ORIGIN AND EVOLUTION OF PHOTOSYNTHETIC REACTION CENTERS

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Abstract. The prototype reaction center may have used protoporphyrin-IX associated with small peptides to transfer electrons or protons across the primitive cell membrane. The precursor of all contemporary reaction centers contained chlorophyll *a* molecules as both primary electron donor and initial electron acceptor and an Fe-S center as secondary acceptor (RC-1 type). The biosynthetic pathway for chlorophyll *a* evolved along with the evolution of a better organized reaction center associated with cytochromes and quinones in a primitive cyclic electron transport system. This reaction center probably functioned initially in photoassimilation, but was easily adapted to CO_2 fixation using H_2 and H_2S as reductants. During this phase bacteriochlorophyll *g* may have evolved from chlorophyll *a* in response to competition for light, and thereby initiated the gram-positive line of eubacteria. A second reaction center (RC-2) evolved from RC-1 between 3.5 and 2.5 Ga ago in response to the competition for reductants for CO_2 fixation. The new organism containing RC-2 in series with RC-1 would have been able to use poor reducing agents such as the abundant aqueous ferrous ion in place of H_2 and H_2S. This new organism is proposed to be the common ancestor of all phototrophic eubacteria except those related to the gram-positive bacteria. All organisms containing bacteriochlorophyll *a* lost either RC-1 or RC-2, while those organisms containing chlorophyll *a* (ancestors of cyanobacteria) added a water-splitting enzyme to RC-2 between 3.0 and 2.5 Ga ago in order to use H_2O in place of hydrated ferrous ion as electron donor for autotrophic photosynthesis.

1. Introduction

The characteristics of contemporary chlorophyll (Chl)-based reaction centers (RCs) have been reviewed recently, and the RCs have been classified (see Figure 1) in terms of five group types: Photosystem (PS)-1, PS-2, purple and filamentous bacteria, green sulfur bacteria and the gram-positive line (Olson and Pierson, 1987).

PS-1 RCs (Setif and Mathis, 1986) contain Chl *a* which functions as primary electron donor (P700) and possibly as initial electron acceptor (Fujita *et al.*, 1978; Shuvalov *et al.*, 1979a, b, c). The secondary acceptors are Fe-S centers (Ke, 1978; Malken, 1977; Shuvalov *et al.*, 1979a; Heathcote *et al.*, 1978a, b; Sauer *et al.*, 1978). PS-1 RCs are found in cyanobacteria and chloroplasts and operate in series with PS-2 RCs to deliver electrons from H_2O to $NAD^+/NADP^+$ for CO_2 fixation. PS-2 RCs (Diner, 1986) also contain Chl *a*, which serves as primary electron donor (P680), but pheophytin (Pheo) *a* probably serves as initial electron acceptor (Fujita *et al.*, 1978; Klevanik *et al.*, 1977; Klimov *et al.*, 1977). Plastoquinone (PQ) serves as the secondary electron acceptor.

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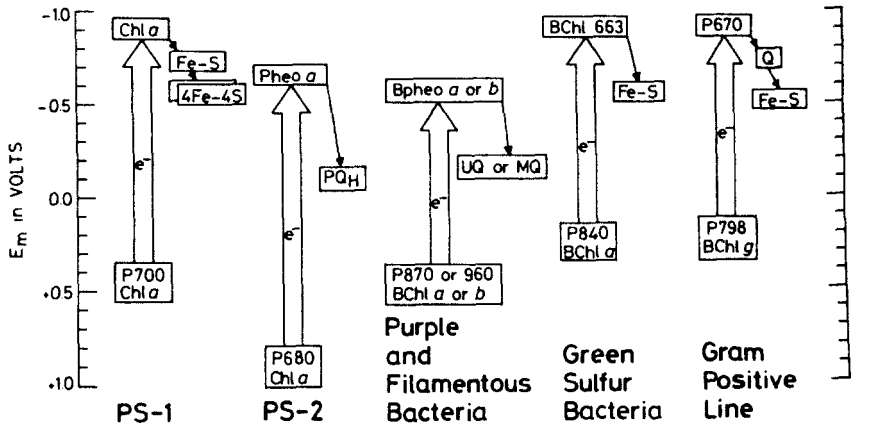

Fig. 1. Photosynthetic reaction centers in contemporary organisms. Secondary electron acceptors (PQ, UQ and MQ) are placed according to their effective midpoint potentials (without proton exchange). From Olson and Pierson (1987).

