the groups in the United States (see Nickelsen and Govindjee 2011, pp. 60–61).

In the second paper, Warburg et al. (1950) wrote that, despite methodological objections that had been raised to the finding of 4 quanta of red light, they had confirmed 3–4 quanta. They attributed the "CO_2 burst" to frothing caused by inadequate shaking of the solution, and stated that the ratio $-CO_2/O_2$ (i.e., γ) was between −0.8 and −1.3—thus presumably countering Emerson's assertion of variable γ values during experimentation. The Warburg group accused Emerson and Lewis of using a carbonate-bicarbonate buffer solution only in order to escape the CO_2 burst in a phosphate buffer.

In the third paper, Warburg and Burk (1950) described nine experiments, one of which was carried out in a carbonate buffer solution. In this experiment, they obtained Emerson's values for the minimum quantum requirement. They interpreted their values for γ as indicating no CO_2 burst (see Nickelsen and Govindjee 2011, p. 65). Apparently referring to their conviction that Einstein's law of photochemical equivalency applied to photosynthesis, Warburg and Burk (1950) concluded (p. 442), with startling confidence (especially for a one-time cancer-researcher such as Warburg), "*The fact must thus be envisaged that in a perfect nature photosynthesis is perfect too*." This thought was echoed later in Warburg (1958) (see Govindjee 1999).

The physiological state of the cells, especially the problem of respiration, was a major concern in all the research. Since respiration was known to continue in the light, the rate of photosynthesis had to be distinguished from that of respiration. The general assumption at the time, later proved incorrect, was that respiration occurred at the same rate in the light as in darkness. Emerson and Lewis, in the 1940s, had tried to limit changes in the respiration rate by using short intervals of light and darkness. In very short intervals, however, transient gas-exchange effects might be occurring, which could lead to different kinds of measuring errors.

James Franck (1949), 1926 Nobel laureate in Physics, noted that, in Warburg's experiments, back reactions might be occurring, in which reducing agents of photosynthesis were reducing half-oxidized respiratory intermediates, or respiratory energy could be bringing about photosynthetic CO_2 reduction.

Regarding the problems encountered in algae culturing, Nickelsen and Govindjee (2011, p. 78) commented, "Indeed, the subject was so complicated that by 1950 many were inclined to believe that almost any factor connected with algae culturing might influence the eventual quantum yield of photosynthesis."

Nishimura et al. (1951, p. 194) criticized Burk and Warburg's assumption that mixing was so efficient in their experiments that there was no time lag in successive light and dark periods. Warburg and Burk, they said, by measuring photosynthesis mainly during 10-minute periods of light alternating with 10 minutes of either darkness or unmeasured light, were not obtaining correct values in either phosphate or carbonate buffer solutions. Nishimura et al. (1951) demonstrated that γ, if calculated separately for light and dark periods, showed large deviations from

−1. Further, Nishimura et al. (1951) explained how, in Warburg's two-vessel system, even minute errors in the manometric readings could greatly change the calculated values of γ, which, in turn, would greatly affect the quantum-yield measurement. Nishimura et al. (1951) nevertheless considered manometry an indispensable method. They argued that only a differential manometer, and simultaneous illumination of both vessels, would enable precise measurements. Further, Nishimura et al. (1951) pointed out that Warburg and Burk's new reports were inconsistent with Warburg's older ones. For example, in his early studies, Warburg had emphasized low light intensities and short durations, whereas by 1950 he and Burk were asserting that efficiencies were highest at high light intensities over long durations. Considering all that was known then, and still holds true today, the slope of the curve of the number of oxygen molecules that are evolved, as a function of the number of photons absorbed, which measures the quantum yield of the process, is highest at low light intensities and becomes smaller at higher light intensities (see Fig. 1). Thus this conclusion by Warburg and Burk (1950) makes no sense. Regardless of their changes in protocol, however, Warburg and his team always managed to obtain about the same value for the minimum quantum requirement.

Despite the technical difficulties of measurement, the weight of the accumulated evidence favored a value of 8–12 quanta, which had been obtained both manometrically and by other means. Warburg, although able to reproduce these values in a carbonate-bicarbonate buffer solution, continued to dismiss them as attributable to sub-optimal photosynthetic ability of the algae at higher pH values, and because only the lowest quantum requirement was of theoretical importance. Thus, Emerson and Warburg did not, at this stage of the controversy, disagree about the values measured in a carbonate-bicarbonate buffer solution. Later, they did.

