Chem 352 - Lecture 9
Photosynthesis

Introduction

The evolution of photosynthesis was a milestone for living system on earth

- It allowed energy to be obtain from an extraterrestrial source.
- It lead to the creation of an oxygenated atmosphere along with a food source for non-photosynthesizing organisms.

Introduction

There are two parts to photosynthesis

- **Light reactions**
  - Shares much in common with the electron transport chain and ATP synthase.
- **Dark reactions**
  - Fixes atmospheric CO_2 and shares much in common with Gluconeogenesis and the Pentose Phosphate Pathway.

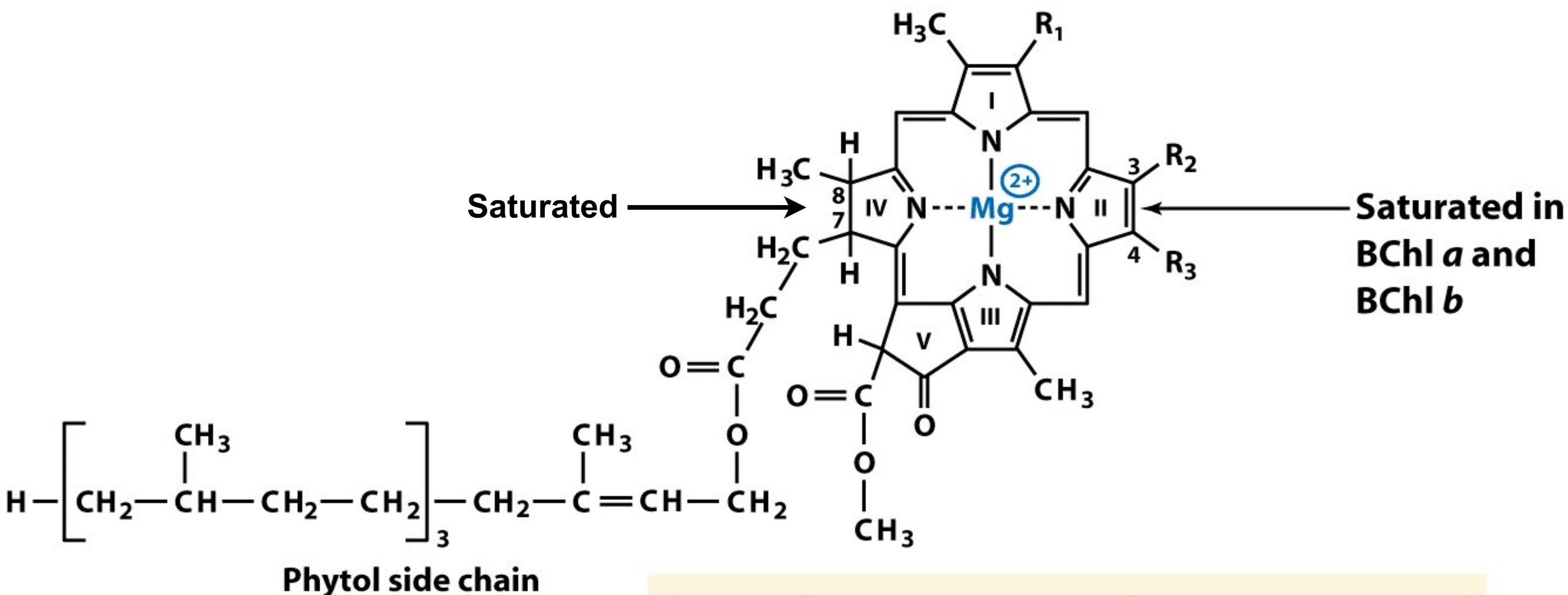
Introduction

- The light reactions take place in complex structures called **photosystems**.
- Light energy is used to energetically excite electrons, and that energy is then used to make either ATP or reduced NADPH + H^+.

Introduction

- The light reactions take place in complex structures called **photosystems**.
- There are two different types of photosystems, PSI and PSII
    - Some organisms have one or the other and some have both.

The Light-gathering Pigments



Chl species	R_1	R_2	R_3
Chl *a*	$-CH=CH_2$	$-CH_3$	$-CH_2-CH_3$
Chl *b*	$-CH=CH_2$	$-C(=O)-H$	$-CH_2-CH_3$
BChl *a*	$-C(=O)-CH_3$	$-CH_3$	$-CH_2-CH_3$
BChl *b*	$-C(=O)-CH_3$	$-CH_3$	$-CH=CH_2$

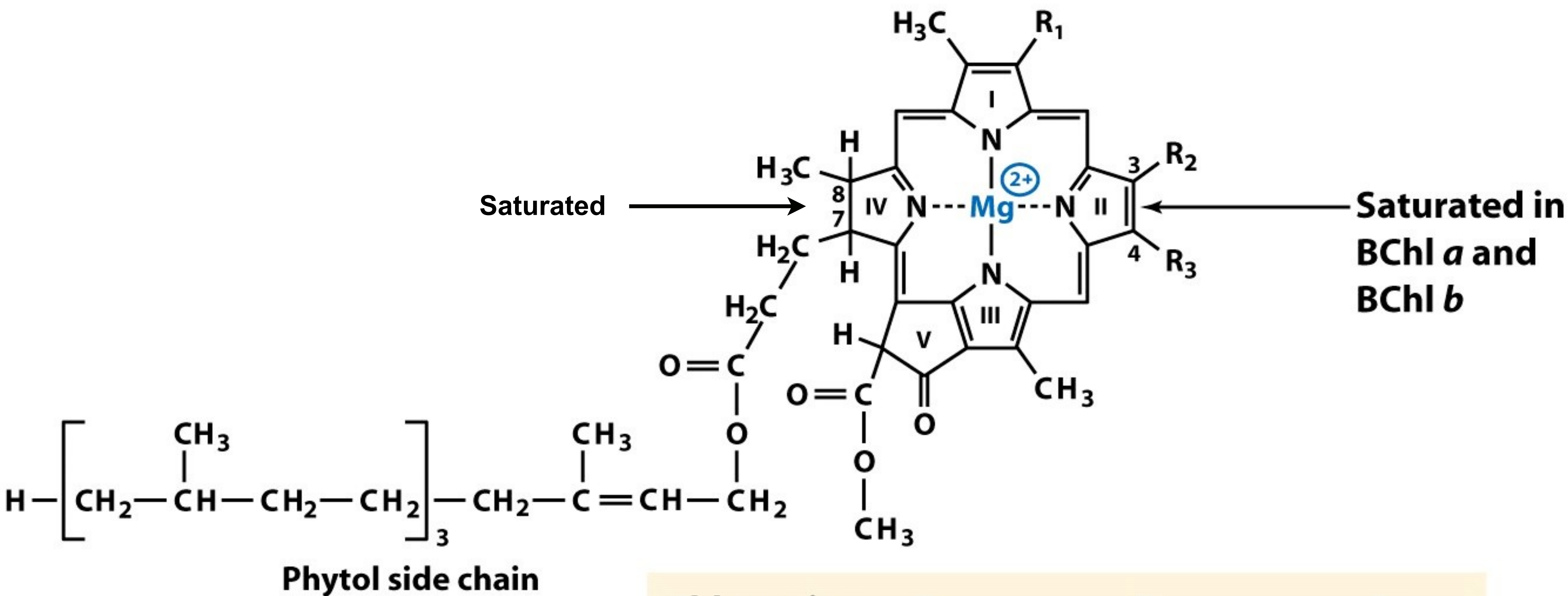
(bacterial)

Oxidation and reduction occurs on the tetrapyrrole ring.

