Anoxygenic Photosynthesis

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Anoxygenic Vs. Oxygenic Photosynthesis

- Green and purple photosynthetic bacteria differ from cyanobacteria and eucaryotic photosynthesizers in several fundamental ways (**table 1).**
- **In particular, green and purple bacteria do not use water** as an electron source or produce O_2 photosynthetically—that is, they are **anoxygenic.**
- There are four groups of green and purple photosynthetic bacteria, each containing several genera:
- Green sulfur bacteria (*Chlorobium),*
- Green nonsulfur bacteria *(Chloroflexus),*
- Purple sulfur bacteria (*Chromatium),*
- Purple nonsulfur bacteria (*Rhodospirillum, Rhodopseudomonas).*

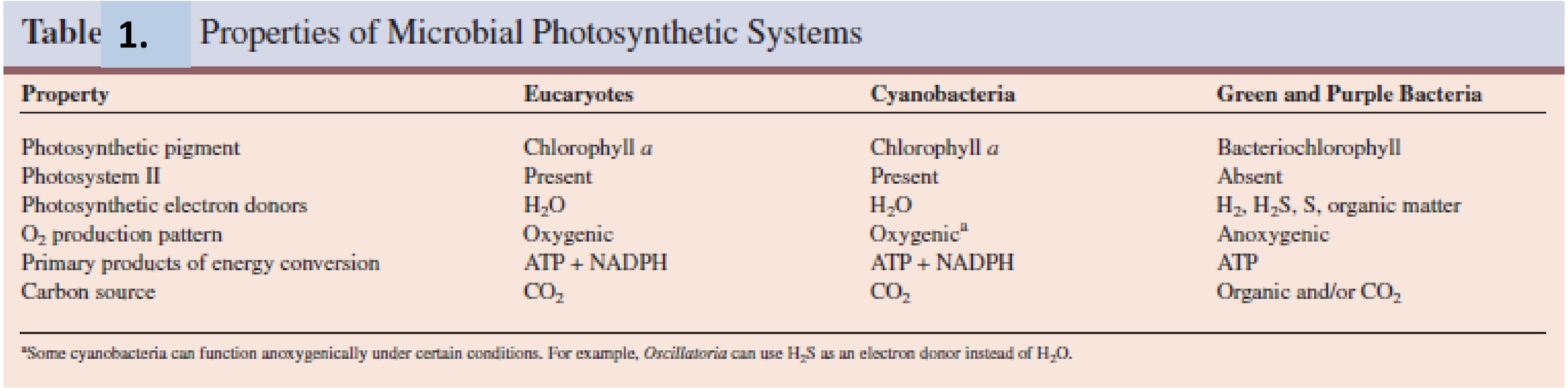


Table 1. Properties of Microbial Photosynthetic Systems

Property	Eucaryotes	Cyanobacteria	Green and Purple Bacteria
Photosynthetic pigment	Chlorophyll *a*	Chlorophyll *a*	Bacteriochlorophyll
Photosystem II	Present	Present	Absent
Photosynthetic electron donors	H_2O	H_2O	H_2, H_2S, S, organic matter
O_2 production pattern	Oxygenic	Oxygenic[a]	Anoxygenic
Primary products of energy conversion	ATP + NADPH	ATP + NADPH	ATP
Carbon source	CO_2	CO_2	Organic and/or CO_2

[a] Some cyanobacteria can function anoxygenically under certain conditions. For example, *Oscillatoria* can use H_2S as an electron donor instead of H_2O.

… **Anoxygenic Vs. Oxygenic Photosynthesis**

- **NADPH is not directly** produced in the photosynthetic light reaction of purple bacteria.
- Green bacteria can reduce NAD directly during the light reaction.
- To synthesize NADH and NADPH, green and purple bacteria must use electron donors like hydrogen, hydrogen sulfide, elemental sulfur, and organic compounds that have more negative reduction potentials than water and are therefore easier to oxidize (better electron donors).
- Finally, green and purple bacteria possess slightly different photosynthetic pigments, **bacteriochlorophylls** many with absorption maxima at longer wavelengths.
- Bacteriochlorophylls a and b have maxima in ether at 775 and 790 nm, respectively.
- In vivo maxima are about 830 to 890 nm (bacteriochlorophyll a) and 1,020 to 1,040 nm (Bchl b).
- This shift of absorption maxima into the infrared region better adapts these bacteria to their ecological niches.

