Photosynthesis

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Content

Literally, the synthesis of chemical compounds using light. The term photosynthesis, however, is used almost exclusively to designate one particularly important natural process: the use of light in the manufacture of organic compounds (primarily certain carbohydrates) from inorganic materials by chlorophyll- or bacteriochlorophyll-containing cells. This process requires a supply of energy in the form of light, since its products contain much more chemical energy than its raw materials. This is clearly shown by the liberation of energy in the reverse process, namely the combustion of organic material with oxygen, which takes place during respiration. *See also:* **Chlorophyll (/content/chlorophyll/132200)**; **Plant respiration (/content/plant-respiration/524600)**; **Respiration (/content/respiration/583400)**

Among chlorophyll-containing plant and algal cells, and in cyanobacteria (formerly known as blue-green algae), photosynthesis involves the oxidation of water (H_2O) to produce oxygen molecules, which are then released into the environment. This is called oxygenic photosynthesis. In contrast, bacterial photosynthesis does not involve O_2 evolution (production). In this case, other electron donors, such as H_2S, are used instead of H_2O. This process is called anoxygenic photosynthesis. Both types of photosynthesis are discussed below.

The light energy absorbed by the pigments of photosynthesizing cells, especially by chlorophyll or bacteriochlorophyll pigments, is efficiently converted into stored chemical energy. Together, the two aspects of photosynthesis—the conversion of inorganic matter into organic matter, and the conversion of light energy into chemical energy—make it the fundamental process of life on Earth: it is the ultimate source of all living matter and of almost all of the energy of life. All types of photosynthesis require light; therefore, photosynthetic organisms are generally restricted to the photic zone, that is, the

narrow region of the Earth near the surface that receives sunlight. The only known exceptions are the anoxygenic photosynthetic bacteria that live near deep-sea hydrothermal vents and utilize the very weak light given out by the hot vents.

The total productivity of photosynthesis on Earth has been estimated in various ways. The most accurate modern method uses satellite remote-sensing data to estimate both land-based and oceanic photosynthesis. These estimates take into consideration the fact that the vegetation in these areas make use of only 1% of the entire solar spectrum on average, or 2% if only visible light is considered. The net primary productivity of photosynthesis on Earth has been determined to be about 115 petagrams of carbon per year [1 petagram (Pg) equals 10^{15} grams or 10^{9} metric tons]. The contributions of land- and ocean-based primary production are roughly equal, although the accumulation of biomass on land is much higher than in the ocean. This is due to the fact that organisms rapidly recycle the fixed carbon in the oceans by consuming it.

Oxygenic photosynthesis

The net overall chemical reaction of oxygenic photosynthesis (by plants, algae, and cyanobacteria) is shown in Eq. (1),

$$H_2O + CO_2 + \text{light energy} \xrightarrow[\text{enzymes}]{\text{chlorophyll}} \{CH_2O\} + O_2 \tag{1}$$

where $\{CH_2O\}$ stands for a carbohydrate (sugar). The photochemical reaction in photosynthesis belongs to the type known as oxidation-reduction, with CO_2 acting as the oxidant (electron acceptor) and water as the reductant (electron donor). The unique characteristic of this particular oxidation-reduction is that it is energetically unfavorable; that is, it converts chemically stable materials into chemically unstable products. Light energy is used to make this “uphill” reaction possible. A considerable part of the light energy used for this process is stored as chemical energy.

Temporal phases of photosynthesis

Photosynthesis is a complex multistage process that consists of nearly a hundred physical processes and chemical reactions. To make this complex process more understandable, it is useful to divide it into four temporal stages. Each phase is based roughly on the time scale in which it occurs. These phases are (1) photon absorption and energy transfer processes in antennas (or antenna chlorophylls, molecules which collect light quanta); (2) primary electron transfer in photochemical reaction centers; (3) electron transport and adenosine triphosphate (ATP) formation; and (4) carbon fixation and export of stable products.

Phase 1 takes place in the femtosecond [1 femtosecond (fs) = 10^{-15} s] to picosecond [1 picoseond (ps) = 10^{-12} s] time scale. Phase 2 takes place in the picosecond to nanosecond time scale [1 nanosecond (ns) = 10^{-9} s]. Phase 3 takes place on the microsecond [1 microsecond (μs) = 10^{-6} s] to millisecond [1 millisecond (ms) = 10^{-3} s) time scale. Phase 4 takes place in the millisecond to second time scale. We will consider each of these phases of photosynthesis in more detail below. The time scales are shown schematically in **Fig. 1**.

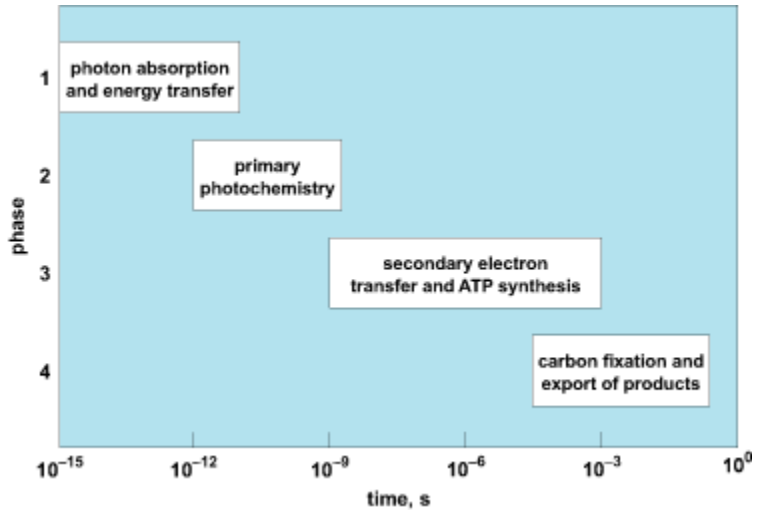

Fig. 1 Four temporal phases of photosynthesis.

Sites of photosynthesis

The photosynthetic process takes place within certain structural elements found in plant cells. All algae, as well as all higher plants, contain pigment-bearing subcellular organelles called chloroplasts. In the leaves of the higher land plants, these are usually flat ellipsoids about 5 micrometers in diameter and 2.3 μm in thickness. Ten to 100 of them may be present in the average parenchyma cell of a leaf. Under the electron microscope, all chloroplasts show a layered structure with alternating lighter and darker layers of roughly 0.01 μm in thickness. These layers are membranes that contain proteins. These membranes are called thylakoid membranes (thylakoid stands for a membrane sac). The proteins bind all of the chlorophyll. The membranes are the sites of the first three phases of photosynthesis. In algae, the number and shape of chloroplasts vary much more. The green unicellular alga *Chlorella* contains only one bell-shaped chloroplast. A typical chloroplast is shown in **Fig. 2**. *See also:* **Cell plastids (/content/cell-plastids/117100)**

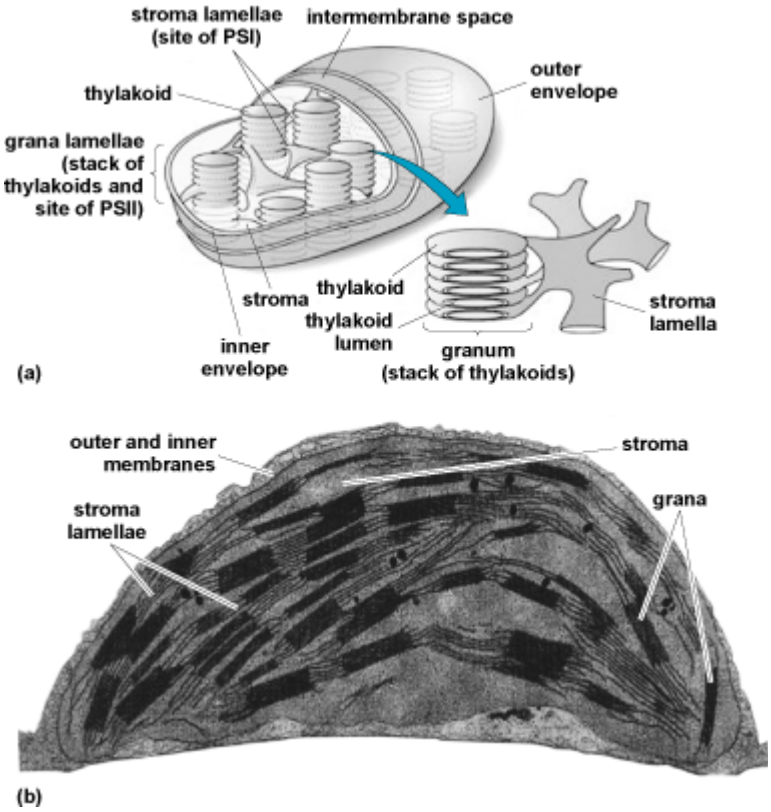

Fig. 2 A typical chloroplast. (*a*) Schematic diagram of a higher plant chloroplast. (*b*) Electron micrograph of a chloroplast. (*After L. Taiz and E. Zeiger, 2006*)

The photochemical apparatus is less complex in cyanobacteria. These cells are prokaryotes and therefore lack a nucleus and organelles such as chloroplasts and mitochondria. The early phases of photosynthesis take place on thylakoid membranes, which extend throughout the interior of the cell.

Quantum energy storage process

In photosynthesis, the energy of light quanta is converted into chemical energy. As seen in Eq. (1), the conversion of 1 mole of CO_2 and 1 mole of H_2O produces 1 mole of a carbohydrate group and 1 mole of oxygen. This reaction results in the storage of about 469 kilojoules of total energy per mole or, under natural conditions, about 502 kJ of potential chemical energy (free energy) per mole. Pigments absorb light in the form of quanta (photons). *See also:* **Absorption of electromagnetic radiation (/content/absorption-of-electromagnetic-radiation/001600)**; **Photon (/content/photon/511100)**

Discovery of two photosystems

A specific mechanism in which two photochemical events cooperate to carry out oxygenic photosynthesis was suggested by experiments of Robert Emerson. Emerson discovered that the “maximum quantum yield of photosynthesis” (number of O_2 molecules evolved per absorbed quantum), while constant at the shorter wavelengths of light (red, orange, yellow, green), declines in the far-red above 680 nanometers (the “red drop”). Later, Emerson and coworkers showed that this low yield could be enhanced if both chlorophyll *a* and *b* are simultaneously excited (only chlorophyll *a* absorbs above 680 nm). This effect, now known as the Emerson enhancement effect, suggests that two different pigments must be excited to perform efficient photosynthesis, thus indicating that two light reactions are involved in photosynthesis. Further, it suggests that one of these pigments is sensitized by light absorption in chlorophyll *a* and one by absorption in another pigment (for example, chlorophyll *b*). Experiments by others enlarged Emerson's observation by suggesting that plants contained two pigment systems. One (called photosystem I, or PSI; sensitizing reaction I) is primarily composed of chlorophyll *a*; the other (called photosystem II, or PSII; sensitizing reaction II) is also composed of chlorophyll *a*, but includes most of chlorophyll *b* or other auxiliary pigments. These other auxiliary pigments include red and blue pigments, called phycobilins, in red algae and cyanobacteria, for example, and the brown pigment fucoxanthol in brown algae and diatoms. Efficient photosynthesis requires the absorption of an equal number of quanta in PSI and in PSII. This ensures that within both systems excitation energy is absorbed by the antenna system and partitioned to each photosystem, where the energy drives the chemical reactions.

Robert Hill proposed that one of these reactions involves the transfer of an electron from an intermediate to cytochrome b_6 (shown later to be a plastoquinone molecule) during the conversion of water to oxygen). The other reaction, he proposed, involves the transfer of an electron from cytochrome *f* to an intermediate in the conversion of CO_2 to carbohydrate. The intermediate transfer of an electron from reduced plastoquinone (plastoquinol) to cytochrome *f* can occur without energy input because the former is a stronger reductant than the latter. There is a great deal of experimental evidence for the existence of two pigment systems and for the key role of plastoquinone and cytochrome *f* in this sequence. Louis N. M. Duysens and Jan Amesz conducted a crucial early experiment showing the existence of two photosystems. In this, they showed that light 1, absorbed by chlorophyll *a*, oxidizes cytochrome *f*, and that light 2 (absorbed in other photosynthetic pigments, including chlorophyll *a*) reduces this oxidized cytochrome *f*. The results suggest that the two light reactions are arranged in series.

Z scheme and the proteins that carry it out

The two photochemical events that were discovered at that time are now known to take place on large protein complexes

embedded in the thylakoid membrane. **Figure 3** shows the four large protein complexes found in the thylakoid membrane, and demonstrates the interactions between photosystems I and II; the cytochrome b_6 *f* complex functions between the photosystems, and the ATP synthase which makes ATP. Arrows show the pathway of electrons and protons (H^+), the latter is essential for the formation of ATP. Note that the membrane has an inherent asymmetry in that the protein complexes are oriented in a particular way in the membrane. This orientation is essential to the proper functioning of photosynthesis.

Figure 4 shows the Z scheme, summarizing the way in which the two photosystems cooperate to carry out electron transfer reactions involved in photosynthesis. It is an energetic diagram, in that the energy of the component, which is measured as the midpoint redox potential E_m, is shown on the *y* axis and the progress of the reaction is shown on the *x* axis. The two vertical arrows represent energy input to the system due to photon absorption.

The structures of all four of the large protein complexes are now known due to x-ray crystallography studies. The combination of the structural pictures in Fig. 3 and **Fig. 5** and the energetic picture in Fig. 4 provides an understanding of the process that neither diagram individually can portray.