Warburg and Burk soon made a more extreme proposal: that photosynthesis operates by a "*one-quantum mechanism*." Their first publication of this hypothesis in English was under the authorship of Burk et al. (1951). Years later, it was published under the authorship of Warburg (1958). Ignoring the criticisms that had been leveled at their work, Burk et al. (1951) asserted that, in very short intervals of light and darkness (i.e., one minute each), during the dark period following a period of high light intensity their system lost ten times more oxygen than during normal respiration. As noted above, the reduction of one molecule of CO_2 to the level of carbohydrate requires about 112 kcal of energy (Rabinowitch and Govindjee 1969, pp. 15; also see pp. 22–28). Burk et al. (1951) evidently rounded this off to 110 kcal (= 110,000 calories) in their calculations, and they wrote (p. 216), "If a single quantum of red light furnishes some 40,000 calories per mole, where do the missing 70,000 calories (110,000–40,000) come from?" They suggested that back reactions in the dark phase would consume two-thirds of the previously produced oxygen, and the 70,000 calories thereby produced would then be used in the subsequent light phase, along with the additional 40,000 calories received through absorption of one quantum of red light, to break down a complex of chlorophyll and a carbonic acid derivative. Thus, 110,000 calories would be available to produce carbohydrate and molecular oxygen. A dark-light cycle would thus require 3 light quanta, with the photochemical process itself using only one of these quanta. Because of the high rate of back reactions, the calculated efficiency was about 100 %.

At a conference held October 29–November 1, 1952, in Gatlinburg, Tennessee, there was a full-fledged open discussion on various aspects of photosynthesis (see Hendricks 1953). Here, supporters of Emerson's work countered Warburg's new claim by presenting data obtained by different techniques, including: polarography (F.S. Brackett and R. Olsen, of the National Institutes of Health, Washington, DC) showing a minimum requirement of 6.5–10 quanta per molecule of oxygen; and mass spectroscopy (^{18}O) data of A.H. Brown (University of Minnesota, Minneapolis) showing that respiration (oxygen consumption) was not affected by light. James Franck described the energy accumulation in photosynthesis, leading Burk to confide to Warburg that these thermodynamic considerations seemed the strongest argument against the four- and one-quantum theory (see Nickelsen and Govindjee 2011, pp. 98–99). Ultimately, the conference did not resolve the controversy.

Emerson worked with Ruth Chalmers and subsequently with Carl Cederstrand (who later did his PhD dissertation with Rabinowitch and Govindjee) to understand Warburg's new findings. Their main goals were: (1) to determine whether there was a time lag between the changes of gas pressure inside the cell and changes in manometric readings; and (2) to see whether transient gas exchanges influenced calculations of photosynthetic efficiency (see Nickelsen and Govindjee 2011, p. 104).

Emerson and Chalmers (1955) used the Warburg-Burk experimental set-up, except that they employed differential manometers, with which pressure could be measured more precisely. Emerson and Chalmers (1955) thereby demonstrated that extremely low values for the minimum quantum requirement could be obtained only by ignoring the experimental results: They found that, even under Warburg and Burk's experimental conditions, time lag had an appreciable effect, mainly due to diffusion between the liquid and gas spaces; and that if no time lag was apparent, it was because other processes within the vessel obscured it. A quantum requirement of about eight per molecule of oxygen was the lowest that could be obtained.

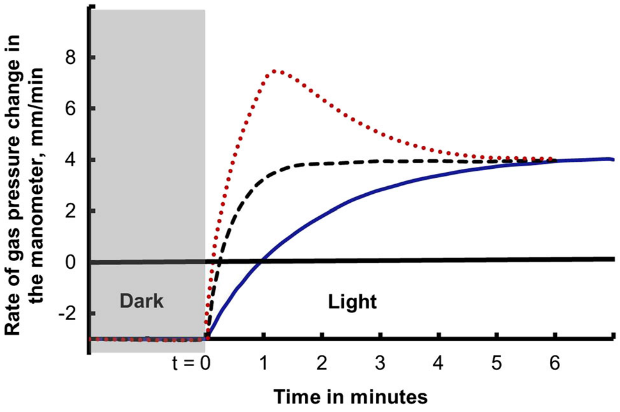

Fig. 6 A diagram of the time course of transition from dark to light. The *solid line* is for transition observed in cells suspended in carbonate/bicarbonate buffer; and the *dotted line* is for cells suspended in acid phosphate medium, as observed by Robert Emerson and coworkers. The dashed line is for cells in acid phosphate medium as published by Warburg and co-workers. Modified and redrawn by A. Stirbet and Govindjee from Emerson and Chalmers (1955, see Fig. 4 on p. 512)