Anoxygenic Photosynthesis

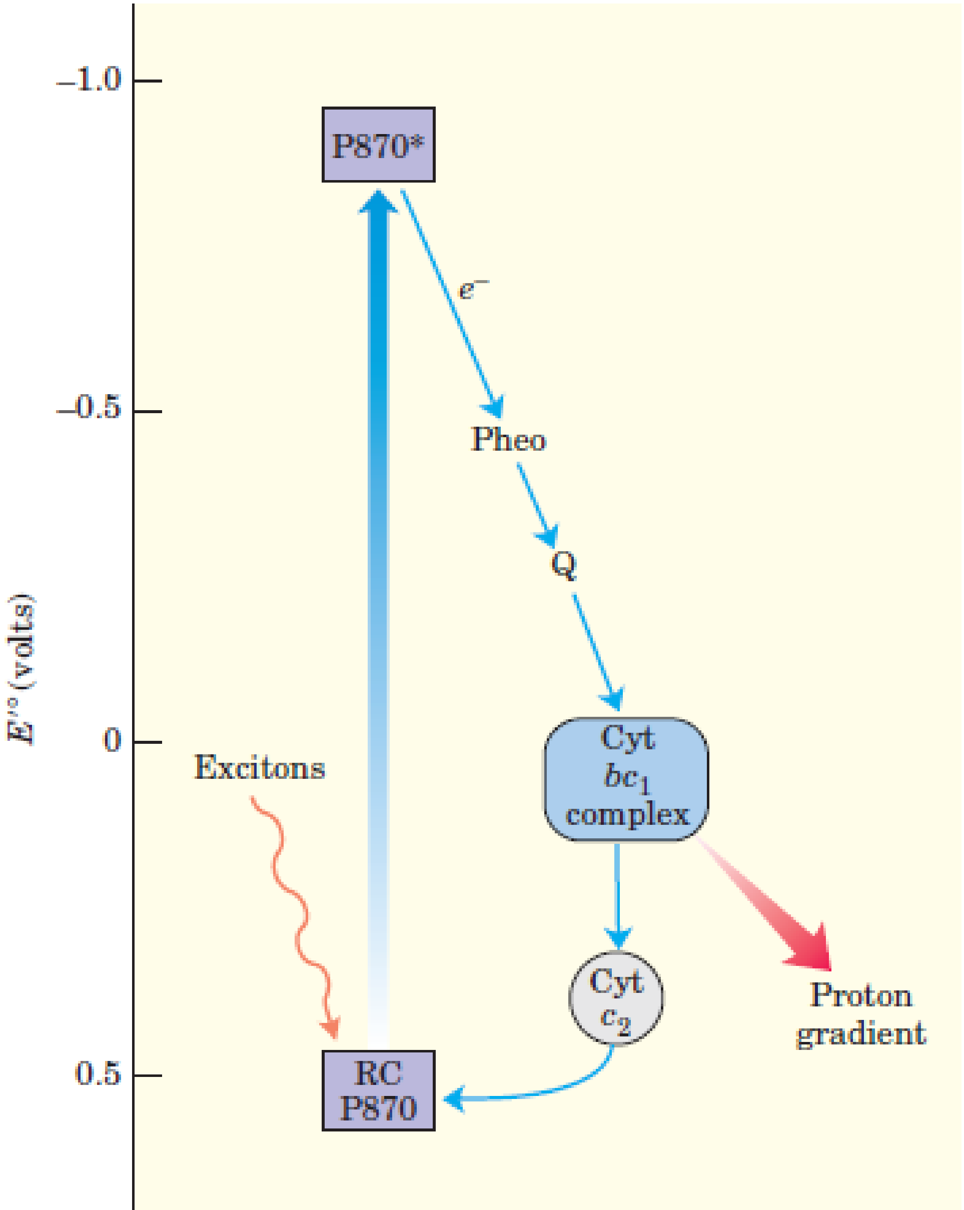
- Photosynthetic bacteria have relatively simple phototransduction machinery, with one of two general types of reaction center.
- One type (found in purple bacteria) passes electrons through **pheophytin** (chlorophyll lacking the central Mg^{2+} ion) to a quinone.
- The other (in green sulfur bacteria) passes electrons through a quinone to an iron-sulfur center.
- Cyanobacteria and plants have two photosystems (PSI, PSII), one of each type, acting in tandem.
- Note that although both green and purple bacteria lack two photosystems, the purple bacteria have a photosynthetic apparatus similar to photosystem II.
- Whereas the green sulfur bacteria have a system similar to photosystem I.

