PHOTOSYNTHESIS: A BRIEF STORY!!!!!

This is ***one*** of the most important biochemical processes in plants and is amongst the most expensive biochemical processes in plant in terms of investment. Photosynthesis is also the major biochemical process that has driven plant form and function. Photosynthetic organisms use solar energy to synthesize carbon compounds that cannot be formed without the input of energy. ***More specifically***, light energy ***drives*** the synthesis of carbohydrates from carbon dioxide and water with the generation of oxygen.

(Sorry everyone – couldn't resist!)

There are two parts to this process: The ***light reactions*** and the ***Carbon reactions***. The main components required by any photosynthetic organisms for this process to occur are:

- H_20 MW 18
- CO_2 MW 44
- Sunlight

The effectiveness of controlling water loss and allowing CO_2 uptake for photosynthesis is called the ***transpiration ratio***. There is a large ratio of water efflux and CO_2 influx. The concentration ratio driving water loss is 50 times larger than that driving CO_2 influx. Furthermore, CO_2 diffuses 1.6 times slower than water, ***due to CO_2 being a larger molecule than water***

Recent estimates indicate that about 200 billion tones of CO_2 are converted to biomass each year. It is also widely considered that 40 % of this is from ***marine phytoplankton***. The bulk of the carbon is incorporated into organic compounds by the carbon reducing reactions (dark reactions) of photosynthesis.

In a nutshell!

The overall process of photosynthesis is a ***redox*** chemical reaction:

Electrons are removed from one chemical species (***oxidation***) and added to another (***reduction***)

Light reduces NADP, which serves as the reducing agent for carbon fixation during the dark reactions

ATP also formed during electron flow from water to NADH and is also used during carbon fixation

Thylakoid (Light) reactions: water oxidized to oxygen, NADP reduced and ATP is formed

Stroma (Carbon) reactions: carbon fixation and reduction reactions

The Light Reactions:

The light reactions are the first step of photosynthesis and occur in the stacks of ***Thylakoids*** known as the ***Granum***. Simply put, the light reactions:

- Harvest light energy
- Convert light energy to chemical energy
- Fix approximately 15-25% of CO_2 taken in into an organic molecule (the rest of the CO_2 influx occurs during the carbon reactions).

<u>There are many components required for this</u>:

- **Chlorophyll:**

Chlorophyll is synthesized during a biosynthetic pathway involving more than 12 gene products the first tow initiated in the mitochondria. Once all of the genes have been expresses the pigment proteins which up chlorophyll are assembled in the thylakoid membrane. Chlorophyll has a complex ring structure, with the basic structure consisting of a porphyrin ring, co-coordinated to a central atom. Structure wise, this is very similar to the heme group of hemoglobin. This ring structure contains loosely bound electrons and is the part of the molecule involved in electron transitions and redox reactions of photosynthesis.

Chlorophyll absorbs light most strongly in the blue portion of the electromagnetic spectrum, followed by the red portion. However, it is a poor absorber of green and near-green portions of the spectrum, hence the green color of chlorophyll-containing tissues

In higher plants there are two types: **Chlorophyll-*a***, which works in conjunction with **Chlorophyll–*b***. The structure of these two pigment types are almost identical, with the difference belonging to the composition of the side-chain, with chlorophyll-*b* containing an extra oxygen molecule on its ring structure.

The different side-groups 'tune' the absorption spectrum to slightly different wavelengths. Light that is not significantly absorbed by chlorophyll-*a*, will instead be captured by chlorophyll-*b*.

- **Photochemical Reaction Centers**

These are a complex of several proteins, pigments and other co-factors assembled together to execute the primary energy conversion reactions of photosynthesis. In the light reactions of higher plant species there are two of these reaction centers, Photosystem II (PS-II) and Photosystem I (PS-I). PS-II is the first system in the reaction series, followed by PS-I. ***Odd, I know, but they are named in the order in which they were isolated and identified for biochemical function***.

PS-II and PS-I are spatially separated in the thylakoid membrane. The PS-II reaction center is located mostly in Granum (Stack of Thylakoids), whilst the PS-I reaction center is located in the Stroma & the edges of the Granum.