Otto Warburg, irritated by the repeated questioning of his findings, requested in 1955 that the US National Academy of Sciences send a commission to Berlin to witness a laboratory demonstration. The Academy's photosynthesis researchers, however, rejected the idea, saying that science should work through its problems in the usual way, not by a committee (see Nickelsen and Govindjee 2011, pp. 107–108).

Emerson and Chalmers' (1955) paper persuaded most researchers that a minimum of ~8 to 10 quanta were required for the evolution of one O_2 molecule. In this paper, a clear CO_2 burst was shown to exist under Warburg's experimental conditions, and its inclusion as O_2 was the only way to obtain the erroneous low value for the minimum quantum requirement (see Fig. 6). Warburg continued to tinker with his experimental set-up, however, always reporting the same low minimum quantum requirement. For example, Warburg et al. (1954, 1955) asserted that, in order to compensate for respiration, high-intensity white background light was not necessary, as Warburg had believed previously, but that low-intensity blue or green light was effective. Warburg called their effects "catalytic." Emerson, although describing Warburg's manometry as "almost mystical," agreed that there are some special effects at certain wavelengths of blue light, as he and Lewis had described in 1943 (see Nickelsen and Govindjee 2011, p. 112).

The Emerson Enhancement Effect

To check Warburg's catalytic-light claim, Emerson et al. (1957) studied photosynthesis efficiencies at different wavelengths, and in the process made an important discovery related to Emerson and Lewis's (1943) finding that at low light intensities photosynthetic efficiency decreased at wavelengths beyond 685 nm (in the red region), even though chlorophyll *a* still absorbs appreciably in this region. The new finding was: The quantum yield at wavelengths longer than 685 nm was enhanced by adding supplementary light of wavelengths between about 644 and 680 nm (also in the red region). Emerson et al. (1957) emphasized that their findings were very different from the catalytic blue light effect reported by Warburg et al. (1954). Their discovery of the *Emerson Enhancement Effect* led Emerson (1958) and Emerson and Chalmers (1958) to conclude that photosynthesis is run by two pigment systems (see Govindjee and Bjorn 2012), while Warburg (1958) continued to study blue light's catalytic effects. Emerson postulated that, in *Chlorella*, the pigments that sensitized the two systems were chlorophyll *a* and chlorophyll *b*. In other algae, he thought that different pigments substituted for chlorophyll *b*. He was correct that there are two pigment systems, but wrong about the role of chlorophyll *b* and other accessory pigments in the reactions. Govindjee and Rabinowitch (1960) and R. Govindjee et al. (1960) clearly established that both pigment systems were run by chlorophyll *a* of different spectral forms (see the *Epilogue*). Clearly, the existence of two pigment systems and two light reactions means that a minimum of 8 quanta are required to oxidize water to O_2, which would be in complete agreement with Einstein's law of photochemical equivalency, and, thus, in our opinion, should have satisfied Warburg.

Epilogue

After Robert Emerson's death, on February 4, 1959, in an airplane crash, Eugene Rabinowitch posthumously published some of Emerson's experimental work, as Emerson and Rabinowitch (1960). In this paper, the ability of shorter-wavelength supplementary light to enhance the decreased photosynthetic efficiency at longer wavelengths was called, for the first time, the "(second) Emerson effect" (and the CO_2 burst was named the "first Emerson effect"). Rabinowitch argued, however, that Emerson erred in attributing the phenomenon to a direct contribution of chlorophyll *b* in *Chlorella*, because fluorescence experiments by Duysens (1952) had shown that almost all the quanta absorbed by chlorophyll *b* were transferred to chlorophyll *a*. Rabinowitch instead stated that chloroplasts have two kinds of chlorophyll *a*: One, the short-wavelength form, accepts more excitation energy from chlorophyll *b* than the other, and the maximum quantum yield could not be obtained when only the long-wavelength spectral