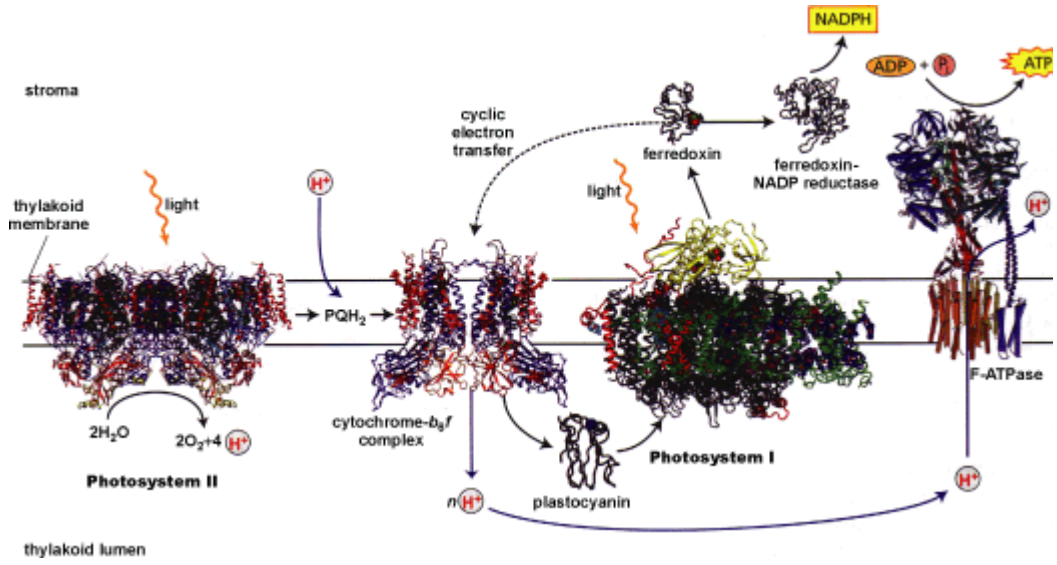

Fig. 3 Structural diagram of the four protein complexes present in the thylakoid membrane, as characterized by x-ray crystallography. Photosystem II (PSII), the cytochrome b_6f complex (cyt b_6f), photosystem I (PSI), and the ATP synthase are shown in the figure. Electron transfer steps are shown as solid arrows while proton flow is indicated by dashed arrows.

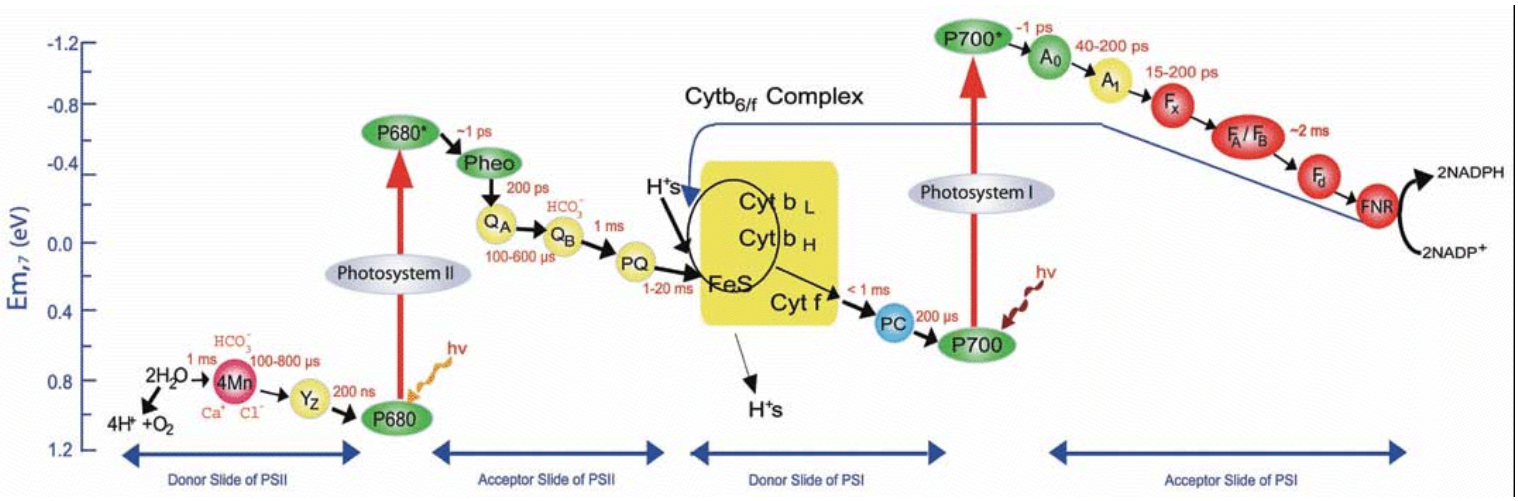

Fig. 4 Z scheme of photosynthesis, representing electron flow and chemical reactions in the two light steps in photosynthesis. Y_z (a tyrosine residue, also referred to as Z) is the electron donor to the oxidized chlorophyll *a* P680 of

PSII, and Mn (manganese-containing protein) is the charge accumulator that leads to O_2 evolution. Pheo (pheophytin) and Chl (a A_0 chlorophyll *a*) are the primary electron acceptors of PSII and PSI, respectively. Q_A and F_X (an iron-sulfur center) are the stable electron acceptors of PSII and PSI, respectively. Q_B is another bound plastoquinone, while PQ is plastoquinone, Cyt is cytochrome, and PC is plastocyanin. A_1 is an electron acceptor of PSI, F_B and F_A are iron-sulfur centers, Fd is ferredoxin, and FNR is ferredoxin $NADP^+$ reductase. E_m is the reduction-oxidation (redox) potential.

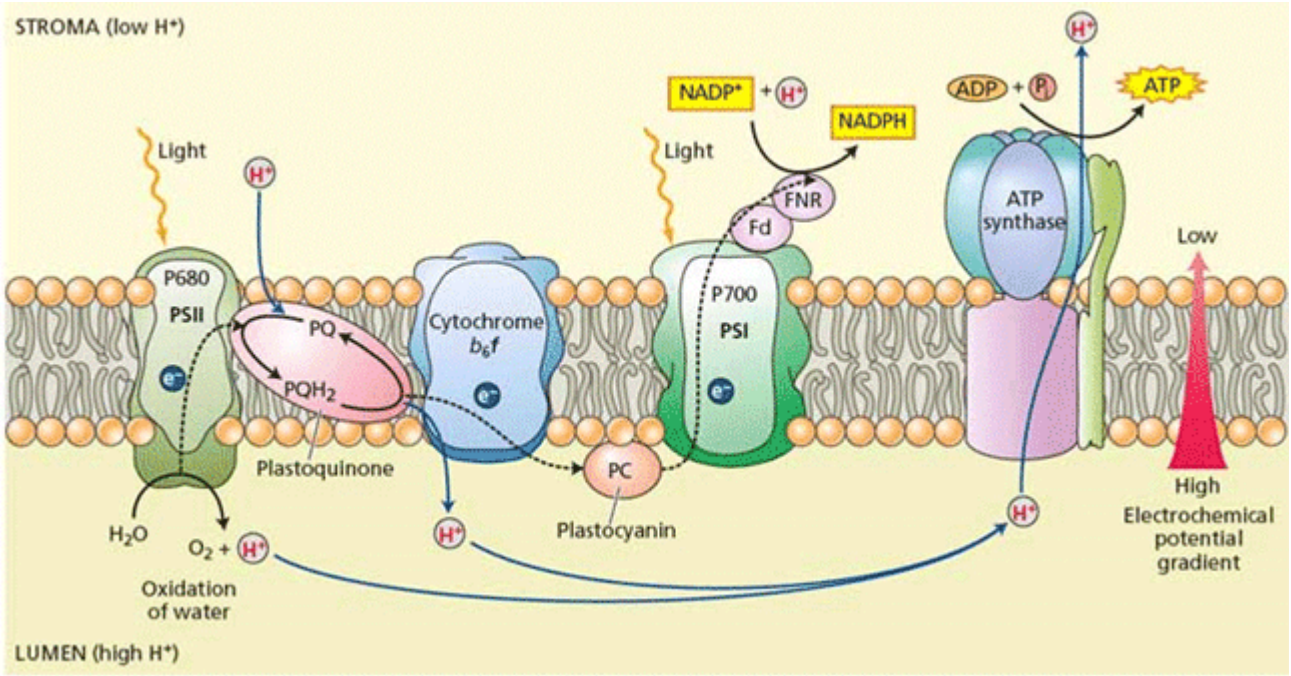

Fig. 5 A diagram of the four major protein complexes of the thylakoid membrane.

Chemical role of chlorophyll

How does the chlorophyll *a* molecule, after excitation by the absorbed quantum of energy, utilize it for an energy-storing photochemical process, such as the transfer of an electron from a reluctant donor, H_2O, to a reluctant acceptor (perhaps $NADP^+$)? The chemical properties of chlorophyll are very different in the excited state from the unexcited or ground state. The excited chlorophyll acts as a very strong reducing agent, so that it easily loses an electron to a nearby acceptor. This is the primary photochemical process in photosynthesis. Support for this concept is provided by observations of reversible photochemical oxidation and of reversible photochemical reduction of chlorophyll in solution, and the comparison of these data with those in more intact systems. Studies of changes in the absorption spectrum of photosynthetic cells in light show that a small fraction of a special form of chlorophyll *a* (including P700), absorbing maximally at 700 and 430 nm, is in an oxidized state during illumination. This is at the heart of the reaction center of PS I. The reaction center Chl's of PS II (including P680) have been suggested also to undergo oxidation-reduction. Furthermore, a chlorophyll *a* molecule appears to be chemically reduced when P700 is oxidized to $P700^+$ in PSI. P700 has been shown to be a pair of Chl *a* and Chl a' molecules. In the above, the P stands for pigment and the numerical designation gives the location, in nanometers, of the maximum decrease in the absorption in the red or the infrared region of the spectrum.

Detailed reactions of PSI and II

The PSII reaction is the one most closely associated with O_2 evolution. The final result of this set of reactions is the oxidation of water to O_2 and the reduction of a plastoquinone (an oxidation-reduction catalyst). Current evidence suggests that light absorbed by the major part of the accessory pigments is ultimately transferred to a special chlorophyll *a* molecule in the PSII reaction center, which is in a favorable position to act as an energy trap. There is a charge separation within 3 picoseconds; this special chlorophyll molecule is oxidized, and a specific pheophytin (Pheo) molecule is reduced (Chl^+ $Pheo^-$). The positive

charge is transferred again within a few picoseconds to a pair of special Chl's nearby (P680). The P680 recovers by accepting an electron from a tyrosine amino acid residue that is represented by Y_Z (referred to as Z below), within 20–400 nanoseconds, as shown in reactions (2).

$$\mathrm{Chl} + h\nu_{\mathrm{II}} \rightarrow \mathrm{Chl}^* \tag{2a}$$

$$\mathrm{Chl}^* + \mathrm{Pheo} \rightarrow \mathrm{Chl}^+ + \mathrm{Pheo}^- \tag{2b}$$

$$\mathrm{Chl}^+\mathrm{P680} \rightarrow \mathrm{P680}^+ + \mathrm{Chl} \tag{2c}$$

$$\mathrm{P680}^+ + \mathrm{Z} \rightarrow \mathrm{P680} + \mathrm{Z}^+ \tag{2d}$$

The components of reactions (2), that is, the special chlorophyll, P680, pheophytin, and Z, and the next intermediates, Q_A and Q_B (bound plastoquinones), are located on a protein complex consisting of two polypeptides, D-1 and D-2 (approximately 32,000 molecular weight each). The oxidation product, the strong oxidant Z^+, is utilized to oxidize water and liberate O_2 and protons (Figs. 4 and 5).

The PS I reaction is the one most closely associated with the reduction of $NADP^+$. Light absorbed by most of the chlorophyll *a* molecules is transferred to a special chlorophyll *a* molecule P700, where the primary charge separation occurs: P700 is oxidized, and another special Chl *a* (A_0) is reduced in about a picosecond, as shown in reactions (3).

$$\mathrm{P700} + h\nu_{I} \rightarrow \mathrm{P700}^* \tag{3a}$$

$$\mathrm{P700}^* + \mathrm{Chl} \rightarrow \mathrm{P700}^+ + \mathrm{Chl}^- \tag{3b}$$

After the primary photochemical processes, several additional steps take place. In PSII, the electrons flow on the electron donor side from H_2O to oxidized tyrosine Z^+ via a manganese (Mn) complex. On the electron acceptor side, electrons flow from $Pheo^-$ to two special plastoquinones called Q_A and Q_B. A bound bicarbonate ion is essential for the electron and proton transfer from photosystem II to the plastoquinone pool. Additional reactions and cofactors connect the two photosystems, including a pool of PQ, the cytochrome b_6 *f* complex which contains cytochrome b_6, cytochrome *f* and the Rieske iron-sulfur protein, and the soluble copper protein plastocyanin. Plastocyanin finally re-reduces $P700^+$ in PSI. On the electron acceptor side of PSI, the electron that is lost from P700 flows from Chl a^- (A^-_0), through an intermediate A_1 (phylloquinone), the iron-sulfur centers (F_X, F_A, F_B), and soluble ferredoxin (Fd) and a flavoprotein called ferredoxin-NADP-reductase, eventually to $NADP^+$, reducing it (Figs. 4 and 5).