Most purple bacteria and all green filamentous bacteria contain RCs with bacteriochlorophyll (BChl) *a* (Olson and Thornber, 1979; Pierson *et al.*, 1983; Pierson and Thornber, 1983; Bruce *et al.*, 1982; den Blanken *et al.*, 1983), whereas some purple bacterial RCs contain BChl *b* (Olson and Thornber, 1979). This type of RC is strikingly similar to the PS-2 type RC in having bacteriopheophytin (BPheo) *a* or *b* as initial acceptor (Olson, 1981; Kirmaier *et al.*, 1983; Parot *et al.*, 1985) and ubiquinone (UQ) or menaquinone (MQ) as secondary acceptor (Olson and Thornber, 1979; Olson, 1981; Blankenship *et al.*, 1983; Vasmel and Amesz,. 1983; Hale *et al.*, 1983). The L- and M-polypeptides associated with RCs from purple bacteria show 22–25% homology with the D-1 polypeptide of PS-2 RCs from spinach chloroplasts (Williams *et al.*, 1984). This homology clearly indicates a single common ancestral polypeptide for L, M, and D-1.

Green sulfur bacteria contain an RC related to PS-1 of cyanobacteria and chloroplasts. The primary electron donor (P840) is BChl *a*, and the secondary electron acceptor is an Fe-S center (Olson and Thornber, 1979; Olson, 1981). The initial acceptor is unique to the green sulfur bacteria: a special lipophilic form of BChl *c* (Brauman *et al.*, 1986; Shuvalov *et al.*, 1986). The gram-positive line (presently represented by a single species *Heliobacterium chlorum* (Woese *et al.*, 1985)) contains the newly discovered BChl *g* (Brockman and Lipinski, 1983), which serves as primary donor (P798) in the RC (Fuller *et al.*, 1985; Prince *et al.*, 1985). The initial acceptor (P670) in this RC (Nuijs *et al.*, 1985) has not been identified chemically as yet, but one of the secondary acceptors is clearly an Fe-S center as in the RCs of green bacteria and PS-1. There is also some evidence for a quinone-like secondary acceptor Q in the RC of *H. chlorum* (Brok *et al.*, 1986).

The relationship between the RC chlorophylls (Chl *a*, BChl *g*, BChl *a*, and BChl *b*) is shown in Figure 2. It is important to recognize that BChl-ide *g* is an isomer of

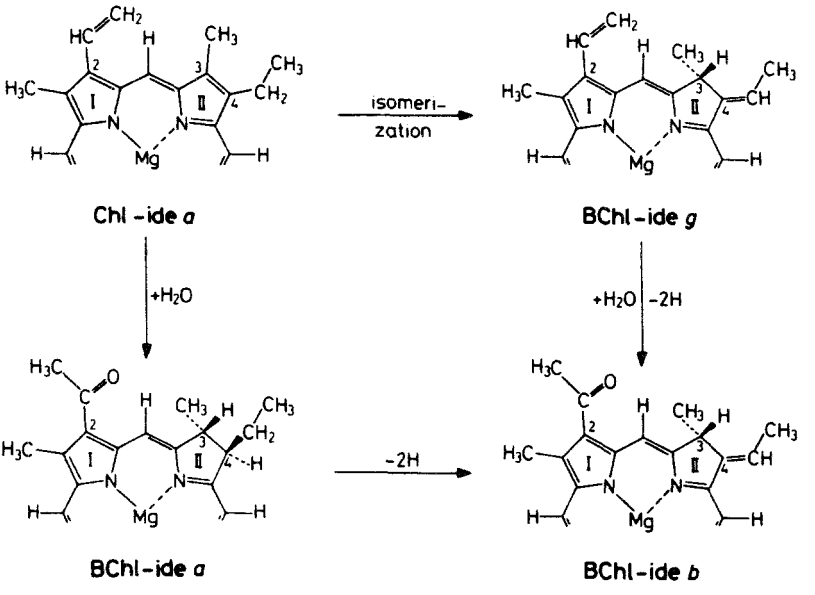

Fig. 2. Comparison of reaction center chlorophyllides: Chl-ide *a*, BChl-ide *g*, BChl-ide *a* and BChl-ide *b*. From Pierson and Olson (1987).

Chl-ide *a*, because the chlorophyll nomenclature obscures this fact. The conversion of Chl-ide *a* to BChl-ide *a* requires at least three enzymic steps in the biosyntehtic pathway worked out in purple bacteria (Olson, 1978, 1981), so we might suppose that BChl *g* is more closely related to Chl *a* than is BChl *a* (or BChl *b*).

The five RC types can be divided into two groups: RC-1 containing Fe-S centers as secondary acceptors and RC-2 containing quinones as secondary acceptors. We suppose that RC-1 is more ancient than RC-2, because RC-2 is associated with oxygen evolution in cyanobacteria and chloroplasts. We believe that oxygen evolution appeared between 3.0 and 2.5 Ga ago, *after* the appearance of CO_2 fixing photosynthesis at least 3.5 Ga ago (Olson and Pierson, 1986). From this point of view the earliest evolution of photosynthetic reaction centers is synonymous with the early evolution of RC-1.

