Evolution of Photosynthesis

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Advanced article

Article Contents

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Photosynthesis is the conversion of radiant energy, as light, into stored chemical energy. The central process is a light-driven separation of electrical charge across a biological membrane. Photochemical reaction centres carry out this process, and their three-dimensional protein structures now indicate that all modern reaction centres are homologous. Reaction centres with light-harvesting complexes comprise photosynthetic units, two of which are required for the oxygenic photosynthesis that now dominates biological energy flow in the biosphere. The evolutionary origin of oxygenic photosynthesis in cyanobacteria had a profound effect on the chemistry of the Earth's atmosphere, on geology and on biology, paving the way for the evolution of complex, multicellular life. Eukaryotic plants and algae maintain the descendents of cyanobacteria as specialised, subcellular, cytoplasmic organelles called chloroplasts. The genes that remain in chloroplasts may be retained to be subject to regulatory control by the photosynthetic electron transport chain.

Introduction

Photosynthesis is a mechanism for conversion of light energy into the chemical energy that is used for endergonic metabolic processes that now form the basis of life on Earth. Whereas the first life forms may have derived their energy from light-independent geothermal convection (Lane *et al*., 2010), light energy now provides most of the energy used by biological systems (Leslie, 2009). **See also**: Prebiotic Chemistry

Two types of photosynthesis have evolved that enable the biological utilisation of light energy. One is present in marine bacteria (Beja *et al*., 2001) and halophilic Archaea and involves the use of bacteriorhodopsin and halorhodopsin for pumping ions (protons and chloride ions, respectively) across a membrane. In this way, light is used to generate an ionic gradient, or proton motive force, across a membrane. This proton motive force is used for adenosine triphosphate (ATP) synthesis or to extrude chloride ions from the cell (see Heberle, 2000 for a review on bacteriorhodopsin, and Kolbe *et al*. (2000) for the 1.8-Å resolution structure of halorhodopsin). ATP is an energy-rich compound (free-energy donor) that is used for many energy-requiring physiological processes in cells. The other type of photosynthetic utilisation of light energy for bioenergetic purposes in cells involves a light-driven charge separation that initiates vectorial electron and proton transport, providing an alternative route to establishment of a proton motive force. **See also**: Halophiles

Photosynthetic electron transport is the process of using light energy to generate a proton gradient across the membrane (used for ATP synthesis) and at the same time to transport electrons (reducing equivalents) that are used for nicotinamide–adenine dinucleotide phosphate, reduced (NADPH) generation. 2′-Phosphate nicotinamide–adenine dinucleotide ($NADP^+$/NADPH) is a common electron carrier in physiological redox reactions. ATP and NADPH are used, for example, for conversion of carbon dioxide to sugars. The source of electrons varies depending on the organism, but of particular importance for the evolution of life on Earth is the use of water as an electron donor. Oxidation of water leads to the formation of free, molecular oxygen. Oxygenic photosynthesis is carried out by plants, algae, cyanobacteria and their relatives, and the quantity of oxygen produced by this process is on the order of 100 million tons per day. Globally, photosynthesis (fixing carbon dioxide and producing oxygen) and respiration (using oxygen and producing carbon dioxide) are antiparallel reactions that occur at similar rates, although

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sequestration of carbon in inorganic form (as carbonates and bicarbonates) has produced an excess of oxygen that is now at a steady-state concentration of approximately 20% by volume of the Earth's atmosphere (Dietrich *et al*., 2006). In contrast, the quantity of carbon dioxide in the air reached, geologically, an all-time low at 0.03% before the industrial revolution and large-scale fossil fuel-burning. **See also**: Biogeochemical Cycles

In addition to oxygenic photosynthesis, photosynthesis using electron donors other than water is carried out in anoxygenic photosynthetic bacteria; this process generally operates under anaerobic conditions. In many cases, the main function of this anoxygenic photosynthesis (with electron donors other than water and therefore not leading to the production of oxygen) is generation of ATP. This type of anoxygenic photosynthesis uses protein complexes that must have derived from those of a photosynthetic ancestor common to both anoxygenic and oxygenic photosynthesis. Therefore, anoxygenic bacterial photosynthesis is likely to be very closely related to the oxygenic photosynthesis that takes place in plants, algae and cyanobacteria. An overview of photosynthesis in many of its aspects is provided in Blankenship (2002). **See also**: Photosynthesis

Photosynthetic Reaction Centres

In photosynthesis, a reaction centre contains a chlorophyll molecule that receives absorbed excitation energy from other molecules and in which the decay of its resulting excited state causes loss of an electron to an acceptor. The reaction centre chlorophyll thus acts as an electron donor and becomes oxidised, while the primary electron acceptor becomes reduced. Photosynthetic reaction centres are also termed 'photochemical reaction centres of photosynthesis'. Operation, or turnover, of reaction centres can be detected by light-induced spectroscopic changes that report on this primary electron transfer. Isolation of reaction centres and structural studies show that all reaction centres, whether from bacteria, algae or green plants, have a common overall structure (**Figure 1**). They are composed of an integral membrane protein complex of essentially a homodimeric or heterodimeric nature to which pigments (carotenoids and chlorophylls) and redox-active cofactors (such as chlorophylls and quinones) are bound. Light energy is absorbed primarily by antenna pigments (chlorophylls and other pigments), which harvest light and transfer it to the reaction centre. Antenna pigments are either linked closely to the photochemical reaction centre (in a core antenna) or in separate protein complexes (in peripheral antennae). Reaction centres and most light-harvesting antennae are intrinsic to the biological membrane in which photosynthesis occurs. In bacteria, these membranes may be the cell membrane, or 'chromatophores', invaginations of the cell membrane that are topologically continuous with it. In eukaryotic plants and algae, photosynthesis occurs in subcellular organelles called chloroplasts, and the primary events of photosynthesis occur in an internal membrane

