The Role of Chlorophyll in Photosynthesis

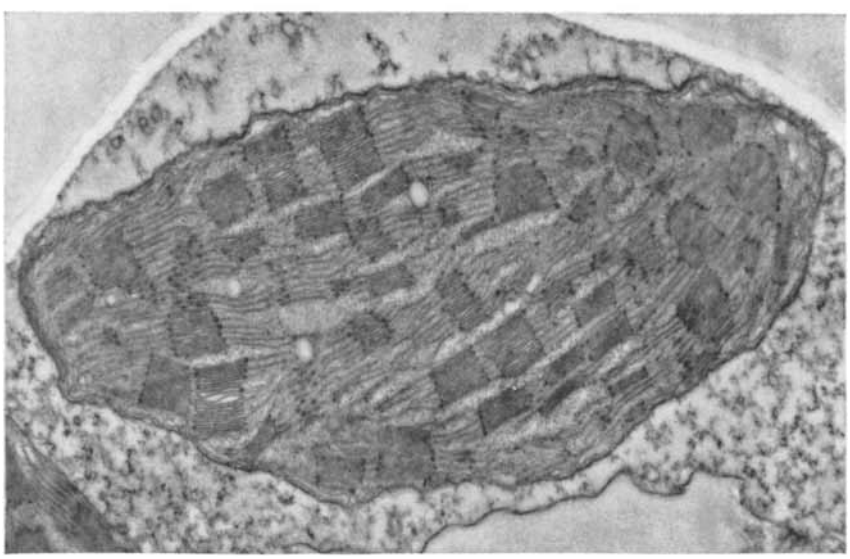
The pigments of plants trap light energy and store it as chemical energy. They do this by catalyzing an oxidation-reduction process in which hydrogen atoms are boosted from water to organic matter

by Eugene I. Rabinowitch and Govindjee

Any effort to understand the basis of life on this planet must always come back to photosynthesis: the process that enables plants to grow by utilizing carbon dioxide (CO_2), water (H_2O) and a tiny amount of minerals. Photosynthesis is the one large-scale process that converts simple, stable, inorganic compounds into the energy-rich combination of organic matter and oxygen and thereby makes abundant life on earth possible. Photosynthesis is the source of all living matter on earth, and of all biological energy.

The overall reaction of photosynthesis can be summarized in the following equation: $CO_2 + H_2O + \text{light} \rightarrow (CH_2O) + O_2 + 112{,}000$ calories of energy per mole. (CH_2O) stands for a carbohydrate; for example, glucose: $(CH_2O)_6$. "Mole" is short for "gram molecule": one gram multiplied by the molecular weight of the substances in question—in this case carbohydrate and oxygen.

When one of us first summarized the state of knowledge of photosynthesis 17 years ago, the whole process was still heavily shrouded in fog [see "Photosynthesis," by Eugene I. Rabinowitch; SCIENTIFIC AMERICAN, August, 1958]. Five years later investigation had penetrated the mists sufficiently to disclose some of the main features of the process [see "Progress in Photosynthesis," by Eugene I. Rabinowitch; SCIENTIFIC AMERICAN, November, 1953]. Since then much new knowledge has been accumulated; in particular the sequence of chemical steps that convert carbon dioxide into carbohydrate is now understood in considerable detail [see "The Path of Carbon in Photosynthesis," by J. A. Bassham; SCIENTIFIC AMERICAN, June, 1962]. The fog has also thinned out in other areas, and the day when the entire sequence of physical and chemical events in photosynthesis will be well understood seems much closer.



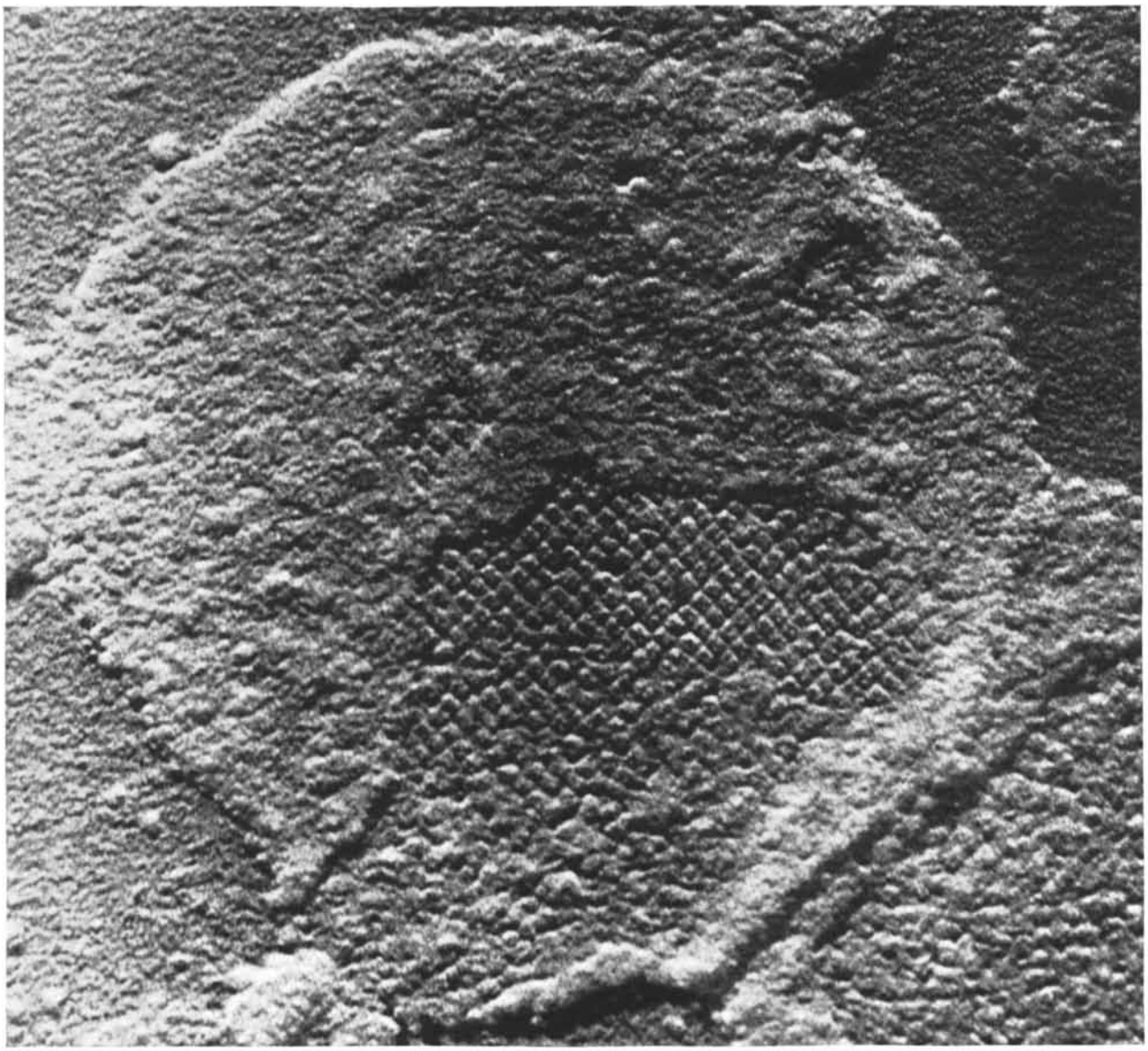
CHLOROPLAST is the organelle in a plant cell within which photosynthesis takes place. The chlorophyll is contained in the "grana," stacks of membranous sacs called lamellae, seen here in cross section. A maize-cell chloroplast is enlarged 19,000 diameters in this electron micrograph made by A. E. Vatter of the University of Colorado Medical Center.