2. Early Evolution of the Reaction Center

Our treatment of this subject (see also Olson and Pierson, 1987) follows closely that of Mercer-Smith and Mauzerall (1984).

As shown in Figure 3 the first RC may have consisted of a porphyrin* (Mauzerall,

* It has been suggested that metalloporphyrins would have been more prevalent than free porphyrins in the environment of the first organism containing photochemical RCs (Fifth ISSOL Meeting and the Eighth International Conference on The Origin of Life, Berkeley, California, U.S.A., 21–25 July, 1986). The line of reasoning presented in this paper assumed that the initial photoactive pigment was a free porphyrin, but a reasonable hypothesis could also be developed with a metalloporphyrin as the initial photoactive pigment.

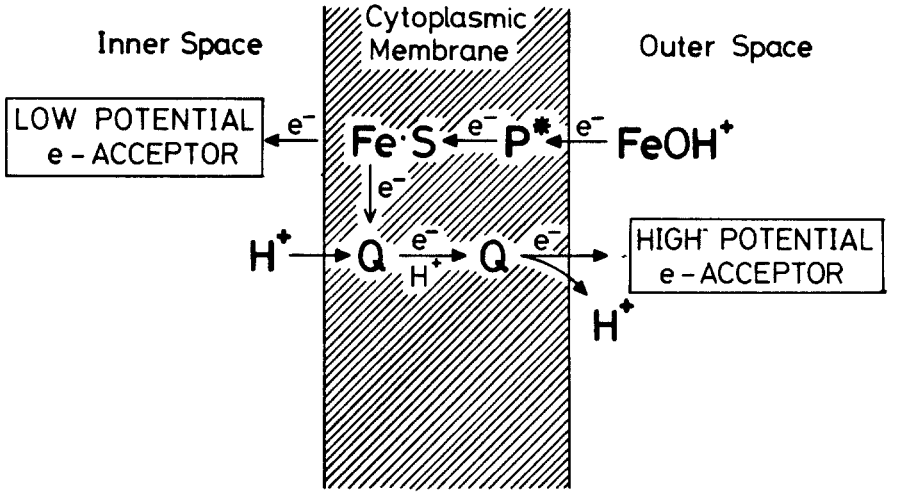

Fig. 3. Primitive reaction center. P* denotes a porphyrin in the excited state, and Q represents a quinone molecule. $FeOH^+$ is a hydrated ferrous ion.

1973; 1977) and an Fe-S center. It may have done little more than transfer an electron from an external donor to an internal acceptor. The first major addition might have been the elaboration of a quinone electron transfer chain for moving electrons *and protons* to the outer space where an external e-acceptor could be reduced in place of the internal e-acceptor. The net result would have been the translocation of one proton across the cytoplasmic membrane from inside to outside. Subsequent evolutionary development may have led to the 'improved' RC shown in Figure 4. The porphyrin in the original RC was presumably replaced by two Chl molecules and one cytochrome (Cyt) *c* molecule. The Cyt *c* molecule might have replaced the external e-acceptor and led to the first completely cyclic electron transfer chain associated with a photochemical RC. As the direct e-donor to Chl, Cyt *c* also might have served as an intermediate in electron transfer from external donors to internal acceptors.

The first RC probably had a very long turnover time (ca. 1 s) compared to the turnover time (ca. 10 ms) for the 'improved' RC (Clayton, 1980). This difference can be understood in terms of the different cross sections for light absorption of the two RCs. The first RC had no accessory light-harvesting pigments, whereas the 'improved' RC probably received excitation energy from a large number of pigment molecules outside the RC. The reduction of excited porphyrin by $FeOH^+$ in the first RC would have been a fast reaction, but the replacement of $FeOH^{2+}$ by $FeOH^+$ could have been a relatively slow process, yet sufficiently fast to keep up with the long turnover time. The reduction of Cyt *c* by $FeOH^+$ in the 'improved' RC may not have been able to keep up with the faster turnover time, and other stronger reductants might have been required to deliver electrons to Cyt *c* fast enough to keep up with the turnover of the RC. This means that $FeOH^+$ might not have been an effective reductant for CO_2 fixation in organisms utilizing a single RC-1 type reaction center such as the 'improved' RC shown in Figure 4.