Light-Harvesting Pigments

- Chlorophylls
- Associated Pigments
  - β-carotene
  - xanthophylls
  - Phycobilins
  - et al.

Light-Harvesting Pigments



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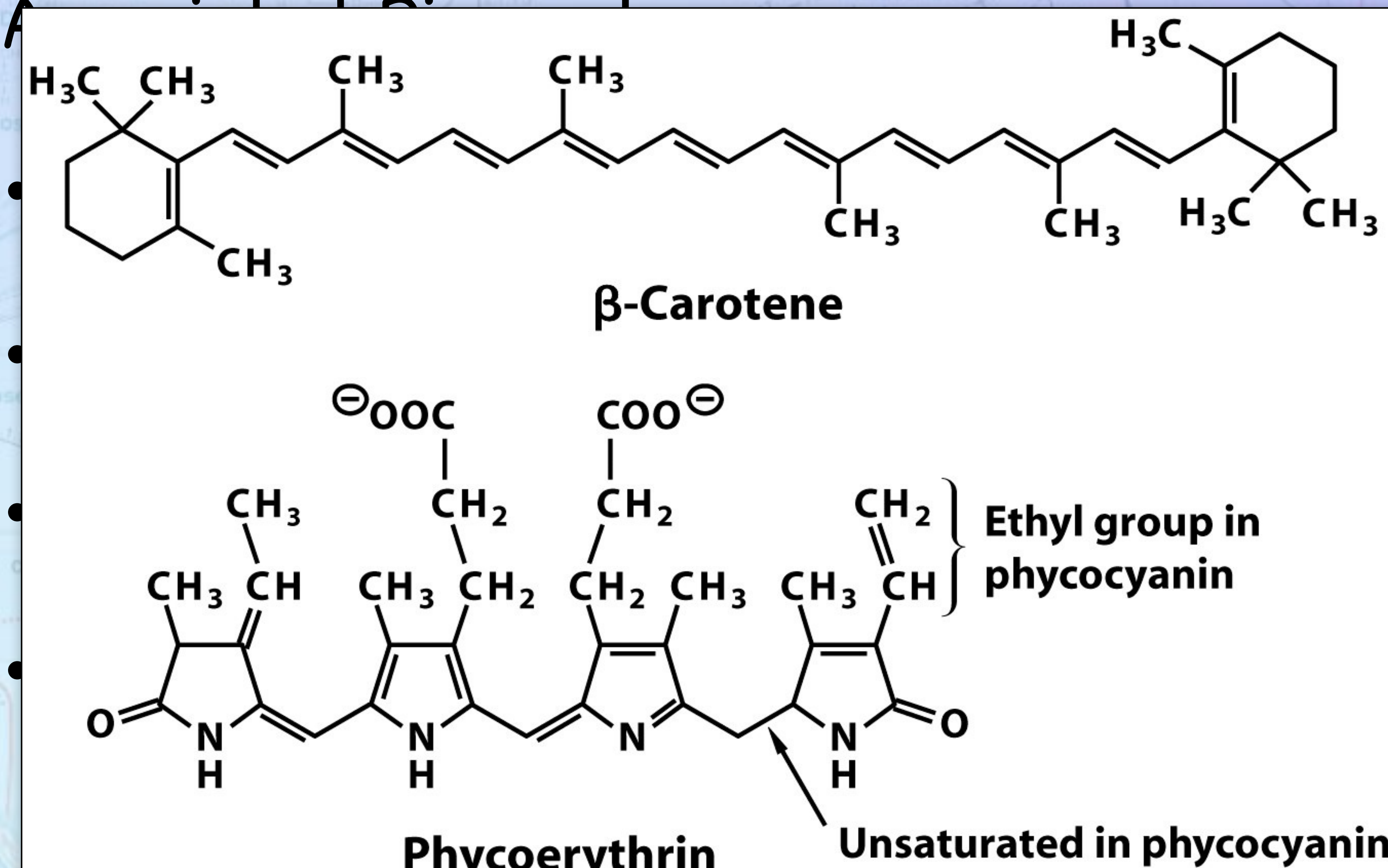
Light-Harvesting Pigments

- Chlorophylls



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Light-Harvesting Pigments

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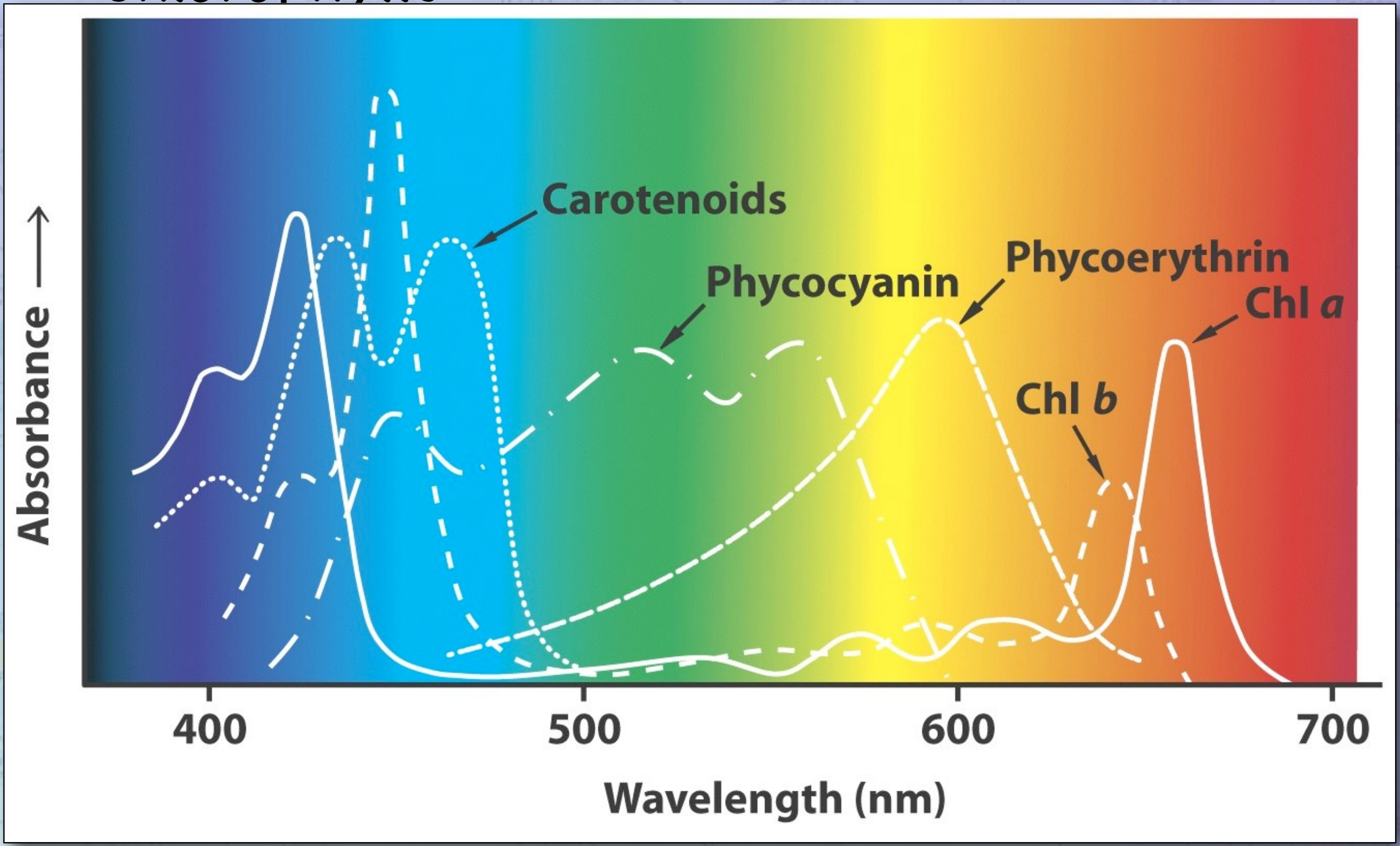