The photosynthetic process apparently consists of three main stages: (1) the removal of hydrogen atoms from water and the production of oxygen molecules; (2) the transfer of the hydrogen atoms from an intermediate compound in the first stage to one in the third stage, and (3) the use of the hydrogen atoms to convert carbon dioxide into a carbohydrate [*see illustration on page 76*].

The least understood of these three stages is the first: the removal of hydrogen atoms from water with the release of oxygen. All that is known is that it entails a series of steps probably requiring several enzymes, one of which contains manganese. The third stage—the production of carbohydrates from carbon dioxide—is the best understood, thanks largely to the work of Melvin Calvin and his co-workers at the University of California at Berkeley. The subject of our article is the second stage: the transfer of hydrogen atoms from the first stage to the third. This is the energy-storing part of photosynthesis; in it, to use the words of Robert Mayer, a discoverer of the law of the conservation of energy, "the fleeting sun rays are fixed and skillfully stored for future use."

The light energy to be converted into chemical energy by photosynthesis is first taken up by plant pigments, primarily the green pigment chlorophyll. In photosynthesis chlorophyll functions as a photocatalyst: when it is in its energized state, which results from the absorption of light, it catalyzes an energy-storing chemical reaction. This

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PHOTOSYNTHETIC UNITS may be the small elements, looking somewhat like cobblestones, visible in this electron micrograph made by Roderic B. Park and John Biggins of the University of California at Berkeley. In the micrograph a single lamella and a part of another one are shadowed with chromium and enlarged 175,000 diameters. Where the membrane is torn away one can see an ordered array of the units, which Park and Biggins call quantasomes and calculate could contain 230 chlorophyll molecules each.

reaction is the primary photochemical process; it is followed by a sequence of secondary "dark"—that is, nonphotochemical—reactions in which no further energy is stored.

Once it was thought that in photosynthesis the primary photochemical process is the decomposition of carbon dioxide into carbon and oxygen, followed by the combination of carbon and water. More recently it has been suggested that the energy of light serves primarily to dissociate water, presumably into hydroxyl radicals (OH) and hydrogen atoms; the hydroxyl radicals would then react to form oxygen molecules. It is better than either of these two formulations to say that the primary photochemical process in photosynthesis is the boosting of hydrogen atoms from a stable association with oxygen in water molecules to a much less stable one with carbon in organic matter. The oxygen atoms "left behind" combine into oxygen molecules, an association also much less stable than the one between oxygen and hydrogen in water. The replacement of stable bonds (between oxygen and hydrogen) by looser bonds (between oxygen and oxygen and between hydrogen and carbon) obviously requires a supply of energy, and it explains why energy is stored in photosynthesis.

The transfer of hydrogen atoms from one molecule to another is called oxidation-reduction. The hydrogen atom is transferred from a donor molecule (a "reductant") to an acceptor molecule (an "oxidant"); after the reaction the donor is said to be oxidized and the acceptor to be reduced. The transfer of an electron can often substitute for the transfer of a hydrogen atom: in an aqueous system (such as the interior of the living cell) there are always hydrogen ions (H^+), and if such an ion combines with the electron acceptor, the acquisition of an electron becomes equivalent to the acquisition of a hydrogen atom (electron + H^+ ion $\rightarrow$ H atom).

The chain of oxidation-reduction reactions in photosynthesis has some links that involve electron transfers and

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others that involve hydrogen-atom transfers. For the sake of simplicity we shall speak of electron transfers, with the understanding that in some cases what is actually transferred is a hydrogen atom. Indeed, the end result of the reactions undoubtedly *is* the transfer of hydrogen atoms.

In the oxidation-reduction reactions of photosynthesis the electrons must be pumped "uphill"; that is why energy must be supplied to make the reaction go. The tiny chlorophyll-containing chloroplasts of the photosynthesizing plant cell act as chemical pumps; they obtain the necessary power from the absorption of light by chlorophyll (and to some extent from absorption by other pigments in the chloroplast). It is important to realize that the energy is stored in the two products organic matter and free oxygen and not in either of them separately. To release the energy by the combustion of the organic matter (or by respiration, which is slow, enzyme-catalyzed combustion) the two products must be brought together again.

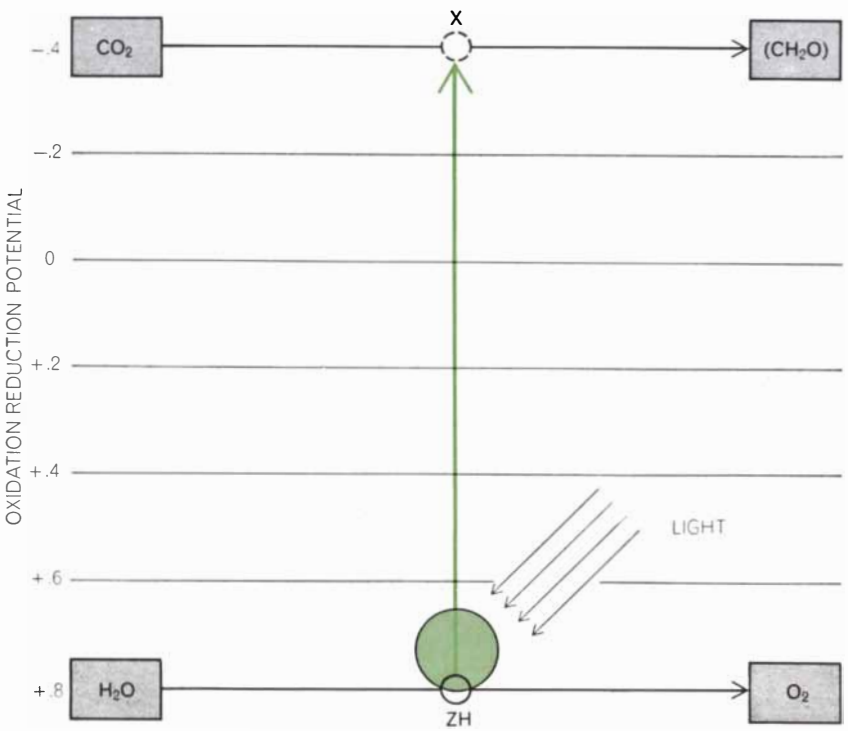
How much energy is stored in the transfer of electrons from water to carbon dioxide, converting the carbon dioxide to carbohydrate and forming a proportionate amount of oxygen?