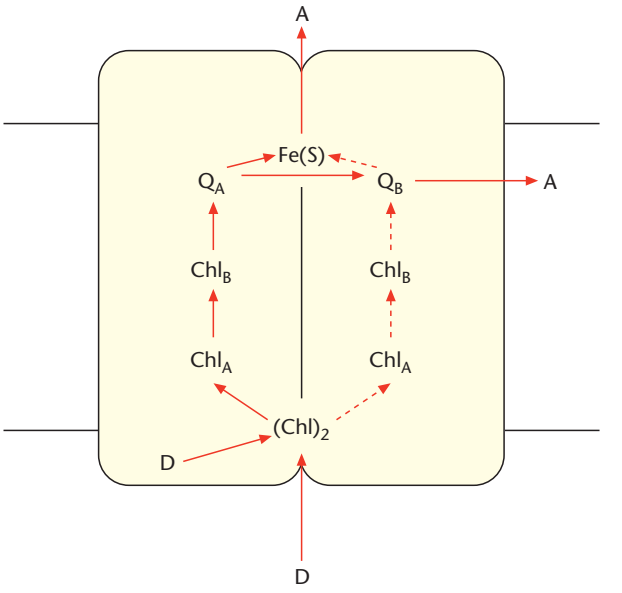

Figure 1 Generic model of a photosynthetic reaction centre in a membrane. The reaction centre consists of a homodimer or heterodimer of polypeptides (indicated by rectangles) that bind cofactors involved in electron transfer. A central component in the photosynthetic reaction centre is the primary donor, indicated by $(Chl)_2$, which is a dimer of chlorophyll *a* or one of its derivatives (such as a bacteriochlorophyll). Upon excitation by light energy, the primary donor transfers an electron through a chlorophyll (or derivative), Chl_A, to another pigment, indicated by Chl_B, which may be a (bacterio)pheophytin or a (bacterio)chlorophyll. This electron transfer takes place within 3–30 ps. Depending on the type of reaction centre, electron transfer can involve one or both of the pathways present in the dimeric reaction centre. In photosystem I-type reaction centres, electrons may flow along both branches (arrows with solid or dotted lines) through the chlorophylls to quinones (Q_A or Q_B) and then to an iron–sulfur centre (FeS) and subsequent acceptors (A) on the cytoplasmic/stromal side of the membrane, without necessarily involving the other quinone in electron transfer. In photosystem II-type reaction centres, however, only one of the branches is used (solid lines), and the two Chls at the right are not involved in electron transfer; they are said to be on the inactive branch of the electron transport chain. The electron in photosystem II-type reaction centres is transferred from Q_A to Q_B through a nonhaem iron (Fe) and then to an acceptor (A) (such as another quinone) in the membrane. In both types of reaction centres, the oxidised primary donor is rereduced by a donor D, which may be either in the membrane or on the lumenal/periplasmic side of the membrane.

called the chloroplast thylakoid. Reaction centres drive electron transport within the thylakoid membrane, and photosynthetic electron transport moves protons from the chloroplast stroma to the thylakoid lumen, an internal compartment homologous with the periplasmic space of photosynthetic bacteria. **See also**: Photosynthesis: Light Reactions

Photosynthetic reaction centres can be divided into two groups. One is the photosystem I-type (or FeS cluster-type) reaction centre group, and the other is the photosystem II-type (or nonhaem iron-type) group. Both catalyse a chain of redox reactions initiated by light energy. A main distinction between these two types of reaction centre is the redox midpoint potential (E_m) range. As indicated in **Figure 2**, photosystem II-type reaction centres are able to

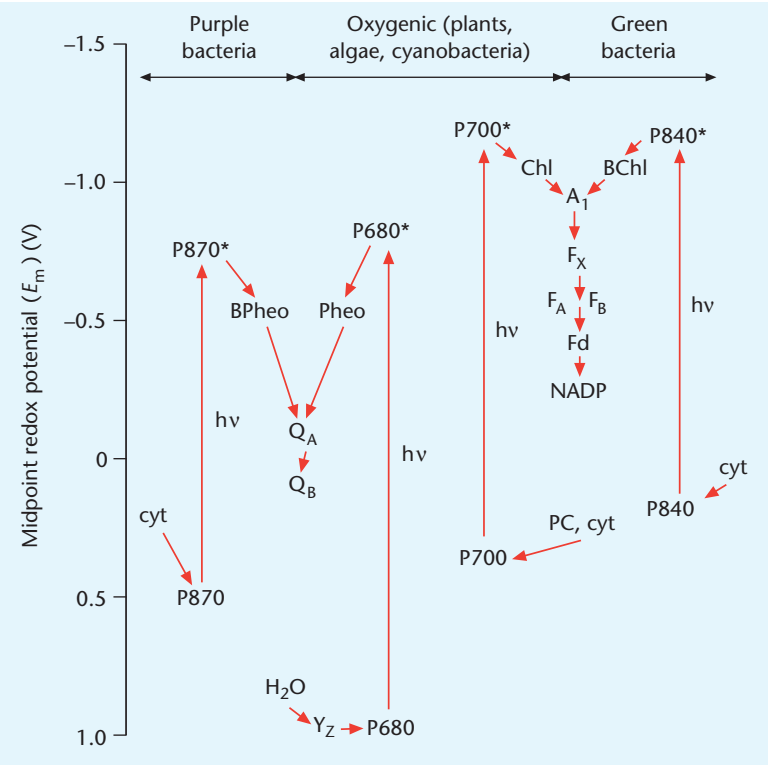

Figure 2 Electron transfer scheme for photosystem II-type (left) and photosystem I-type (right) reaction centres. Vertically, the electron transport components have been arranged according to their redox midpoint potential. A more negative midpoint potential means that components are stronger electron donors (reductants), and a more positive potential is indicative of a stronger oxidant. The two examples of photosystem II-type reaction centres indicated in this scheme are those from *Rhodobacter sphaeroides*, a purple nonsulfur bacterium (left), and photosystem II (middle left). The two examples of photosystem I-type reaction centres shown here are photosystem I (middle right) and the reaction centre from *Chlorobium tepidum*, a green sulfur bacterium (right). Abbreviations: A_1, quinone-type electron acceptor (vitamin K_1 in photosystem I and in *C. tepidum*); BChl, bacteriochlorophyll; BPheo, bacteriopheophytin; Chl, chlorophyll; cyt, cytochrome; F_A, F_B and F_X, Fe_4S_4 centres; Fd, ferredoxin; hν, light; P870, P680, P700 and P840, the primary donors (Bchl *a*, Chl *a*, Chl *a*/*a*¢ and BChl *a*, respectively) in the reaction centres of *R. sphaeroides*, photosystem II, photosystem I and *C. tepidum*, respectively; PC, plastocyanin; Pheo, pheophytin (chlorophyll without a central magnesium ions) and Q_A and Q_B, the primary and secondary quinone-type electron acceptors (these quinones are ubiquinones in *Rhodobacter*, and plastoquinone in photosystem II).