The reaction center of **Photosystem II**:

- Absorbs red light at 680 nm
- Produces a strong oxidant, capable of oxidizing water
- Also produces a weak reductant

The core of PS-II consists of two subunits. Photosystem II obtains electrons by oxidizing water in a process called photolysis. Molecular oxygen is a byproduct of this process, ***and it is this reaction that supplies the atmosphere with oxygen***. This reaction is catalysed by a reactive centre in photosystem II containing four ***manganese*** ions. Manganese is used because it is capable of existing in four oxidation states: Mn^{2+}, Mn^{3+}, Mn^{4+} and Mn^{5+}. Manganese also forms strong bonds with oxygen-containing molecules, such as water. Every time the PS-II reaction center absorbs a photon, it emits an electron, gaining a positive charge. This charge is neutralized by the extraction of an electron from the manganese centre, which sits directly below it. It should be remembered that the process of oxidizing two molecules of water requires four electrons.

The reaction center of **Photosystem I:**

- Absorbs far-red light at 700 nm.
- Produces a strong reductant, capable of reducing NADP
- Also produces a weak oxidant

As with photosystem II and the bacterial reaction centre, a pair of chlorophyll *a* molecules initiates photo-induced charge separation. This pair is referred to as P700, in reference to the wavelength at which the chlorophyll molecules absorb light maximally. The P700 lies in the centre of the protein. Once photo-induced charge separation has been initiated, the electron travels down a pathway through a chlorophyll-*a* molecule situated directly above the P700, through a quinone molecule situated directly above that, through three 4Fe-4S clusters, and finally to an interchangeable ferredoxin complex.

Each of the two reaction centers are surrounded by 15 chlorophyll molecules (both –*a* and -*b*). The fatty acid chain strictures of chlorophyll act as an antenna which literally tunes the wavelengths of light to allow the maximum possible absorbance of light for photosynthesis to occur.

- **Pheophytin**

Biochemically, pheophytin is a chlorophyll molecule lacking a central Mg^{2+}. This molecule acts as the first electron carrier intermediate in the photosystem. After P680 becomes excited to $P680^{*}$, it transfers an electron to pheophytin, which converts the molecule into a negatively charged radical. The negatively charged pheophytin radical quickly passes its extra electron to two consecutive plastoquinone molecules. Eventually, the electrons pass through the cytochrome b_6f molecule and leaves PS- II.

- **Plastoquinone**

This is a quinone molecule which is involved in the electron transport chain, and is characterized by a phenol-type six carbon ring structure. Plastoquinone is reduced (accepts two protons (H^+) from the stromal matrix of the chloroplast, coupled to two electrons (e^-) from PS-II), forming plastoquinol. It transports the protons to the lumen of thylakoid discs, while the electrons continue through the electron transport chain into the cytochrome b_6f protein complex.

- **Cytochrome b6f complex.**

This is a dimer, with each monomer made up of eight subunits, which consist of four large subunits: a 32 kDa cytochrome, a 25 kDa cytochrome with a low- and high-potential heme group, a 19 kDa iron-sulfur protein containing a [2Fe-2S] cluster, and a 17 kDa subunit IV; along with four small subunits (3-4 kDa): PetG, PetL, PetM, and PetN. The total molecular weight is 217 kDa. This complex functions to mediate the transfer of electrons between the two photosynthetic reaction center complexes, from PS-II to PS-I, while transferring protons from the chloroplast stroma across the thylakoid membrane into the lumen Electron transport via cytochrome b_6f is responsible for creating the proton gradient that drives the synthesis of ATP in chloroplasts.

- **Plastocyanin**

This is an important copper-containing protein involved in electron-transfer. The protein is monomeric, with a molecular weight around 1.5 KDa, and 99 amino acids in most vascular plants. Although the molecular surface of plastocyanins differs within plant species, the structure of the copper binding site is generally conserved.

- **Ferredoxin.**

These are iron-sulfur proteins that mediate electron transfer in a range of metabolic reactions. These are small proteins containing iron and sulfur atoms organized as iron-sulfur clusters. These biological "capacitors" can accept or discharge electrons, the effect being change in the oxidation states (+2 or +3) of the iron atoms. This way, ferredoxin acts as electron transfer agents in biological redox reactions.

- **Nicotinamide adenine dinucleotide phosphate**, (**$NADP^+$**)

This is a coenzyme used in anabolic reactions, which require NADPH as a reducing agent. NADPH is the reduced form of $NADP^+$. $NADP^+$ differs from NAD^+ in the presence of an additional phosphate group on the 2' position of the ribose ring that carries the adenine moiety. In plants, NADPH is produced by ferredoxin-$NADP^+$ reductase in the last step of the electron chain of the light reactions of photosynthesis. It is used as reducing power for the biosynthetic reactions in the Calvin cycle to assimilate carbon dioxide.