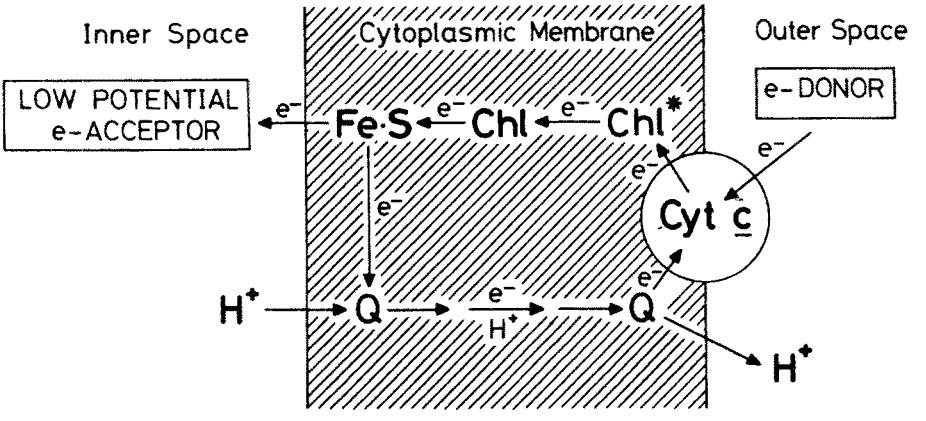

Fig. 4. Improved reaction center. Chl* denotes an excited chlorophyll, and Cyt *c* represents cytochrome *c*. See text for details.

According to the Granick (1965, 1967) hypothesis the history of 'photosynthetic' RCs in eubacteria is recapitulated in the biosynthetic pathway of Chl *a* and BChl *a*. This means, for example, that Chl *a* might have functioned before BChl *a* even existed. Likewise protochlorophyll *a* might have functioned before Chl *a*, and protoporphyrin-IX and Mg protoporphyrin-IX might have functioned in primitive RCs before protochlorophyll *a* existed.

The first macrocycle in the biosynthetic pathway leading to protoporphyrin-IX is uroporphyrinogen-III followed by coproporphyrinogen-III and protoporphyrinogen-IX. These porphyrinogens are colorless and could not have functioned in biological RCs. Protoporphyrin-IX, on the other hand, has a strong absorption band at 408 nm. When similar porphyrins (uroporphyrin, coproporphyrin, mesoporphyrin, and hematoporphyrin) are illuminated with white or blue (410-nm) light in the presence of ethylenediamine tetraacetic acid (EDTA), H_2 and oxidized EDTA are produced in the presence of a platinum catalyst (Mercer-Smith and Mauzerall, 1984). The photochemistry is summarized in the following equations where P = pigment and D = secondary electron donor (EDTA):

$$P \xrightarrow{\text{light}} P^*. \tag{1}$$

$$P^* + D \longrightarrow P^- + D^+. \tag{2}$$

$$2P^- + 2H^+ \xrightarrow{\text{catalyst}} 2P + H_2. \tag{3}$$

In contrast the photochemistry of a contemporary photosynthetic RC can be summarized as follows:

$$P \xrightarrow{\text{light}} P^*. \tag{1}$$

$$P^* + I \longrightarrow P^+ + I^-. \quad (2)$$

$$I^- + X \longrightarrow I + X^-. \quad (3)$$

$$D + P^+ \longrightarrow D^+ + P. \quad (4)$$

Thus in porphyrin photochemistry the primary change separation leaves the originally excited porphyrin (*P*) in the reduced state, whereas in contemporary RCs the primary charge separation leaves the originally excited chlorophyll (*P*) in the oxidized state (Mauzerall, 1977). We may suppose therefore that in ancient RCs containing porphyrins but no chlorophyll, the primary photochemical electron transfer required a donor molecule such as $FeOH^+$ to react with the excited acceptor molecule (porphyrin). The reduced porphyrin molecule might then have donated one electron to a low potential Fe-S center which then might have reacted with a low potential acceptor such as ferredoxin as shown in Figure. 3.

An RC based on protoporphyrin-IX would have been subject to at least one important limitation: Energy transfer between pigment molecules would have been relatively poor because of the weak absorption band at 633 nm as shown in Table I. Therefore one might expect a phototrophic organism using protoporphyrin to

TABLE I

Absorption characteristics of chlorophylls found in reaction centers and their precursor pigments. Absorptivity (ϵ) values are listed beneath the appropriate wavelengths (λ) for 5 pigments. Absorptivity ratios (ϵ/ϵ_{max}) are given in italics for two pigments.