Oxidation-reduction energy can conveniently be measured in terms of electrochemical potential. Between a given donor of electrons and a given acceptor there is a certain difference of oxidation-reduction potentials. This difference depends not only on the nature of the two reacting substances but also on the nature of the products of the reaction; it is characteristic of the two oxidation-reduction "couples." For example, when oxygen is reduced to water (H_2O) its potential is +.81 volt, but when it is reduced to hydrogen peroxide (H_2O_2) the potential is +.27 volt. The more positive the potential, the stronger is the oxidative power of the couple; the more negative the potential, the stronger is its reducing power.

When two oxidation-reduction couples are brought together, the one containing the stronger oxidant tends to oxidize the one containing the stronger reductant. In photosynthesis, however, a weak oxidant (CO_2) must oxidize a weak reductant (H_2O), producing a strong oxidant (O_2) and a strong reductant (a carbohydrate). This calls for a massive investment of energy. The specific amount needed is given by the difference between the oxidation-reduction potentials of the two couples involved in the reaction: oxygen-water and carbon-dioxide–carbohydrate. The oxygen-water potential is about +.8 volt; the carbon-dioxide–carbohydrate potential, about −.4 volt. The transfer of a single electron from water to carbon dioxide thus requires +.8 minus −.4, or 1.2, electron volts of energy. For a molecule of carbon dioxide to be reduced to CH_2O—the elementary molecular group of a carbohydrate—*four* electrons (or hydrogen atoms) must be transferred; hence the total energy needed is 4.8 electron volts. This works out to 112,000 calories per mole of carbon dioxide reduced and of oxygen liberated. In short, the pumping of electrons in the second stage of photosynthesis entails the storage of 112,000 calories of energy per mole for each set of four electrons transferred.

We know the identity of the primary electron donor in photosynthesis (water) and of the ultimate electron acceptor (carbon dioxide), but what are the intermediates involved in the transfer of electrons from the first stage to the third? This has become the focal problem in recent studies of the photosynthetic process. As a matter of fact, it is not yet definitely known what compound releases electrons from the first stage, and what compound receives them in the third; that is why these compounds are respectively labeled *ZH* and *X* in the illustration at the left. About the donor, *ZH*, we have almost no information; the following considerations suggest the possible nature of the primary acceptor, *X*.

From the study of the mechanism of respiration we are familiar with an important oxidation-reduction catalyst: nicotinamide adenine dinucleotide phosphate, or NADP (formerly known as triphosphopyridine nucleotide, or TPN). NADP has an oxidation-reduction potential of about −.32 volt, thus in itself it is not a strong enough reductant to provide the −.4-electron-volt potential needed to reduce carbon dioxide to carbohydrate. NADP can achieve this feat, however, if it is supplied with additional energy in the form of the high-energy compound adenosine triphosphate, or ATP. A molecule of ATP supplies about 10,000 calories per mole when its terminal phosphate group is split off, and this is enough to provide the needed boost to the reducing power of NADP. Furthermore, we know that NADP is reduced when cell-free preparations of chloroplasts are illuminated. Put together, these two facts led to the now widely accepted hypothesis that the sec-



THREE STAGES of photosynthesis are the removal of hydrogen from water with the release of oxygen (*bottom arrow*), the transfer (*vertical arrow*) of the hydrogen by energy from light trapped by chlorophyll (*color*) and the use of the hydrogen to reduce carbon dioxide to carbohydrate (*top arrow*). In this scheme the oxidation-reduction potentials involved are indicated by the scale at the left, and the hypothetical "primary reductant" and "primary acceptor" intermediates are designated as *ZH* and *X* respectively.

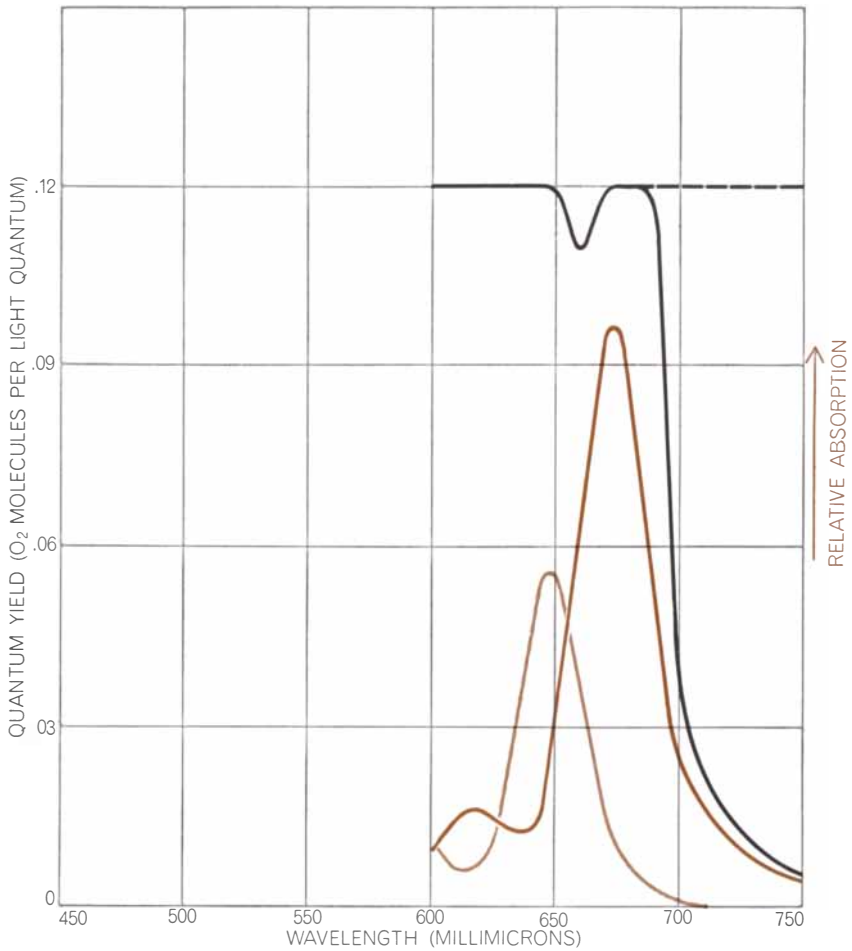
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ond stage of photosynthesis manufactures both ATP and reduced NADP and feeds them into the third stage.

