Photosynthesis - Photosynthetic carbon reduction (PCR)

- Overview
- Calvin-Benson cycle (C_3 pathway)
- Regulation
- Photorespiration
- C_4 Photosynthesis
- CAM photosynthesis
Overview

- Three stages:
- CO$_2$ reduced to triose phosphate
- Uses ATP and NADPH from light reactions
- Occurs in the stroma
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2$  

• Light energy converted to chemical energy of ATP and NADPH
• $\text{CO}_2$ is reduced, water is oxidized
• $K_{\text{eq}} = 10^{-496}$
Calvin-Benson cycle ($C_3$ pathway)

- Discovery
- use of $^{14}$CO$_2$ and the green alga; Chlorella
- 2 sec exposure
- 1st product a $C_3$ acid
- Researchers found a 5 carbon acceptor molecule
- Ribulose 1,5-bisphosphate (RuBP)
Stages of Calvin-Benson cycle

- Three stages
- carboxylation
- reduction
- regeneration
Carboxylation

- Rubisco (large subunits= 55kd and small sub-unit 13kd), 30% of total leaf protein
- coded by chloroplast (lg) and nuclear (small) genes
- 16 sub-units (8 lg/8small)
- spontaneous reaction no energy required, $\Delta G = -51.9 \text{ kJ/mol}$
- Maximal Catalytic rate = 3/s
- $K_m (\text{CO}_2)= 12 \text{ um}$
- forms 2 (3-PGA)
Reduction

- Two steps
- Requires 2 ATP & NADPH
- Forms triose phosphate
Stage 3: Regeneration

- reforms RuBP
- requires 1 ATP
- Overall: 3 ATP/2 NADPH
### Summary

**TABLE 8.1**
Reactions of the Calvin cycle (Part 1)

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ribulose-1,5-bisphosphate</td>
<td>6 Ribulose-1,5-bisphosphate + 6 CO₂ + 6 H₂O → 12 (3-phosphoglycerate) + 12 H⁺</td>
</tr>
<tr>
<td>carboxylase/oxygenase</td>
<td></td>
</tr>
<tr>
<td>2. 3-Phosphoglycerate kinase</td>
<td>12 (3-Phosphoglycerate) + 12 ATP → 12 (1,3-bisphosphoglycerate) + 12 ADP</td>
</tr>
<tr>
<td>3. NADP:glyceraldehyde-3-phosphate</td>
<td>12 (1,3-Bisphosphoglycerate) + 12 NADPH + 12 H⁺ → 12 glyceraldehye-3-phosphate + 12 NADP⁺ + 12 P_i</td>
</tr>
<tr>
<td>dehydrogenase</td>
<td></td>
</tr>
<tr>
<td>4. Triose phosphate isomerase</td>
<td>5 Glyceraldehyde-3-phosphate → 5 dihydroxyacetone-3-phosphate</td>
</tr>
<tr>
<td>5. Aldolase</td>
<td>3 Glyceraldehyde-3-phosphate + 3 dihydroxyacetone-3-phosphate → 3 fructose-1,6-bisphosphate</td>
</tr>
<tr>
<td>6. Fructose-1,6-bisphosphatase</td>
<td>3 Fructose-1,6-bisphosphate + 3 H₂O → 3 fructose-6-phosphate + 3 P_i</td>
</tr>
<tr>
<td>7. Transketolase</td>
<td>2 Fructose-6-phosphate + 2 glyceraldehyde-3-phosphate → 2 erythrose-4-phosphate + 2 xylulose-5-phosphate</td>
</tr>
</tbody>
</table>

*Note: P_i stands for inorganic phosphate.*
Regulation of Calvin Cycle

- **Rubisco**
- light activates electron transport
- pH stroma goes up from 7 → 8
- Mg\(^{2+}\) increases in stroma
- NADPH allosteric activator
- Rubisco Activase catalyzes carbamate formation
  - CO\(_2\) required
Regeneration Enzymes

- Light activated through PS I
- Ferrodoxin-Thioredoxin
- Gly 3-P dehydrogenase
- FBPase
- Sedoheptulose 1,7 Bis phosphotase
- Ribulose 5-P kinase
<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubisco</td>
<td>Carbon fixation in the Calvin cycle</td>
</tr>
<tr>
<td>Fructose 1,6-bisphosphatase</td>
<td>Gluconeogenesis</td>
</tr>
<tr>
<td>Glyceraldehyde 3-phosphate dehydrogenase</td>
<td>Calvin cycle, gluconeogenesis, glycolysis</td>
</tr>
<tr>
<td>Sedoheptulose bisphosphatase</td>
<td>Calvin cycle</td>
</tr>
<tr>
<td>Glucose 6-phosphate dehydrogenase</td>
<td>Pentose phosphate pathway</td>
</tr>
<tr>
<td>Phenylalanine ammonia lyase</td>
<td>Lignin synthesis</td>
</tr>
<tr>
<td>Ribulose 5′-phosphate kinase</td>
<td>Calvin cycle</td>
</tr>
<tr>
<td>NADP⁺-malate dehydrogenase</td>
<td>C₄ pathway</td>
</tr>
</tbody>
</table>
Photorespiration

