# PHOTOSYNTHESIS

Photosynthesis (light synthesis) is often described as a process allowing living organisms to use light energy to drive the anabolic reactions required to build sugar molecules from inorganic carbon (CO_2); however, this is misleading, because light energy is never used directly to drive carbon-fixing reactions. Furthermore, the chemical equation often used to represent photosynthesis ($6CO_2 + 6H_2O$ + light energy $\rightarrow C_6H_{12}O_6 + 6O_2$) is not always applicable because not all **phototrophs** (organisms capable of using light energy) can fix CO_2 into organic compounds, and not all **autotrophs** (organisms capable of using inorganic carbon sources) can capture light energy. Also, not all **photoautotrophs** produce oxygen as a by-product of their photosynthetic activity. To better understand photosynthesis, it is necessary to recognize that it involves two entirely different processes; **photophosphorylation** (using light energy to drive the synthesis of ATP), and a series of chemical reactions allowing organisms to "fix" inorganic carbon into organic compounds, e.g., the **Calvin-Benson cycle**.

Photophosphorylation reactions (the light dependent reactions of photosynthesis) require molecules capable of responding to light energy. **Archaea** in the genus *Halobacterium* use the red-colored pigment **bacteriorhodopsin** for this process. When activated by light, bacteriorhodopsin molecules transport hydrogen protons across cellular membranes and create a proton-motive force. As protons flow back (passively, down their concentration and electrical gradient) through **ATP-synthase**, the potential energy they provide is used to bind ADP and PO_4 into ATP.

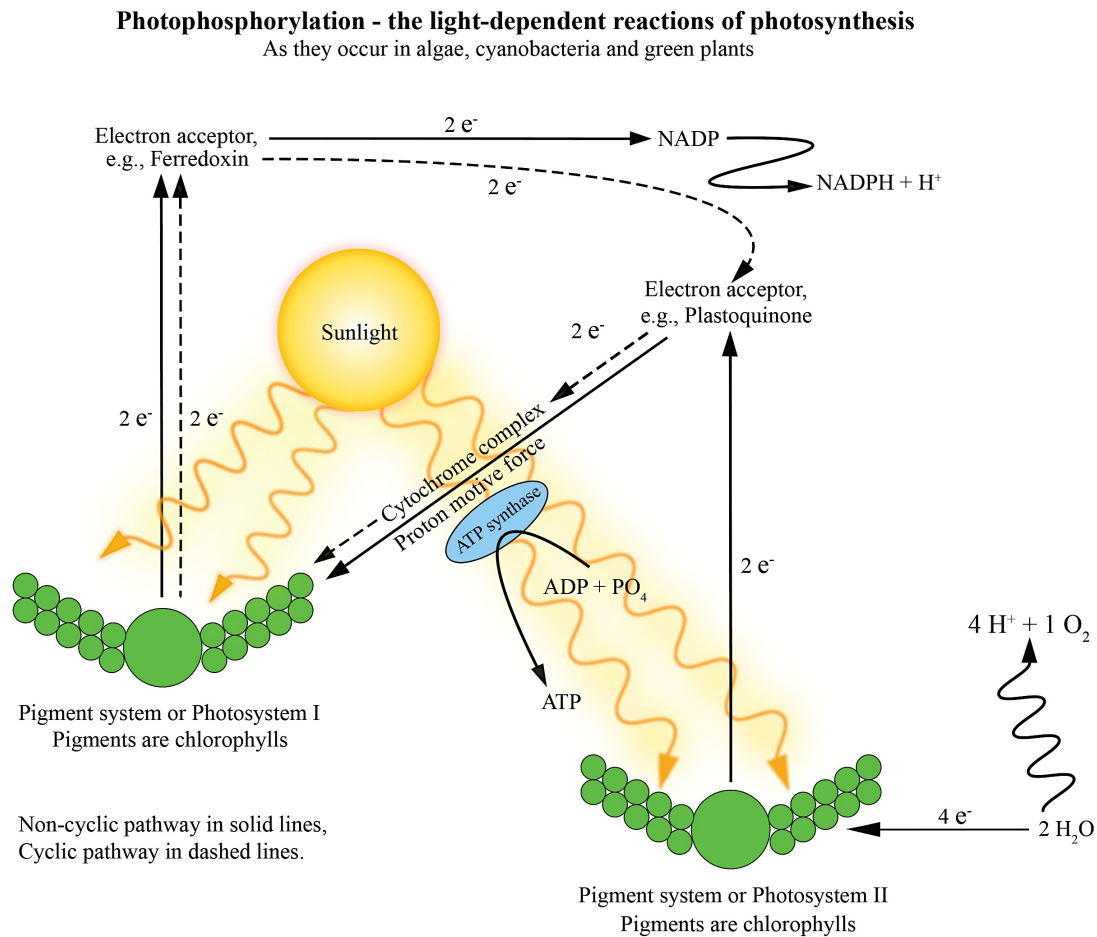**Photophosphorylation - the light-dependent reactions of photosynthesis**
As they occur in the anoxygenic phototrophic bacteria