Pigment	λ (nm), ϵ(mM^{-1} cm^{-1}) or ϵ/ϵ_{max} (%)						Reference
Protoporphyrin-IX	404	503	536	576	605	633	Smith (1975)
dimethyl ester (ether)	158	15	12	7	2	7	
Mg Protoporphyrin	419	510	553	591			Jones (1963)
monomethyl ester (ether)	*100*	*1*	*6*	*6*			
Protochlorophyll *a*	432	438	533	570	602	622	Houssier and
(ether)	182	137	4	8	5	22	Sauer (1970)
Chlorophyll *a*	410	430	530	578	615	662	Houssier and
(ether)	85	118	3	8	13	90	Sauer (1970); Sauer *et al.* (1966)
Bacteriochlorophyll *g*	408	418	470	575		763	Brockmann and
(dioxane)	*100*	*95*	*27*	*21*		*51*	Lipinski (1983)
Bacteriochlorophyll *a*	357	392		573		770	Sauer *et al.*
(ether)	73	47		22		96	(1966)
Bacteriochlorophyll *b*	368	408		578		794	Steiner (1984)
(ether)	86	77		26		106	

contain a large number of RCs with no accessory light-harvesting molecules. The introduction of Mg into the protoporphyrin molecule would not have substantially changed the situation with respect to energy transfer, but presumably would have changed the character of the primary charge separation to the 'chlorophyll' type (Mauzerall, 1977). In addition we may suppose that Fe was also introduced into protoporphyrin either before or after Mg, so that heme could serve as a secondary electron donor to the RC.

With the introduction of ring V in protochlorophyll *a*, the red absorption band (622 nm) was doubled or tripled in oscillator strength (see Table I), and according to Förster theory the rate of energy transfer was also doubled or tripled compared to the cases of protoporphyrin-IX or Mg protoporphyrin-IX.

In Chl *a* the red absorption band (662 nm) is about quadrupled in strength (see Table I), and the rate of energy transfer is also quadrupled in comparison to the situation in protochlorophyll *a*. Furthermore Chl *a* can effectively use both red and blue light for photochemistry.

Bacteriochlorophylls *g*, *a*, and *b* are specialized for absorbing light in the far-red as shown in Table I. Reaction centers containing these chlorophylls are, however, limited in the amount of excitation energy that they can convert to useful chemical free energy (Olson, 1970; 1978).

All pigments in contemporary prokaryotes are associated with proteins in pigment-protein complexes. The proteins affect the absorption characteristics of the pigments, orient them within the membrane, and help determine their function. Orientation within the membrane would have been important even in very early RCs in order to acheive an asymmetric charge distribution across the membrane.

Simple associations of porphyrins with peptides can be achieved abiologically (Kolesnikov *et al.*, 1981), and one need not assume that the early RC proteins were very complex. Increasing complexity could have increased the efficiency of the system, and eventually a well-developed RC protein would have evolved. In Figure 4 we indicate that the earliest RC pigment-protein complex containing Chl was an RC-1 type, which later gave rise to RC-2.

3. Origin of Photosystem-2 and Oxygen Evolution

The geological evidence for substantial amounts of oxygen in the atmosphere 1.7 Ga ago is quite convincing, and there is general agreement that the major influx of oxygen came from photosynthesis. The fossil record approx. 2.0 Ga ago is consistent with the existence of oxygen-evolving cyanobacteria at that time (Schopf, 1974; Hofmann and Schopf, 1983). We believe that oxygen-evolving photosynthesis began to function sometime between 3 and 2.5 Ga ago after a series of mutations which led first to the evolution of the PS-2 reaction center, and then to the evolution of the water-splitting enzyme.

The evolutionary pressure for a second RC in series with the PS-1 reaction center was the general depletion of sources of reducing power for autotrophic

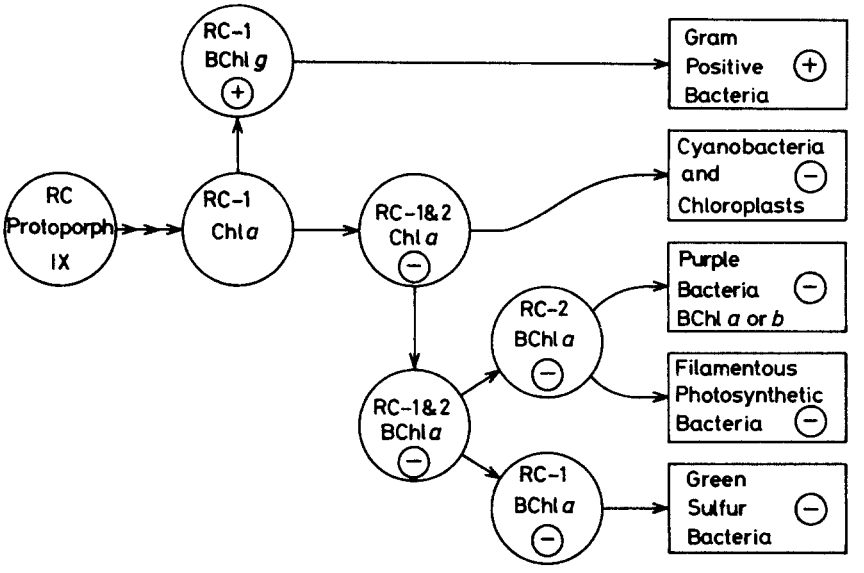

Fig. 5. Early evolution of reaction centers: Hypothetical relationships which might explain extant eubacterial 'phyla' containing photosynthetic members. Gram-positive (+) and gram-negative (−) organisms are indicated. See text for details.