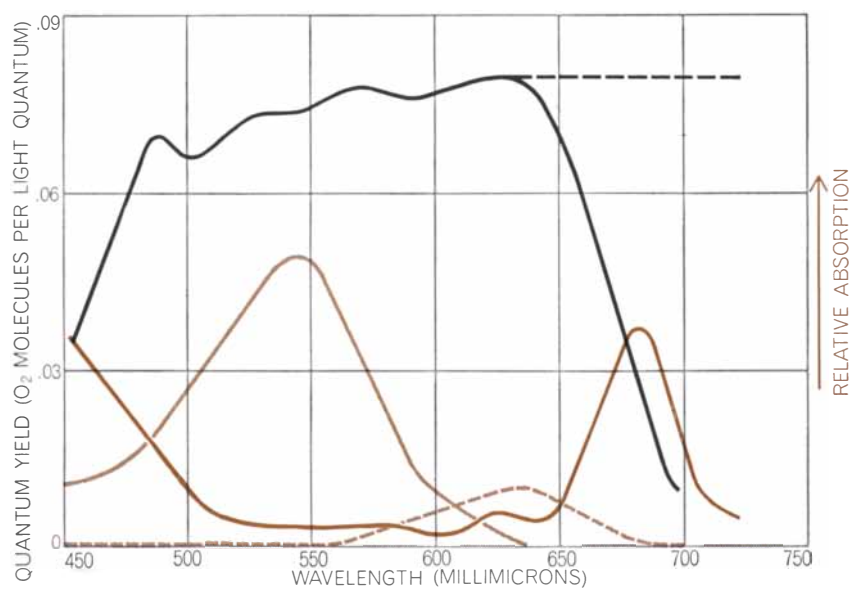
At first it was assumed that NADP is identical with *X*, the primary acceptor in our scheme. Subsequent experiments by various workers—notably Anthony San Pietro at Johns Hopkins University and Daniel I. Arnon and his colleagues at the University of California at Berkeley—suggested, however, that NADP is preceded in the "bucket brigade" of electron transfer by ferredoxin, a protein that contains iron. This compound has an oxidation-reduction potential of about —.42 volt; therefore if it is reduced in light it can bring about the reduction of NADP by a "dark" reaction requiring no additional energy supply.

More recently Bessel Kok of the Research Institute for Advanced Studies in Baltimore has found evidence suggesting that compound *X* may be a still stronger reductant, with a potential of about —.6 volt. If this is so, plants have the alternatives of either applying this stronger reductant directly to the reduction of carbon dioxide or letting it reduce first ferredoxin and then NADP and using reduced NADP to reduce carbon dioxide. It seems a roundabout procedure to create a reductant sufficiently strong for the task at hand, then to sacrifice a part of its reducing power and finally to use ATP to compensate for the loss. It is not unknown, however, for nature to resort to devious ways in order to achieve its aims.

For photosynthesis to be a self-contained process the required high-energy phosphate ATP must be itself manufactured by photosynthesis. The formation of ATP has in fact been detected in illuminated fragments of bacteria by Albert W. Frenkel of the University of Minnesota and in chloroplast fragments by Arnon and his co-workers [see "The Role of Light in Photosynthesis," by Daniel I. Arnon: SCIENTIFIC AMERICAN, November, 1960]. As a matter of fact, ATP is needed not only to act as a booster in the reduction of an intermediate in the carbon cycle by reduced NADP but also for another step in the third stage of photosynthesis. According to a sequence of reactions worked out in 1951 by Andrew A. Benson and his colleagues at the University of California at Berkeley, carbon dioxide enters photosynthesis by first reacting with a "carbon dioxide acceptor," a special sugar phosphate called ribulose diphosphate. It turns out that the production of this compound from its precursor—

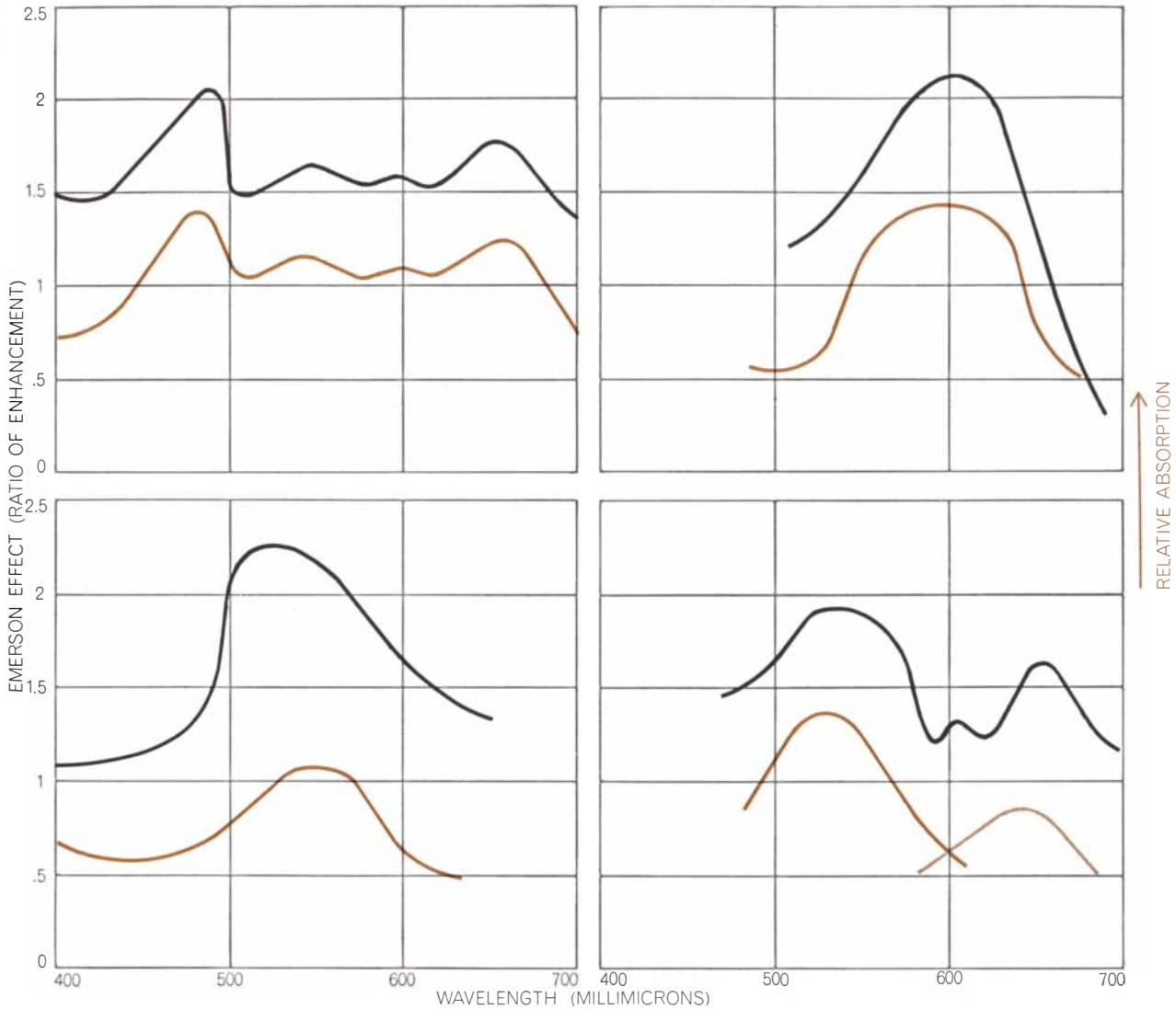


"RED DROP," the drop in quantum yield (*black curve*) of oxygen in photosynthesis under long-wave illumination, is demonstrated in the green alga *Chlorella pyrenoidosa*. Peak efficiency is restored (*broken line*) by supplementary shorter-wave illumination. Absorption curves of chlorophylls *a* (*solid color*) and *b* (*light color*) are also shown. This illustration and the next two are based on data of the late Robert Emerson of the University of Illinois.