use electron donors with very positive midpoint redox potentials but do not generate strong reductants (a typical electron acceptor is a quinone), whereas photosystem I-type reaction centres generate strong reductants (easily capable of $NADP^+$ reduction) and need electron donors of relatively low redox potential. In the case of oxygenic photosynthesis, the two types of reaction centres are both needed and work in series. In photosystem II, water serves as the ultimate electron donor. However, the E_m of the ultimate electron acceptor at the acceptor side, Q_B, is too positive to be able to reduce nicotinamide–adenine dinucleotide (NAD^+) or $NADP^+$ without having additional driving force (such as a proton gradient). In contrast, oxidised photosystem I-type reaction centres are rather weak oxidants and cannot oxidise water but can oxidise electron carriers that ultimately received their electrons from photosystem II. **See also**: Photosystem II

Another difference between the two types of reaction centre is the nature of the terminal electron acceptor. In photosystem I-type reaction centres, electrons go from the quinone (**Figure 1**) to Fe_4S_4 centres that transfer electrons to ferredoxin or flavodoxin and eventually to $NADP^+$. The structural homologue of F_X, the first electron-accepting Fe_4S_4 centre in photosystem I-type reaction centres, appears to be the nonhaem iron in photosystem II-type reaction centre. However, in contrast to F_X, the nonhaem iron does not serve as an electron transport intermediate under normal conditions. Instead, electrons pass from one quinone to a second quinone, which is subsequently released from the reaction centre complex into the membrane. **See also**: Photosystem I

Because of the functional differences between photosystem I-type and photosystem II-type reaction centres, these centres initially were once viewed as originating from different evolutionary lineages. However, there are two reasons why a single reaction centre ancestor is highly probable: (1) the reaction centres are so similar functionally that they can be described by one unified model (**Figure 1** and **Figure 2**) and (2) the similarity between the two types of reaction centres is structurally compelling (Schubert *et al.*, 1998). **See also**: Mitochondria: Structure and Role in Respiration

Ancestral Reaction Centre

Although it now seems clear that all photosynthetic reaction centres have a common evolutionary origin, the question remains as to what an ancestral reaction centre complex may have looked like and how reaction centres have evolved. Schopf (1993) has interpreted structures found in 3.5 billion-year-old stromatolites to be the remains of cyanobacteria. Therefore, reaction centres from cyanobacteria (oxygenic organisms with two different types of photosynthetic reaction centres operating in series) may be among the oldest photosynthetic structures. However, cyanobacterial photosynthesis has two features that are thought to be advanced: (1) the capability to oxidise water and produce oxygen and (2) two photosynthetic reaction complexes working in series. Therefore, if Schopf's interpretation is correct, one might assume that oxygenic photosynthetic organisms already existed in the early Archaean aeon (Olson, 2006). Alternatively, ancient stromatolites might have been built by anoxygenic precursors of cyanobacteria (Allen, 2005). Note that other authors argue that these stromatolites had an abiotic origin (Brasier *et al*., 2006). **See also**: Earth: Changes Through Time

The important questions that are still open are what the ancestral reaction centre may have looked like, what its origin may have been and what could have been the selection pressure for two types of reaction centres to develop. The function of the original reaction centre was probably the generation of both ATP and reducing equivalents. Arguing from this functional perspective, purple nonsulfur bacteria and green bacteria and heliobacteria fit the bill of potentially being close to the photosynthetic ancestor. Purple bacteria as well as presumably the green bacteria and heliobacteria have a predominantly cyclic electron transfer pathway in which electrons from the acceptor side are shuttled back to the donor side through the cytochrome b-c_1 complex or its equivalent. A proton gradient results, which may be used for ATP synthesis, ion transport or other processes. On the basis of sequence comparison of enzymes involved in (bacterio)chlorophyll synthesis in photosynthetic organisms, it has been argued that purple bacteria are the most ancient photosynthetic organisms that still have living descendants (Xiong *et al*., 2000). However, the primary structure of the type II purple bacterial reaction centre is far removed from that of photosystems II and I, particularly in terms of the antenna system. A possible structural homology between type II reaction centres and cytochrome b (Xiong *et al*., 2000) is depicted in **Figure 3**. **See also**: Electron Carriers: Proteins and Cofactors in Oxidative Phosphorylation

One interpretation of this homology is that photosynthetic complexes in purple bacteria may have resulted from lateral gene transfer, even though the source of these genes is not apparent. None the less, because photosynthetic genes are located in major clusters in many purple bacteria, gene transfer events leading to introduction of an entire photosynthetic pathway would not need to be very complicated. Alternatively, the nonphotosynthetic close relatives of purple photosynthetic bacteria (including representatives of the genera *Bradyrhizobium* and *Paracoccus*) may have lost the ability to perform photosynthesis. In any case, the hypothesis that purple bacteria are the most ancient photosynthetic organisms with living descendants (Xiong *et al*., 2000) does not seem to be supported by this line of evidence. **See also**: Phototrophic Purple Bacteria

Another possibility is that the ancestral reaction centre resembled a simple, probably homodimeric, photosystem I-type reaction centre, perhaps similar to that in heliobacteria or *Chlorobium* (Baymann *et al*., 2001). From this, the photosystems and the purple bacterial reaction centre may have developed by gene duplication and divergence events. All reaction centres, except those from Heliobacteriaceae and Chlorobiaceae (two families of photosynthetic bacteria), contain a heterodimeric pair of central polypeptides. These two bacterial families contain only a single reaction centre gene and are presumed to contain a homodimeric protein in their reaction centre. As a homodimeric arrangement is viewed to be more ancient than a heterodimeric one, one might expect the reaction centre in heliobacteria and Chlorobiaceae to be most related to the common ancestor. However, this is not clear from 16S ribosomal ribonucleic acid (rRNA) sequence analysis. According to this analysis, the two families with homodimeric reaction centres do not branch off particularly early in the phylogenetic tree and are closely interwoven with other groups (Woese *et al*., 1985; Stackebrandt *et al*., 1996). However, a large photosynthesis gene cluster of heliobacteria has been sequenced, and on the basis of these results, an evolutionary analysis of photosynthesis was presented (Xiong *et al*., 1998). In this analysis, heliobacteria were placed closest to cyanobacteria and, when genes not specific for photosynthesis were considered, were placed closest to Gram-positive bacteria (particularly bacilli). A close relationship between Chlorobiaceae and cyanobacteria is found by comparing sigma factor sequences (Gruber and Bryant, 1998); sigma factors are RNA polymerase subunits that are involved with promoter recognition (Shimizu *et al*., 2010). Cyanobacteria and bacteria with a homodimeric reaction centre are rather closely related phylogenetically. If the photosynthetic bacteria with a homodimeric reaction centre were evolutionarily ancient, this would support the notion that cyanobacteria are among the most ancient photosynthetic organisms (Bryant and Frigaard, 2006). **See also**: Cyanobacteria