photosynthesis. Sometime after 3.5 Ga ago the local environments with H_2 or reduced sulfur compounds became fewer and fewer, and some photosynthetic autotrophs began to adapt to weaker and weaker reductants in the environment. At a certain point a second reaction center (RC-2) evolved from RC-1 in order to extract electrons from the new reductants (Olson, 1981; Olson and Pierson, 1987). The conversion from RC-1 to RC-2 could have been achieved by elimination of the Fe-5 center and direct electron transfer from the initial e-acceptor to a quinone.

The nature of the new reductants is not really known, but the most widespread source of reducing power at that time was ferrous ion, and the redox potential for $Fe(OH)^+/Fe(OH)^{2+}$ (pH 7) is about +0.34 V (P. S. Braterman, personal communication). Cohen (1984) has demonstrated that Fe^{2+} can be used by some cyanobacteria to support photosynthesis. Although originally thought to donate electrons to RC-1 (Cohen, 1984), it now appears that Fe^{2+} also donates to RC-2 (Y. Cohen, personal communication). If Fe^{2+} was ever used as a reductant for CO_2 fixation, it might well have required two photosystems in series, but no water-splitting enzyme.

Once there were two kinds of Chl *a* containg RCs linked in series in the same organism, the evolutionary advantage would have been tremendous. For then, and only then, would it have been possible to extract electrons from water and to deliver then to CO_2 as in the cyanobacteria (Olson, 1970, 1978). However, in certain specialized environments with H_2S and/or dissolved organic compounds there would have been no advantage in having two different RCs, especially if there had

been a switch from Chl *a* to BChl *a* for light-harvesting purposes driven by competition for light in dense mat communities. Under these conditions two different RCs would have been redundant for cyclic electron flow, although RC-1 would probably have been favored for the direct reduction of ferredoxin. As shown in Figure 5 the green sulfur bacteria are thought to be the descendents of those early BChl *a*-containing organisms which evolved under autotrophic conditions with a good supply of H_2S. In these bacteria RC-1 was retained, while RC-2 was lost. The purple bacteria and filamentous photosynthetic bacteria are thought to be descended from those early BChl *a*-containing organisms which evolved under heterotrophic conditions with a good supply of soluble organic compounds. In this line of evolution RC-2 was retained, while RC-1 was lost. The cyanobacteria are thought to have evolved from those early Chl *a*-containing orgnisms with both RC-1 and RC-2 Both RCs have been retained for the most efficient conversion of solar energy to chemical free energy yet devised by biological evolution.

Figure 5 presents a highly speculative phylogeny for the five extant eubacterial 'phyla' containing photosynthetic members. This phylogeny is based mainly on the type of primary electron donor (chlorophyll), initial electron acceptor, and secondary electron acceptor in each RC. Our scheme 'explains' a lot of comparative biochemistry and ecology, but at the present time it can neither be proven nor disproven by the comparison of 16S RNA catalogs (Olson and Pierson, 1987). Nonetheless our scheme can help people organize their thinking about the possible evolution of reaction centers in photosynthetic prokaryotes. With this in mind we summarize our point of view as follows:

4. Summary

Phase 1: The prototype RC may have used a porphyrin molecule and an Fe-S center associated with small peptides to create a charge separation across the primitive cell membrane.

Phase 2: The precursor of all contemporary RCs contained Chl *a* and an Fe-S center (RC-1 type). During the transition from Phase 1 to Phase 2 the biosynthetic pathway for Chl *a* evolved along with the evolution of a cyclic electron transport pathway containing quinone and cytochrome. This RC could function either in photoassimilation or CO_2 fixation using H_2 or H_2S as reductants.

Phase 3: BChl *g* may have evolved from Chl *a* in response to competition for light, and thereby started the gram-positive line of eubacteria.

Phase 4: RC-2 evolved from RC-1 between 3.5 and 2.5 Ga ago in response to the competition for reductants for CO_2 fixation. The new organism containing RC-2 in series with RC-1 may have used the abundant $Fe(OH)^+$ in place of H_2 and H_2S. However it did *not* evolve oxygen. The new organism is proposed to be the common

ancestor of all gram-negative phototrophic eubacteria except those containing BChl *g*.