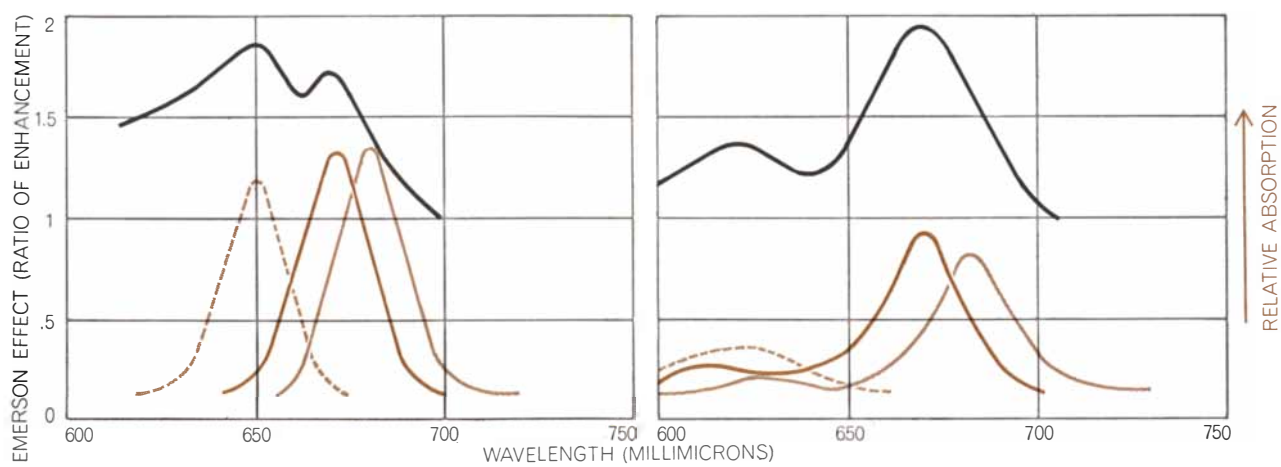


QUANTUM YIELD is similarly affected by long-wave illumination in the red alga *Porphyridium cruentum* (*black curve*). Yield drops to less than half of its maximum when absorption by chlorophyll *a* (*solid-color curve*) is at its peak. Absorption of the pigments phycoerythrin (*light-color curve*) and phycocyanin (*broken-color curve*) are also shown.

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EMERSON EFFECT is shown for *Chlorella* (*top left*), the blue-green alga *Anacystis nidulans* (*top right*), *Porphyridium* (*bottom left*) and the diatom *Navicula minima* (*bottom right*). In each case the black curve shows the action spectrum of the Emerson effect, or the degree of enhancement in quantum yield as the wavelength of the supplementary illumination is varied. The curve of the action spectrum turns out to be parallel to the absorption curves (*color*) of the various accessory pigments: chlorophyll *b* in *Chlorella*, phycocyanin in *Anacystis*, phycoerythrin in *Porphyridium* and fucoxanthol (*solid color*) and chlorophyll *c* (*light color*) in *Navicula*.



DETAILED ACTION SPECTRA of the Emerson effect reveal the presence of chlorophyll *a* 670 in *Chlorella* (*left*) and *Navicula* (*right*). The Emerson-effect peaks coincide with the absorption peaks of chlorophyll *a* 670 (*solid color*) as well as of chlorophyll *b* in *Chlorella* and chlorophyll *c* in *Navicula* (*broken curves*). The chlorophyll *a* absorption curve is also shown (*light-color curve*).

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ribulose monophosphate—calls for a molecule of ATP.

ATP is produced both in chloroplasts and in mitochondria, the tiny intracellular bodies that are the site of the energy-liberating stage of respiration in animals as well as plants. The mitochondria produce ATP as their main function, exporting it as packaged energy for many life processes. The chloroplasts, on the other hand, make ATP only as an auxiliary source of energy for certain internal purposes. The energy of the light falling on the chloroplasts is stored mostly as oxidation-reduction energy by the uphill transfer of electrons. Only a relatively small fraction is diverted to the formation of ATP, and this fraction too ultimately becomes part of the oxidation-reduction energy of the final products of photosynthesis: oxygen and carbohydrate.

Let us now consider the uphill transport of electrons in greater detail. Recent investigations have yielded considerable information about this stage. Apparently the pumping of the electrons is a two-step affair, and among the most important intermediates in it are the catalysts called cytochromes.

The idea of a two-step electron-transfer process grew from a consideration of the energy economy of photosynthesis. Precise measurements, particularly those made by the late Robert Emerson and his co-workers at the University of Illinois, showed that the reduction of one molecule of carbon dioxide to carbohydrate, and the liberation of one molecule of oxygen, requires a minimum of eight quanta of light energy. The maximum quantum yield of photosynthesis, defined as the number of oxygen molecules that can be released for each quantum of light absorbed by the plant cell, is thus 1/8, or 12 percent. Since the transfer of four electrons is involved in the reduction of one carbon dioxide molecule, it was suggested that it takes two light quanta to move each electron.

Emerson and his colleagues went on to determine the quantum yield of photosynthesis in monochromatic light of different wavelengths throughout the visible spectrum. They found that the yield, although it remained constant at about 12 percent in most of the spectrum, dropped sharply near the spectrum's far-red end [*see illustrations on page 77*]. This decline in the quantum yield, called the "red drop," begins at a wavelength of 680 millimicrons in green plants and at 650 millimicrons in red algae.

There are two chlorophylls present in green plants: chlorophyll *a* and chlorophyll *b*. Only chlorophyll *a* absorbs light at wavelengths longer than 680 millimicrons; the absorption of chlorophyll *b* rises to a peak at 650 millimicrons and becomes negligible at about 680 millimicrons. Emerson found that the quantum yield of photosynthesis at the far-red end of the spectrum beyond 680 millimicrons can be brought to the full efficiency of 12 percent by simultaneously exposing the plant to a second beam of light with a wavelength of 650 millimicrons. In other words, when light primarily absorbed by chlorophyll *a* was supplemented by light primarily absorbed by chlorophyll *b*, both beams gave rise to oxygen at the full rate. This relative excess in photosynthesis when a plant is exposed to two beams of light simultaneously, as compared with the yield produced by the same two beams separately, is known as the Emerson effect, or enhancement.