Early Evolution

In energy conversion by living cells, electron and proton transport are vectorial, which is to say that these reactions possess both magnitude and direction, in space – from one side of a membrane to the other. The earliest living cells are likely to have possessed the transmembrane gradient of hydrogen ion concentration that was later supplemented

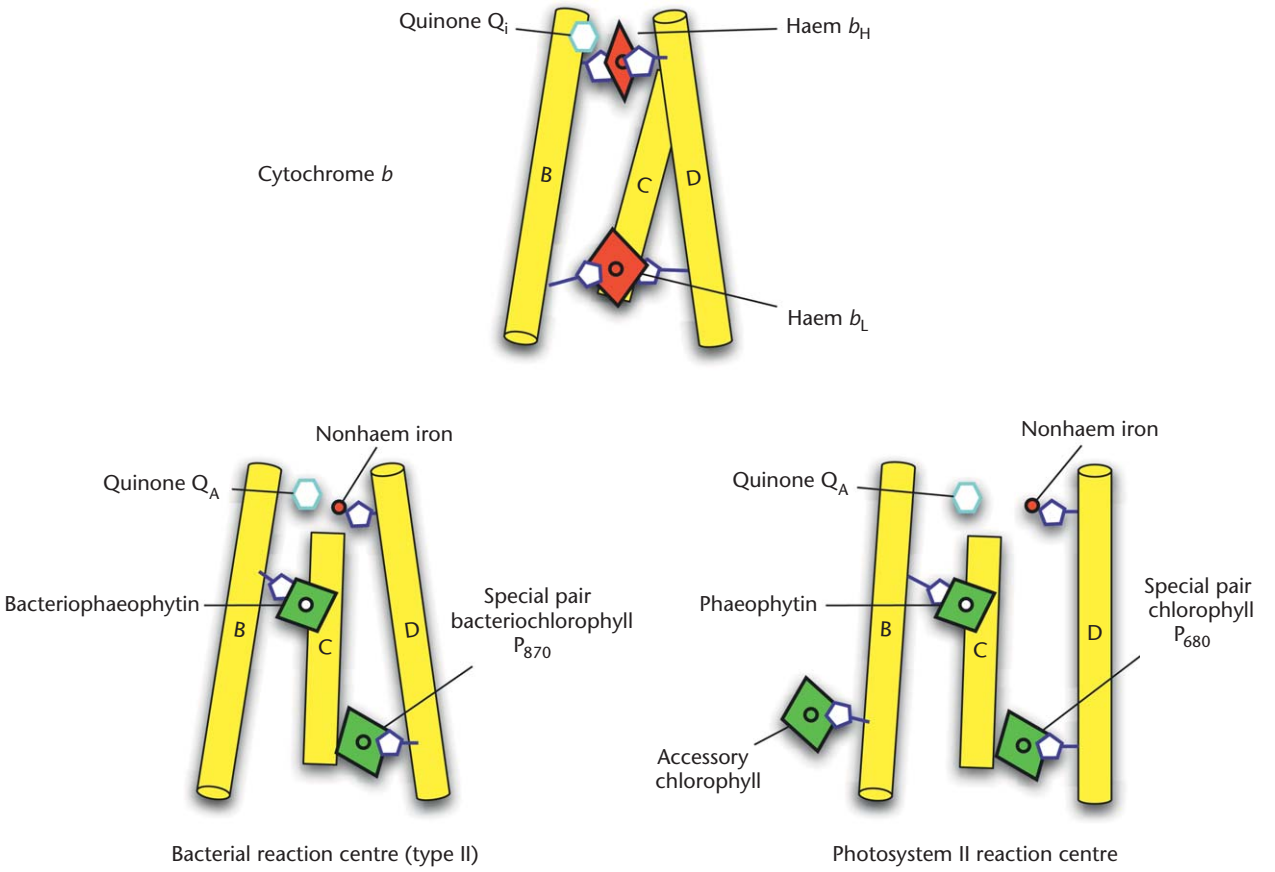

Figure 3 Possible structural homology between type II reaction centres and cytochrome *b*, as proposed by Xiong *et al.* (2000). Haem groups (red) of cytochrome *b* become substituted by chlorin rings (green) of (bacterio)chlorophyll and (bacterio)phaeophytin in the transition from cytochrome to reaction centre and occupy positions spanning the membrane by means of ligation to conserved histidine side chains (blue).

by biological electron transport, including photosynthetic electron transport (Lane *et al.*, 2010). The fundamental feature of photosynthetic reaction centres is thus light-driven, transmembrane charge separation. **See also**: Cell Membrane Features

Regardless of which type of reaction centre may have been most ancient, an important question is how the initial reaction centre may have formed. Even a heliobacterial homodimeric reaction centre has 11 membrane-spanning regions per subunit, and it is unlikely that such a complex structure would have formed spontaneously. As the simplest way to form a major membrane protein complex is to string together membrane-spanning domains, a first approach is to determine whether sequence similarities exist between individual transmembrane domains of antenna and reaction centre proteins. Alignment of individual transmembrane domains of these proteins shows several interesting patterns of evolutionary significance (**Figure 4**). First of all, many even-numbered transmembrane helices (going from the periplasmic/lumenal side to the cytoplasmic/stromal side of the membrane in the core light-harvesting antenna of the two types of photosystems as well as the chlorophyll Prochlorophyte chlorophyll binding protein A (PcbA)) have a common pattern. This similarity includes conservation of residues (such as histidine, asparagine and lysine) that may provide an axial ligand to magnesium ions in chlorophyll and conservation of the size of hydrophobic residues at many positions. **See also**: Membrane Proteins