Purple Nonsulfur Bacterial Photosynthesis

(The Pheophytin-Quinone Reaction Center

(Type II Reaction Center)

- The photosynthetic machinery in purple bacteria consists of three basic modules:
  - Single reaction center (P_{870})
  - Cytochrome bc1 electron transfer complex
  - ATP synthase
- Illumination drives electrons through pheophytin and a quinone to the cytochrome *bc1* complex.
- After passing through the complex, electrons flow through cytochrome *c2* back to the reaction center, restoring its preillumination state.
- This light-driven cyclic flow of electrons provides the energy for proton pumping by the cytochrome bc1 complex.
- Powered by the resulting proton gradient, ATP synthase produces ATP.
- Purple bacteria face a further problem because they also require NADH or NADPH for CO_2 incorporation.
- They may synthesize NADH in at least two ways:
  - If they are growing in the presence of hydrogen gas, which has a reduction potential more negative than that of NAD^+, the hydrogen can be used directly to produce NADH.
  - Like chemolithotrophs, many photosynthetic purple bacteria use proton motive force to reverse the flow of electrons in an electron transport chain and move them from inorganic or organic donors to NAD^+.



Purple bacteria
(pheophytin-quinone type)

Molecular Mechanism

- A pair of bacteriochlorophylls—the “special pair,” designated $(Chl)_2$—is the site of the initial photochemistry in the bacterial reaction center.
- Energy from a photon absorbed by one of the many antenna chlorophyll molecules surrounding the reaction center reaches $(Chl)_2$ by exciton transfer.
- The $(Chl)_2$ donates an electron that passes through a neighbouring chlorophyll monomer to pheophytin (Pheo).
- This produces two radicals, one positively charged (the special pair of chlorophylls) and one negatively charged (the pheophytin):

$$(\mathrm{Chl})_2 + 1\ \mathrm{exciton} \longrightarrow (\mathrm{Chl})_2^{*} \qquad \text{(excitation)}$$

$$(\mathrm{Chl})_2^{*} + \mathrm{Pheo} \longrightarrow \cdot(\mathrm{Chl})_2^{+} + \cdot\mathrm{Pheo}^{-} \qquad \text{(charge separation)}$$

- The pheophytin radical now passes its electron to a tightly bound molecule of quinone (Q_A), converting it to a semiquinone radical, which immediately donates its extra electron to a second, loosely bound quinone (Q_B).

… Molecular Mechanism

- Two such electron transfers convert Q_B to its fully reduced form, Q_BH_2, which is free to diffuse in the membrane bilayer, away from the reaction center to the cytochrome bc1 complex:

$$2 \cdot \text{Pheo}^- + 2H^+ + Q_B \longrightarrow 2\ \text{Pheo} + Q_BH_2 \qquad \text{(quinone reduction)}$$