Light-Harvesting Pigments

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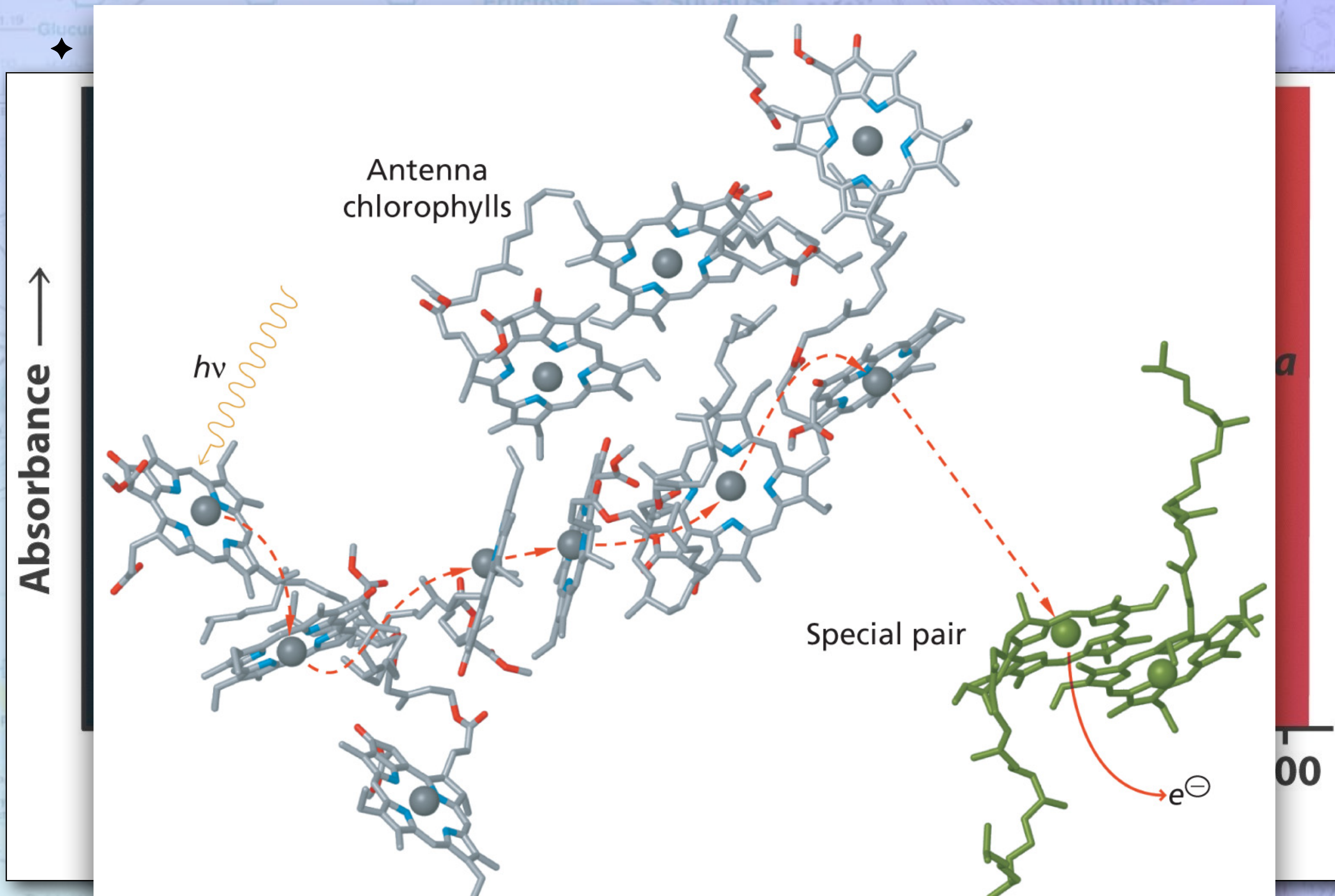
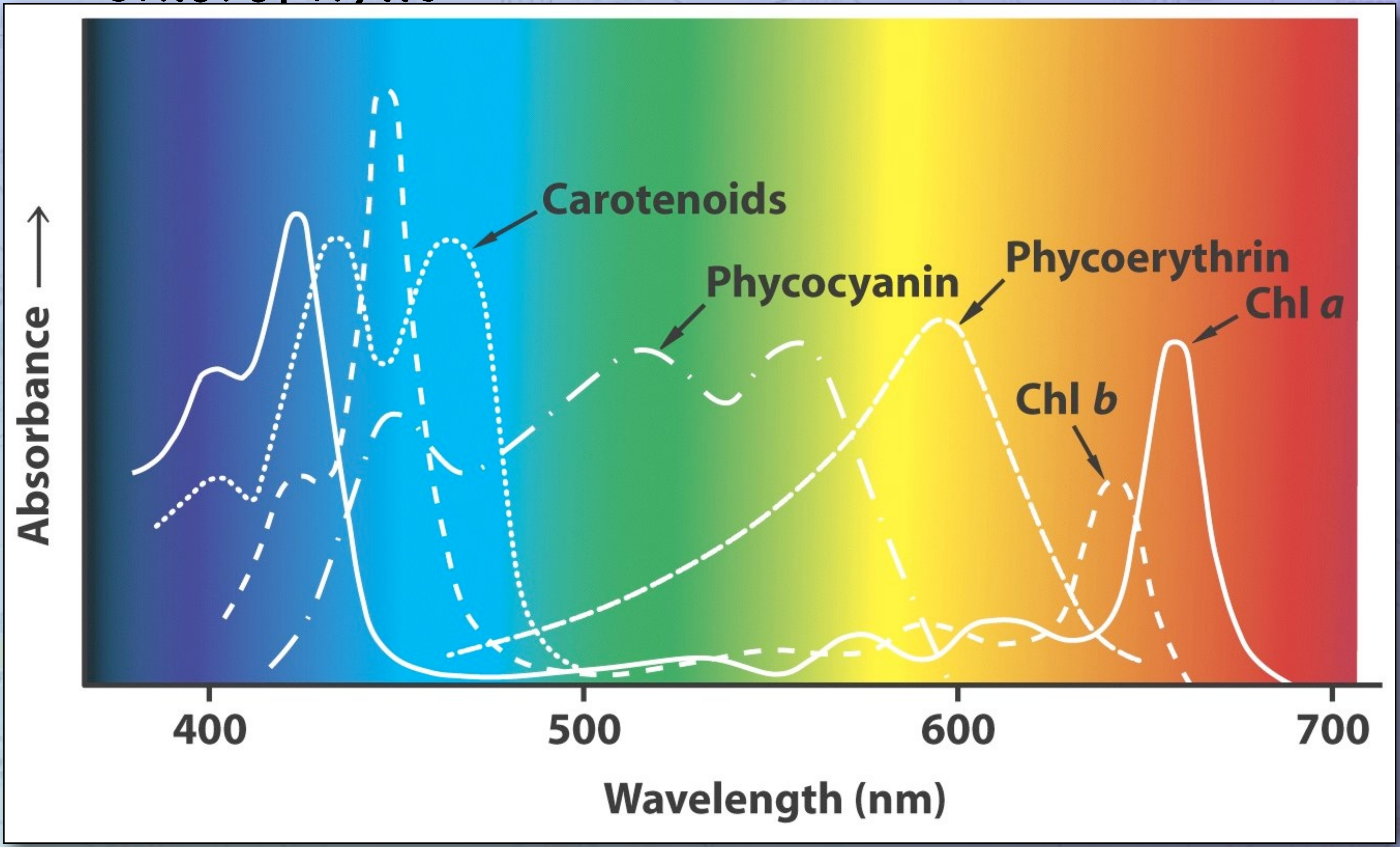