It seems reasonable to interpret the weak similarities between single transmembrane regions of reaction centre and antenna proteins as evidence for a small number of common one-helix ancestors that have given rise to the diverse spectrum of reaction centre and antenna proteins known today. However, detailed structural information on all or most of these complexes will be needed to determine whether the sequence alignments presented here indeed represent structural similarities between single-helix regions. None the less, if this is correct, one may argue that multiple duplication events involving proteins, each with a single membrane-spanning helix, may have led to the formation of a myriad of different photosynthetic reaction centres and integral membrane antennae. A scheme outlining the possible duplication events is shown in **Figure 5**. In this scheme, the most ancient reaction centre may be simpler than any of the existing ones and have consisted of

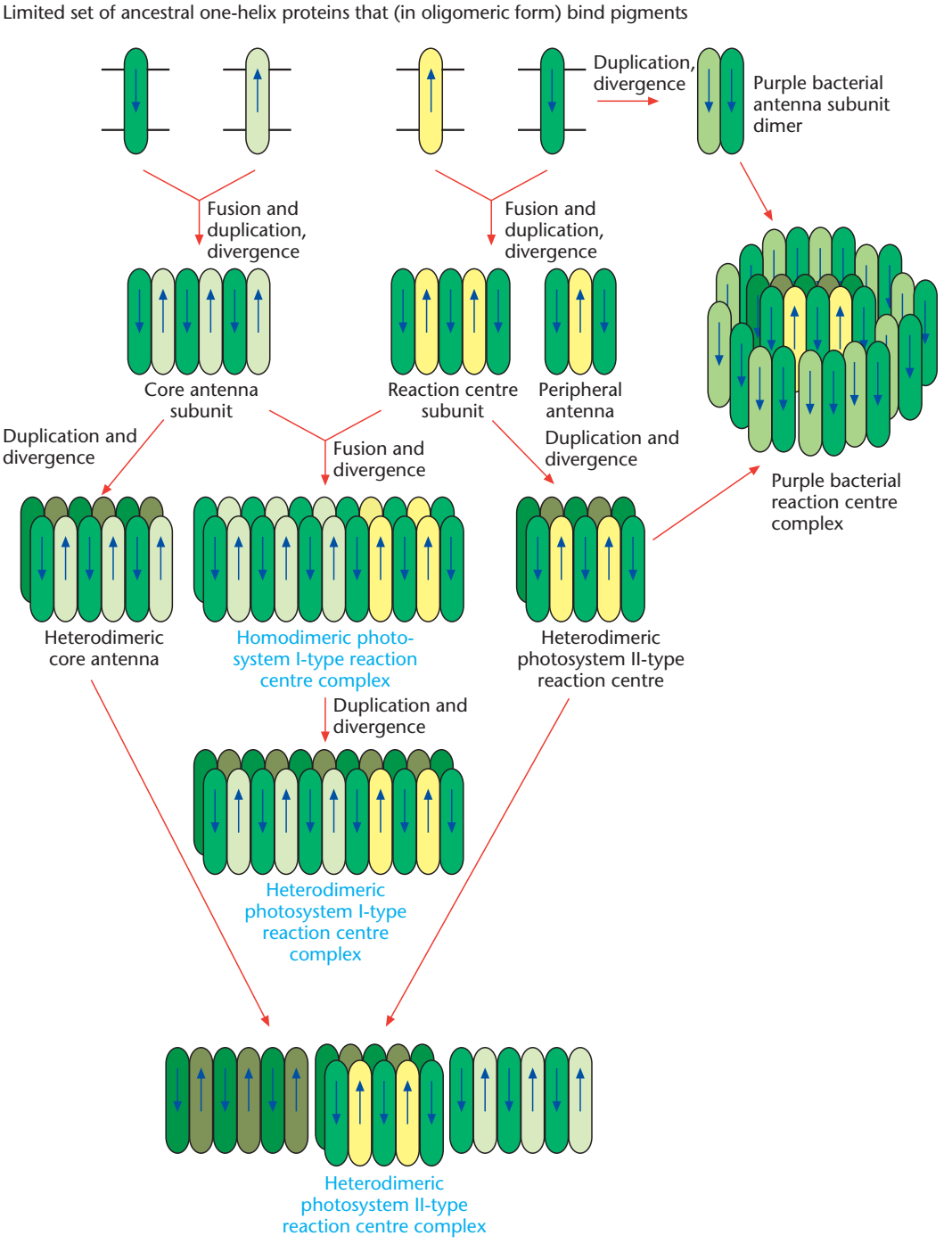

Figure 4 A possible evolutionary relationship between reaction centres and light-harvesting complexes. Initially, two small pigment-binding membrane proteins, each with a single membrane-spanning helix, may have given rise to a simple reaction centre by gene duplication, divergence and possibly fusion. Other but perhaps similar pigment-binding membrane proteins may have undergone duplication, divergence and fusion events, leading to multihelix core antenna proteins. Fusion of a core antenna and a reaction centre protein is expected to have led to homodimeric photosystem I-type reaction centres such as those of heliobacteria. The homodimeric reaction centres may have evolved to heterodimeric ones by another round of gene duplication and divergence. Core antenna proteins and five-helix reaction centre proteins may have duplicated to form heterodimeric photosystem II-type reaction centre complexes. Reaction centres from purple bacteria may have formed by combination of a heterodimeric photosystem II-type reaction centre with single-helix antenna proteins, possibly similar to one of the ancestral one-helix pigment-binding proteins.