Mechanism of O_2 evolution

The mechanism of O_2 evolution is the least known part of photosynthesis. All oxygen liberated in photosynthesis originates in water. Based on the measurements, by Pierre Joliot and Bessel Kok, of the amount of O_2 evolved in single brief (10-μs) saturating light flashes, it has been shown that four oxidizing equivalents must accumulate on the O_2-evolving complex before it can oxidize H_2O to O_2. There is a period 4 oscillation in the pattern of O_2/flash as a function of flash number (**Fig. 6***a*, left). The system is an oxygen “clock” in which the state (S) of the O_2-evolving complex undergoes sequential reactions, and the subscripts on S represent the oxidizing equivalents accumulated on the complex; the system starts in the dark in S_1 state (Fig. 6*b*, right).

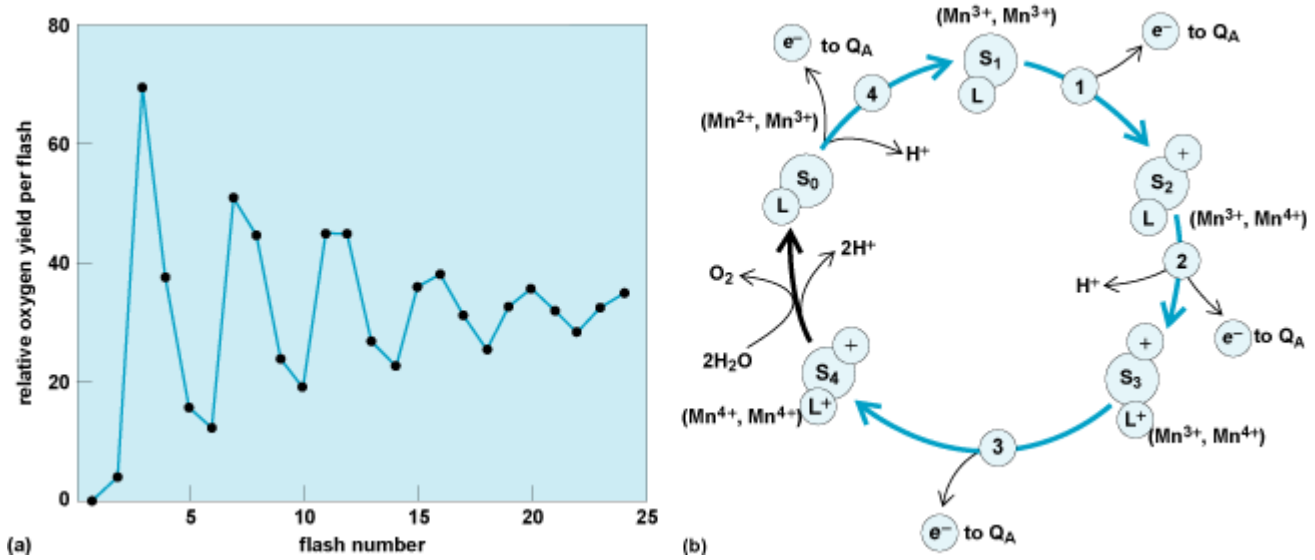

Fig. 6 Oxygen clock. (*a*) Pattern of oxygen evolution from dark-adapted chloroplasts when illuminated by a series of intense brief flashes. (*b*) S-state mechanism to describe oxygen evolution pattern. The oxygen-evolving complex can exist in five distinct states, S_0–S_4. Light activates PSII, which in turn advances the system through the states one step for each photochemical turnover of the PSII reaction center. When state S_4 is reached, oxygen is produced and the clock is reset to S_0.

Manganese (Mn) is required for O_2 evolution. Plants grown in a manganese-deficient medium lose their capacity to evolve O_2. The charge accumulator of the reaction mechanism is a manganese complex; manganese is known to exist in several valence states. In addition to manganese, chloride and calcium ions also function at the O_2-evolving site, though the mechanism of action is not known. The O_2-evolving complex includes at least four "intrinsic" proteins having molecular weights of 34,000, 32,000, 9000, and 4500 (D-1, D-2, and two subunits of cytochrome *b*-559). In addition, three "extrinsic" polypeptides of molecular weights 33,000, 24,000, and 18,000 are also involved. In cyanobacteria, the 24,000 and the 18,000 molecular weight proteins are replaced by a cytochrome *c* and another low molecular weight protein. Further research is needed to understand the detailed chemical mechanism of O_2 evolution.

Photophosphorylation

Inner cytoplasmic membranes from photosynthetic bacteria, cyanobacterial cells, and chloroplasts from green plants and algae—when illuminated in the presence of adenosine diphosphate (ADP) and inorganic phosphate (P_i)—use light energy to synthesize adenosine triphosphate (ATP). About 42 kJ of converted light energy in this reaction is stored in each mole of the high-energy phosphate, ATP. This photophosphorylation is coupled with energy-releasing steps in photosynthesis, such as the electron flow from PSII to PSI. When phosphorylation is associated with noncyclic electron flow from H_2O to $NADP^+$, it is called noncyclic photophosphorylation. *See also:* **Adenosine triphosphate (ATP) (/content/adenosine-triphosphate-atp/010700)**

Under certain conditions, electrons in PSI, instead of going to $NADP^+$, may return to an intermediate (such as a cytochrome, plastoquinone, plastocyanin, or P700) and thus close the cycle. This type of cyclic electron flow, mediated by added cofactors and ADP and inorganic phosphate, also leads to the production of ATP and has been termed cyclic phosphorylation; it has been shown to exist under certain experimental conditions in vivo.

The mechanism of ATP formation is very different from the electron transfer processes described earlier. Light produces a high-energy state, and then the actual phosphorylation occurs in the dark. André Jagendorf and coworkers found that if chloroplasts are first suspended in an acidic medium and then transferred to an alkaline medium in the presence of ADP and P_i, ATP formation occurs without the need of light. All of these experiments were explained in terms of a hypothesis proposed

by Peter Mitchell, in which light produces a H^+ ion gradient (ΔpH) across the lamellar membranes in the chloroplasts, and the energy dissipation of this H^+ ion gradient via the ATP synthase (sometimes called the coupling factor, a protein complex present in the lamellae) leads to phosphorylation. In addition, an electric field (ΔΨ) generated across the thylakoid membrane as a result of the initial light-induced charge separation can also drive photophosphorylation. Reagents that dissipate the electric field or the H^+ gradient also inhibit phosphorylation. The two together are referred to as proton motive force.

The ATP synthase is shown schematically in Fig. 5, and its structure is shown in Fig. 3. It has two parts, a section that is embedded in the thylakoid membrane and a section that protrudes into the stroma. Recent evidence demonstrates that the ATP synthase is a rotary motor, and most of the membrane-associated part rotates, while H^+'s are translocated across the membrane. Mechanical energy in this rotary motion is coupled to the formation of high-energy phosphate bonds in ATP. The chemical mechanism of this process is not yet well understood.

Photosynthetic unit

The concentration of the special chlorophyll *a* molecules (P700 or P680) that engage in the chemical reactions is very low, only one in several hundred chlorophyll molecules; energy absorbed by other pigments is effectively transferred to the reaction centers. The collection of antenna molecules along with their associated photosystems are often referred to as photosynthetic units.

Robert Emerson and William Arnold showed how the light reaction in photosynthesis can be separated from the dark reaction by the use of brief, intense light flashes, separated by intervals of darkness of variable duration. They found that the yield of a single flash was maximum when the interval between the consecutive light flashes was at least 0.04 s at 1°C (33°F). This, then, is the minimum time required for the efficient utilization of the products from the light reactions. Emerson and Arnold further observed that, under optimal conditions, the maximum yield from a single flash was one O_2 molecule per 2400 chlorophyll molecules present. However, it is now known that the two light-reaction mechanism of photosynthesis requires the transfer of four electrons twice for every molecule of oxygen evolved. Thus there are at least eight photoacts leading to the evolution of one O_2 molecule. Therefore, the ratio of one O_2 per 2400 chlorophylls means one photoact per 300 chlorophyll molecules. By using spinach grown in moderate to high light intensity, we know that there is one active PSII (P680) and one active PSI (P700) for a total of about 600 chlorophyll molecules present. If these chlorophyll molecules are equally divided in PSI and II, there is one reaction center per 300 chlorophyll molecules in each system. This is the commonly accepted size of one physical unit in higher plants, algae, and cyanobacteria.

Accessory antenna pigments

In addition to chlorophyll *a* (the one pigment present in nearly all oxygenic photosynthetic organisms), there are other chlorophylls, such as chlorophyll *b* in the green algae and higher plants. In brown algae, chlorophyll *c* replaces chlorophyll *b*. In a marine cyanobacterium *Acaryochloris marina*, most of Chl *a* is replaced by Chl *d*. There are also nonchlorophyllous pigments belonging to two groups: (1) the carotenoids, so called because of similarity to the orange pigment of carrots, are a variable assortment of pigments found in all photosynthetic higher plants and in algae. (2) The phycobilins, or vegetable bile pigments, are chemically related to animal bile pigments. The phycobilins are either red (phycoerythrin) or blue (phycocyanin). Both types are present in special granules called phycobilisomes in red algae (Rhodophyta) and cyanobacteria: the red pigment in red algae, and the blue pigment in cyanobacteria. Another phycocyanin called allophycocyanin is also present in cyanobacteria. All of these pigments are associated with specific proteins to form so-called antenna pigment proteins. The structures of many of these antenna complexes are known, and the energy transfer processes have been investigated using ultrafast laser techniques. *See also:* **Carotenoids (/content/carotenoids/110600)**; **Chlorophyll (/content/chlorophyll/132200)**; **Phycobilin (/content/phycobilin/512600)**

Light absorbed by accessory pigments does contribute to energy storage in photosynthesis. This is simply demonstrated from measurements of the so-called action spectra of photosynthesis. In such measurements, photosynthesis is excited by monochromatic light, and the production of oxygen per incident quantum of light is measured as a function of wavelength. The observed spectral variations in the yield of photosynthesis can be related to the proportion of light absorbed at each wavelength by the different pigments in the cells. Measurements of this kind have led to the conclusion that quanta absorbed by most carotenoids are 50–80% as effective as those absorbed by chlorophyll *a* in contributing energy to photosynthesis. An exception is fucoxanthol, the carotenoid that accounts for the color of brown algae (Phaeophyta) and that of the diatoms; it supplies light energy to photosynthesis about as effectively as chlorophyll *a*. The red and blue pigments of the Rhodophyta and cyanobacteria are also highly effective. They can be as effective as chlorophyll or somewhat less, depending, among other things, on the physiological status of the organism and the color of the light to which they have become adapted. The primary function of all these pigments is to harvest the light energy and transfer it to reaction-center chlorophyll molecules. However, in addition, several xanthophylls (violaxanthin, antheraxanthin, and zeaxanthin) and lutein are involved in photoprotecting photosynthetic organisms against excess light. In many cases, excess light energy is lost as “heat” via deexcitation of chlorophyll directly or via transfer to zeaxanthin.

Energy transfer between pigment molecules in antenna system

Chlorophyll *a* in vivo is weakly fluorescent, that is, some of the light quanta absorbed by it (up to 6%) are reemitted as light (**Fig. 7**, white curve). Observations of the action spectrum of chlorophyll *a* fluorescence in different oxygenic organisms closely parallel the action spectrum of photosynthesis. In other words, fluorescence of chlorophyll *a* is excited also by light absorbed by the accessory pigments. Excitation of chlorophyll *a* fluorescence by light quanta absorbed by phycoerythrin requires transfer of the excitation energy from the excited phycoerythrin molecule to a nearby chlorophyll molecule (somewhat as in acoustic resonance, where striking one bell causes a nearby bell to ring). Therefore, light quanta absorbed by accessory pigments, such as carotenoids and phycobilins, contribute to photosynthesis by being transferred to chlorophyll *a*. By this mechanism, red algae, growing relatively deep under the sea where only green light penetrates, can supply the energy of this light to chlorophyll *a*, which has very weak absorption in the green region of the spectrum.

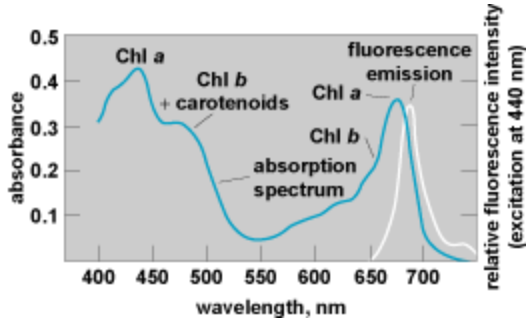

Fig. 7 Absorption spectrum of a maize (*Zea mays*) chloroplast suspension. Pigments responsible for specific bands are shown. Also shown is the fluorescence emission of chloroplasts from a maize chloroplast.

Excitation energy is transferred efficiently in the chloroplasts from accessory pigments to chlorophyll *a*. A similar transfer (often referred to as energy migration) occurs also between different chlorophyll *a* molecules themselves. Excitation-energy transfer among chlorophyll *a* molecules or among phycobilin molecules, and excitation-energy transfer from accessory pigments (donor molecules) to chlorophyll *a* (acceptor molecules) or from various short-wavelength forms of chlorophyll *a* to the long-wavelength forms of chlorophyll *a*, has been demonstrated. The most widely accepted hypothesis, Förster's hypothesis, is that energy transfer is preceded by thermal relaxation in the donor molecules. The efficiency of energy transfer depends upon three basic factors: orientation of acceptor molecules with respect to the donor molecule; overlap of the fluorescence spectrum of the donor molecule with the absorption spectrum of the acceptor molecule; and the distance

between the two molecules. The function of most of the pigments (including most of the chlorophyll *a* molecules) is to act as an antenna, harvest the energy, and transfer to very few (1 in 300) reaction-center Chl molecules, depending upon the pigment system. Energy is thus trapped and used for photochemistry. *See also:* **Chlorophyll (/content/chlorophyll/132200)**; **Plant pigment (/content/plant-pigment/524550)**

[Contributions of Rajni Govindjee to this article are acknowledged.]