Light-Harvesting Pigments

- Chlorophylls



Light-Harvesting Pigments

- Chlorophylls
- Associated Pigments
  - β-carotene
  - xanthophylls
  - Phycobilins
  - et al.

Light-Harvesting Pigments

Photosystems have a special pair of chlorophylls called the **special pair**.

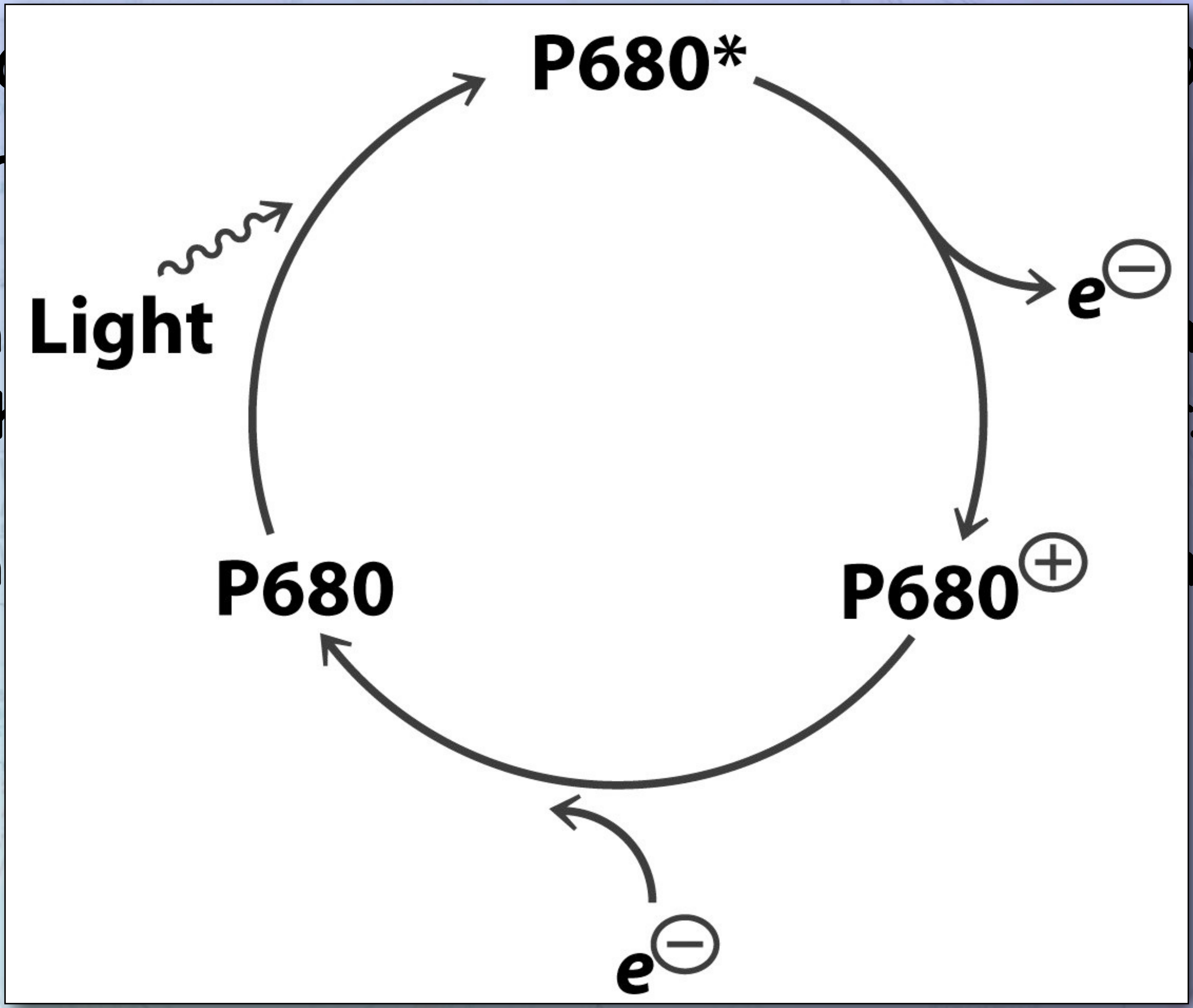
- This is where light energy is used to remove a high energy electron from special pair.
- This makes them a strong oxidizing agent.

Light-Harvesting Pigments

Phot[...] [...]f

chlor[...] [...]r.

- Th[...] [...]nove a k[...] [...].
- Th[...] [...]t.