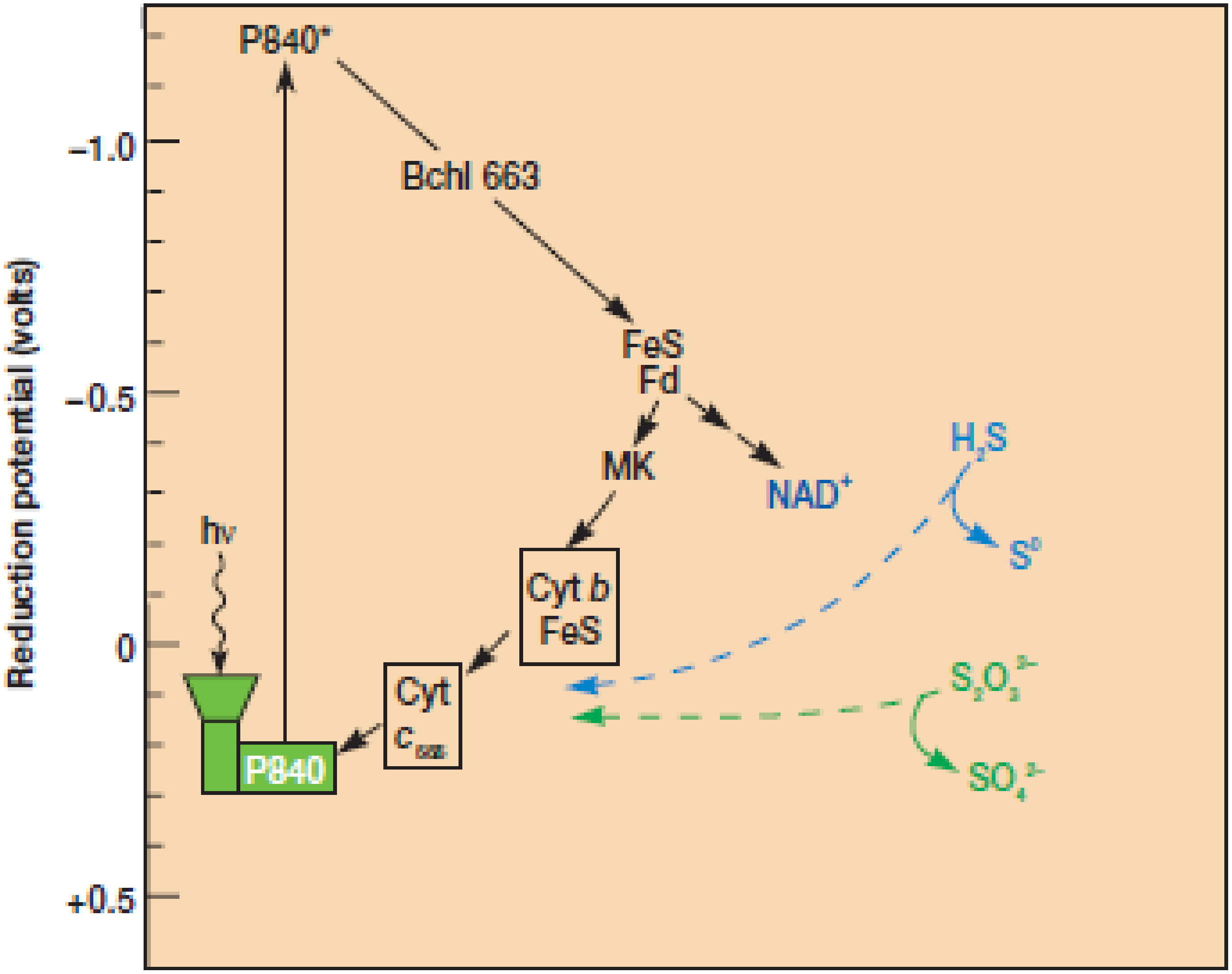
- the cytochrome *bc1* complex of purple bacteria carries electrons from a quinol donor (QH_2) to an electron acceptor (electron depleted form of P870, $(Chl)_2$), using the energy of electron transfer to pump protons across the membrane, producing a proton motive force.
- Electrons move from the cytochrome bc1 complex to P870 via a soluble c-type cytochrome, cytochrome c2.
- *The* electron transfer process completes the cycle, returning the reaction center to its unbleached state, ready to absorb another exciton from antenna chlorophyll.

Green Sulfur Bacterial Photosynthesis

The Fe-S Reaction Center

(Type I Reaction Center)

- Photosynthesis in green sulfur bacteria involves the same three modules as in purple bacteria, but the process differs in several respects and involves additional enzymatic reactions.
- Excitation causes an electron to move from the reaction center to the cytochrome bc1 complex via a quinone (MK, Menaquinone) carrier.
- Electron transfer through this complex powers proton transport and creates the proton-motive force used for ATP synthesis.
- However, in contrast to the cyclic flow of electrons in purple bacteria, some electrons flow from the reaction center to an iron-sulfur protein, **ferredoxin, which then** passes electrons via ferredoxin: NAD reductase to NAD, producing NADH.
- The electrons taken from the reaction center to reduce NAD are replaced by the oxidation of H_2S to elemental S, then to SO_4^{2-}, in the reaction that defines the green sulfur bacteria.
- This oxidation of H_2S by bacteria is chemically analogous to the oxidation of H_2O by oxygenic plants.


Reduction potential (volts)
−1.0
−0.5
0
+0.5
P840*
Bchl 663
FeS
Fd
MK
NAD$^+$
H_2S
S^0
Cyt *b*
FeS
hν
Cyt
c$_{555}$
P840
$S_2O_3^{2-}$
SO_4^{2-}

Questions

- Explain detailed process of anoxygenic photosynthesis of green and purple bacteria.
- How anoxygenic photosynthesis differ from oxygenic photosynthesis?
- Explain molecular mechanism of anoxygenic green sulfur bacterial photosynthesis.