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Govindjee

Carbon Dioxide Fixation

The light-dependent conversion of radiant energy into chemical energy as adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADPH) serves as a prelude to the utilization of these compounds for the reductive fixation of CO_2 into organic molecules. Such molecules, broadly designated as photosynthates, are usually but not invariably in the form of carbohydrates such as glucose polymers or sucrose, and form the base for the nutrition of all living things, as well as serving as the starting material for fuel, fiber, animal feed, oil, and other compounds used by people. Collectively, the biochemical processes by which CO_2 is assimilated into organic molecules are known as the photosynthetic dark reactions, not because they must occur in darkness but because, in contrast to the photosynthetic light reactions, light is not required. (We do recognize, however, that several enzymes need to be light-activated before they can function; see "Regulation of C_3 cycle enzymes" below.) CO_2 fixation by photosynthetic organisms is an important mechanism by which this "greenhouse" gaseous molecule is removed from the atmosphere during carbon cycling on Earth. Approximately 100 pentagrams of carbon (1 pentagram equals 10^9 metric tons) as CO_2 is assimilated annually into organic molecules by photosynthesis (about half of this amount is assimilated by photosynthetic marine algae).

The route by which CO_2 is assimilated had been studied for over a century when it was discovered that photosynthesis leads to the accumulation of sugars and starch. Details of the biochemical pathway leading to CO_2 assimilation were worked out in the 1950s, when the availability of paper chromatographic techniques and $^{14}CO_2$ allowed Melvin Calvin, Andrew A. Benson, and James A. Bassham to develop the outline of the reductive pentose phosphate cycle (Calvin was awarded a Nobel Prize in Chemistry in 1961), now usually called the C_3 cycle. The name C_3 cycle refers to the first stable product generated from CO_2, which is a three-carbon organic molecule. The C_3 cycle forms the primary, or basic (with other, feeder pathways occurring in some plant types), route for the formation of photosynthate from CO_2.

C_3 photosynthesis

The essential details of C_3 photosynthesis can be seen in **Fig. 8**. The entire cycle can be separated into three phases —carboxylation, reduction, and regeneration. Since the smallest intermediate in the cycle consists of three carbons, we will start with three molecules of CO_2. During the initial carboxylation phase, these three molecules of CO_2 are combined with three molecules of the five-carbon compound ribulose 1,5-bisphosphate (RuBP) in a reaction catalyzed by the enzyme RuBP carboxylase/oxygenase (rubisco) to form three molecules of an intermediate, unstable enzyme-bound six-carbon compound. These unstable molecules are hydrolyzed by the enzyme into six molecules of the three-carbon compound phosphoglyceric acid (PGA). These products of the carboxylation phase, the six (three-carbon) PGA molecules, are phosphorylated by six molecules of ATP (releasing ADP to be used for photophosphorylation via the light reactions) to form six 1,3-bisphosphoglycerate (1,3-BP) molecules. The resulting compounds are reduced (that is, in the reduction phase of the C_3 cycle) by the NADPH formed in photosynthetic light reactions to form six molecules of the three-carbon compound phosphoglyceraldehyde (PGAL). PGAL is isomerized to form another three-carbon compound, dihydroxyacetone phosphate (DHAP). PGAL, the aldehyde, and DHAP, the ketone, are energetically equivalent, reduced compounds and can be

considered the products of the reductive phase of the C_3 photosynthetic cycle. PGAL and DHAP together form the triose phosphate (TP) pool of the chloroplast. The chloroplast TP pool is primarily composed of PGAL; the isomerase responsible for PGAL:DHAP interconversion favors PGAL formation.

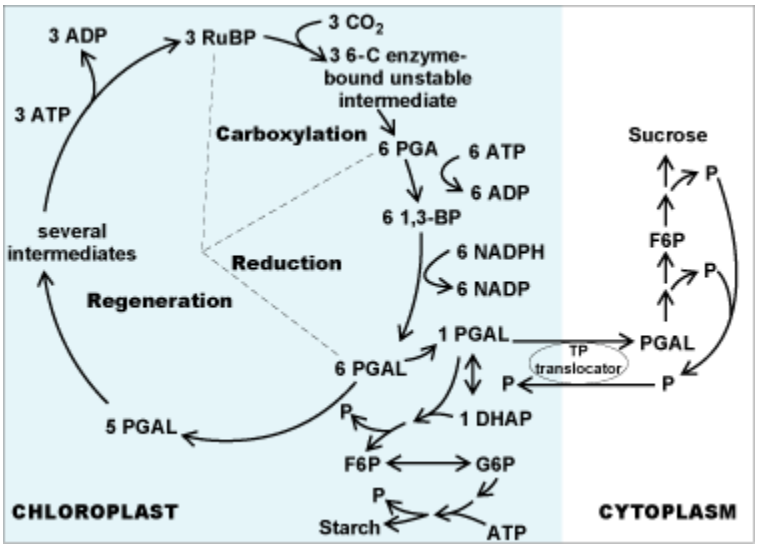

Fig. 8 Schematic outline of the C_3 (Calvin-Benson-Bassham) CO_2 assimilation cycle (the three phases are noted), showing the partitioning of assimilated carbon into starch within the chloroplast [via the phosphorylated 6-C intermediates, fructose-6-phosphate (F6P) and glucose-6-phosphate (G6P)], and the assimilate efflux (through the three-carbon triose phosphate [TP] transporter) across the chloroplast inner envelope to the cytoplasm (in exchange for inorganic phosphate) leading to sucrose synthesis. For the reactions of the C_3 cycle, shown in the chloroplast, the relative numbers of molecules involved in each specific step are shown to the left of the substrate and/or product.

The rest of the C_3 photosynthetic cycle (the regeneration phase) involves enzymatic steps that allow regeneration of RuBP, the initial carboxylation substrate. One molecule of PGAL is made available for combination with DHAP isomerized from a second PGAL (requiring a second “turn” of the Calvin-Benson-Bassham cycle wheel) to form a six-carbon sugar. The other five PGAL molecules, through a complex series of enzymatic reactions, are rearranged into three molecules of RuBP, which can again be carboxylated with CO_2 to continue the cycle.

It should be noted that the enzyme that incorporates CO_2 into an organic compound, RuBP carboxylase/oxygenase (rubisco), also allows oxygen (O_2) to react with RuBP, hence the “oxygenase” in the name. This reaction initiates the process called photorespiration, which results in the release of one previously incorporated molecule of CO_2 for every two molecules of O_2 that are allowed to react. *See also:* **Photorespiration (/content/photorespiration/511500)**

Due to its low catalytic efficiency, rubisco (**Fig. 9**) can be up to half of the soluble protein in C_3 chloroplasts, and most likely it is the most abundant protein found in nature. Rubisco is a large and complex enzyme, comprising eight large polypeptide subunits and eight small subunits. Interestingly, the small subunit polypeptide is produced (as a larger precursor form) in the cytoplasm from mRNA which is encoded in the nucleus. The precursor polypeptide is then transported across the chloroplast membrane (the mature form of this polypeptide cannot be transported in this manner); processed into the shorter, mature polypeptide; and then combined with large subunits (encoded in the chloroplast DNA and produced in the stroma) to form the mature enzyme.

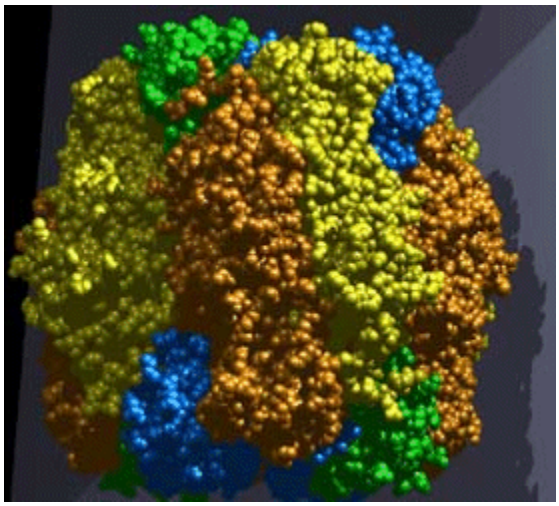

Fig. 9 Structural model of Rubisco.

The net product of two “turns” of the cycle, a six-carbon sugar (G6P or F6P), is formed either within the chloroplast in a pathway leading to starch (a polymer of many glucose molecules) or externally in the cytoplasm in a pathway leading to sucrose (condensed from two six-carbon sugars, glucose and fructose). This partitioning of newly formed photosynthate leads to two distinct pools; starch is stored in the photosynthesizing “source” leaf cells, and sucrose is available either for immediate metabolic requirements within the cell or for export to “sinks” such as developing reproductive structures, roots, or other leaves. Factors within the photosynthesizing cell, such as energy requirements in different compartments (mitochondria, cytoplasm, and chloroplasts), along with energy needs of the plant (such as increased sink requirements during different developmental stages) and external, environmental factors (such as light intensity and duration) ultimately regulate the partitioning of newly formed photosynthetic product (PGAL) into starch or sucrose. *See also:* **Plant metabolism (/content/plant-metabolism/523400)**

This profound control of photosynthate partitioning is accomplished through regulation of PGAL export from the chloroplast to the cytoplasm, as well as by regulation of the enzymes that convert PGAL to sucrose in the cytoplasm and starch in the chloroplast. Under conditions where sink demand is low (and sucrose is not transported through the phloem away from source leaf cells), metabolic effectors accumulate in the cytoplasm that lower the activities of the sucrose-forming enzymes and increase the activities of the starch-forming enzymes. This results in a condition that reduces PGAL export from the chloroplast, and hence more PGAL is retained in the chloroplast for starch formation. Also, under conditions which cause low chloroplast PGAL levels (such as low light), PGAL transport out of the chloroplast is restricted, resulting in decreased substrate for sucrose formation, increasing the relative amount of starch production. The energy status of the cell affects sucrose formation (and therefore photosynthate partitioning) because cytoplasmic uridine triphosphate (used in the formation of sucrose) level is dependent on ATP generation, and also because PGAL export to the cytoplasm is coupled obligatorily to inorganic phosphate (formed when ATP is metabolized in the cytoplasm) import into the chloroplast.

In addition to providing carbon skeletons for starch and sucrose synthesis, PGAL is fed back into the C_3 cycle to allow for the regenerative phase of the reactions to synthesize more RuBP, the carboxylation substrate. We have known for quite some time that the maximal measurable activities of fructose 1,6-bisphophatase (FBPase) and sedoheptulose 1,7-bisphosphatase (SBPase), two enzymes involved in RuBP regeneration, are not much greater than the rate of photosynthetic carbon assimilation and concomitant carbon flow through the C_3 cycle. Thus, carbon flow through these enzymes might contribute to rate limitation of photosynthetic carbon assimilation. Studies with transgenic plants overexpressing these enzymes support this contention; increasing the amount of either enzyme led to a higher level of the carboxylation substrate RuBP as well as higher photosynthetic rates.

The autocatalytic nature of the cycle (that is, more substrate for initial carboxylation can be generated as carbon flows through the steps of the pathway) can be best understood by considering that the net product of one “turn” of the cycle (representing three carboxylations), that is, a PGAL molecule, can be fed back into the cycle. Thus the rate of carboxylation during an initial lag phase (as chloroplasts are initially illuminated) is dependent on the level of newly formed RuBP. If all newly fixed carbon were fed back into the cycle, the level of RuBP would double after five carboxylations. Since the rate of photosynthetic carbon fixation is initially dependent on the level of intermediates such as the substrate (RuBP) for the carboxylation reaction, the next five carboxylations would occur in a shorter amount of time, resulting in an exponential increase in the rate of photosynthesis until factors other than intermediate levels become limiting.

Regulation of C_3 cycle enzymes

The photosynthetic carbon assimilation cycle is regulated at a number of enzymatic steps. The initial carboxylation catalyst, rubisco, as well as some of the enzymes involved in the regeneration phase, including glyceraldehyde-3-phosphate dehydrogenase, phosphoribulose kinase, SBPase, and FBPase, require activation. These enzymes are inactivated in the dark and activated in the light. Several conditions are required for activation, including high concentrations of Mg^{2+}, high pH, and a reductant (supplied in the chloroplast by the enzyme thioredoxin). Thioredoxin is reduced by NADPH generated in the light. Thioredoxin acts as a protein disulfide oxidoreductase, converting disulfide (S-S) bonds of the target proteins (all of the above enzymes except rubisco) to a reduced (−SH) form. Rubisco activity is also modulated by a specific mechanism involving another enzyme, called rubisco activase. All of the aforementioned activating conditions within the chloroplast stroma are facilitated by light-dependent processes but are reversed in darkness. This regulatory mechanism conveniently allows for the synthesis pathway to be “shut off,” preventing a futile cycle during the night, when starch reserves are mobilized to meet cell energy requirements via intermediates which, if C_3 cycle enzymes were activated, would be reconverted to starch.