Pigment system or photosystem
Pigments are bacteriochlorophylls
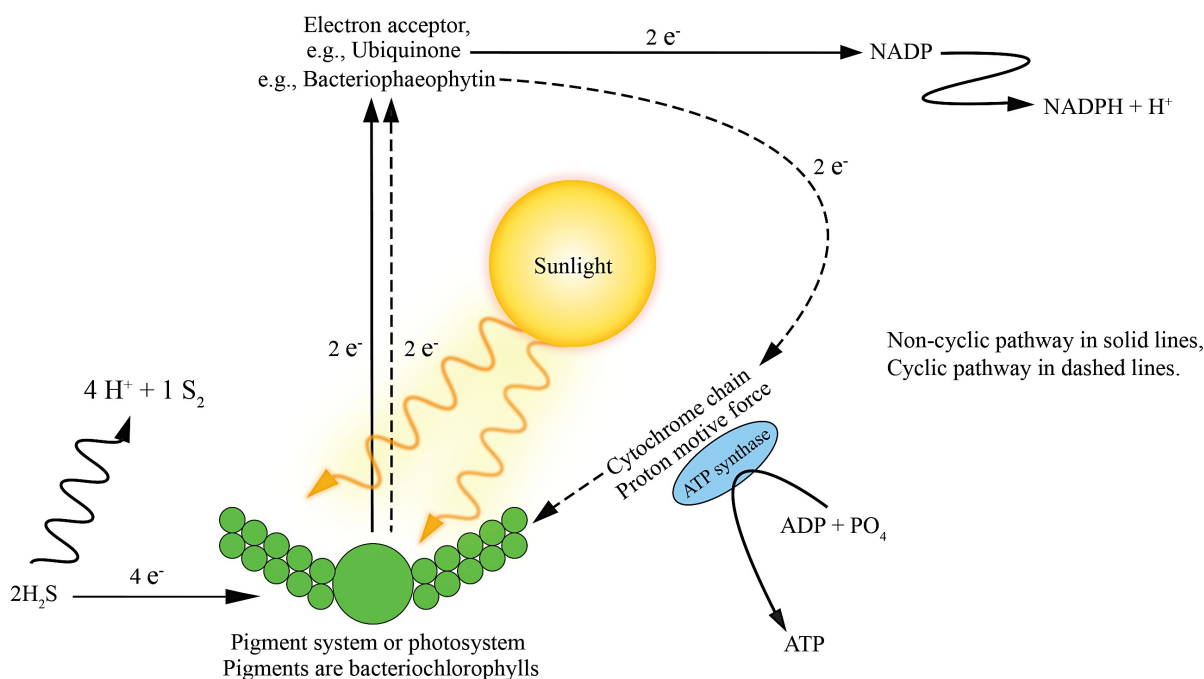
Anoxygenic phototrophic bacteria use **bacteriochlorophylls** (various combinations of a, b, c, d, and e) to "capture" light energy. The pigments respond to light by giving off electrons that are passed to electron acceptors of various types. During cyclic photophosphorylation (dashed lines) the electrons can pass to **bacteriophaeophytin**, and then to a cytochrome complex. The cytochromes transport hydrogen protons across membranes (cell membranes) generating a proton motive force. As the protons flow back (passively) through **ATP-synthase**, their potential energy is used to bind ADP to PO_4 forming ATP.

When the anoxygenic phototrophic bacteria pass electrons along a non-cyclic pathway, they can use a different electron acceptor (e.g., **ubiquinone**) and ultimately pass the electrons to NADP reducing it to **NADPH + H$^+$**. Although this is a high-energy molecule, the process involved in forming it is technically not phosphorylation (it is reduction). Electrons that pass to NADP do not return to the pigments, so these must be replaced. Bacteriochlorophylls cannot "pull" electrons away from water molecules, but they can "pull" them away from **hydrogen sulfide** (H$_2$S) resulting in the formation of elemental sulfur.