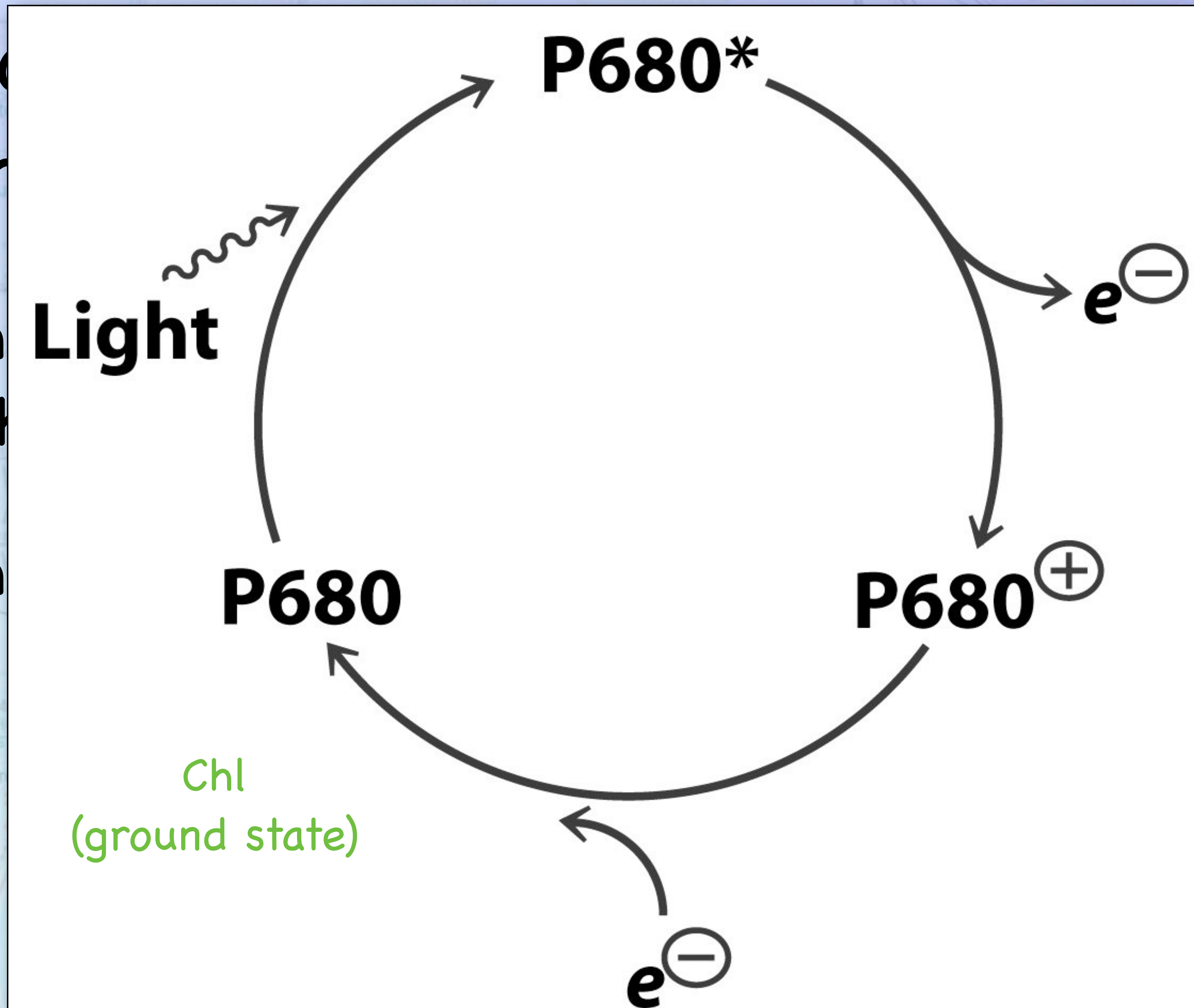


Light-Harvesting Pigments

Phot… …f

chlor… …r.

- Th… …move
  a k… …:
- Th… …t.

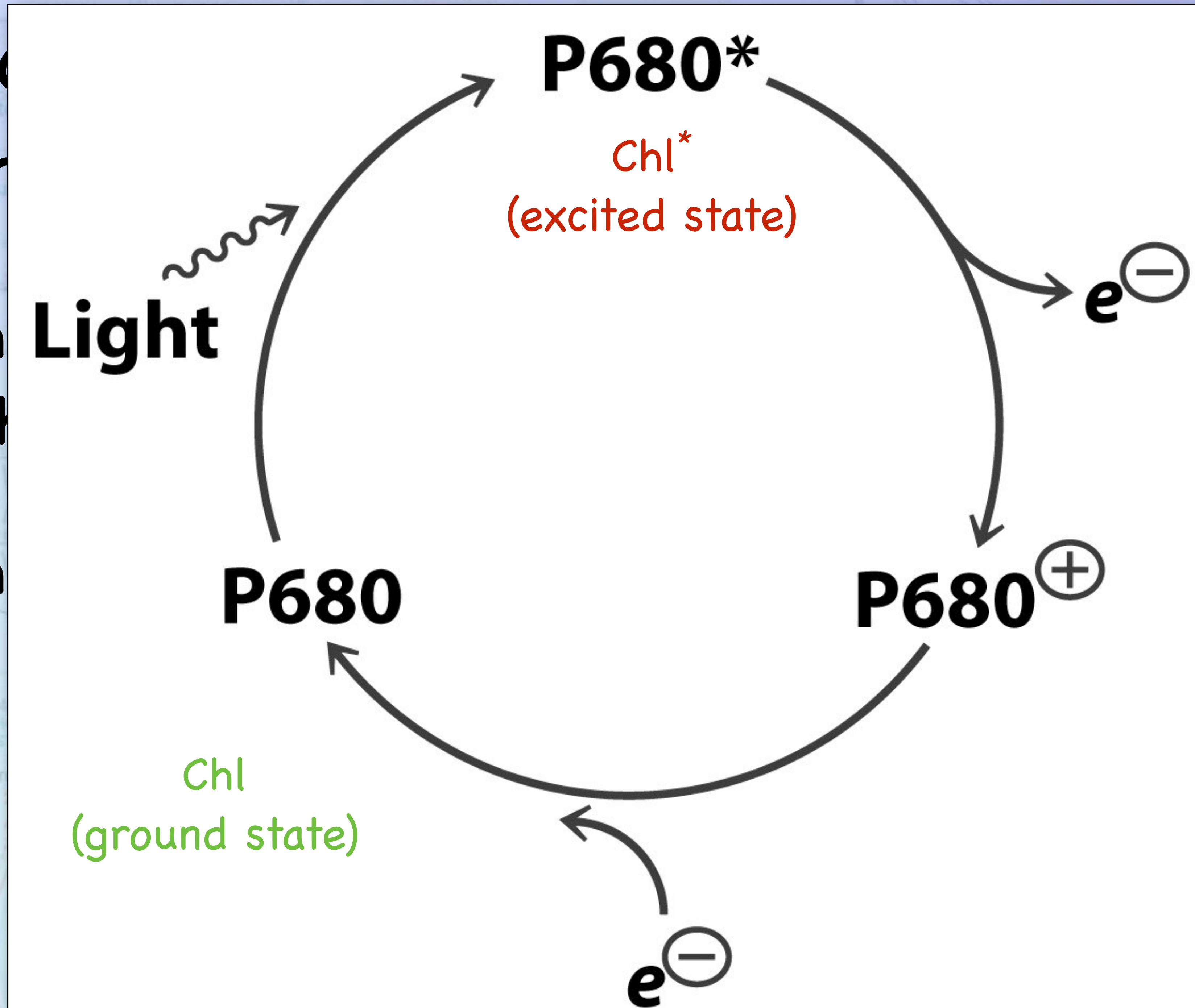


Light-Harvesting Pigments

Phot … of

chlor … r.