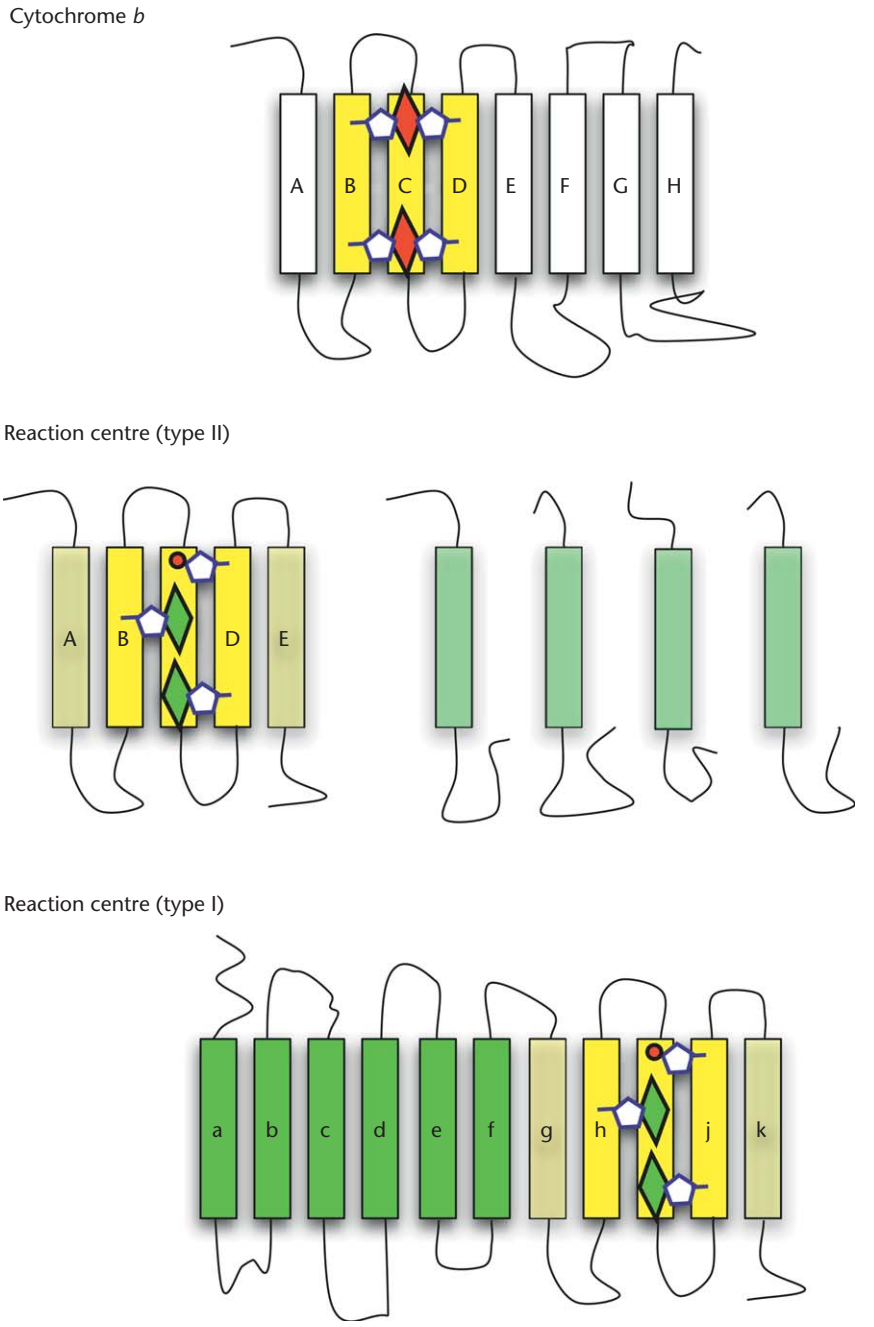

Figure 5 Relationship between type I and type II reaction centres based on numbers and origin of their component transmembrane helices. A type II reaction centre has its origin in cytochrome *b* (as in **Figure 3**), and the core of the reaction centre consists of five membrane-spanning helices A to E. Gene fusion leads to addition of six additional helices (a to f) from a light-harvesting antenna protein to form the larger reaction centre core of type I reaction centres, including photosystem I.

transmembrane helices that together bound chromophores that were capable of redox reactions and that could eventually reduce an electron acceptor at the other side of the membrane. Antenna complexes may thus have been a later addition, using similar protein and pigment building blocks as for the reaction centre but not allowing redox chemistry of pigments. **See also**: Light-harvesting Complex

The scheme in **Figure 5** suggests that the ancestral reaction centre subunit may have been of the five-helix (photosystem II-like) type. This may have functioned as a homodimer. The homodimeric photosystem I-type reaction centre may have evolved from this reaction centre by addition of six membrane-spanning helices per subunit, representing the antenna complex. The evolution of a

putative homodimeric photosystem II-like reaction centre subunit to current photosystem II and purple bacterial heterodimeric reaction centres may have followed either of two paths. As the two reaction centre subunits of purple bacteria are closer to each other than to the subunits of photosystem II, the homodimeric ancestors of purple bacterial reaction centres and photosystem II may have split and only then may the heterodimer have developed independently in the two systems. The alternative, which is equally likely, is that heterodimeric reaction centres evolved before photosystem II and the purple bacterial reaction centres separated. The heterodimeric reaction centre would have merely served to distinguish the two acceptor-side quinones from each other, and subsequent evolutionary changes optimised reaction centre function under the conditions needed. Purely comparing the levels of sequence identity in the two systems does not necessarily provide an accurate picture, as it is likely that, in heterodimers, mutations in one subunit favour comparable mutations in the other subunit. A similar coevolution of pairs of mutations has been established for 16S rRNA. In any case, at the moment, the early evolution of reaction centre complexes remains speculative. **See also**: Phylogeny Based on 16S rRNA/DNA

Electron Donors to Photosynthetic Reaction Centres

Another interesting question is what the ancient electron donors for photosynthesis may have been. If photosynthesis is operated solely in a circular fashion (from the cytochrome *bc* complex electrons return to the primary donor of the photosystem), no net electron donors are required. However, even though ATP can be generated in this process, no reducing equivalents that can be used for carbon dioxide fixation can be produced. To be capable of carbon dioxide fixation, external donors must be available. Assuming that the fossil record has been interpreted correctly and cyanobacteria are at least 3.5 billion years old, water has been used as an electron donor for photosystem II for a long time. To be able to use water as a source of electrons, a very high midpoint potential of the primary donor is required (>0.82 V) and a rather complex water-splitting system is used. Therefore, water may be a donor for only the more evolved photosynthetic apparatus. Instead, ferrous ion, sulfide or other easily oxidisable compounds may have been donors for the ancestral photosynthetic machinery. A reaction centre with a relatively low midpoint redox potential of the primary donor (such as the photosystem I-type reaction centre) may have evolved initially, as it could use light to convert rather weak reductants to stronger ones that could be used for carbon dioxide fixation. Therefore, a photosystem I-type reaction centre may have generated compounds suitable for carbon dioxide fixation. However, if water, a very poor reductant, is the source of electrons, the operation of two photosystems in series is needed to generate NADPH, the reductant for carbon dioxide fixation. In the evolution of water-oxidising systems, one may consider whether intermediate scenarios with other electron donors (such as hydrogen peroxide) may have occurred, presenting a transition from more reducing electron donors to water (Blankenship and Hartman, 1998). However, hydrogen peroxide is unlikely to have accumulated in the early atmosphere or even in cells, as catalase and peroxidases are likely to have been ancient inventions: these enzymes are necessary and ubiquitous as, in the presence of ferrous ions, hydrogen peroxide may form highly toxic hydroxyl radicals. Therefore, the hydrogen peroxide concentration may have been insufficient to provide a major source of electrons. Instead, a reaction centre with a highly oxidising primary donor may have evolved that was capable of oxidising water and that subsequently acquired the capacity to do so more efficiently. **See also**: Green Nonsulfur Bacteria; Green Sulfur Bacteria