C_4 photosynthesis

Initially, the C_3 cycle was thought to be the only route for CO_2 assimilation, although it was recognized by plant anatomists that some rapidly growing plants (such as maize, sugarcane, and sorghum) possessed an unusual organization of the photosynthetic tissues in their leaves (Kranz morphology). Work by Hugo Kortschak, Constance Hartt, and colleagues in Hawaii as well as that of M. D. (Hal) Hatch and Roger Slack in Australia demonstrated that plants having the Kranz anatomy utilized an additional CO_2 assimilation route now known as the C_4-dicarboxylic acid pathway (**Fig. 10**). Carbon dioxide enters a mesophyll cell where it is combined (in the form of bicarbonate) with the three-carbon compound phosphoenolpyruvate (PEP) via the enzyme PEP carboxylase to form a four-carbon acid, oxaloacetate, which is reduced to malic acid or transaminated to aspartic acid. The four-carbon acid moves into bundle sheath cells where the acid is decarboxylated and the CO_2 reassimilated via the C_3 cycle. The resulting three-carbon compound, pyruvic acid, moves back into the mesophyll cell and is transformed into PEP (at the cost of 2 ATP molecules) via the enzyme pyruvate phosphate dikinase located in the mesophyll chloroplasts to complete the cycle. The net effect of this cycle is to increase the CO_2 concentration around rubisco, thereby reducing photorespiration via the competing oxygenase activity of this enzyme.

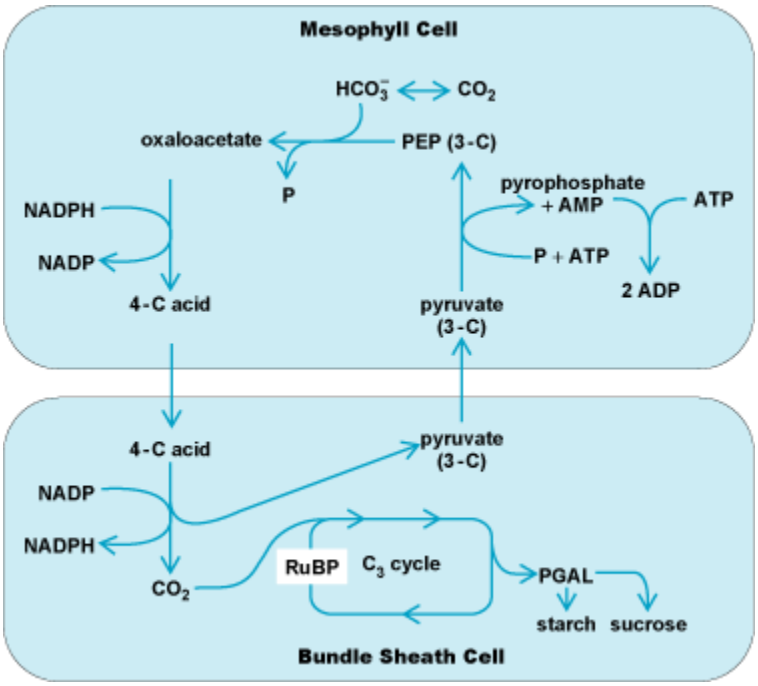

Fig. 10 Schematic outline of the C_4 carbon dioxide assimilation process in the two cell types of a NADP-ME-type plant.

As depicted in Fig. 10, extensive transport of metabolites must occur between the two cell types that are found in most C_4 plants. The diffusion of metabolites between two cell types is facilitated by the presence of plasmodesmata connecting the cells to form a cytoplasmic continuum. However, in some cases the two cell types, mesophyll and bundle sheath, are not necessarily adjacent (sedges are an example). Exotic plants have now been found that perform C_4 photosynthesis in single cells in which the chloroplasts that initially combine carbon dioxide with PEP are spatially separated from the chloroplasts where the carbon dioxide is reassimilated via the C_3 cycle.

C_4 metabolism is classified into three types, depending on the primary decarboxylation reaction used with the four-carbon acid in the bundle sheath cells. The majority of C_4 species (exemplified by sugarcane, maize, crabgrass, and sorghum) are of type 1 (see below), and employ NADP-malic enzyme (NADP-ME) for decarboxylation. NAD-malic enzyme (NAD-ME) C_4 plants (type 2) include amaranthus, atriplex, millet, pigweed, and purslane. Type 3 C_4 types use phosphoenolpyruvate carboxykinase (PCK) for decarboxylation and include *Panicum* grasses. The decarboxylases are also located in different intracellular compartments as indicated:1.

NADP-ME type,

$$\mathrm{NADP^+} + \text{malic acid} \xrightarrow{\text{NADP-malic enzyme (chloroplasts)}} \text{pyruvic acid} + \mathrm{CO_2} + \mathrm{NADPH} \tag{6}$$

2.
NAD-ME type,

$$\mathrm{NAD^+} + \text{malic acid} \xrightarrow{\text{NAD-malic enzyme (mitochondria)}} \text{pyruvic acid} + \mathrm{CO_2} + \mathrm{NADH} \tag{7}$$

3.
PCK type,

$$\text{Oxaloacetic acid} + \text{ATP} \xrightarrow{\text{phosphoenolpyruvate carboxykinase (cytosol)}} \text{PEP} + CO_2 + \text{ADP} \quad (8)$$

In addition to differing decarboxylation reactions, the particulars of the CO_2 fixation pathway in NAD-ME and PCK plant types differ from those depicted in Fig. 10 with respect to the three-carbon compound transported from bundle sheath to mesophyll cells. With NAD-ME types, the three-carbon compound can be either pyruvic acid or alanine, and in PCK types this compound is PEP. Therefore, the three variations in the C_4 pathway necessarily predicate different energy (ATP and NADPH) usage in the two cell types. The generation of ATP from ADP, and NADPH from NADP via noncyclic electron flow through photosystem I (PSI) and photosystem II (PSII), is tightly coupled: neither compound can be produced without sufficient substrate for both. Therefore, the different usage of ATP and NADPH in the mesophyll and bundle sheath chloroplasts of the three C_4 plant types (due both to variations in the pathway of carbon flow in the photosynthetic cycle and to variations in partitioning of portions of the pathway between cell types) is supported by variations in the photochemical apparatus which allow for differing ability to produce ATP without concomitant NADPH production. These alternative pathways of ATP production (which result in different ratios of ATP:NADPH produced) are cyclic and pseudocyclic photophosphorylation, with the cyclic pathway considered the major pathway of uncoupled ATP production in chloroplasts, and the pseudocyclic pathway possibly acting as a “fine-tuning” modulator.

Variations in the photochemical apparatus that indicate enhanced cyclic photophosphorylation capacity (utilizing only PSI) are a high chlorophyll *a*/*b* ratio, low Chl/P700 ratio, and a low PSII reaction. These characteristics are found in bundle sheath chloroplasts of NADP-ME-type plants, indicating that the primary function of the photochemical apparatus in these chloroplasts is the generation of ATP. NADPH is supplied via the decarboxylation of malic acid to support the C_3 cycle activity (PGA conversion to PGAL) in these chloroplasts. Assays of chlorophyll *a*/*b* ratio, Chl/P700 ratio, and PS II activity indicate that NAD-ME mesophyll chloroplasts also have a primary role of cyclic photophosphorylation, while NAD-ME bundle sheath chloroplasts have a primary role of noncyclic electron flow. In PCK-type plants, mesophyll chloroplasts appear to have a photochemical apparatus similar to C_3 chloroplasts, while bundle sheath chloroplasts appear to have a low PSII activity. The enhanced ability of PCK bundle sheath chloroplasts to produce ATP via cyclic photophosphorylation supplies the extra ATP needed to convert pyruvic acid to PEP. These variations in the C_4 pathway and photochemical apparatus among the C_4 plant types demonstrate the close relationship that has evolved between light reactions and the biochemical processes of carbon dioxide assimilation, and show the highly integrated cooperation between the cell types involved.

Benefits of C_4 cycle

The concentration of CO_2 in air is presently about 0.037% by volume (and increasing with time due to burning of fossil fuels), a concentration that does not fully saturate the C_3 cycle when it is operating at capacity due to the low affinity of rubisco for CO_2. It would be necessary to have about 0.1% CO_2 to saturate photosynthesis in C_3 plants, which can be achieved only under controlled conditions (CO_2-enriched greenhouses or growth chambers). Leaf photosynthesis in C_4 plants, however, is fully saturated at air CO_2 concentrations. Thus, C_4 photosynthesis may be considered to be an evolutionary adaptation to current-day CO_2 levels in air. During the C_4 cycle, CO_2 is rapidly captured via biochemical reactions in mesophyll chloroplasts and released near rubisco in bundle sheath chloroplasts. This serves to increase the CO_2 concentration around the enzyme, increasing its catalytic efficiency and decreasing its reaction with O_2 and thus photorespiration; thus the ambient concentration of CO_2 in air is not rate-limiting. The spatial compartmentalization of portions of CO_2 assimilation into the two cell types not only allows C_4 plants to assimilate air CO_2 rapidly with minimal photorespiration, but also partly explains other physiological characteristics and responses to the external environment of C_4 plants. C_4 plants have a higher efficiency of water use. Water vapor exits from leaves through the same stomatal pores through which CO_2 enters the leaf. Since the C_4 plant is more efficient at fixing CO_2 than C_3 plants, more CO_2 is incorporated per unit water lost. C_4 plants have a greater efficiency of nitrogen usage. Since rubisco is produced only in bundle sheath cells in C_4 plants, only 10–35% of the leaf

nitrogen is tied up in this enzyme, as opposed to 40–60% in C_3 plants. Since C_4 plants have to "expend" less carbon on producing the protein rubisco, they have higher rates of sugar formation, which can facilitate the rapid growth rates seen in such C_4 plants as maize, sugarcane, sorghurn, and crabgrass. Other differences in response to the environment between C_3 and C_4 plants are as follows: C_4 plants exhibit a nonsaturating response curve of leaf photosynthesis to light levels found in nature. In addition, C_4 plants tolerate more salinity and higher temperatures than do C_3 plants. The higher energy requirements of C_4 plants (2 ATPs per CO_2 assimilated) are also reflected by the fact that quantum yields of photosynthesis for C_3 plants are higher than for those possessing the auxiliary C_4 system. At 2% oxygen partial pressure and 30°C, maximum quantum yield for C_3 plants is about 0.073 mole CO_2 assimilated per absorbed Einstein (an Einstein is a mole of photons) of light, while for C_4 plants the maximum quantum yield is 0.054. However, at normal O_2 partial pressures (21% O_2), quantum yields are almost identical. This is due to the presence of high photorespiration in C_3 plants, and thus represents a net quantum yield rather than a true photosynthetic yield. *See also:* **Photorespiration (/content/photorespiration/511500)**

Crassulacean acid metabolism photosynthesis

Under arid and desert conditions, where soil water is in short supply, transpiration during the day when temperatures are high and humidity is low may rapidly deplete the plant of water, leading to desiccation and death. By keeping stomata closed during the day, water can be conserved, but the uptake of CO_2, which occurs entirely through the stomata, is prevented. Desert plants in the Crassulaceae, Cactaceae, Euphorbiaceae, and 15 other families have evolved, apparently independently of C_4 plants, a similar strategy of concentrating and assimilating CO_2 by which the CO_2 is taken in at night when the stomata open; water loss is low because of the reduced temperatures and correspondingly higher humidities. Although these succulent plants with thick, fleshy leaves were known since the nineteenth century as being unusual, the biochemical understanding of the process did not occur until the 1960s and 1970s when the details of C_4 photosynthesis were being worked out. It was first studied in plants of the Crassulaceae; thus, the process has been called crassulacean acid metabolism (CAM).

In contrast to C_4, where two cell types usually cooperate, the entire CAM process occurs within an individual cell; the separation of C_4 and C_3 is thus temporal rather than spatial. At night, CO_2 combines with PEP through the action of PEP carboxylase, resulting in the formation of oxaloacetic acid and its conversion into malic acid. The PEP is formed from starch or sugar via the glycolytic route of respiration. Thus, there is a daily reciprocal relationship between starch (a storage product of C_3 photosynthesis) and the accumulation of malic acid (the terminal product of nighttime CO_2 assimilation; **Fig. 11**).

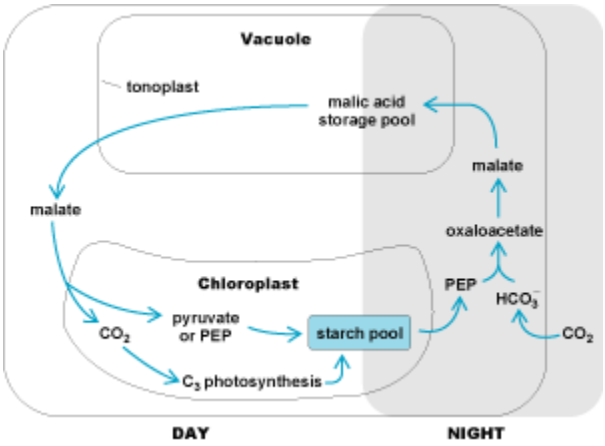

Fig. 11 Scheme for the flow of CO_2 within a single crassulacean acid metabolism (CAM) cell over a day, showing initial dark CO_2 fixation, malic acid storage in the vacuole at night, followed by decarboxylation and the C_3 cycle the next day.

As in C_4 plants, there may be variations in the decarboxylase that provides the CO_2 for assimilation via the C_3 cycle. In some CAM plants (such as pineapple) PCK is used, while in others (cactus) the decarboxylase is the NADP-malic enzyme

(NADP-ME type). A few CAM species use NAD-ME for decarboxylation. Since the stomata are closed most of the day, decarboxylation of the stored malate (or oxaloacetate) results in an elevation of its concentration around rubisco. The **table** summarizes the major physiological differences between C_3, C_4, and CAM plants.