On the basis of his discovery Emerson concluded that photosynthesis involves two photochemical processes: one using energy supplied by chlorophyll *a*, the other using energy supplied by chlorophyll *b* or some other "accessory" pigment. Experimenting with various combinations of a constant far-red beam with beams of shorter wavelength, and using four different types of algae (green, red, blue-green and brown), Emerson's group found that the strongest enhancement always occurred when the second beam was absorbed mainly by the most important accessory pigment (the green pigment chlorophyll *b* in green cells, the red pigment phycoerythrin in red algae, the blue pigment phycocyanin in blue-green algae and the reddish pigment fucoxanthol in brown algae). Such results suggested that these other pigments are not mere accessories of chlorophyll *a* but have an important function of their own in photosynthesis [*see top illustration on opposite page*].

Certain findings concerning the behavior of pigments in living plant cells, however, seemed to make this conclusion untenable. Illuminated plant cells fluoresce; that is, pigment molecules energized by the absorption of light quanta reemit some of the absorbed energy as fluorescent light. The source of fluorescence can be identified, because each substance has its own characteristic fluorescence spectrum. The main fluorescing pigment in plants always proves to be chlorophyll *a*, even when the light is absorbed by another pigment. This had first been shown for brown algae in a study conducted in 1943 by H. J. Dutton, W. H. Manning and B. B. Duggar at the University of Wisconsin; later the finding was extended to other organisms by L. N. M. Duysens of the University of Leiden. Known as sensitized fluorescence, the phenomenon indicates that the initial absorber has transferred its energy of excitation to chlorophyll *a;* the transfer is effected by a kind of resonance process. Careful measurements have shown that certain accessory pigments—chlorophyll *b,* phycoerythrin, phycocyanin and fucoxanthol—pass on to chlorophyll *a* between 80 and 100 percent of the light quanta they absorb. For some other accessory pigments—for example carotene—the transfer is less efficient.

This puts accessory pigments back in the role of being mere adjuncts to chlorophyll *a*. True, they can contribute, by means of resonance transfer, light energy to photosynthesis, thereby improving the supply of energy in regions of the spectrum where chlorophyll *a* is a poor absorber. Chlorophyll *a,* however, collects all this energy before it is used in the primary photochemical process. Why, then, the enhancement effect? Why should chlorophyll *a* need, in order to give rise to full-rate photosynthesis, one "secondhand" quantum obtained by resonance transfer from another absorber in addition to the one quantum it had absorbed itself?

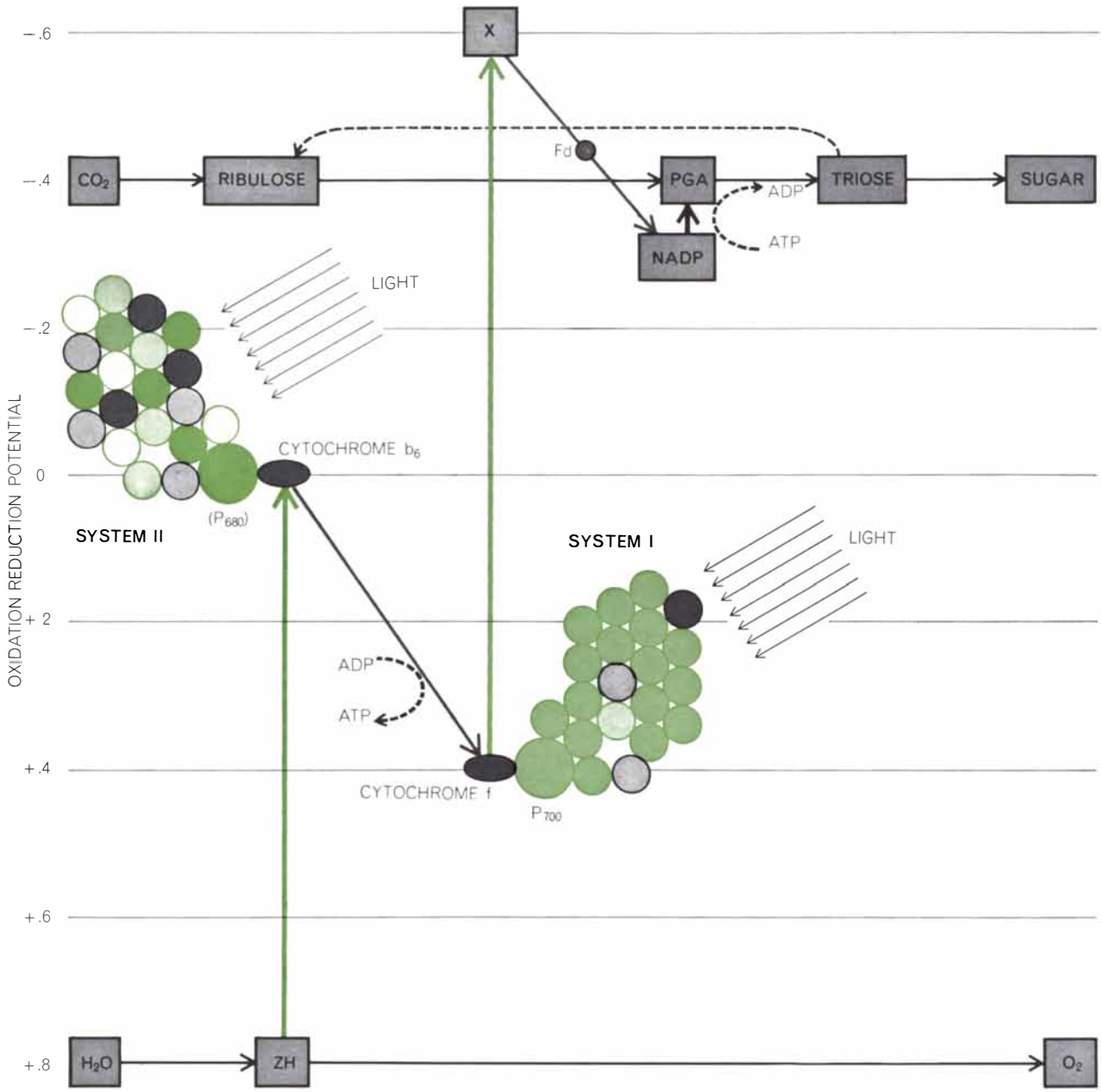
A better understanding of this paradox resulted from the discovery that there apparently exist in the cell not only chlorophyll *a* and chlorophyll *b* but also two forms of chlorophyll *a*. These two forms have different light-absorption characteristics, and they probably also have different photochemical functions.