With all this in mind, the net-reaction of all light-dependent reactions in oxygenic photosynthesis is:

$$\mathbf{2H_2O + 2NADP^+ + 3ADP + 3P_i \rightarrow O_2 + 2NADPH + 3ATP}$$

The Carbon Reactions:

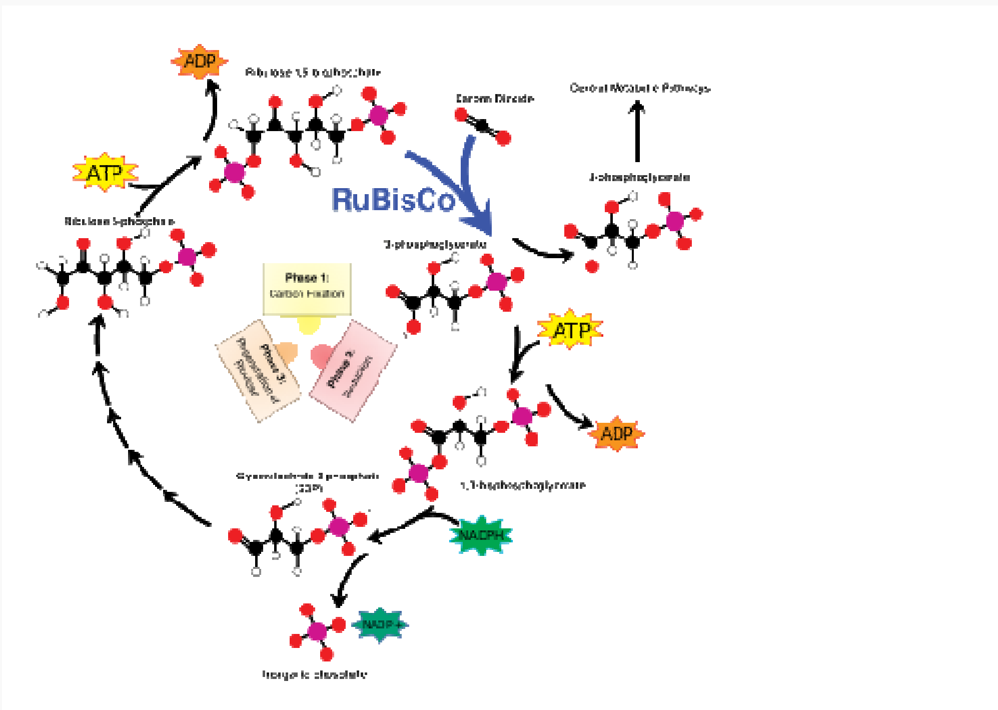
The Carbon Reactions occur mostly within the stroma. Simply put the carbon reactions:

- Expend chemical energy
- Fix Carbon [convert CO_2 to organic form]
- Produce glucose, which can now serve as a building block to make: polysaccharides, other monosaccharides, fats, amino acids, and nucleotides

<u>What is required for this?</u>

The enzyme RuBisCO captures CO_2 from the atmosphere and in a process that requires the newly formed NADPH, called the Calvin-Benson Cycle, releases three-carbon sugars, which are later combined to form sucrose and starch. The overall equation for the light-independent reactions in green plants is:

$$3\ CO_2 + 9\ ATP + 6\ NADPH + 6\ H^+ \rightarrow C_3H_6O_3\text{-phosphate} + 9\ ADP + 8\ P_i + 6\ NADP^+ + 3\ H_2O$$



An overview of the Calvin cycle and carbon fixation.

To be more specific, carbon fixation produces an intermediate product, which is then converted to the final carbohydrate products. The carbon skeletons produced by photosynthesis are then variously used to form other organic compounds, such as the building material cellulose, as precursors for lipid and amino acid biosynthesis, or as a fuel in cellular respiration. The latter occurs not only in plants but also in animals when the energy from plants gets passed through a food chain.

The fixation or reduction of carbon dioxide is a process in which carbon dioxide combines with a five-carbon sugar, ribulose 1,5-bisphosphate (RuBP), to yield two molecules of a three-carbon compound, glycerate 3-phosphate (GP), also known as 3-phosphoglycerate (PGA). GP, in the presence of ATP and NADPH from the light-dependent stages, is reduced to glyceraldehyde 3-phosphate (G3P). This product is also referred to as 3-phosphoglyceraldehyde (PGAL) or even as triose phosphate. Triose is a 3-carbon sugar. Most (5 out of 6 molecules) of the G3P produced is used to regenerate RuBP so the process can continue. The 1 out of 6 molecules of the triose phosphates not "recycled" often condense to form hexose phosphates, which ultimately yield sucrose, starch and cellulose. The sugars produced during carbon metabolism yield carbon skeletons that can be used for other metabolic reactions like the production of amino acids and lipids.