Some characteristics of the three major plant groups

Characteristics	C_3	C_4	CAM
Leaf anatomy in cross section	Diffuse distribution of organelles in mesophyll and palisade cells with less chloroplasts in bundle sheath cells if present	Layer of bundle sheath cells around vascular tissue with a high concentration of chloroplasts; layers of mesophyll cells around bundle sheath	Spongy, often lacking palisade cells; mesophyll cells have large vacuoles
Theoretical energy requirement for net CO_2 fixation (CO_2:ATP:NADPH)	1:3:2	1:5:2	1:6.5:2
Carboxylating enzyme	Rubisco	PEP carboxylase, then rubisco	Darkness: PEP carboxylase; light: mainly rubisco
CO_2 compensation concentration, ppm CO_2	30–70	0–10	0–5 in dark
Transpiration ratio, g H_2O/g dry weight increase	450–950	250–350	50–55
Maximum net photosynthetic rate, mg CO_2/(dm^2 leaf)(h)	15–40	40–80	1–4
Photosynthesis sensitive to high O_2	Yes	No	Yes
Photorespiration detectable	Yes	Only in bundle sheath	Difficult to detect
Leaf chlorophyll *a*/*b* ratio	2.8 ± 0.4	3.9 ± 0.6	2.5–3
Maximum growth rate, g dry wt/(dm^2 leaf)(day)	0.5–2	4–5	0.015–0.018
Optimum temperature for photosynthesis	15–25° C (59–77° F)	30–40° C (86–104° F)	About 35° C (95° F)

Other CO_2 assimilation mechanisms

Both the C_4 cycle and CAM involve the synthesis of oxaloacetic acid, which is also one of the intermediates in the tricarboxylic acid (TCA) cycle of respiration. In the late 1960s a light-driven reversal of the TCA cycle was discovered. This CO_2 fixation cycle, called the reductive carboxylic acid cycle, results in the net synthesis of pyruvic acid via the reversal of the three decarboxylation steps in the TCA cycle (pyruvic acid to acetyl coenzyme A, isocitric acid to α-ketoglutaric acid, and succinyl CoA to succinic acid). The pathway has been detected in some photosynthetic bacteria. *See also:* **Citric acid cycle (/content/citric-acid-cycle/366100)**

In most photosynthetic bacteria, the C_3 cycle is functional despite some differences in detail. The green sulfur bacteria, however, carry out C_3 photosynthesis poorly or not at all. *Chlorobium thiosulfatophilum* (alternate name: *Chlorobium limicola*), lacking the key enzyme rubisco, utilizes a reductive carboxylic acid cycle in which reduced ferredoxin drives the TCA cycle in reverse, resulting in carboxylation reactions much like those of the reductive carboxylic acid cycle. Heterocysts of cyanobacteria do not have a functional C_3 cycle because, in contrast to the normal cells of these bacteria, the heterocyst cell (implicated in nitrogen fixation) lacks the key enzyme rubisco. Here, CO_2 fixation in heterocysts may occur through PEP carboxylase as in C_4 and CAM photosynthesis. Guard cells in C_3 plants, which regulate the opening of stomatal pores for gas

exchange in leaves, also lack rubisco and apparently use PEP carboxylase exclusively to fix CO_2.

[Contributions of the late Martin Gibbs to this article are acknowledged.]

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Bacterial Photosynthesis

Certain bacteria have the ability to perform photosynthesis. This was first noticed by Sergey Vinogradsky in 1889 and was later extensively investigated by Cornelis B. Van Niel, who gave a general equation for bacterial photosynthesis. This is shown in reaction (9).

$$2H_2A + CO_2 + \text{light} \xrightarrow[\text{enzymes}]{\text{bacteriochlorophyll}} \{CH_2O\} + 2A + H_2O \tag{9}$$

where A represents any one of a number of reductants, most commonly S (sulfur).

Photosynthetic bacteria cannot use water as the hydrogen donor and are incapable of evolving oxygen. They are therefore called anoxygenic photosynthetic bacteria. The prokaryotic cyanobacteria (formerly called blue-green algae) are excluded in this discussion of bacterial photosynthesis, since their photosynthetic system closely resembles that found in eukaryotic algae and higher plants discussed above. Anoxygenic photosynthetic bacteria can be classified in four major groups:

1. *Proteobacteria*. Two groups with somewhat different properties are known.

(A) Nonsulfur purple bacteria (Rhodospirillaceae). In these bacteria, H_2A is usually an organic H_2 donor, such as succinate or malate; however, these bacteria can be adapted to use hydrogen gas as the reductant. They require vitamins for their growth and usually grow anaerobically in light, but they can also grow aerobically in the dark by using respiration to utilize organic compounds from the environment. They are thus facultative photoheterotrophs. Examples of this group are *Rhodospirillum rubrum* and *Rhodobacter sphaeroides*.

(B) Sulfur purple bacteria (Chromatiaceae). These cannot grow aerobically, and H_2A is an inorganic sulfur compound, such as hydrogen sulfide, H_2S; the carbon source can be CO_2. These bacteria are called obligate photoautotrophic anaerobes. An example is *Chromatium vinosum* (alternate name: *Allochromatium vinosum*).

2. *Green sulfur bacteria* (Chlorobiaceae). These bacteria are capable of using the same chemicals as Chromatiaceae but, in addition, use other organic H_2 donors. They may then be called photoautotrophic and photoheterotrophic obligate anaerobes. An example of the green sulfur bacteria is *Chlorobium tepidum*.

3. *Green gliding bacteria* (Chloroflexaceae) [also known as filamentous anoxygenic phototrophs, FAP]. These are primarily photoorganotrophic bacteria which can grow under anaerobic conditions in light by photosynthesis or in aerobic conditions in the dark by using respiration to utilize organic compounds from the environment. They are thermophilic bacteria found in hot springs around the world. They also distinguish themselves among the photosynthetic bacteria by possessing mobility. An example is *Chloroflexus aurantiacus*.

4. *Heliobacteria* (Heliobacteriaceae). These are strictly anaerobic bacteria that contain bacteriochlorophyll *g*. They grow primarily using organic substrates and have not been shown to carry out autotrophic growth using only light and inorganic

substrates. An example is *Heliobacterium chlorum*.

Like plants, algae, and cyanobacteria, anoxygenic photosynthetic bacteria are capable of photophosphorylation, which is the production of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and inorganic phosphate (P_i) using light as the primary energy source. Several investigators have suggested that the sole function of the light reaction in bacteria is to make ATP from ADP and Pi. The hydrolysis energy of ATP (or the proton-motive force that precedes ATP formation) can then be used to drive the reduction of CO_2 to carbohydrate by H_2A in reaction (9).

Photochemical apparatus

Photosynthetic bacteria do not have specialized organelles such as the chloroplasts of green plants. Electron micrographs of certain photosynthetic bacteria show tiny spherical sacs, with double-layered walls, as a result of invaginations which form stacks of membranes (**Fig. 12***a*). Other photosynthetic bacteria have invaginations which form thylakoids (Fig. 12*b*). These intracytoplasmic membranes, often called chromatophores, contain the photosynthetic apparatus and can be isolated easily by mechanical disruption of bacteria followed by differential centrifugation. Isolated chromatophores are often used for biochemical and biophysical studies of bacterial photosynthesis.

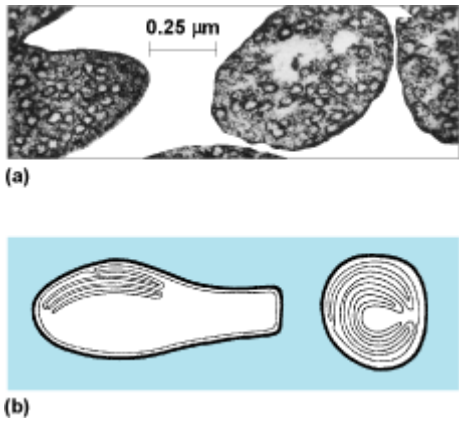


Fig. 12 Photosynthetic bacteria. (*a*) Electron micrograph of *Rhodobacter sphaeroides* with vesicle-like invaginations (*from T. W. Goodwin, ed., Biochemistry of Chloroplasts, vol. 1, Academic Press, 1966*). (*b*) Pictorial representation of a stacked invagination in a photosynthetic bacterium; at left is a longitudinal section and at right is a transverse section (*after R. Whittenbury and A. G. McLee, Archiv. für Mikrobiologie, 59:324–334, 1967*).

Reaction centers

The pigment bacteriochlorophyll (BChl) is a necessary component for bacterial photosynthesis. There are specialized BChl molecules in bacteria which engage in the primary chemical reactions of photosynthesis. In addition to these specialized molecules, there are 40– 50 BChl molecules referred to as antenna pigments, whose sole function is to harvest light energy and transfer it to reaction center molecules. This is similar to the photosynthetic unit of plants, algae, and cyanobacteria. Each reaction center contains a special pair (dimer) of BChl molecules that engage in chemical reactions after they trap the absorbed light energy. They are also called the energy traps of bacterial photosynthesis.

The energy trap in *Rhodobacter sphaeroides* has been identified as P870. Such identification is carried out with a difference (absorption) spectrophotometer. In this instrument a weak monochromatic measuring beam monitors the absorption of the sample; a brief but bright actinic light given at right angles to the measuring beam initiates photosynthesis. When photosynthesis occurs, changes in absorption take place. **Figure 13***a* shows the absorption spectrum of reaction centers isolated from *R. sphaeroides*. These changes are measured as a function of the wavelength of measuring light. A plot of the change induced in *R. sphaeroides* reaction centers by an actinic light flash, as a function of the wavelength of measuring

light, is the difference absorption spectrum (Fig. 13*b*). This spectrum is due largely to the photooxidation of the BChl dimer, P870.

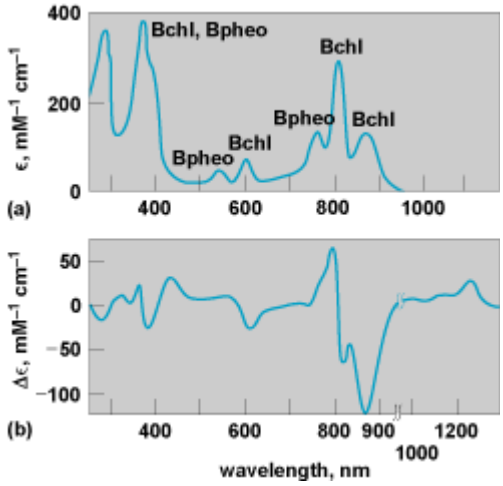


Fig. 13 Plots of (*a*) absorption spectrum and (*b*) the light-induced absorption changes in it, as occurring in reaction centers isolated from carotenoidless mutant R-26 of *Rhodobacter sphaeroides*. In *a*, bands attributed to bacteriochlorophyll and bacteriopheophytin are labeled BChl and BPheo, respectively. The ordinate in a is the millimolar extinction coefficient; in *b*, it is the differential extinction coefficient. (*After R. K. Clayton, Photosynthesis: Physical Mechanisms and Chemical Patterns, Cambridge University Press, 1980*)

If P870 is the energy trap, then the following criteria must be met: (1) It must undergo a reduction or oxidation reaction, since this is the essential reaction of photosynthesis. The decrease in absorption at 870 nm (Fig. 13) is an oxidation reaction since chemical oxidants cause a similar change. (2) The quantum yield (number of trap molecules oxidized per absorbed photon) must be very high (close to 1.0). (3) The primary light reaction should occur at very low temperatures, down to 1 K (−460°F or −273°C). (4) The above photochemical reaction should be extremely fast, that is, in the picosecond range.

All the above criteria are fulfilled by P870, and thus it is the reaction center of bacterial photosynthesis in *Rhodobacter sphaeroides*. Among other reaction centers that have been identified and studied extensively are P890 in *Chromatium vinosum*, P960 in *Rhodopseudomonas viridis* (also called *Blastochloris viridis*), P840 in *Chlorobium limicola* and P798 *Helicobacterium chlorum*. Each species of bacteria has only one type of reaction center, unlike plants, algae, and cyanobacteria, which utilize two types of reaction centers, PSI and PSII, that include P680 and P700, respectively. The reaction centers from oxygenic photosynthetic organisms have been identified by means similar to those used for bacterial reaction centers. Reaction centers have been isolated as pure proteins, which has served the important function of providing a well-defined system in which primary reactions of photosynthesis can be studied. A milestone in bacterial photosynthesis was reached in the early 1980s by the crystallization and determination of the three-dimensional structure of *Rhodopseudomonas viridis* reaction centers by Hartmut Michel, Johann Deisenhofer, and Robert Huber, who received the 1988 Nobel Prize in Chemistry for their work. These crystals enabled an atomic resolution of the molecular structure of the reaction center to be obtained.

Although isolated reaction centers are able to absorb light and convert it to chemical energy, the antenna pigment system in chromatophores (or in whole cells) absorbs most (>90%) of the light. The antenna transfers this energy to the reaction center. Antenna BChl molecules are bound to protein in a specific manner; this binding and pigment-pigment interactions modify the properties of the pigment and define the absorption maxima and the width of the absorption band. An example is B800 (B represents BChl, and the number indicates the wavelength of one of the absorption peaks in nanometers) found in *Rhodobacter sphaeroides* (**Fig. 14**).