Homodimeric versus Heterodimeric Reaction Centres

The scheme presented in **Figure 5** more or less sidesteps the issue of whether photosystem II-type or photosystem I-type reaction centres are more ancient: taken at face value, the scheme would place them at roughly the same place evolutionarily. The original reaction centre complex may have consisted of a homodimer of five-helix subunits, but simpler scenarios cannot be excluded. In principle, a couple of transmembrane helices would already be sufficient to be able to bind all cofactors needed. As no organisms with a photosynthetic reaction centre resembling such a simple arrangement are known, the issue of what the ancestral reaction centre may have looked like remains purely within the realm of speculation. **See also**: Protein Quaternary Structure: Subunit–Subunit Interactions

In principle, a homodimer is generally viewed to be an evolutionary precursor of a heterodimer. However, this does not necessarily imply that the current homodimeric reaction centres, as found in heliobacteria and *Chlorobium*, are any older in a geological sense than the heterodimeric ones from, for example, purple bacteria or other photosystem II-type reaction centres. The reason for this caution is that one needs to consider the functional advantages that a heterodimeric reaction centre may have in the two cases: the evolutionary pressure towards a heterodimer may have been different in the photosystem II-type versus the photosystem I-type reaction centres. A heterodimeric reaction centre presents the opportunity to have electrons flow along only one branch and to distinguish functionally between the two quinones at the acceptor side. This is important for photosystem II-type reaction centres as the first quinone (Q_A) is reduced to the semiquinone form and is then oxidised rapidly by the second quinone (Q_B), which serves as the 'two-electron gate'. At Q_B, two electrons are

gathered before reduced Q_B exchanges with the quinone pool in the membrane. Having a direct path of electron flow between Q_B and the primary donor would enhance recombination reactions and therefore reduce the efficiency of energy conversion. Therefore, an efficient photosystem II-type reaction centre seems almost to require a heterodimeric arrangement to obtain efficient photosynthetic reactions. This is less of an issue for photosystem I-type reaction centres, as electrons flow to F_X and beyond in a set of one-electron redox reactions without stable accumulation of single charges on a quinone that may recombine readily with the oxidised primary donor. Therefore, the advantage of a heterodimeric arrangement in photosystem I-type reaction centres is less apparent than in photosystem II-type reaction centres. A heterodimeric reaction centre arrangement may be a virtual requirement for an efficient photosystem II-type reaction centre, and from the possible existence of cyanobacteria and photosynthetic oxygen evolution activity several billion years ago, it is apparent that this arrangement may already have formed very early on in the evolution of life. With this in mind, one needs to consider what steps are needed to generate a heterodimeric, photosystem II-type reaction centre versus a homodimeric, photosystem I-type complex. A change in several amino acid residues in the environment of the primary donor has been shown to have profound effects on its midpoint potential, and redox-active amino acid residues can be introduced close to the primary donor as well (Kalman *et al.*, 1999). By analogy, the potential of the intermediate electron acceptor and of the quinone may be changed considerably by modifying the chemical nature of the cofactor or the cofactor's protein environment. Therefore, on an evolutionarily rather short time scale, it should be possible to change the redox midpoint potentials of the cofactors with a relatively small number of mutations. What may be a conceptually larger jump is to have the two quinones become functionally distinct, so that one serves as a one-electron acceptor (Q_A) and the other (Q_B) is a two-electron acceptor with a more positive midpoint potential. This would require a heterodimeric arrangement. What has been the driving force leading to this heterodimeric arrangement is as yet unknown. **See also**: Quinone Cofactors

Which Came First: Type I or Type II Reaction Centres?

It is also possible to envisage that the first photosynthetic reaction centre was a charge-separating adjunct to an established electron transport chain and thus capable of both linear and cyclic electron transfer. Separation into type I and type II photochemical reaction centres would then have arisen by selection favouring one or other mode of electron transport, according to environmental availability of an electron donor (**Figure 6**). **See also**: Photoautotrophy

A further proposal is that type I and type II reaction centre genes were retained in a single, anoxygenic lineage, but never expressed at the same time, their expression being subject to a redox regulatory control of transcription that eliminated crosstalk between two electron transport chains, each functioning under special environmental conditions (Allen, 2005). The type I reaction centre was induced by availability of hydrogen sulfide as an electron donor. When hydrogen sulfide became depleted, type I genes were repressed and type II genes were induced, providing for a type II reaction centre driving purely cyclic, proton-motive electron transport for ATP synthesis in photoheterotrophic growth. This hypothetical, two-light reaction, anoxygenic phototroph might be the organism that built stromatolites before the advent of oxygenic cyanobacteria. **See also**: Transcription Activation at Bacterial Promoters

The scheme in **Figure 6** also envisages the possibility of loss of the redox switch becoming selectively advantageous if, and only if, a catalyst of water oxidation (Allen and Martin, 2007) became adventitiously attached to the donor side of the type II reaction centre. The selective advantage of this arrangement was that electrons could flow, for the first time, all the way from water to ferredoxin and $NADP^+$. **See also**: Photophosphorylation

Chloroplasts and the Origin of Plants

In essence, little has happened to the light reactions of photosynthesis since the advent of oxygen evolution and the cooperation, in series, of photosystem I (Nelson and Ben-Shem, 2005) and photosystem II (Rutherford and Faller, 2003). However, the endosymbiosis that turned cyanobacteria eventually into chloroplasts (Martin *et al.*, 2002) had consequences for the eventual colonisation of the land, because multicellular organisms could tap into and manage water supply in otherwise inhospitable environments. Terrestrial life also depends on the ozone layer of the Earth's atmosphere. Ozone absorbs ionising ultraviolet light and itself is a product of the free oxygen produced in photosynthesis. **See also**: Plant Chloroplasts and Other Plastids

