Photosynthesis: CO$_2$ assimilation and sugar metabolism
Energy Transduction       Carbon Assimilation

Chloroplast

H₂O

Light

CO₂

NADP⁺

ADP + Pᵢ

NADPH

ATP

[CH₂O]
(sugar)

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The second half of photosynthesis is reducing CO$_2$ from the atmosphere into a simple sugar. A key enzyme you should know is RUBISCO. This enzyme catalyzes the key step in carbon fixation, adding CO$_2$ to a 5-carbon acceptor.
RUBISCO
Ribulose bisphosphate carboxylase oxygenase

“Fixes” $10^{11}$ tons CO$_2$/ yr
Most abundant protein in the biosphere, 40 million tons
  How?  $\approx 50\%$ of soluble protein in leaves
  Why?  Slow enzyme, need a lot to get the job done

Multimeric enzyme = 8 large subunits and 8 small subunits (different in PS bacteria)
  • large subunit = 56 Kda, encoded in chloroplast genome
  • small subunit = 14 Kda, encoded in nuclear genome (evidence of organellar DNA transfer to nucleus)

RuBP (5C) + CO$_2$ $\rightarrow$ 2 phosphoglycerate (3C + P)
  Note, not reduced at this stage, same energy as CO$_2$. 
CO₂ assimilation is most easily understood as a three stage cycle: 1) carboxylation, 2) reduction, and 3) regeneration of the acceptor (ribulose-1,5-bisphosphate)
The carboxylation phase

\[ 3 \left( \begin{array}{c} \text{H}_2\text{C} \text{OP} \\ \text{C} = \text{O} \\ \text{H} = \text{C} \text{OH} \\ \text{H}_2\text{C} \text{OP} \end{array} \right) + 3 \text{CO}_2 + 3 \text{H}_2\text{O} \rightarrow 6 \left( \begin{array}{c} \text{CO}_2\text{H} \\ \text{H} = \text{C} \text{OH} \\ \text{H}_2\text{C} \text{OP} \end{array} \right) \]

The reduction phase

\[ 6 \text{ATP} \rightarrow 6 \text{ADP} + 6 \text{NADPH} + 6 \text{NADP}^+ \]

\[ 6 \text{H}^+ \]

\[ 6 \text{PO}_4\text{H}^{2-} \]

\[ \text{P} = \text{PO}_3^{2-} \]

\[ \text{P}_i = \text{PO}_4\text{H}^{2-} \]
The reduction step happens after the CO₂ addition, where the ATP and NADPH made in the light reactions are used to make sugar. Thus, the two reactions are directly linked (one can not happen without the other)!
One 3-carbon sugar called a Triosephosphate

\[ P = \text{PO}_3^{2-} \]
\[ P_1 = \text{PO}_4H^{2-} \]
The Calvin Cycle regenerates the 5-carbon acceptor.
What are the fates of the triosephosphate (3C) product of photosynthesis?

1) Calvin cycle - regeneration of RuBP

2) Substrate for fatty acid and amino acid biosynthesis in the chloroplast

3) STARCH biosynthesis - short-term storage of carbon the chloroplast
   After condensation into a 6-carbon hexose, glucose-1-phosphate is pulled off and added to ATP forming ADP-glucose. ADP-glucose is added to a starch primer by Starch Synthase.

4) Export into the cytoplasm where it is the substrate for SUCROSE synthesis
   The 3-carbon triosephosphate is condensed into a hexose. One product is glucose -1-Phosphate. This is added to UTP, forming UDP-gucose. UDP-glucose plus fructose-6-phpsphate form Sucrose-Phosphate. This reaction is catalyzed by the enzyme, Sucrose Phosphate Synthase.
Key enzymes:

1) Starch synthase:
   ADP-G + primer --------> starch (amylose)

2) Sucrose-phosphate synthase
   F-6-P + UDP-G --------------> sucrose-phosphate + UDP

3) The Phosphate Translocator
Why not store and transport triosephosphate?

