

THE BEGINNING OF PHOTOSYNTHESIS

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Abstract. There is no evolutionary continuity between photochemical abiosynthesis and bacterial photosynthesis. Rather, the photosynthetic bacteria are descendants of fermenters that did not use light. Photosynthesis and respiration, both using electron flow coupled with phosphorylation, have a common origin ('conversion hypothesis'), but photosynthesis came first. Anaerobic (nitrate or sulphate) respiration cannot have preceded photosynthesis as neither nitrate nor sulphate existed on the early earth. Sulphate was made first by photosynthetic sulphur bacteria. Nitrate arose even later, namely, in the aerobic biosphere produced by the blue-green algae, the first 'phytotrophs'. Photophosphorylation may have originated through the combination with membrane function of substrate level phosphorylation in reactions of photoproducts. Cyclic photophosphorylation arose while the biosphere was still reducing. It was supplemented later by processes for the light-based production of reducing power (NADH), ATP-powered electron flow, and subsequently light-powered electron flow with ATP production (noncyclic photophosphorylation). These later processes served the assimilation of CO₂.

1. It is widely thought that the organic compounds in the prebiotic soup were mainly produced by ultraviolet (uv) light. Some authors hold that already the earliest organisms utilized the energy of light (Gaffron, 1965; Granick, 1965). Thus continuity in the action of light from prebiotic to biotic times is suggested.

Fermenters base their energy metabolism, by definition, on dark redox reactions between organic compounds, coupled to phosphorylation on a substrate level. Since a separate origin of the fermenters would imply a polyphyletic origin of life, and therefore appears unlikely, it must be assumed from Gaffron's and Granick's point of view that the fermenters are descended from photosynthesizers.

We shall not accept this. In contrast to the machinery for fermentation, that for photosynthesis always has a complicated solid-phase structure. Photosynthesis in liquid phase is unknown. The components of the photosynthetic electron flow (redox) chain are arranged in spatial order: the loci of electron flow and of photophosphorylation are membranes. Organisms with this degree of structure can hardly have been the first.

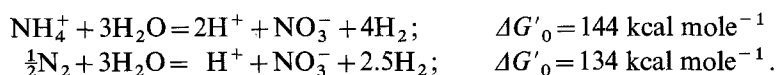
More probably, the fermenters preceded the photosynthesizers. Indeed this is the majority view. But what are the relative positions in evolution of the photosynthesizers and the respirers? Like the photosynthesizers, the respirers have ordered electron flow, coupled to phosphorylation. Moreover, both groups – and no other – have cytochromes. Therefore, it has been proposed (Broda, 1970, 1971) that photosynthesis and respiration always evolved one from the other, and never arose independently ('conversion hypothesis'). Which process came first?

2. Aerobic respiration clearly was impossible before photosynthesis, as there was almost no free oxygen in the biosphere. The biosphere acquired oxygen (became oxygenic) only through the activity of the most advanced photosynthesizers, the blue-green algae. From this point of view, only anaerobic respiration might have

antedated photosynthesis. This would imply a tremendous time interval between the origins of anaerobic and of aerobic respiration. The former would have arisen before, the latter after photosynthesis.

Two groups of anaerobic respirers exist, the dissimilatory nitrate and sulphate reducers. In these organisms, nitrate or sulphate substitutes for oxygen as the terminal electron acceptor. Anaerobic respiration has indeed much in common with aerobic respiration. Electron flow is coupled to phosphorylation, and cytochromes participate in the process.

According to Egami (see Takahashi *et al.*, 1963), nitrate respiration antedated oxygen respiration. These authors think that nitrate respiration arose from a supposed variant of fermentation, nitrate fermentation. However, in absence of free oxygen the synthesis of nitrate would have been highly endergonic:

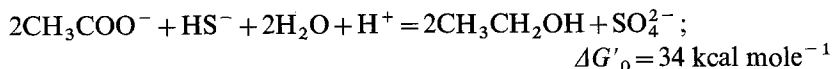


Thus the anoxygenic biosphere did not contain nitrate. Presumably nitrate was formed later – in the oxygenic atmosphere – by chemolithotrophs, namely, the nitrifiers.

It is a curious feature of Egami's hypothesis that photosynthesis has no role. We have seen that nitrate respiration must have awaited the emergence of free oxygen, and, consequently, of photosynthesis.

3. Early sulphate respiration has been assumed by Peck (1966), Klein and Cronquist (1967) and Postgate (1968). But did sulphate exist in the early biosphere? Peck admits that not much sulphate was there before life began. Indeed, little sulphate has been found in the oldest rocks (Cloud, 1968, 1972). This is not surprising, as sulphate is unstable in a reducing biosphere (see Broda, 1971).