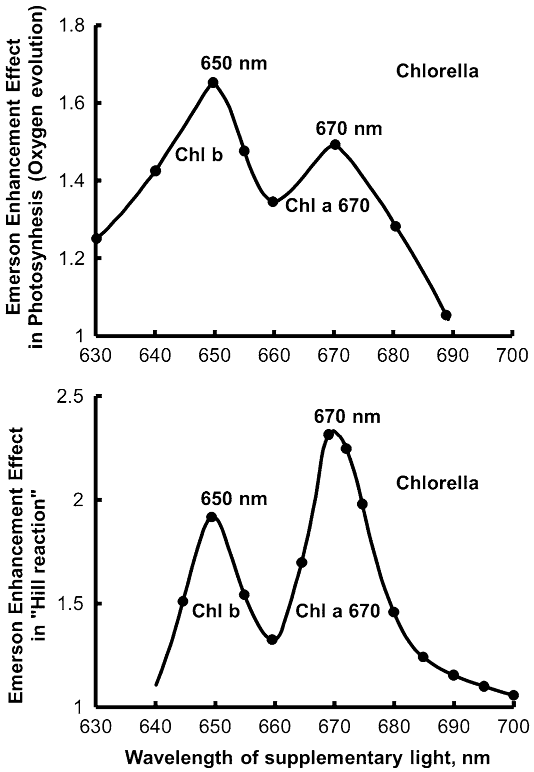

Fig. 7 Action spectra of the Emerson Enhancement Effect in photosynthesis (*upper graph*; Govindjee and Rabinowitch 1960) and in Quinone-Hill reaction (*lower graph*; R. Govindjee et al. 1960) in *Chlorella* cells. In both cases, far-red light beam (Photosystem I) was kept constant and enhancement was measured by varying the wavelength of the orange-red light (Photosystem II). Both established that Chl *a* 670 was present in the same photosystem that had Chl *b*; further, the Hill reaction data suggested that the observed effect was in photosynthesis, not in respiration since the para-benzoquinone used in the experiment had fully inhibited respiration. The figures were modified and redrawn by A. Stirbet and Govindjee from earlier plots by Govindjee and Bjorn (2012, see p. 9)

form of chlorophyll *a*, by itself, absorbed the light (see discussion in Nickelsen and Govindjee 2011, p. 118). This was precisely the point established by the action spectra of the (second) Emerson effect (which became known as the Emerson Enhancement Effect) showing that the short-wave absorbing form of Chlorophyll *a* (Chlorophyll *a* 670) was in the same system as Chlorophyll *b* (see Fig. 7, upper graph; Govindjee and Rabinowitch 1960; cf. Rabinowitch and Govindjee, 1961).

Govindjee recalls that the idea that chlorophyll (Chl) *b* cannot carry out a light reaction by itself, since it transfers all its absorbed energy to Chl *a*, was already being actively discussed, especially by Steve Brody, during the weekly "photosynthesis seminars" in the "Photosynthesis Project" at UIUC during 1957–1958. After the seminars, Govindjee would walk back with Emerson to Govindjee's apartment, which was on the way to Emerson's home. Almost every time, Govindjee would ask Emerson to explain why he did not accept this idea, Emerson always gave the same answer: "I am an experimentalist; only my experiments can dictate the answer." We now know that Emerson had missed seeing Chl *a* in the system in which Chl *b* (or other auxiliary pigment) was present because the Hg–Cd lamp Emerson was using did not emit light at the wavelengths that Chl *a* absorbs. In hindsight it seems that he had full faith that Chl *a* could not be involved because of the "Red drop" he had discovered in the region Chl *a* absorbed. It was the experiment of Govindjee and Rabinowitch (1960) that solved the dilemma because Govindjee used a tungsten lamp, which provided all wavelengths of light, including those that could be absorbed by Chl *a*.