The cyanobacterial ancestory of chloroplasts is indicated by the retention, in chloroplasts, of small, specialised, and yet still quasi-autonomous genetic systems (Martin *et al.*, 1998). In eukaryotes, the genes for proteins of photosynthetic reaction centres are always located in chloroplast deoxyribonucleic acid (DNA) and never in the cell nucleus. Recent investigations (Puthiyaveetil *et al.*, 2008; Shimizu *et al.*, 2010) conclude that chloroplasts have retained not just the machinery of oxygenic photosynthesis but also prokaryotic elements of a conserved signal transduction pathway (Puthiyaveetil and Allen, 2009) that exerts regulatory control over transcription of the reaction centre genes contained in their DNA (Pfannschmidt *et al.*, 1999). Thus, evidence is accumulating for the hypothesis that the function of cytoplasmic genomes is to provide for a direct

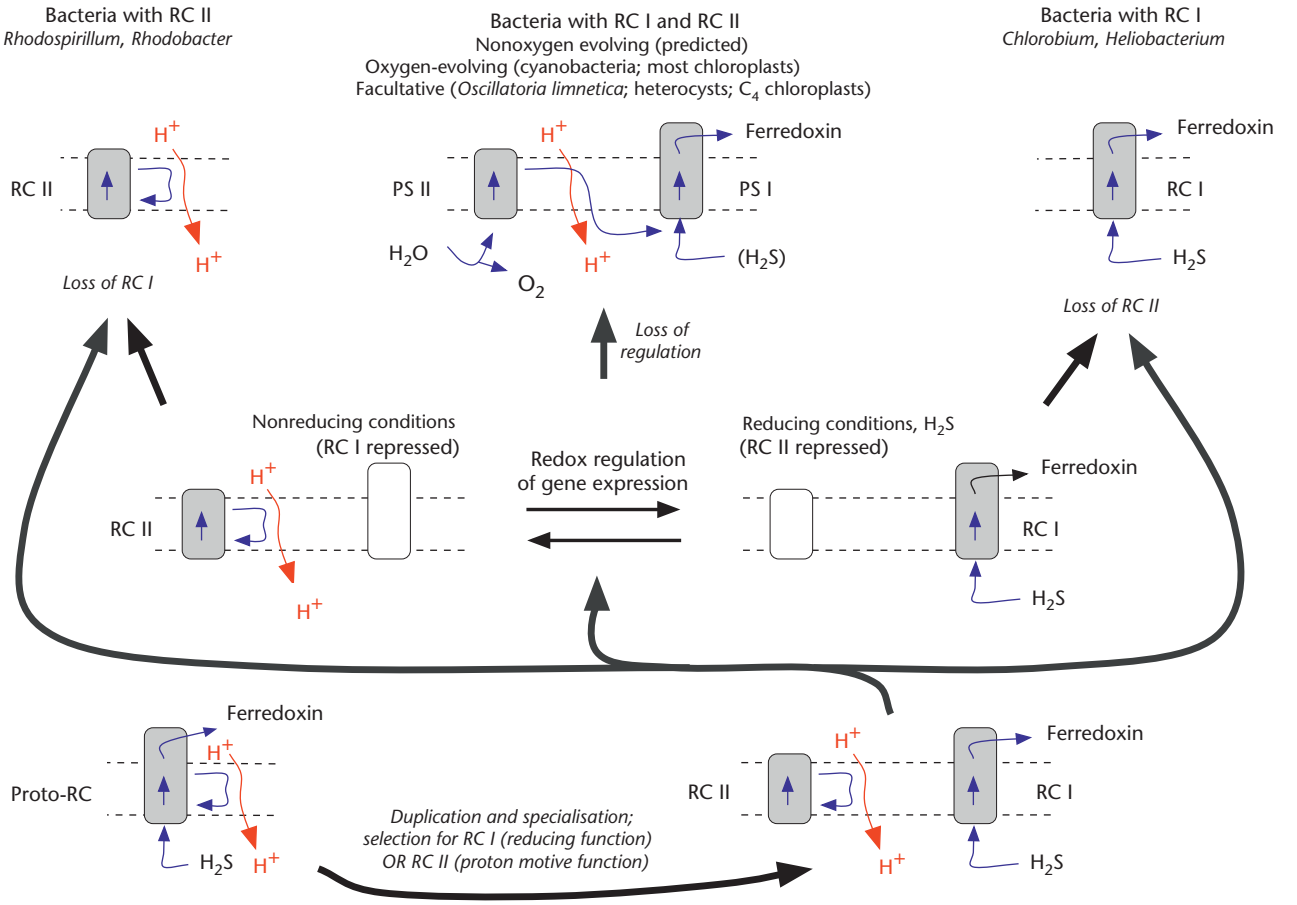

Figure 6 Retention of type I and type II centres, selected by a redox switch. Adapted from Allen (2005). Type I (RC I) and type II (RC II) reaction centres separate, allowing specialisation and eventual loss of the redundant reaction centre in photoautochemotrophic (type I-containing) lineages (e.g. *Chlorobium* and *Heliobacillus* spp.) and in photoheteroorganotrophic (type II-containing) lineages (e.g. *Rhodobacter*, *Rhodospirillum* spp.). However, a versatile, facultatively chemoautotrophic photosynthetic bacterium retains genes for both type I and type II reaction centres. In this hypothetical ancestor of cyanobacteria and chloroplasts, expression of type I centre genes in the presence of hydrogen sulfide is accompanied by silent type II genes. Type II genes are themselves induced under nonreducing conditions, when type I genes become repressed. Eventually, loss of regulatory control allows coexistence of type I and type II reaction centres, with complementary functions. In place of hydrogen sulfide, the type II centre, as photosystem II (PS II), oxidises water, liberating oxygen, and donating electrons to the type I centre, as photosystem I (PS I).

regulatory link between reaction centre gene transcription and the relative rates of electron transfer between photosystem I and photosystem II (Allen, 2003). **See also**: Chloroplast Genome

The ability to balance expression of genes for different classes of reaction centre may have been as decisive in the evolution of plants and eukaryotic algae as it was in origin of oxygenic photosynthesis in cyanobacteria (Allen, 2005). It is tempting to speculate that the same mode of action – redox regulation of gene expression (Bauer *et al*., 2003; Eraso and Kaplan, 2002) – is also achieved by evolutionarily conserved components.

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