According to Peck, sulphate was made in the anoxygenic biosphere by fermenters in reactions unknown in the present world, namely, by oxidation of sulphide with organics. However, such reactions with plausible oxidants are endergonic. For instance, with acetate we have:



and with water (for comparison);



Realistically, ΔG was still more positive than $\Delta G'_0$, as the concentration of HS^- in presence of Fe^{++} is limited by the solubility of FeS . From the solubility product of FeS (3.7×10^{-19}) follows that, e.g., in neutral 10^{-3} M Fe^{++} the concentration of HS^- must have been less than 3×10^{-8} M. Consequently, $\Delta G - \Delta G'_0 > 10.2$. Of course, the values of $\Delta G'$ could be depressed by assuming lower concentrations of the organic

products than of the organic reactants, but this seems unrealistic in respect of the primeval, reducing biosphere.

Thus no sulphate could arise in fermentations. It is proposed (Broda, 1970, 1971) that sulphate was made first by photosynthetic bacteria. Purple bacteria are known which make sulphate as a by-product in the phototransfer of electron from sulphide to ferredoxin. The sulphate produced by early photosynthetic bacteria then served the sulphate respirers as an electron acceptor in 'sulphureta', closed ecosystems. In accordance with the conversion hypothesis the sulphate respirers are assumed to have descended from photosynthetic bacteria.

It is concluded that all respiring bacteria (oxygen, sulphate and nitrate respirers) evolved from photosynthetic bacteria, and that the photosynthetic bacteria evolved from fermenters. Hence chlorophyll type pigments are older than cytochromes.

4. How can photosynthesis have evolved from fermentation? Transitional forms are unknown now, and so we are left to mere speculation. What is the most plausible process?

Bacterial photosynthesis, as we know it now, provides both ATP and reducing power (NADH). According to Arnon (1959), the primary function of photosynthesis was the production of ATP. (Of course, ATP may have been preceded by another energy-rich compound, e.g., inorganic pyrophosphate.) Other authors have given precedence to NADH production (Duysens, 1964; Gaffron, 1965). Also the present author (1970) was at one time so inclined.

One argument for the primary role of ATP in photosynthesis is that even now in some conditions only ATP – no NADH – is required by photosynthetic bacteria, e.g., for the photoassimilation of alcohols. This may be an ancient process. A further argument is that NADH could be made, when needed, in a dark reaction by reduction of NAD by H_2 ; the biosphere was still reducing when photosynthesis began.

Through the life processes of the fermenters, the stores of suitable substrates for redox reactions yielding ATP diminished. The first task of light may have been replenishment of suitable redox systems through reversal of the exergonic reactions by light.

Endergonic redox reactions can be forced by light. Thus NAD is reduced by ascorbic acid in pyridine in presence of chlorophyll (Krasnovsky and Voinovskaya, 1952). In early cells, both products of light reactions, reductant and oxidant, were found in the same compartment, and therefore the possibility for useless back reactions was great (see Gaffron, 1965). Systems were only useful where such direct back reactions were slow, and hence back reactions coupled to phosphorylation could compete with them. This idea is not far-fetched. After all, in presence of the necessary catalysts, glycolysis with phosphorylation competes with the direct 'split' of glucose into lactic acid – a reaction slow enough to be purely fictive.

5. The yield of ATP in the back reaction could be improved through spatial separation of oxidant and reductant by a barrier, i.e., a membrane. Nowadays all cells

have at least a plasma membrane. Quite plausibly the early fermenters, too, were separated by membranes from the aqueous medium, and the membranes were, then as now, the location of the mechanism for transport. Invaginations of the plasma membrane are now common, and the thylakoids of the photosynthetic bacteria surely originated as internal extensions of the plasma membrane.

It seems that a light-powered phosphorylating redox system combined with a necessarily asymmetric transporting membrane, in such a way that the products of the light reaction (oxidant and reductant) appeared on different sides of the membrane. According to Mitchell (1970)

it is an evolutionarily attractive proposition that the proton-translocating oxidoreduction loop system and the reversible proton-translocating ATPase may have arisen separately... and that the accidental occurrence of both systems in the same cell may then have provided the means of storing the free energy of oxidoreduction in ATP....

Subsequently the membrane could be improved by stepwise insertion of compounds suitably spaced in respect to redox potential, including cytochromes, and by coupling electron flow along this chain to phosphorylation.

Gradually the biosphere ceased being reducing. Further evolution will not be discussed here, but clearly for the mobilisation of the abundant carbon in biospheric CO₂ additional reducing power was needed. NADH was probably provided first by ATP-powered noncyclic electron flow ('reversed flow'), and later by light-powered noncyclic electron flow with production of ATP. Increasingly, inorganics (sulphides, ferrous salts) were employed as additional sources of electrons (photolithotrophy). When these sources approached exhaustion, water itself was applied. This was achieved by plants, first by the blue-green algae, through the 2-quanta process. The relationship of bacterial and plant photosynthesis has, of course, been explained in the momentous work of Van Niel (see Van Niel, 1962). The mechanism of photosynthesis in higher plants seem to be essentially identical with that in algae, even blue-green algae. The plant's way of making metabolic energy might merit a separate name: (photo)phytotrophy.

Note added in proof. The question of the instability of sulphate in reducing conditions will be taken up again in a forthcoming book (E. Broda, *The Evolution of the Bioenergetic Processes*, Pergamon Press, Oxford). Reference will be made there to the important work of H. D. Holland.

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