Two pigments and two light reactions, operating in a "Z"-scheme (as described by Hill and Bendall 1960; see Govindjee and Bjorn 2012 for earlier contributions by others) soon became the standard model in photosynthesis (see Nickelsen 2009a, 2012). One of the photosystems, Photosystem II, oxidizes water and reduces cytochrome *f* (Wydrzynski and Satoh 2005), and the other, Photosystem I, oxidizes reduced cytochrome *f* and reduces $NADP^+$ (Golbeck 2006). The Z-scheme accounts nicely for the observed minimum quantum requirement of 8, because each of the 4 electrons from water requires 2 quanta, one in each photosystem. Because there is also a cyclic electron flow around Photosystem I, this number is often 10–12 (see current versions of Z-Schemes in, e.g., Govindjee and Bjorn (2012) and Orr and Govindjee (2013)). The Z-scheme was decisive in resolving the quantum-yield controversy. The *Emerson Enhancement Effect* was explained by a two-pigment system and two-light-reaction scheme. The long-wave limit of Photosystem II produces the *Red Drop*, and at wavelengths beyond the red drop, a supplementary beam of shorter wavelength is required in order for Photosystem II to supply electrons to Photosystem I.

Because measurements of the minimum quantum requirement were made via the net oxygen exchange, the finding of a minimum requirement of 8–10 could easily have been due to effects on respiration. Rajni Govindjee, however, established that the Emerson Enhancement Effect occurred in the light reactions of photosynthesis, not in respiration (R. Govindjee et al. 1960, 1962, 1964; see Fig. 7, lower graph). R. Govindjee et al. (1960) had used para-benzoquinone (p-BQ) as an electron acceptor for the Hill reaction in *Chlorella* cells; further, p-BQ also inhibits respiration. However, R. Govindjee et al. (1962, 1964) had discovered the Emerson Enhancement Effect in electron flow from water to $NADP^+$. Additional proof came from mass spectroscopic ^{18}O measurements in *Chlorella* (Govindjee et al. 1963). All the new research showed 8–10 quanta as a minimum requirement for the release of one oxygen molecule.

As noted earlier, Emerson died on Feb. 4, 1959. In 1963, in Gif-sur-Yvette, France, Eugene Rabinowitch overheard Warburg saying, "*now the problem is solved,*" (Rabinowitch to Govindjee, unpublished conversation in Urbana, Illinois, in September 1964). The implication might be that since his major opponent was no more, Warburg's views would be accepted by others, especially when Warburg recounted the conditions that Emerson had not followed. Several years later, to respond definitively to this challenge by Warburg, Govindjee and Rajni Govindjee decided to repeat the measurements in *Chlorella* cells. R. Govindjee et al. (1968) confirmed the number of 8–10 quanta, under the conditions that Otto Warburg had claimed, in 1963 and later, that Emerson had not used: (1) young synchronous cells of *Chlorella*; and (2) the presence of 10 % CO_2. In addition, Senger and Bishop (1967) had also measured a minimum quantum requirement of 10–11 per oxygen evolved in younger (8 h) versus 16–17 quanta in older (16 h) *Scenedesmus* cells. Further, Ng and Bassham (1968) published a minimum requirement of 9–12 quanta in *Chlorella* by measuring both oxygen release and carbon dioxide uptake. Requirements of no fewer than 8 quanta per oxygen were also reported years later by Ley and Mauzerall (1982) and Skillman (2008).

Warburg remained unconvinced to his death. In his final paper, published under the authorship of Warburg et al. (1969), he reported a value of approximately 12 quanta per O_2 molecule at the lowest light intensity used; a linear extrapolation to zero light intensity would give a value of 8–10 quanta per O_2 molecule! Although this result agreed with measurements made by Warburg's critics, Warburg et al. (1969) interpreted it as indicating that the *Chlorella* cells contained a large amount of "free," photochemically inert, chlorophyll. They postulated that there is a complex of chlorophyll bound to carbonic acid, and they called it 'photolyte.' They said that the minimum quantum requirement had to be calculated only from the amount of photolyte, even though there was no evidence for its existence. Warburg's concept of photolyte conformed to his long-held belief that the oxygen that was evolved in photosynthesis came from CO_2, an idea that harked back to Willstätter and Stoll (1918) and even much earlier (see Hill 2012). Research conducted by van Niel (1932, 1941), Hill (1937, 1939), and Ruben et al. (1941), however, had indicated that the O_2 came instead from water. Warburg et al. (1969) calculated, at all light intensities, roughly the same value—i.e., 3 quanta per O_2—as Warburg had calculated before he had differentiated between free chlorophyll and photolyte.