In the living cell chlorophyll *a* absorbs light most strongly in a broad band with its peak between 670 and 680 millimicrons. In our laboratory at the University of Illinois we undertook to plot the Emerson effect more carefully than before as a function of the wavelength of the enhancing light. We found that for green and brown cells the resulting curve showed, in addition to peaks corresponding to strong absorption by the accessory pigments, a peak at 670 millimicrons that must be due to chlorophyll *a* itself [*see bottom illustration on opposite page*]. It was this finding that suggested the existence of two forms of chlorophyll *a*. The form that absorbs light at the longer wavelengths—mainly above 680 millimicrons—seemed to belong to one pigment system, now often called System I. The form that absorbs at 670 millimicrons seemed to

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belong to another pigment system: System II. In the second system the form of chlorophyll *a* that absorbs at 670 millimicrons is strongly assisted by accessory pigments, probably by resonance transfer of their excitation energy. Careful analysis of the absorption band of chlorophyll *a* by C. Stacy French of the Carnegie Institution of Washington's Department of Plant Biology, and also in our laboratory, confirmed that the band is double, with one peak near 670 millimicrons (at 668 millimicrons) and another band at 683 millimicrons [*see bottom illustration on page 78*].

If chlorophyll *a* is extracted from living plants, there is only one product; we must therefore assume that in the living cell the two forms differ in the way molecules of chlorophyll *a* are clumped together, or in the way they are associated with different chemical partners (proteins, lipids or other substances). Be this as it may, the important implication of the new finding is that photosynthesizing cells possess two light-absorbing systems, one containing a form of chlorophyll *a* absorbing around 683 millimicrons and the other a form absorbing around 670. The latter system includes chlorophyll *b* (in green-plant cells) or other accessory pigments (in brown, red and blue-green algae). Further investigation—particularly of red algae—has suggested, however, that the distribu-



HYDROGEN TRANSFER in photosynthesis is now conceived of as a two-step process involving two pigment systems. Hydrogen atoms (or electrons) from the donor (*ZH*) are boosted to cytochrome b_6 by energy collected in System II and trapped by a hypothetical "pigment 680" (*P 680*). The pigments of System II include chlorophyll *a* 670 and such accessory pigments as chlorophyll *b* or *c*, phycoerythrin or phycocyanin, depending on the plant. The electrons are passed "downhill" to cytochrome *f*, synthesizing adenosine triphosphate (*ATP*) in the process. Energy from System I (primarily chlorophyll *a*, with some accessory pigments), trapped by pigment 700 (*P 700*), boosts the electrons to a receptor (*X*), whence they move via ferredoxin (*Fd*) to nicotinamide adenine dinucleotide phosphate (*NADP*). Energy from ATP helps to move the electrons to phosphoglyceric acid (*PGA*) and into the carbon cycle.

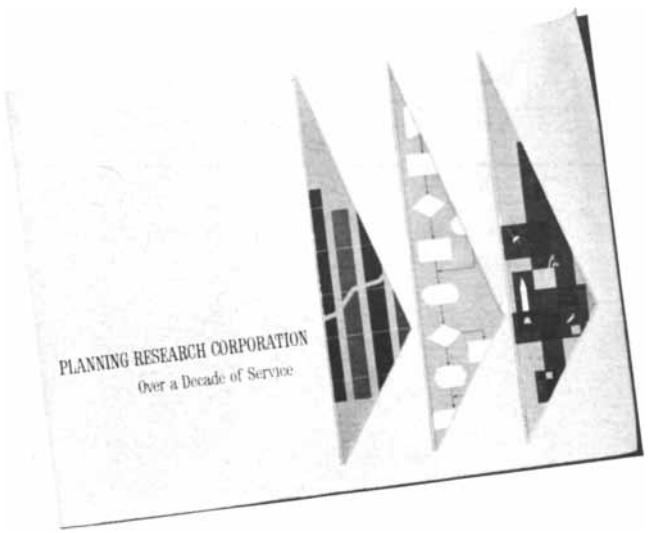
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tion of these two components in the two systems may be less clear-cut. In red algae a large fraction of the chlorophyll *a* absorbing at 670 millimicrons seems to belong to System I rather than System II.

In all likelihood the two systems provide energy for two different photochemical reactions, and efficiency in photosynthesis requires that the rates of the two reactions be equal. What are these reactions? This question brings us to another significant finding, which suggested the participation of cytochromes in photosynthesis.

Cytochromes are proteins that carry an iron atom in an attached chemical group. They are found in all mitochondria, where they serve to catalyze the reactions of respiration. Robert Hill and his co-workers at the University of Cambridge first found that chloroplasts also contain cytochromes—two kinds of them. One, which they named cytochrome *f*, has a positive oxidation-reduction potential of about .4 volt. The other, which they named cytochrome b_6, has a potential of about 0 volt. In 1960 Hill, together with Fay Bendall, proposed an ingenious hypothesis as to how the two cytochromes might act as intermediate carriers of electrons and connect the two photochemical systems [*see illustration on opposite page*]. They suggested that cytochrome b_6 receives an electron by a photochemical reaction from the electron donor *ZH;* the electron is then passed on to cytochrome *f* by a "downhill" reaction requiring no light energy. (The oxidation-reduction potential of cytochrome *f* is much more positive than that of cytochrome b_6.) A second photochemical reaction moves the electron uphill again, from cytochrome *f* to the electron-acceptor *X* in the third stage of photosynthesis. In this sequence the photochemical reactions store energy and the reaction between the two cytochromes releases energy. Some of the released energy, however, can be salvaged by the formation of an ATP molecule; this occurs in the transfer of electrons among cytochromes in respiration. In this way ATP is obtained without spending extra light quanta on its formation, which the tight energy economy of photosynthesis does not allow.

Experiments by Duysens and his associates confirmed this hypothesis, by showing that the absorption of light by System I causes the oxidation of a cytochrome, whereas the absorption of light by System II causes its reduction. This is exactly what we would expect. The illustration on the opposite page shows that the light reaction of System II