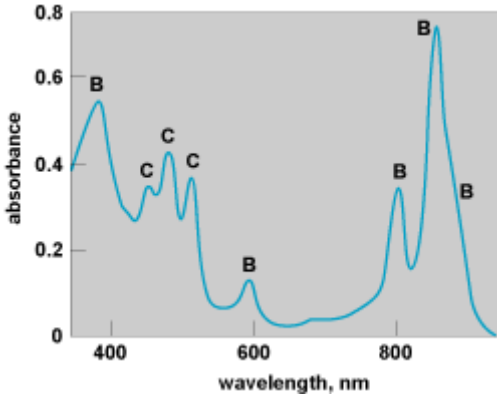


Fig. 14 Absorption spectrum of chromatophores from the bacterium *Rhodobacter sphaeroides*. Absorption bands attributed to BChl *a* are labeled as B, and those attributed to carotenoids as C. (*After R. K. Clayton, Photosynthesis: Physical Mechanisms and Chemical Patterns, Cambridge University Press, 1981*)

Components of photosynthetic bacteria

These bacteria contain the usual components of living material: proteins, lipids, carbohydrates, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and various metals. However, the specific components of interest to the electron transport system of bacterial photosynthesis are quinones, pyridine nucleotides, and various iron-containing proteins (cytochromes, ferredoxins, Rieske iron-sulfur centers, and others) in addition to the photosynthetic pigments which capture light energy.

In contrast to plastoquinones found in plants, bacteria contain substituted benzoquinones called ubiquinones (UQ or coenzyme Q) and substituted naphthoquinones called menaquinones (MK or vitamin K_2) which act as electron acceptors. The purple bacteria have a pool of UQ (about 25 UQ per reaction center) which mediates transfer of electrons and protons between protein complexes in the chromatophore membrane. However, MK is found only in some bacteria, sometimes in a smaller quantity (about 1–2 MK molecules per reaction center) than the more plentiful UQ. In these organisms, menaquinone's function is probably limited to electron transfer within the reaction center. Other organisms contain only menaquinone. In contrast to plants which contain NADP, the major pyridine nucleotide in bacteria is nicotinamide adenine dinucleotide (NAD); it is present in large quantities and seems to be active in photosynthesis. Among the various cytochromes, the *c*-type cytochromes and the *b*-type cytochromes are the important ones for bacterial photosynthesis.

Pigments

Most photosynthetic bacteria contain BChl *a*, a tetrahydroporphyrin. The chlorophyll of green plants, algae, and cyanobacteria, by contrast, is a dihydroporphyrin. In diethyl ether, BChl *a* has absorption maxima at 365, 605, and 770 nm. The infrared band of various antenna BChl *a* has maxima at 800 (B800), 850 (B850), or 890 nm (B890). These antenna absorption bands in the bacterial cell are due to the formation of complexes of BChl *a* with different proteins. *See also:* **Chlorophyll (/content/chlorophyll/132200)**

The reaction center protein (composed of L, M, and H subunits) from *Rhodobacter sphaeroides* binds four BChl *a* and two bacteriopheophytin (BPh; similar to BChl but does not contain magnesium). Two of the BChl form the energy trap P870. Another BChl and a BPh are involved in the transfer of electrons within the protein. The exact locations of these chromophores in the reaction center protein was first established in the crystals of *Rhodopseudomonas viridis* reaction centers (**Fig. 15***a*). Similar information is now available for *Rhodobacter sphaeroides* reaction centers (Fig. 15*b*).

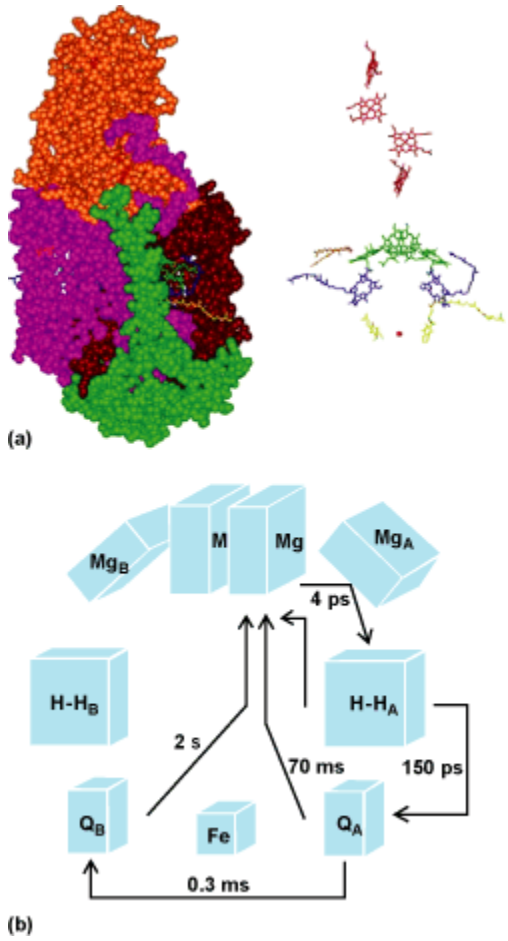


Fig. 15 Reaction centers of bacteria. (*a*) Structure of the reaction center of the purple nonsulfur bacterium *Rhodopseudomonas viridis* as determined by x-ray analysis of the crystalline preparation. In this diagram, the left side shows the complete structure in a space-filling representation. On the right side, the protein has been removed for clarity and only the components of the electron transport chains are shown (*after R. E. Blankenship, Molecular Mechanisms of Photosynthesis, Blackwell Science, Oxford, 2002*). (*b*) A simplified representation of the donor-acceptor complex based on the x-ray data and on spectroscopic data for *Rhodobacter sphaeroides*. The blocks define the aromatic ring systems of bacteriochlorophyll (M-Mg and Mg), bacteriopheophytin (H-H), the quinones (Q), which are ubiquinone and menaquinone, and Fe^{2+}. M-Mg is the primary electron donor, a dimer of bacteriochlorophyll *a* (*Rhodobacter sphaeroides*) or *b* (*Rhodopseudomonas viridis*). Subscripts A and B label the two potential electron transfer pathways, of which only pathway A appears active. The arrows show the various electron transfer reactions with their half-times. Note that Q_B is absent in the crystal of *Rhodopseudomonas viridis* (*after J. F. Norris and G. Van Brakel, Photosynthesis, in Govindjee, J. Amesz, and D. C. Fork, eds., Light Emission by Plants and Bacteria, Academic Press, 1986*).

The bacterium *Rhodopseudomonas viridis* utilizes an antenna with an infrared absorption band at 1015 nm. The isolated BChl from this species has absorption maxima at 368, 582, and 795 nm in diethyl ether, and has been designated BChl *b*. The reaction center of *R. viridis*, P960, uses BChl *b* and BPh *b* much in the same way as P870 in other bacteria utilizes Bchl *a*. Here, there is an “uphill” energy transfer from the antenna to its reaction center.

The green bacterium *Chlorobium* sp. contains a small amount of BChl *a* but a large quantity of another type of chlorophyll called chlorobium chlorophylls, BChl *c, d* or *e*, depending on the species. The BChl *a* has been shown to be associated with the reaction center, and some antenna complexes while the BChl *c* acts only as antenna. It is located in chlorosome complexes, which are appressed to the cytoplasmic side of the cell membrane and contain about 200,000 molecules of chlorobium chlorophyll.

The second group of pigments is the carotenoids, which have absorption peaks from 450 to 550 nm. The carotenoids of photosynthetic bacteria are of great variety and include some which are found in green plants, for example, the lycopenes. However, some are typical only of bacteria: γ-carotene, which is found in large quantities in green sulfur bacteria, and

spirilloxanthol, which is found mainly in purple bacteria. Carotenoids function to prevent photooxidation and destruction of antenna bacteriochlorophyll. They also function in bacterial photosynthesis by transferring their absorbed energy to bacteriochlorophyll. Similar roles are found for carotenoids in plants and cyanobacteria.

Transfer of excitation energy

Light energy absorbed by the carotenoids is transferred to BChl with varying efficiency (30–90%), as demonstrated by the method of sensitized fluorescence. (Similar methods have been used for demonstrating energy transfer from carotenoids, chlorophyll *b*, and phycobilins to chlorophyll *a* in oxygenic photosynthesizers.) When light energy is absorbed by carotenoids, only the fluorescence of bacteriochlorophyll (B875) is observed. By the same method, energy transfer with efficiencies approaching 100% has been demonstrated from B800 to B850 to B875. The high quantum yield (almost 1.0) of P870 oxidation, when bacteria are excited in the antenna pigments, is a clear demonstration of an extremely efficient excitation energy transfer by antenna pigments and trapping in reaction centers.

The lifetime of the excited state of antenna BChl in the bacterial cell is of the order of 30–50 ps. The excitation energy must be channeled from the antenna pigments to the energy traps within this time for efficient photosynthesis to occur. In reaction center preparations, it takes only 3 ps to create a definitively stable charge separation (see below) after the absorption of light. Moreover, the lifetime of the physical state or states preceding P870 oxidation is <3 ps. Thus, it appears that within a few picoseconds of receiving excitation energy, the reaction center has converted the absorbed light energy into chemical energy. Similar reactions occur in plants, algae, and cyanobacteria.

Mechanisms of electron transport

The first act of photosynthesis is the absorption of light by various pigments. As discussed above, light energy absorbed by the carotenoids B800 and B850 is transferred to B875 and finally to the reaction centers, where the primary reaction occurs: the oxidation of the reaction center BChl dimer leads to bleaching of P870 and reduction of an acceptor (**Fig. 16**). In the current model, P (short for P870 and so on) is oxidized to P^+ and an intermediate I is reduced to I^- within a few picoseconds; I includes a BChl monomer and a BPh molecule. The reduced I^- transfers the electron to an iron-quinone complex, reducing the primary quinone (Q_A) to a semiquinone within 100–200 ps. For most anoxygenic bacteria, Q_A is ubiquinone, though for those containing both menaquinone and ubiquinone the menaquinone functions as Q_A. Although an iron atom is in this complex and is within 0.5–1.0 nm of the quinone, its presence is not necessary for the reduction of Q_A, nor does the iron undergo redox changes. The function of this nonheme iron in the reaction center is unknown. In plants, algae, and cyanobacteria, PSII contains Q_A, which is a bound plastoquinone; the function of the iron there is also unknown.

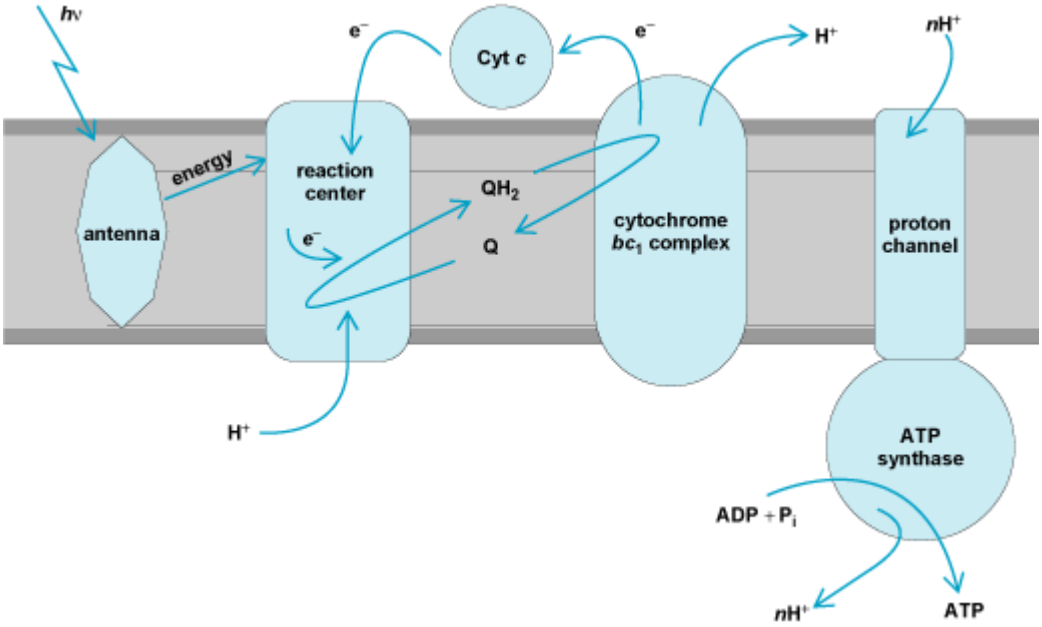


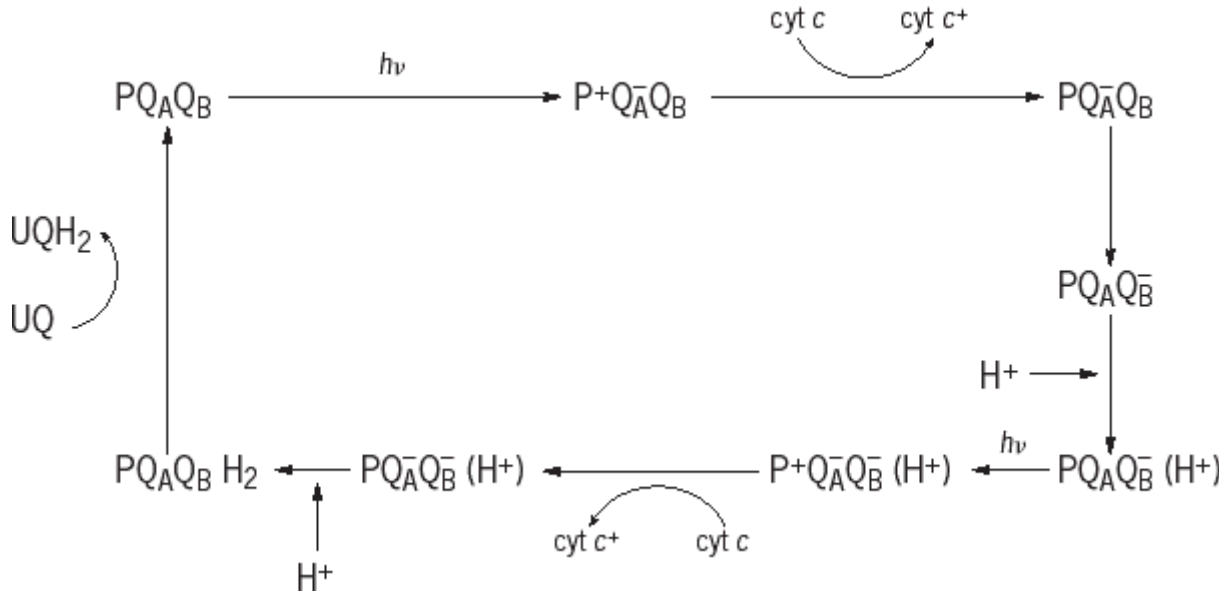
Fig. 16 Electron and proton transport in purple photosynthetic bacteria. For details and explanation of symbols, see the text. The shapes of the proteins are largely hypothetical.