Two majors problems: 1) osmotic and 2) tie-up essential nutrient - Phosphate

Why make STARCH?

Photosynthetic output during the day is greater than needed by the cell or exported to other organs. Consequently, photosynthetic mesohphyll cells store excess carbohydrate as starch, and/or sucrose, for utilization at night. At night, some carbohydrate is broken down for respiration (energy), but a lot is exported to supply non-photosynthetic cells. Starch, versus sucrose, is often the major storage form of daily excess because it has no osmotic impact on the cell.
Pathways of starch and sucrose biosynthesis from triosephosphate
“carbon partitioning inside the photosynthetic cell”

Chloroplast

- ATP + NADPH
- PGA
- CO₂
- Ru1,5 BP
- ATP
- Triose-P
- F1,6 BP
- F-6-P
- G-1-P + ATP
- G-6-P
- Triosephosphate
- Starch

Cytoplasm

- Pi or PGA
- ATP + NADH
- Triose-P
- F1,6 BP
- F-6-P
- G-1-P
- G-6-P
- Sucrose-phosphate synthase
- Sucrose-phosphate + UDP
- Sucrose
- Export or short term storage
Fate of assimilated carbon over a 24 hr period

<table>
<thead>
<tr>
<th></th>
<th>Soybean mg CH$_2$O/ dm$^2$</th>
<th>Spinach mg CH$_2$O/ dm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon exported (during the day)</td>
<td>184</td>
<td>132</td>
</tr>
<tr>
<td>Sucrose stored</td>
<td>6.8</td>
<td>96</td>
</tr>
<tr>
<td>Starch stored</td>
<td>74</td>
<td>42</td>
</tr>
<tr>
<td>Carbon exported at night</td>
<td>80.8</td>
<td>138</td>
</tr>
<tr>
<td>TOTAL Carbon</td>
<td>268</td>
<td>271</td>
</tr>
</tbody>
</table>
H₂O LIGHT

Chloroplast

ATP NADPH

O₂ NADP⁺

CO₂

CO₂

NADP⁺

ADP

Pi

ATP

NADPH

[CH₂O] (sugar)

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BUT, there is a problem with RUBISCO!
In addition to adding CO$_2$, it can also add O$_2$ (hence the name)
Metabolism of 2-phosphoglycolate is expensive. It results in the release of CO₂ and NH₄⁺. The NH₄⁺ must be quickly added to a carbon skeleton to make an amino acid because it is toxic and re-assimilating the CO₂ costs ATP and NADPH.

This is called Photorespiration. In C₃ plants, costs 20% - 30% of the energy!
Photosynthesis:

$\text{CO}_2$ and the Water

“catch 22”
The water - carbon dioxide paradox!

Leaf cross section

Vein

Stomata

CO₂ + O₂

Mesophyll

5 µm

Outer membrane

Intermembrane space

Inner membrane

Thylakoid granum

Stroma

Thylakoid space

Mesophyll cell

1 µm
Water is a real issue as plants acquire CO$_2$. Thus, some plants have developed novel strategies to minimize water loss during CO$_2$ uptake.

How do they do that???
C₄ Plants

- C₄ plants decrease water loss by using a different enzyme (not RUBISCO) for the initial capture of CO₂ from the atmosphere. This other enzyme has about a 10-fold higher affinity for CO₂ and this means the diffusion gradient for CO₂ into the leaf is much greater than cells using only RUBISCO. This enzyme, PEP carboxylase, incorporates CO₂ into four-carbon compounds in mesophyll cells (hence C₄).

- These four-carbon compounds are exported to bundle-sheath cells, where they release CO₂ that is then used in the Calvin cycle.
Because of PEP carboxylase, the diffusion gradient for CO₂ into the leaf is larger than for RUBISCO driven plants. Therefore, the stomatal pore can be closed down while still getting the same amount of CO₂ in, and with a smaller pore, LESS water is lost!.