- Th … move
  a … .
- Th … nt.



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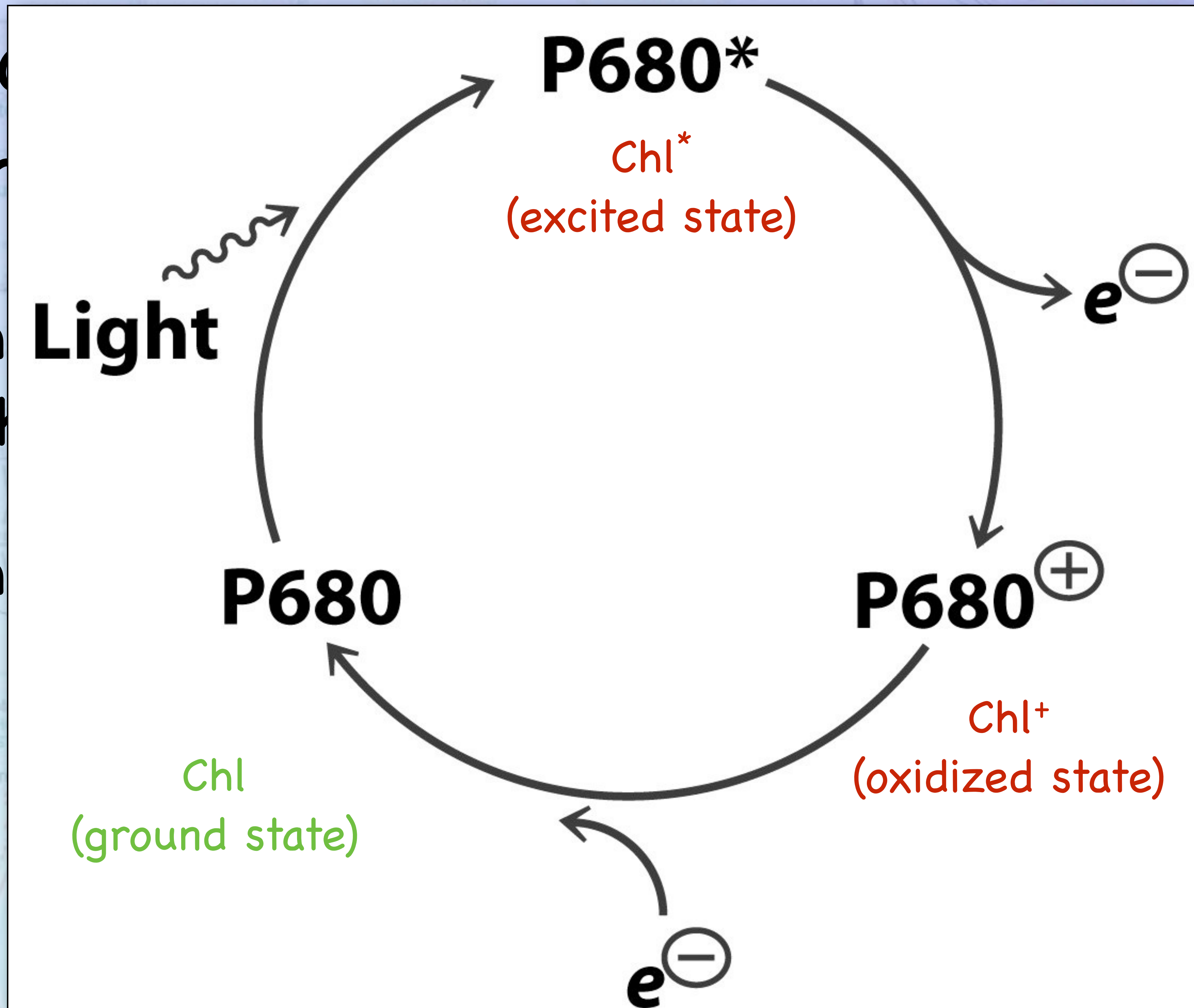

Light-Harvesting Pigments

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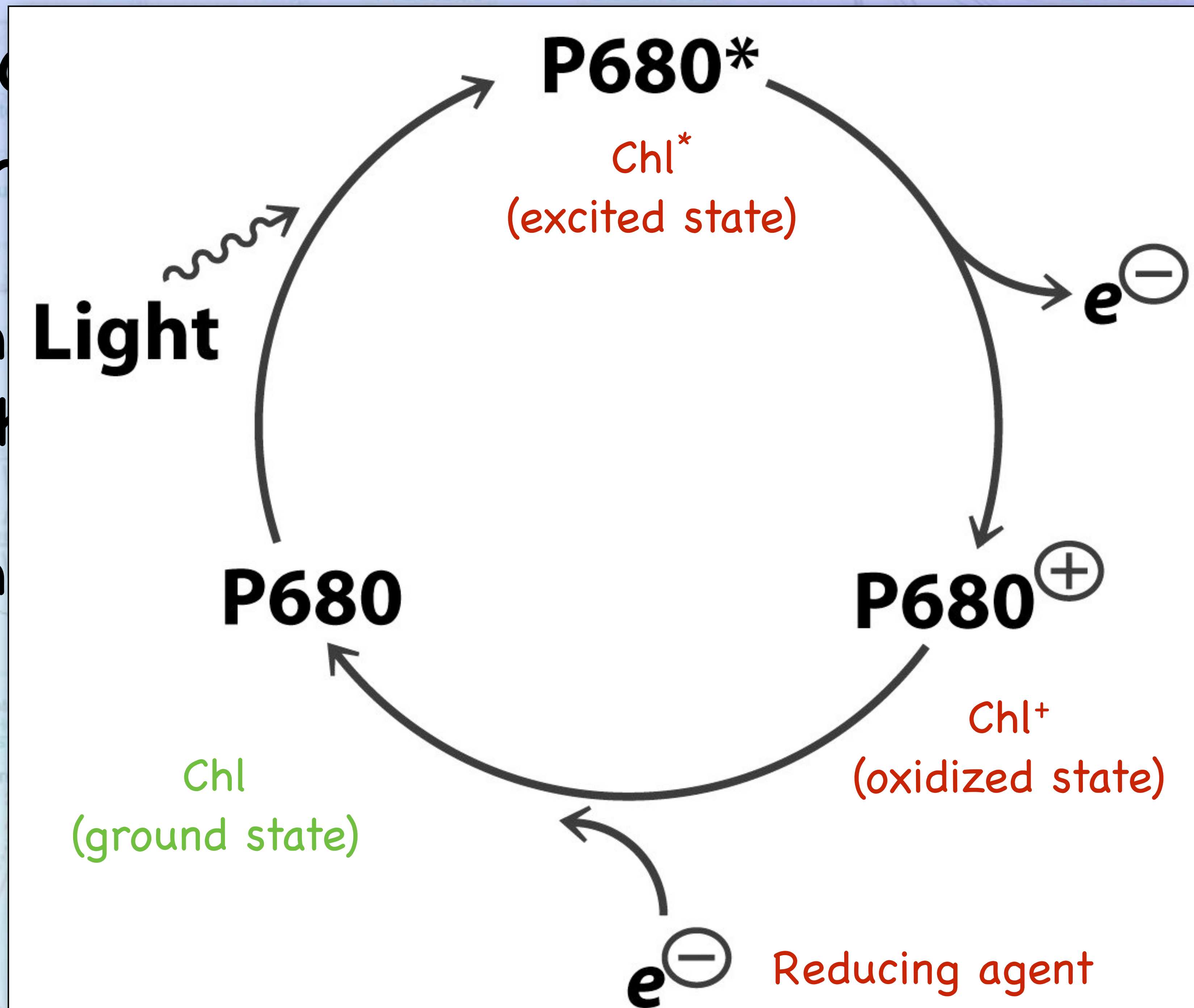