Phase 5: The continued competition for light in mat communities stimulated the evolution of BChl *a* from Chl *a*. The first BChl *a*-containing organisms contained both RC-1 and RC-2, but no longer linked in series. Again these organisms did *not* evolve oxygen. One line of evolution dropped RC-1 and led to the purple bacteria and the filamentous bacteria. The other line dropped RC-2 and led to the green sulfur bacteria.

Phase 6: Those organisms containing Chl *a*, RC-1 and RC-2 added a water-splitting enzyme to RC-2 between 3.0 and 2.5 Ga ago in order to use H_2O in place of $Fe(OH)^+$ as electron donor for autotrophic photosynthesis. This completed the foundation for contemporary oxygen-evolving photosynthesis by cyanobacteria and chloroplasts.

Note added in proof: While we have suggested certain times for the occurrence of the major events in the evolution of reaction centers, we want to emphasize that it is the relative sequence of events that we are describing and not the actual time when they occurred. It is impossible to know when the first water-splitting reaction center actually evolved. Since there is general agreement that oxygen was increasing in the atmosphere around 2.0 Ga ago, then water-splitting must have evolved prior to this time. It may very well have evolved much before this, however, perhaps as much as 3.0 Ga ago. We have no way of knowing how long such a reaction center functioned before the organisms possessing it became widely distributed and the oxygen produced by it actually accumulated. It certainly seems likely that the evolution of RC-2 from RC-1 initially without water-splitting occurred prior to 3.0 Ga ago.

References

Brauman, T., Vasmel, H., Grimme, L. H., and Amesz,J.: 1986, *Biochim. Biophys. Acta* **848**, 83.
Blankenship, R. E., Feick, R., Bruce, B. D., Kirmaier, C., Holten, D., and Fuller, R. C.: 1983, *J. Cell Biochem.* **22**, 251.
Brockmann, H., Jr. and Lipinski, A.: 1983, *Arch. Microbiol.* **136**, 17.
Brok, M., Vasmel, H., Horikx, J. T. G., and Hoff, A. J.: 1986, *FEBS Lett.* **194**, 322.
Bruce, B. D., Fuller, R. C., and Blankenship, R. E.: 1982, *Proc. Natl. Acad. Sci. U.S.A.* **79**, 6532.
Clayton, R. K.: 1980, *Photosynthesis: Physical Mechanisms and Chemical Patterns*, Cambridge University Press, Cambridge, p. 28.
Cohen, Y.: 1984, in M. J. Klug and C. A. Reddy (eds.), *Current Perspectives in Microbial Ecology* Amer. Soc. for Microbiol., Washington, D.C., p. 435.
den Blanken, H. J., Vasmel, H., Jongenelis, A. P. J. M., Hoff, A., and Amesz, J.: 1983, *FEBS Lett.* **161**, 185.
Diner, B. A.: in L. A. Staehlein and C. J. Arntzen (eds.), *Encyclopedia of Plant Physiology New Series*, Vol. 19, Springer-Verlag, Berlin, p. 422.
Fujita, I., Davis, M. S., and Fajer, J.: 1978, *J. Am. Chem. Soc.* **100**, 6280.
Fuller, R. C., Sprague, S. G., Gest, H., and Blankenship, R. E.: 1985, *FEBS Lett.* **182**, 345.