Photophosphorylation - the light-dependent reactions of photosynthesis
As they occur in algae, cyanobacteria and green plants

Electron acceptor,
e.g., Ferredoxin   —— 2 e$^-$ ——→ NADP
                     ---- 2 e$^-$ ----→ NADPH + H$^+$

Sunlight

2 e$^-$ 2 e$^-$

Electron acceptor,
e.g., Plastoquinone

2 e$^-$

Cytochrome complex
Proton motive force

ATP synthase

ADP + PO$_4$

2 e$^-$

ATP

4 H$^+$ + 1 O$_2$

Pigment system or Photosystem I
Pigments are chlorophylls

Non-cyclic pathway in solid lines,
Cyclic pathway in dashed lines.

4 e$^-$ 2 H$_2$O

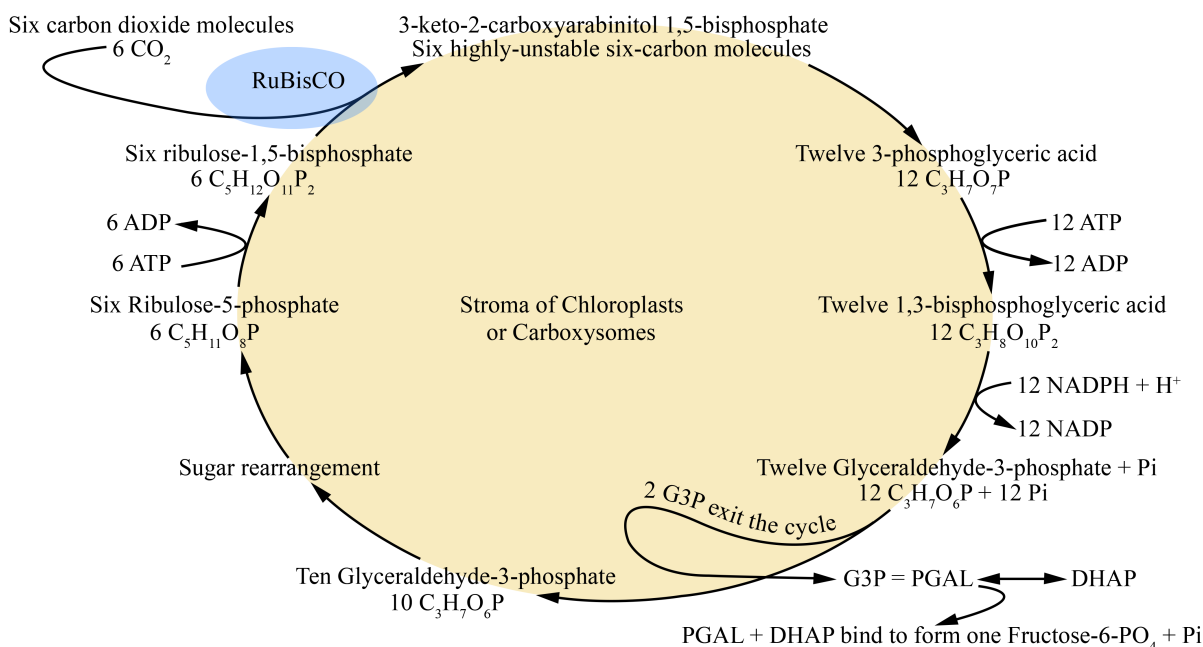Pigment system or Photosystem II
Pigments are chlorophylls

Algae and **cyanobacteria** (as well as green plants) use **chlorophyll** molecules (various combinations of a, b, and c) to capture light energy. Chlorophyll molecules respond to light by giving up electrons, and these are passed to various types of electron acceptors. During **non-cyclic photophosphorylation**, the electrons leaving photosystem II pass to **plastoquinone** and from there to a cytochrome complex (cytochrome b$_6$f). The cytochromes transport hydrogen protons across membranes (into **thylakoids**) generating a proton motive force. As the protons flow back (passively) through **ATP-synthase**, their potential energy is used to bind ADP and PO$_4$ into ATP. The cytochrome complex also passes electrons from photosystem II to the pigments of photosystem I, and these replace the electrons passed from photosystem I to **ferredoxin** (an iron-sulfur protein). The electrons passed to ferredoxin are ultimately passed to NADP reducing it to **NADPH + H$^+$** (thus this process yields both ATP and NADPH + H$^+$). The pigments of photosystem II can replace their missing electrons by "pulling" them away from water molecules, and as a result, form **molecular oxygen** (O$_2$) as a waste gas (algae and cyanobacteria are **oxygenic**). Algae and cyanobacteria can also run a type of cyclic photophosphorylation (dashed line). During this process they produce ATP, but do not form NADPH + H$^+$ and do not form oxygen. Pigment molecules other than chlorophylls are often associated with photosystems. Some of these are the carotenoid and phycobilin pigments described earlier as being found in some types of algae.