Key Concepts
1. PEP carboxylase
2. Bundle-sheath
CAM Plants

• CAM plants also use PEP carboxylase, but their BIG difference is that they open their stomata at night, incorporating CO$_2$ into organic acids

• Stomata close during the day, and CO$_2$ is released from organic acids and used in the Calvin cycle

• Thus, in C$_4$, CO$_2$ uptake is spatially separated form RUBISCO. In CAM plants, it is temporally separated!
Bundle-sheath cell

Mesophyll cell

1. CO₂ incorporated into four-carbon organic acids (carbon fixation)

2. Organic acids release CO₂ to Calvin cycle

Sugarcane

Pineapple

C₄

CALVIN CYCLE

Sugar

Day

Night

Organic acid

CO₂

Spatial separation of steps

(b) Temporal separation of steps

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$C_4$ plants grow very well because of the water use efficiency (corn as example). Moreover, high CO$_2$ in bundle sheath eliminates (±) photorespiration.

CAM plants grow slowly because they are limited by how much organic acid they can store overnight. Many desert plants use CAM because of high heat, low relative humidity and low water availability.
In low light, photosynthesis is limited by light energy. As light increases, CO$_2$ limits photosynthesis. Full sun is 2000 $\mu$mol m$^{-2}$ s$^{-1}$. 

![Graph showing the relationship between photosynthetic CO$_2$ assimilation and absorbed light.]
In high light, too much energy will harm the chloroplast.
What happens with excess light energy?

1. Generate heat

2. Remove through energy consuming chemical reactions

3. Irreversible photodamage - repair when possible or sacrifice the leaf
Plants move chloroplasts to optimize photosynthesis and, in high light, to protect them from too much energy!
This is also a problem for algae!!
OK, based on light reactions and CO2 assimilation, what are potential targets for improvement in photosynthesis?
A note comparing energy availability in higher plants
What are the energy molecules for biofuels?

Useful substrates (feedstocks) for biofuels are: starch, cellulose and lipids. Starch and cellulose are polymers of glucose. Lipids are fatty acids linked to a "head" group.

Relative energy content:

Fatty acids in lipids = 39 kJ/gram

Carbohydrate (glucose) = 17 kJ/gram

Diesel = 48 kJ/gram
Cellulose

Starch

Lipid

TAG
What is the distribution of these energy molecules in plants?

**Corn seed (typical values, dry weight):**
Carbohydrate (starch) 30 – 50%
Protein = 7-27%
Oil = 5 – 16% (high oil equals low yield)

Note protein and starch are inversely correlated.
Average dw yields = 150 bu/acre = 8,400 lbs/acre

**Soybean seed:**
Oil = 19%
Protein = 38%
Soluble sugar (sucrose) = 10%
Insoluble sugar = 23%
Mineral = 5%

Average dw yield = 40 bu/acre = 2400 lb/acre
OK, what is the energy content per acre for corn and soybean?

**Corn (carbohydrate)**
4000 lb/acre x 454g/lb x 17 kJ/g = 30,872,000 kJ/acre

**Soybean (oil)**
480 lb/acre x 454 g/lb x 39 kJ/g = 8,498,990 kJ/acre

Thus, soybean yields only 27% of the energy of corn.

What about new energy crops? For Miscanthus, dry wt yields of cellulose is approaching 40,000 lb/acre, or about 10-times more energy than available in starch from corn seed. That is why long-term biofuel solutions from higher plants focus on cellulose.

What about oil from algae. Recent calculation of maximum production at 5,000 gal/acre/yr, which equals:
7 lb/gal x 454 g/lb x 5000 gal/acre/yr x 39 kJ/g = 619,710,000 kJ/acre/yr

That is about 20-times the energy available from starch in corn seed, if one can get close to maximum production possibility.