Granick, S.: 1965, in V. Bryson and H. L. Vogel (eds.), *Evolving Genes and Proteins*, Academic Press, New York, p. 67.
Granick, S.: 1967, in T. W. Goodwin (ed.), *Biochemistry of Chloroplasts*, Vol. II, Academic Press, New York, p. 373.
Hale, M. B., Blankenship, R. E., and Fuller, R. C.: 1983, *Biochim Biophys. Acta* **723**, 376.
Heathcote, P., Williams-Smith, D. L., and Evans, M. C. W.: 1978a, *Biochem. J.* **170**, 373.
Heathcote, P., Williams-Smith, D. L., Sihra, C. K., and Evans, M. C. W.: 1978b, *Biochim. Biophys. Acta* **503**, 333.
Hofmann, H. J. and Schopf, J. W.: 1983, in J. W. Schopf (ed.), *Earth's Earliest Biosphere*, Princeton Univ. Press, Princeton, New Jersey, p. 321.
Houssier, C. and Sauer, K.: 1970, *J. Am. Chem. Soc.* **92**, 779.
Jones, O. T. G.: 1963, *Biochem. J.* **86**, 429.
Ke, B.: 1978, in D. R. Sanadi and L. P. Vernon (eds.), *Current Topics in Bioenergetics*, Vol. 7, Academic Press, New York, p. 75.
Kirmaier, C., Holten, D., Feick, R., and Blankenship, R. E.: 1983, *FEBS Lett.* **158**, 73.
Klevanik, A. V., Klimov, V. V., Shuvalov, V. A., and Krasnovskii, A. A.: 1977, *Dokl. Akad. Nauk USSR* **236**, 241.
Klimov, V. V., Klevanik, A. V., Shuvalov, V. A., and Krasnovskii, A. A.: 1977, *FEBS Lett.* **82**, 183.
Kolesnikov, M. P., Voronova, N. I., and Egorov, I. A.: 1981, *Origins of Life* **11**, 223.
Malkin, R.: 1978, *FEBS Lett.* **87**, 329.
Mauzerall, D.: 1973, *Ann. New York Acad. Sci.* **206**, 483.
Mauzerall, D.: 1977, in A. Trebst and M. Avron (eds.), *Encyclopedia of Plant Physiology New Series*, Vol. 5, Springer-Verlag, Berlin, p. 117.
Mercer-Smith, J. A. and Mauzerall, D. C.: 1984, *Photochem. Photobiol.* **39**, 397.
Nuijs, A. M., van Dorssen, R. J., Duysens, L. N. M., and Amesz, J.: 1985, *Proc. Natl. Acad. Sci. U.S.A.* **82**, 6865.
Olson, J. M.: 1970, *Science* **168**, 438.
Olson, J. M.: 1978, *Evolutionary Biology* **11**, 1.
Olson, J. M.: 1981, *BioSystems* **14**, 89.
Olson, J. M. and Pierson, B. K.: 1986, *Photosyn. Res.* **9**, 251.
Olson, J. M. and Pierson, B. K.: 1987, *Int. Rev. Cytol.* **108** 209.
Olson, J. M. and Thornber, J. P.: 1979, in R. A. Capaldi (ed.), *Membrane Proteins in Energy Transduction* Marcel Dekker, New York, p. 279.
Parot, P., Delmas, N., Garcia, D., and Vermeglio, A.: 1985, *Biochim. Biophys. Acta* **809**, 137.
Pierson, B. K. and Olson, J. M.: 1987, in J. Amesz (ed.), *New Comprehensive Biochemistry – Photosynthesis*, Elsevier, Amsterdam, p. 21.
Pierson, B. K. and Thornber, J. P.: 1983, *Proc. Natl. Acad. Sci. U.S.A.* **80**, 80.
Pierson, B. K., Thornber, J. P., and Seftor, R. E. B.: 1983, *Biochim. Biophys. Acta* **723**, 322.
Prince, R. C., Gest, H., and Blankenship, R. E.: 1986, *Biochim. Biophys. Acta* **810**, 377.
Sauer, K., Mathis, P., Acker, S., and van Best, J. A.: 1978, *Biochim. Biophys. Acta* **503**, 120.
Sauer, K., Smith, J. R. L., and Schultz, A. J.: 1966, *J. Am. Chem. Soc.* **88**, 2681.
Schopf, J. W.: 1974, *Evolutionary Biology* **7**, 1.
Schopf, J. W.: 1983, in J. W. Schopf (ed), *Earth's Earliest Biosphere*, Princeton Univ. Press, Princeton, New Jersey, p. 3.
Setif, P. and Mathis, P.: 1986, in L. A. Staehelin and C. J. Arntzen (eds.), *Encyclopedia of Plant Physiology New Series*, Vol. 19, Springer-Verlag, Berlin, p. 476.
Shuvalov, V. A., Amesz, J., and Duysens, L. N. M.: 1986, *Biochim. Biophys. Acta* **851**, 1.
Shuvalov, V. A., Dolan, E., and Ke, B.: 1979a, *Proc. Natl. Acad. Sci. U.S.A.* **76**, 770.
Shuvalov, V. A., Ke, B., and Dolan, E.: 1979b, *FEBS Lett.* **100**, 5.
Shuvalov, V. A., Klevanik, A. V., Sharkov, A. V., Kryukov, P. G., and Ke, B.: 1979c, *FEBS Lett.* **107**, 313.
Smith, K. M.: 1975, in K. M. Smith (ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, p. 871.
Steiner, R.: 1984, Ph.D. Thesis, University of Munich.
Vasmel, H. and Amesz, J.: 1983, *Biochim. Biophys. Acta* **724**, 118.
Vasmel, H., Meiburg, R. F., Kramer, H. J. M., de Vos, L. J., and Amesz, J.: 1983, *Biochim. Biophys. Acta* **724**, 333.

Williams, J. C., Steiner, L. A., Feher, G., and Simons, M. I.: 1984, *Proc. Natl. Acad. Sci. U.S.A.* **81**, 7303.

Woese, C. R., Debrunner-Vossbrinck, B. A., Oyaizu, H., Stackebrandt, E., and Ludwig, W.: 1985, *Science* **229**, 762.