During the 1950s, advances in spectroscopy and the use of carbon-14 as a tracer had already increased understanding of photosynthesis significantly. Most researchers by then had accepted that CO_2 was not photochemically split, with the release of oxygen, and was not directly reduced to carbohydrate. Instead, it entered a complex reaction cycle (the "dark" cycle) that had been discovered in the 1950s by a Berkeley team led by Melvin Calvin and Andrew Benson (Calvin et al. 1950; see Bassham et al. 1954; Benson 2002; Bassham 2003; Nickelsen and Govindjee 2011, p. 120). In 1961, Calvin received the Nobel Prize in Chemistry for discovering the path of carbon in photosynthesis, leaving out Benson, who had done most of the earlier pioneering work on this subject, but this is another story (see BBC movie "Botany: A Blooming History, Episode 2, The Power of Plants" 2010; Govindjee 2010; Benson 2010; Buchanan 2012; Buchanan and Wong 2013).

Warburg et al. (1969) still thought that, because water oxidation required the removal of 4 electrons to release one molecule of oxygen, the minimum requirement had to be 4 light quanta per oxygen, based on the law of photochemical equivalency. Warburg was indeed correct that this law applies to photosynthesis, and had he accepted—as had most researchers since about 1960—that there were two light reactions and two pigment systems, he probably also would have accepted a minimum quantum requirement of 8 per oxygen. Govindjee (1999) commented, "*In view of the fact that both Warburg and Emerson were ideal experimentalists, the 'resolution' of the measured values brings relief to us*."

Warburg ultimately failed to demonstrate that the changes he made in his experimental protocols were relevant. Instead, his changes, especially in later years, seem arbitrary, and he often did not describe his set-ups precisely. The range of experimental conditions he used failed to produce a corresponding range of experimental results, and even when he did obtain the same results as other researchers, he devised convoluted explanations for them rather than accept them at face value. Perhaps it has to do with the frailty of the human mind—when "ego" dominates and scientific logic takes a back seat. According to Martin Kamen (1989, 1995), A.J. Liebling, a *New Yorker* magazine writer, had mused that "*if you are smart enough and work hard enough you can pick yourself up by the scruff of your neck and throw yourself out in the street!*" Kamen (1989) postulated that Warburg had done precisely that, buoyed by a belief that "nature tends toward perfection and experiments showing otherwise in photosynthesis were faulty." Warburg (1958) had written, "In summary, one can say that, with the fixing of the conditions of culture and measurement, the dispute concerning the efficiency of utilization of sun-light is finally decided. *It is a decision in favor of nature.* The reaction by which nature transforms the energy of sunlight into chemical energy, and upon which the existence of the organic world is based, is not so imperfect that the greater part of the applied light energy is lost; on the contrary, *the reaction is, like the world itself, nearly perfect.*"

Although Warburg claimed as late as 1970 (the year of his death) that he had solved the problem of photosynthesis, he stated, "[I have] wasted my time and energy in controversy, when I should have been going on doing new experiments" (see Nickelsen and Govindjee 2011, p. 124). As almost everyone else in the field concurred that the controversy had wasted researchers' time, it conceivably could have ended much earlier and more fruitful research could have been pursued (Nickelsen and Govindjee 2011, p. 124).

As a result of the damage to his reputation, Warburg's finding (Warburg and Krippahl 1958) that very small amounts of carbon dioxide were necessary in order for the Hill reaction (i.e., photosynthesis without carbon fixation) to function tended to be ignored.[1] Although Warburg was wrong in believing that CO_2 is the source of oxygen, CO_2 (as bicarbonate) does play a key role in electron and proton transport in Photosystem II, particularly on its electron acceptor, the plastoquinone, side, as discovered in the laboratory of Govindjee.

For details on the bicarbonate effect on Photosystem II, see, e.g., reviews by Govindjee and van Rensen (1978), van Rensen et al. (1999), and Shevela et al. (2012). We note that Umena et al. (2011) showed, in a 1.9 Å resolution structure of Photosystem II, that bicarbonate is indeed bound on non-heme iron that sits between the primary and secondary electron acceptor plastoquinones. The work of Stemler et al. (1974) (see Stemler 1982; El-Shintinawy and Govindjee 1990; Klimov et al. 1995) has shown that there is also a bicarbonate effect on the electron donor side of Photosystem II; however, it is the research group of Johannes Messinger (Koroidov et al. 2014) that has shown that indeed bicarbonate plays a role in accepting protons released during water oxidation on the electron donor side of Photosystem II.