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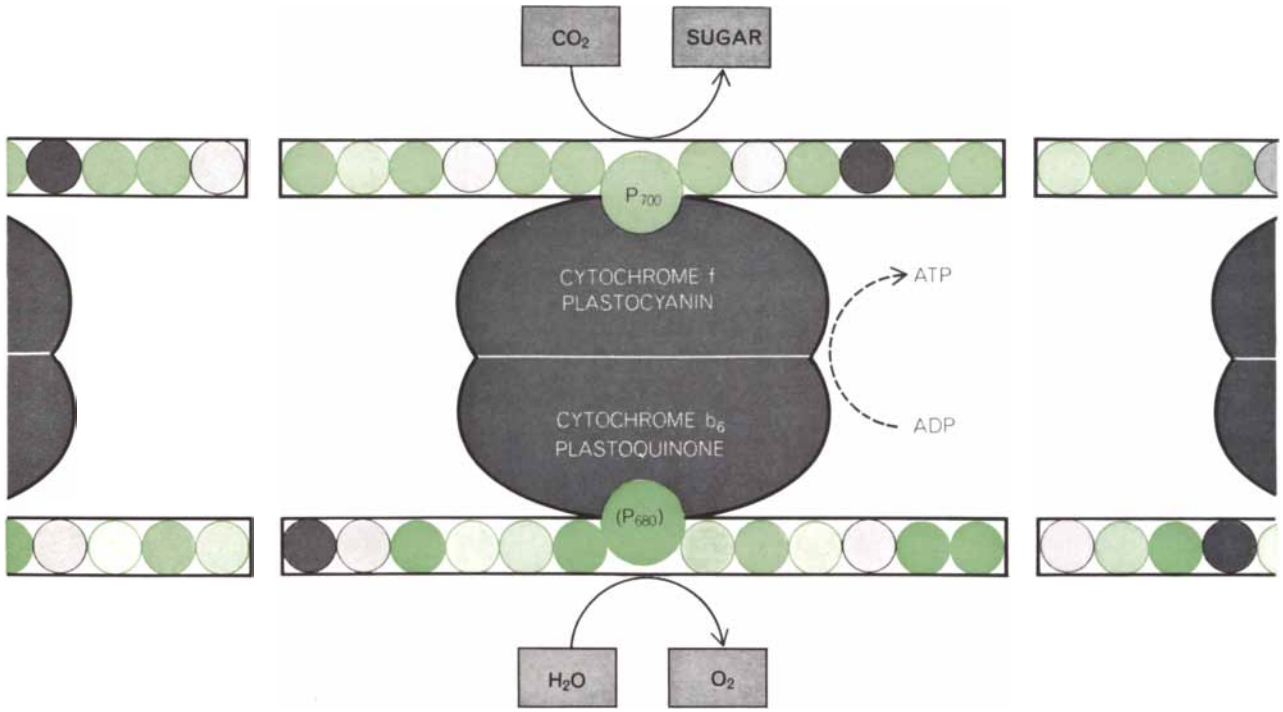
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HYPOTHETICAL ARRANGEMENT of pigments in a chloroplast lamella would have System I in a monomolecular layer at the top and System II at the bottom. The space between the two pigment layers might contain the compounds responsible for the transport of hydrogen atoms (or electrons). The water-to-oxygen cycle would then be linked to System II and the carbon cycle to System I.

should flood the intermediates between the two photochemical reactions with electrons taken from *ZH;* the light reaction of System I should drain these electrons away, sending them up to the acceptor *X* and into the third stage of photosynthesis.

This, then, describes in a general way the oxidation-reduction process by which the chloroplasts store the energy of light in photosynthesis. Several other investigators have contributed evidence for the two-step mechanism; notable among them are French, Kok, Arnon, Horst Witt of the Max-Vollmer Institute in Berlin and their colleagues. In detail the process probably is much more complex than our scheme suggests. Its "downhill" central part seems to include, in addition to the two cytochromes, certain compounds of the group known as quinones and also plastocyanin, a protein that contains copper.

What is known of the submicroscopic structure in which the reactions of the second stage of photosynthesis take place? There is much evidence that the photosynthetic apparatus consists of "units" within the chloroplasts, each unit containing about 300 chlorophyll molecules. This picture first emerged from experiments conducted in 1932 by Emerson and William Arnold on photosynthesis during flashes of light; it was later supported by various other observations. The pigment molecules are packed so closely in the unit that when one of them is excited by light it readily transfers its excitation to a neighbor by resonance. The energy goes on traveling through the unit, rather as the steel ball in a pinball machine bounces around among the pins and turns on one light after another. Eventually the migrating energy quantum arrives at the entrance to an enzymatic "conveyor belt," where it is trapped and utilized either to load an electron onto the belt or to unload one from it. (The steel-ball analogy should not be taken literally; the migration of energy is a quantum-mechanical phenomenon, and the quantum's location can only be defined in terms of probability; its entrapment depends on the probability of finding it at the entrance to the conveyor belt.)

How is the quantum trapped? The trap must be a pigment molecule with what is called a lower excited state; the migrating quantum can stumble into such a molecule but cannot come out of it. Kok has found evidence that System I contains a small amount of a special form of chlorophyll called pigment 700 because it absorbs light at a wavelength of 700 millimicrons; this pigment could serve as a trap for the quantum bouncing around in System I. There seems to be a proper amount of pigment 700: about one molecule per unit. Furthermore, experiments suggest that pigment 700 is oxidized by light absorbed in System I and reduced by light absorbed in System II. It has an oxidation-reduction potential of about +.4 volt. All these properties fit the role we have assigned pigment 700 in our scheme: collecting energy from a 300-molecule unit in System I, using it to transfer an electron to the acceptor *X* and recovering the electron from cytochrome *f* [*see illustration on page 80*].

One suspects that there should be a counterpart of pigment 700 in System II, but so far none has been convincingly demonstrated. We believe, however, that a pigment we have tentatively named pigment 680—from the anticipated position of its absorption band—does serve as an energy trap in System II. Its existence is supported by the discovery of a new fluorescent emission band of chlorophyll at 693 millimicrons, which is compatible with absorption at 680 millimicrons. This band is emitted by certain algae when they are exposed to strong light of the wavelengths absorbed by System II.

What is the spatial organization of the pigment systems in the electron-boosting mechanism of the second stage of photosynthesis? It seems that the two systems may be arranged in two mono-

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molecular layers, with a protein layer between them containing the enzymatic conveyor belt [*see illustration on opposite page*]. The chloroplasts are known from electron microscope studies to consist of a set of lamellae: thin alternating layers of protein and fatty material piled one atop the other. Each layer appears to consist of particles arrayed rather like cobblestones in a pavement. The particles were first observed in electron micrographs made by E. Steinmann of the Technische Hochschule in Zurich; subsequently Roderic B. Park and John Biggins of the University of California at Berkeley made clearer micrographs of the particles and named them quantasomes [*see illustration on page 75*]. The units comprising Systems I and II may operate independently or they may be sufficiently close together to exchange energy by resonance, when such exchange is needed to maintain a balanced rate of operation by the two systems.

The picture of the energy-storing second stage of photosynthesis presented in this article is, of course, still only a working hypothesis. Alternative hypotheses are possible, one of which we shall briefly describe. For many years the late James Franck, who shared the Nobel prize in physics for 1925, tried to develop a plausible physicochemical mechanism of photosynthesis. In 1963 he proposed, together with Jerome L. Rosenberg of the University of Pittsburgh, a concept according to which the two consecutive photochemical steps occur in one and the same energy trap. In other words, according to Franck, the same chlorophyll molecule that takes the electron away from the initial donor *ZH* and transfers it to a cytochrome then supplies energy for the transfer of the electron from the cytochrome to the acceptor *X*. In the first transfer, Franck suggested, the chlorophyll *a* molecule functions in the short-lived "singlet" excited state (in which the valence electrons have opposite spins); in the second transfer it functions in the long-lived "triplet" state (in which the valence electrons have parallel spins). Franck's hypothesis avoids certain difficulties of the "two trap" theory, but new difficulties arise in their place. On balance the two-trap picture seems to us the more plausible one at present.

No doubt this picture will change as more information emerges. It is merely a first effort to penetrate the inner sanctum of photosynthesis, the photocatalytic laboratory in which the energy of sunlight is converted into the chemical energy of life.



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