Photosystem II (PSII)

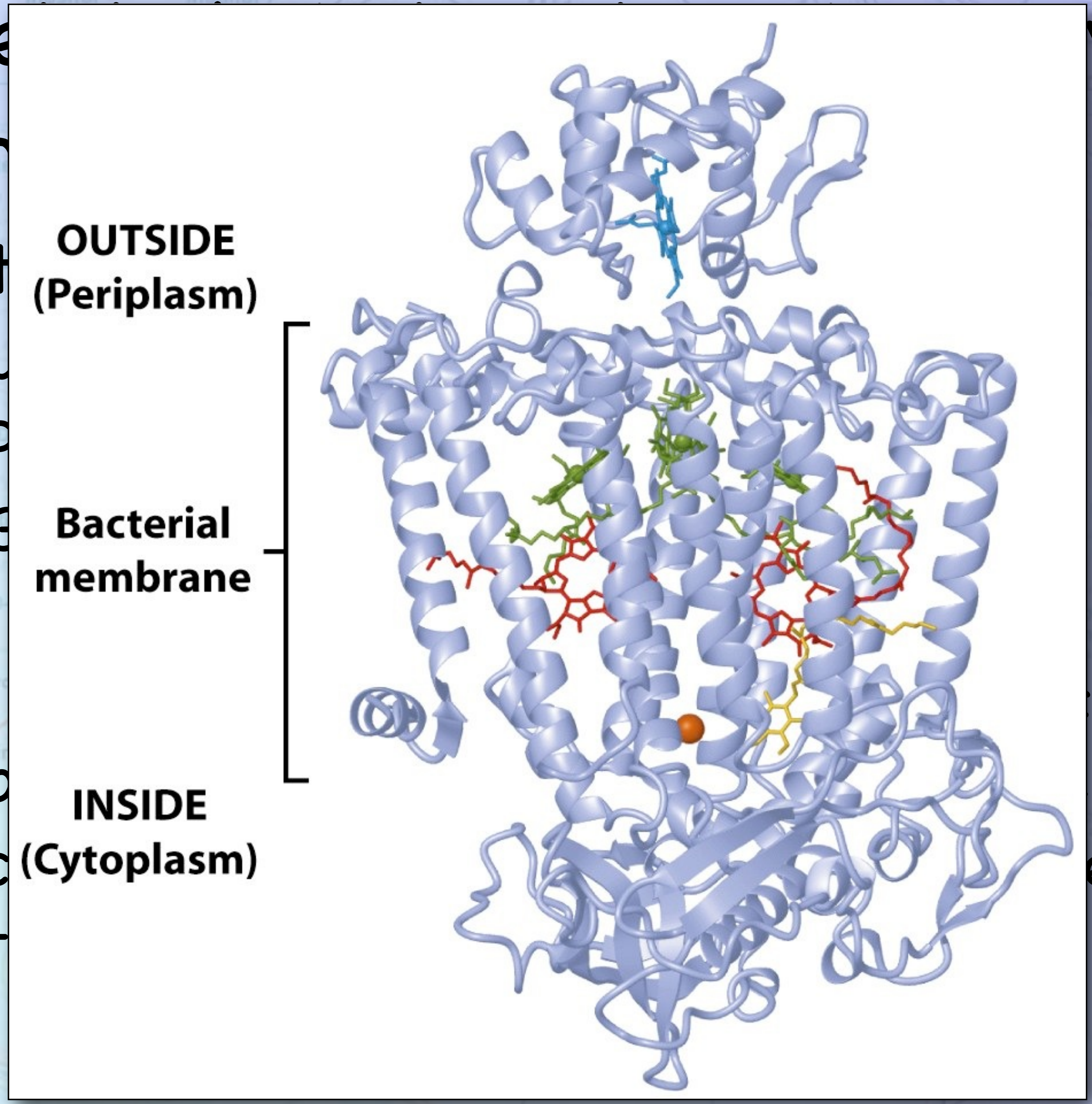
Two related photosystems have evolved in the the last 2.8 billion years.

- Photosystem II (PSII)
  - Found in
    - Purple bacteria
    - Green filamentous bacteria
      - both are strict anaerobes
- PSII is combined with cytochrome bc to create a proton gradient that is used to synthesize ATP.
    - cytochrome bc is complex III from the electron transport chain.

Photosystem II (PSII)

Two re... volved in the th...

- Phot...
  - Fou...
    - P...
    - G...
      - ...
- PSII ... create a proto... ATP.
  - c... e electron t...