Despite the bitterness of the quantum-yield controversy, it produced a large volume of correspondence and frequent scientific meetings, which advanced the knowledge and understanding of photosynthesis. Warburg's report of the curious effects of blue light inspired Emerson to pursue this line of research again, having already found in 1943 that short-wavelength light had peculiar effects. Had he not pursued this phenomenon, Emerson might not have hit upon the *Enhancement Effect* (Nickelsen and Govindjee 2011, p. 127). In addition, exploration of the complex relationship between photosynthesis and respiration, and the problems of algae cultivation, benefited photosynthesis research considerably. Thus, even the detours in the path of the research were not totally in vain.

Kok (1948) had discovered that the quantum yield of photosynthesis abruptly increases below the compensation point (i.e., when the rate of photosynthesis equals the rate of respiration); this became known as the "Kok effect." Sharp et al. (1984) showed that this effect is due to a suppression of dark respiration, giving a false increase in efficiency of photosynthesis. Its possible relevance to the Warburg-Emerson controversy no longer exists as originally suggested (see a thorough discussion of all the experiments on the maximum quantum yield of photosynthesis until 1951 in Chapter 29 of Rabinowitch (1951)).

Although the existence of two light reactions and two pigment systems is well-established, the idea that one light reaction may be sufficient has been published off and on (e.g., Arnon and Barber 1990; Greenbaum et al. 1995), but these publications have not survived the test of time (Blankenship 2014). Yes, sometimes one light reaction (run by Photosystem II only) can sustain photosynthesis for a short time in the presence of glucose, but then the energy for the entire process comes from other chemical reactions as well, and the process is rather temporary (Wang et al. 2012; cf. Govindjee et al. 1967). A three-light-reaction scheme was presented by Arnon et al. (1971), but it has not been tested by others, or even seriously examined.

For a discussion of the thermodynamic efficiency of photosynthesis, see, e.g., Emerson (1958), Duysens (1958,

Fig. 8 A photograph of Kärin Nickelsen and Govindjee, in Nickelsen's office at the University of Bern when they were working on their 2011 book. Govindjee is wearing Emerson's apron that he had used during the 1940s–1950s, while doing his experiments; he is also wearing a red tie of the kind Emerson wore when he did his experiments in his lab; in addition, Govindjee is holding a 1928 book by Otto Warburg (see Warburg 1928). Photograph by Rajni Govindjee

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[1] John F. Allen told us about his recollection of an exchange at a Photochemistry Discussion Group meeting at London's Royal Institution in 1975. Sir George Porter was organizer and chair. Helmut Metzner had just given a talk on the possible role of bicarbonate/CO_2 in the Hill reaction. Porter addressed Robin Hill in the audience, "*But, CO_2 is not required for your reaction; is it*? Robin replied "*Yes, it is*." (See Shevela et al. 2012 for a complete perspective on this issue.)

Fig. 9 2014 photographs of the authors. *Left* Jane F. Hill; *right* Govindjee; photographs taken by William A. Hill, and Rajni Govindjee, respectively

1962), Ross and Calvin (1967), Knox (1969), Parson (1978), Bolton and Hall (1991, and references cited therein), and Mauzerall (2013). Bolton and Hall (1991) pointed out that the high efficiencies suggested by Pirt (1986) and by Osborne and Geider (1987) cannot be supported on theoretical grounds. All of them clearly reject the view that oxygenic photosynthesis can ever take place with 70 % efficiency (Otto Warburg), but they can with 35 % efficiency (Robert Emerson and others). For maximum quantum yield of photosynthesis under field conditions, see Baker et al. (1989).

We end this Historical Corner perspective with the following quote from *Panchatantra*: "*The firefly seems afire, the sky looks flat; yet sky and fly are neither this nor that*" (see Ryder 1957). What this means to us is that all scientific conclusions must be continually questioned, including those of our teachers, Nobel-laureates or not, and, especially, our own!

Figure 8 shows a photograph of Kärin Nickelsen and Govindjee while they were working on their 2011 book, *The Maximum Quantum Yield Controversy: Otto Warburg and the 'Midwest Gang.'* Figure 9 shows photographs of the authors of this paper.

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