Organisms that function as **autotrophs** use many of the high-energy molecules produced in association with photophosphorylation (ATP and NADPH + H$^+$) to drive reactions that can "fix" inorganic carbon (e.g., carbon dioxide) into organic compounds. Because these reactions do not require light, they are sometimes referred to as the light independent reactions (or dark reactions) of photosynthesis. The cyclic series of reactions shown below is one example of an **anabolic pathway** used to "fix" carbon. It is not the only one, but is a pathway used by many different types of autotrophs.

The Calvin-Benson-Bassham Cycle
Light Independent or Dark Reactions of Photosynthesis

Six carbon dioxide molecules
6 CO_2

RuBisCO

3-keto-2-carboxyarabinitol 1,5-bisphosphate
Six highly-unstable six-carbon molecules

Six ribulose-1,5-bisphosphate
6 $C_5H_{12}O_{11}P_2$

Twelve 3-phosphoglyceric acid
12 $C_3H_7O_7P$

6 ADP
6 ATP

12 ATP
12 ADP

Six Ribulose-5-phosphate
6 $C_5H_{11}O_8P$

Stroma of Chloroplasts
or Carboxysomes

Twelve 1,3-bisphosphoglyceric acid
12 $C_3H_8O_{10}P_2$

12 NADPH + H$^+$
12 NADP

Sugar rearrangement

Twelve Glyceraldehyde-3-phosphate + Pi
12 $C_3H_7O_6P$ + 12 Pi

2 G3P exit the cycle

Ten Glyceraldehyde-3-phosphate
10 $C_3H_7O_6P$

G3P = PGAL ⇌ DHAP

PGAL + DHAP bind to form one Fructose-6-PO_4 + Pi

The first enzyme in the Calvin-Benson-Bassham Cycle (aka Calvin Cycle or **Calvin-Benson cycle**) is **ribulose-1,5-bisphosphate carboxylase/oxygenase** (RuBisCO). This enzyme catalyzes reactions binding inorganic carbon in the form of carbon dioxide to ribulose-1,5-bisphosphate, thereby "fixing" CO_2 into organic compounds. In the diagram, six CO_2 molecules are "fixed" at the start of the cycle. Each six-carbon compound formed is highly unstable and almost immediately breaks into two, three-carbon compounds (3-phosphoglyceric acid molecules). These are then phosphorylated (a step requiring ATP) to form two molecules of 1,3-bisphosphoglyceric acid. NADPH + H+ is then used to reduce each 1,3-bisphosphoglyceric acid forming glyceraldehyde-3-phosphate (G3P), a molecule also called phosphoglyceraldehyde (PGAL), and two inorganic phosphates (Pi). Phosphoglyceraldehyde (PGAL) is in equilibrium with dihydroxyacetone phosphate (DHAP), so both types of molecules form. One PGAL and one DHAP can exit the cycle and form fructose-6-phosphate plus Pi. This sugar can then be used to form glucose, polysaccharides and various other organic compounds. The remaining ten PGAL molecules (30 carbons) undergo a rearrangement to form six, five-carbon molecules of ribulose-5-phosphate (30 carbons). Then ATP is used to phosphorylate these forming six molecules of ribulose-1,5-bisphosphate, and the cycle is ready to start again.
RuBisCO is probably the most abundant protein on the planet, but is somewhat inefficient (it catalyzes reactions rather slowly). It is typically concentrated within confined spaces, e.g., the **stroma** of chloroplasts or within **carboxysomes** (prokaryotes), and is influenced by a number of factors e.g., CO_2 concentration, pH, temperature, availability of Mg^{++} (a cofactor), PO_4, ATP/ADP ratio, etc. In plants and some algae, another enzyme called RuBisCO activase is required for RuBisCO function. This enzyme is inactivated by heat so heat-stressed plants cannot fix CO_2 properly. **Bad news given climate change!**