- React w/O₂
- Km (O₂) = 250 um
- Atmosphere = 21% O₂
- CO₂ limiting conditions: such as drought, high temperatures
- Three organelles
  - chloroplast
  - mitochondria
  - peroxisome
- loss of fixed CO₂
Photorespiration
Adaptations to limited CO₂

- C₄ pathway: C₄ acid 1st product
- Discovered by Hatch and Slack in sugar cane
- Shuttle system
- PEP carboxylase
- Increase CO₂ at site of Calvin cycle
- Under high light/high temperature conditions
C₄ pathway
# Reactions

## TABLE 8.3
Reactions of the C₄ photosynthetic carbon cycle

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Phosphoenolpyruvate (PEP) carboxylase</td>
<td>Phosphoenolpyruvate + HCO₃⁻ → oxaloacetate + Pᵢ</td>
</tr>
<tr>
<td>2. NADP:malate dehydrogenase</td>
<td>Oxaloacetate + NADPH + H⁺ → malate + NADP⁺</td>
</tr>
<tr>
<td>3. Aspartate aminotransferase</td>
<td>Oxaloacetate + glutamate → aspartate + α-ketoglutarate</td>
</tr>
<tr>
<td>4. NAD(P) malic enzyme</td>
<td>Malate + NAD(P)⁺ → pyruvate + CO₂ + NAD(P)H + H⁺</td>
</tr>
<tr>
<td>5. Phosphoenolpyruvate carboxykinase</td>
<td>Oxaloacetate + ATP → phosphoenolpyruvate + CO₂ + ADP</td>
</tr>
<tr>
<td>6. Alanine aminotransferase</td>
<td>Pyruvate + glutamate ↔ alanine + α-ketoglutarate</td>
</tr>
<tr>
<td>7. Adenylate kinase</td>
<td>AMP + ATP → 2 ADP</td>
</tr>
<tr>
<td>8. Pyruvate–orthophosphate dikinase</td>
<td>Pyruvate + Pᵢ + ATP → phosphoenolpyruvate + AMP + PPᵢ</td>
</tr>
<tr>
<td>9. Pyrophosphatase</td>
<td>PPᵢ + H₂O → 2 Pᵢ</td>
</tr>
</tbody>
</table>

*Note: Pᵢ and PPᵢ stand for inorganic phosphate and pyrophosphate, respectively.*
## Energetics

### TABLE 8.4
Energetics of the C₄ photosynthetic carbon cycle

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products/Intermediates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoenolpyruvate + H₂O + NADPH + CO₂ (mesophyll)</td>
<td>→ malate + NADP⁺ + P₁ (mesophyll)</td>
</tr>
<tr>
<td>Malate + NADP⁺</td>
<td>→ pyruvate + NADPH + CO₂ (bundle sheath)</td>
</tr>
<tr>
<td>Pyruvate + P₁ + ATP</td>
<td>→ phosphoenolpyruvate + AMP + PP₁ (mesophyll)</td>
</tr>
<tr>
<td>PP₁ + H₂O</td>
<td>→ 2 P₁ (mesophyll)</td>
</tr>
<tr>
<td>AMP + ATP</td>
<td>→ 2ADP</td>
</tr>
</tbody>
</table>

**Net:** CO₂ (mesophyll) + ATP + 2 H₂O → CO₂ (bundle sheath) + 2ADP + 2 P₁

**Cost of concentrating CO₂ within the bundle sheath cell = 2 ATP per CO₂**

Note: As shown in reaction 1 of Table 8.3, the H₂O and CO₂ shown in the first line of this table actually react with phosphoenolpyruvate as HCO₃⁻. P₁ and PP₁ stand for inorganic phosphate and pyrophosphate, respectively.
Regulation

- Thioredoxin: NADP: malate dehydrogenase
- PEP carboxylase: covalent modification by phosphorylation/dephosphorylation; regulated by phosphorylation by PEP carboxylase-kinase to make active
- Pyruvate Pi dikinase: ADP-dependent phosphorylation when light intensity drops
Crassulacean Acid Metabolism

• Initial CO₂ fixation step which occurs at night.
• After the initial carboxylation, malic acid (the first stable product after fixation) is then sequestered into the central vacuole during the night period.
• In the following light period, the stomata close and the malic acid returns to the cytoplasm for decarboxylation.
• The released CO₂ is then assimilated through the C₃ pathway.
Pathway

Dark: Stomata opened
- CO₂ uptake and fixation: leaf acidification
- Atmospheric CO₂
- Open stoma permits entry of CO₂ and loss of H₂O

Light: Stomata closed
- Decarboxylation of stored malate and refixation of internal CO₂: deacidification
- Closed stoma prevents H₂O loss and CO₂ uptake