The photooxidized donor BChl dimer, P^+, can be re-reduced by a cytochrome *c* in 1–30 μs, thus oxidizing the cytochrome. In *Rhodobacter sphaeroides* and a number of other species, this cytochrome is soluble Cyt c_2. In other bacteria (for example, *Rhodopseudomonas viridis*) the cytochrome that donates electrons to P^+ is an integral part of the reaction center. The photochemical reactions and the electron transfers in the reaction center are summarized in reaction (10).

$$\mathrm{PIQ_A} \xrightarrow{h\nu} \mathrm{P^*IQ_A} \xrightarrow{3\ \mathrm{ps}} \mathrm{P^+I^-Q_A} \xrightarrow{200\ \mathrm{ps}}$$

$$\mathrm{P^+IQ_A^-} \xrightarrow[1\text{–}30\ \mu\mathrm{s}]{\mathrm{cyt}\ c \rightarrow \mathrm{cyt}\ c^+} \mathrm{PIQ_A^-} \qquad (10)$$

After this set of reactions, the electron is transferred from Q^-_A to Q_B (a bound UQ), producing $Q_AQ^-_B$. In a subsequent absorption of a photon, the $Q^-_AQ^-_B$ state is created, which is followed by electron transfer from Q_A^- to Q^-_B, forming Q_BH_2 with the uptake of two protons. The bound quinol (Q_BH_2) is replaced by a UQ molecule. This cycle is known as the two-electron gate and is summarized in reaction (11)



(11)

[omitting the early photochemical steps illustrated in reaction (10)]. The same cycle occurs in photosystem II, except that the electron donor to P^+ is tyrosine Z, and Q_BH_2 is another plastoquinol instead of ubiquinol. The molecular detail is so similar in oxygenic and anoxygenic photosynthesizers that many of the herbicides which act to inhibit PSII electron transfer from $Q^-{}_A$ to Q_B are also potent inhibitors of electron transfer from $Q^-{}_A$ to Q_B in photosynthetic bacteria. However, one difference involves a unique role of $CO_2/HCO_3{}^-$ in reaction (11) in PSII of plants and cyanobacteria, but not in photosynthetic bacteria. Bicarbonate has been shown to be bound on the electron acceptor side of PSII, but not in photosynthetic bacteria.

Protons are taken up from the cytoplasm at the same time as the electrons reduce the quinones. The first proton does not bind directly to the semiquinone ($Q^-{}_A$ or $Q^-{}_B$), but instead it binds to a protonatable amino acid of the reaction center. The net result from the absorption of two photons is the formation of a ubiquinol in the membrane, the oxidation of two Cyt *c*, and the removal of two protons from the cytoplasm of the bacterial cell. In plants and cyanobacteria, the quinol is plastoquinol, and it is water that is ultimately oxidized.

The doubly reduced ubiquinone (QH_2, quinol) through a cyclic pathway serves to re-reduce the oxidized cytochrome (cyt c^+). This cyclic reaction (Fig. 16) is coupled to the production of ATP via the creation of a proton gradient (more accurately a proton motive force) across the membrane. Just as in plants, the proton motive force (which includes two components: a membrane potential, and a proton gradient) is used to drive ATP synthesis. Protons move down the potential gradient through the ATPase to contribute energy to drive the ADP + $P_i \rightarrow$ ATP reaction.

This overall mechanism is consistent with P. Mitchell's chemiosmotic theory. The quinol produced by the two-electron gate mechanism binds to the cytochrome *b-c* complex (an integral membrane protein) which contains two *b* cytochromes, a *c* cytochrome, a Rieske iron-sulfur center, and two quinone-binding sites. Plants also contain a similar complex, where cytochrome *b* is replaced by cytochrome b_6, and cytochrome *c* is replaced by cytochrome *f*. The mechanism is strikingly similar, on a molecular level, to that of noncyclic electron transfer from photosystem II to plastocyanin via the plastoquinone pool and the cytochrome *b-f* complex. In all likelihood, it includes a pathway called a Q cycle by Mitchell; this cycle incorporates two different redox-linked pathways for the electrons. For each quinol oxidized by this complex, two molecules of Cyt *c* are reduced, two protons are removed from the quinol, an additional two protons are removed from the cytoplasm, and these four protons are released into the intermembrane space. Absorption of two photons leads to the translocation of four protons across the membrane. Structural and mechanistic data on ATPases indicate that 3–5 H^+'s are needed to make an ATP (Fig. 16).

The mechanism described here for the generation of ATP from light energy is largely from studies on *Rhodobacter*

sphaeroides and is generally valid for other purple photosynthetic bacteria.

The mechanisms for oxidizing the reduced substrate H_2A [reaction (9)] are known in much less detail than those for photophosphorylation. Most substrates feed electrons into the quinone pool, and the resulting quinol can be used by the cytochrome *b-c* complex. An example is succinate, which reduces quinone via a succinate dehydrogenase. In bacteria that have a low potential cytochrome *c* bound to the reaction center (such as Cyt c_{551} in *Chromatium vinosum*), electrons from some substrates can possibly be fed into the reaction center through this cytochrome. The electrons for the reduction of NAD^+ in purple photosynthetic bacteria are from the quinone pool, but these electrons require additional energy gained from the hydrolysis of ATP or action of the proton motive force.

Alternatively, especially in some green bacteria, the primary stable acceptor of electrons in the reaction center may not be a quinone but an acceptor with a negative enough oxidation-reduction potential to directly reduce NAD^+. In several green bacteria, this electron acceptor has been shown to be an iron-sulfur (Fe·S) center instead of a quinone. The midpoint redox potential of this Fe·S center is much lower than that for the quinone acceptor in the purple photosynthetic bacteria. This Fe·S center can then directly reduce a ferredoxin, and this can drive the $NAD^+ \rightarrow NADH$ reaction. The reduced ferredoxin may also feed electrons into a cytochrome *b* complex from which a soluble Cyt *c* could be reduced, thus allowing cyclic electron transfer to occur. This scheme is very reminiscent of PSI-driven reactions in oxygenic photosynthesis. However, not all green photosynthetic bacteria follow the above pattern, but instead they resemble more the purple photosynthetic bacteria.

The reduced pyridine nucleotide NADH and the ATP made in the light reactions are then utilized to convert carbon sources into carbohydrates. The pathway of carbon in anoxygenic photosynthetic bacteria involves a reversed tricarboxylic acid (Krebs) cycle or another cycle called the hydroxyproprionate cycle. *See also:* **Bacterial physiology and metabolism (/content/bacterial-physiology-and-metabolism/069000)**

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Bibliography

R. E. Blankenship, *Molecular Mechanisms of Photosynthesis*, Blackwell Science, Oxford, 2002

B. Demmig-Adams et al. (eds.), *Photoprotection, Photoinhibition, Gene Regulation, and Environment*, Springer, Dordrecht, 2005

P. G. Falkowski and J. A. Raven, *Aquatic Photosynthesis*, 2d ed., Princeton University Press, Princeton, 2007

J. H. Golbeck (ed.), *Photosystem I: The Light-Driven Plastocyanin: Ferredoxin Oxidoreductase*, Springer, Dordrecht, 2006

Govindjee et al. (eds.), *Discoveries in Photosynthesis*, Springer, Dordrecht, 2005

B. R. Green and W. W. Parson (eds.), *Light-Harvesting Antennas in Photosynthesis*, Springer, Dordrecht, 2003

B. Grimm et al. (eds.), *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*, Springer, Dordrecht, 2006

B. Ke, *Photosynthsis: Photobiochemistry and Photobiophysics*, Springer, Dordrecht, 2001

A. W. D. Larkum et al. (eds.), *Photosynthesis in Algae*, Springer, Dordrecht, 2003

R. C. Leegood et al. (eds.), *Photosynthesis: Physiology and Metabolism*, Springer, Dordrecht, 2000

G. Papageorgiou and Govindjee (eds.), *Chlorophyll a Fluorescence: A Signature of Photosynthesis*, Springer, Dordrecht,

2005

R. R. Wise and J. K. Hoober (eds.), *The Structure and Function of Plastids*, Springer, Dordrecht, 2006

T. Wydrzynski and K. Satoh (eds.), *Photosystem II: The Light-Driven Water-Plastoquinone Oxidoreductase*, Springer, Dordrecht, 2005

Additional Readings

J. A. Bassham, Mapping the carbon reduction cycle: A personal retrospective. *Photosynth. Res.*, 76:35–52, 2003 DOI: 10.1023/A:1024929725022 (http://dx.doi.org/10.1023/A:1024929725022)

A. A. Benson, Following the path of carbon in photosynthesis: A personal story. *Photosynth. Res.*, 73:29–49, 2002 DOI: 10.1023/A:1020427619771 (http://dx.doi.org/10.1023/A:1020427619771)

C. C. Black and C. B. Osmond, Crasulacean Acid Metabolism photosynthesis: Working the night shift, *Photosynth. Res.*, 76:329–341, 2003 DOI: 10.1023/A:1024978220193 (http://dx.doi.org/10.1023/A:1024978220193)

R. K. Clayton, Research on photosynthetic reaction centers from 1932–1987, *Photosynth. Res.*, 73:63–71, 2002 DOI: 10.1023/A:1020412729766 (http://dx.doi.org/10.1023/A:1020412729766)

W. A. Cramer, Ironies in photosynthetic electron transport: A personal perspective. *Photosynth. Res.*, 80:293–305, 2004 DOI: 10.1023/B:PRES.0000030600.28313.58 (http://dx.doi.org/10.1023/B:PRES.0000030600.28313.58)

J. J. Eaton-Rye, B. C. Tripathy, and T. D. Sharkey (eds.), *Photosynthesis: Plastid Biology, Energy Conversion and Carbon Assimilation*, Springer Science+Business Media, Dordrecht, Netherlands, 2012

H. Gest and R. E. Blankenship, Time line of discoveries: Anoxygenic bacterial photosynthesis, *Photosynth. Res.*, 80:59–70, 2004 DOI: 10.1023/B:PRES.0000030448.24695.ec (http://dx.doi.org/10.1023/B:PRES.0000030448.24695.ec)

Govindjee and D. Krogmann, Discoveries in oxygenic photosynthesis (1727–2003): A perspective, *Photosynth. Res.*, 80:15–57, 2004 DOI: 10.1023/B:PRES.0000030443.63979.e6 (http://dx.doi.org/10.1023/B:PRES.0000030443.63979.e6)

D. D. Hall and K. K. Rao, *Photosynthesis*, 6th ed., Cambridge University Press, 1999

M. D. Hatch, C_4 photosynthesis: Discovery and resolution, *Photosynth. Res.*, 73:251–256, 2002 DOI: 10.1023/A:1020471718805 (http://dx.doi.org/10.1023/A:1020471718805)

W. Junge, Protons, proteins and ATP, *Photosynth. Res.*, 80:197–221, 2004 DOI: 10.1023/B:PRES.0000030677.98474.74 (http://dx.doi.org/10.1023/B:PRES.0000030677.98474.74)

A. Lytovchenko et al., Tomato fruit photosynthesis is seemingly unimportant in primary metabolism and ripening but plays a considerable role in seed development, *Plant Physiol.*, 157(4):1650–1663, 2011 DOI: 10.1104/pp.111.186874 (http://dx.doi.org/10.1104/pp.111.186874)

I. McConnell, G. Li, and G. W. Brudvig, Energy conversion in natural and artificial photosynthesis, *Chem. Biol.*, 17(5):434–447, 2010 DOI: 10.1016/j.chembiol.2010.05.005 (http://dx.doi.org/10.1016/j.chembiol.2010.05.005)

W. L. Ogren, Affixing the O to Rubisco: Discovery of the source of photorespiratory glycolate and its regulation, *Photosynth. Res.*, 76:53–63, 2003 DOI: 10.1023/A:1024913925002 (http://dx.doi.org/10.1023/A:1024913925002)

A. R. Portis, Jr. and M. E. Salvucci, The discovery of Rubisco activase—yet another story of serendipity, *Photosynth. Res.*, 73:257–264, 2002 DOI: 10.1023/A:1020423802875 (http://dx.doi.org/10.1023/A:1020423802875)

Y. Saga, Y. Shibata, and H. Tamiaki, Spectral properties of single light-harvesting complexes in bacterial photosynthesis, *J. Photochem. Photobiol. C Photochem. Rev.*, 11(1):15–24, 2010 DOI: 10.1016/j.jphotochemrev.2010.02.002 (http://dx.doi.org/10.1016/j.jphotochemrev.2010.02.002)

A. Vermeglio, The two-electron gate in photosynthetic bacteria, *Photosynth. Res.*, 73:83–86, 2002 DOI: 10.1023/A:1020429114745 (http://dx.doi.org/10.1023/A:1020429114745)