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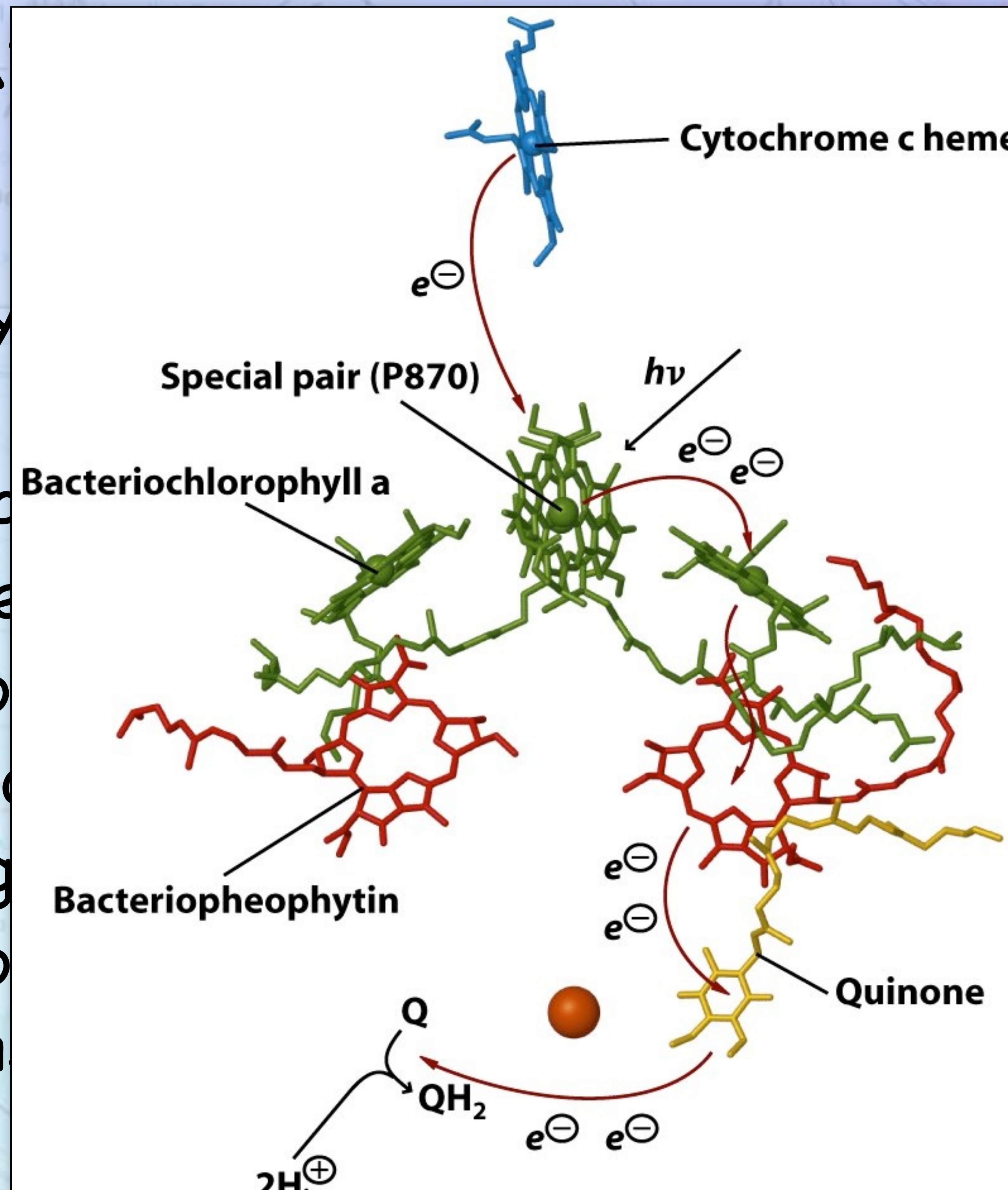

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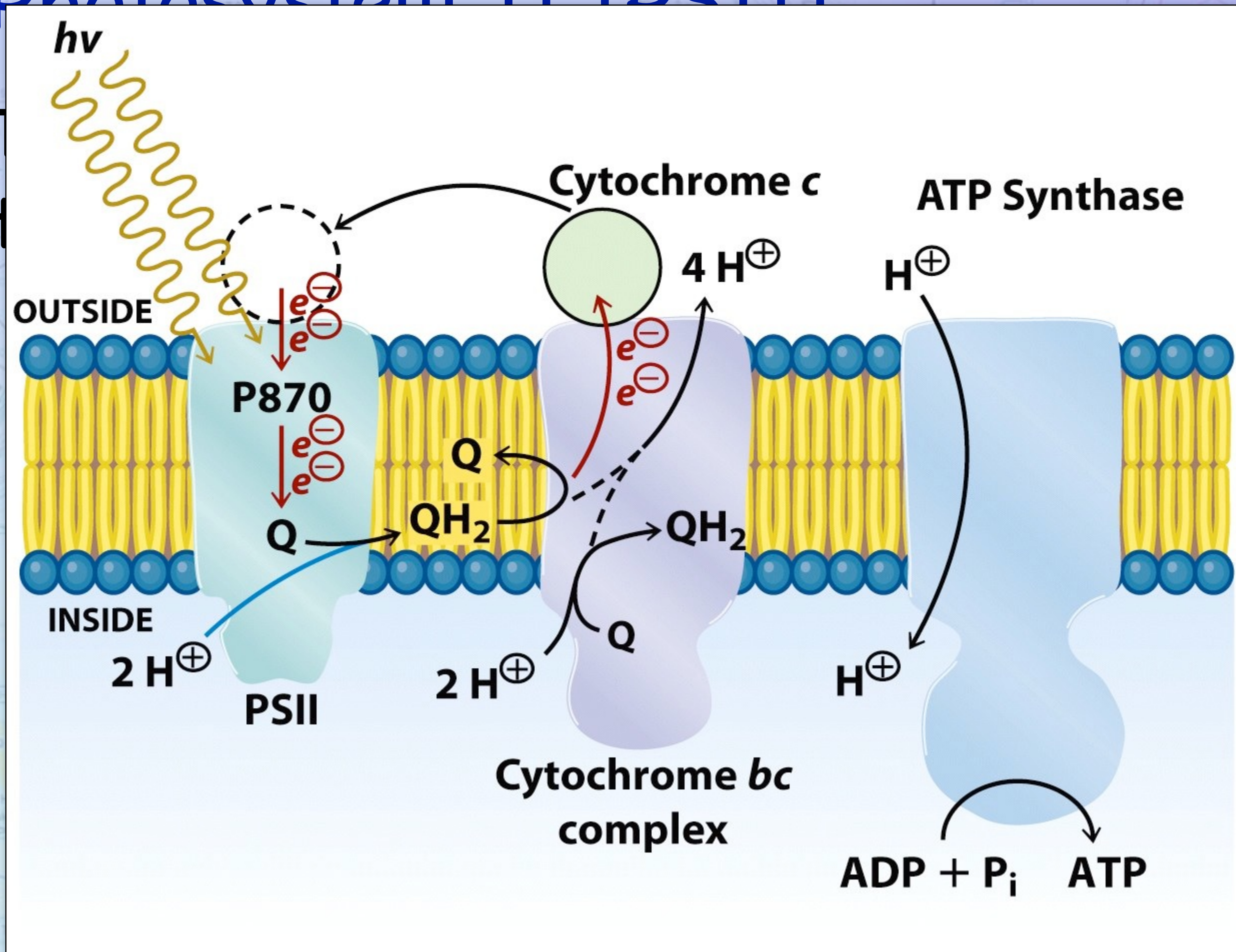

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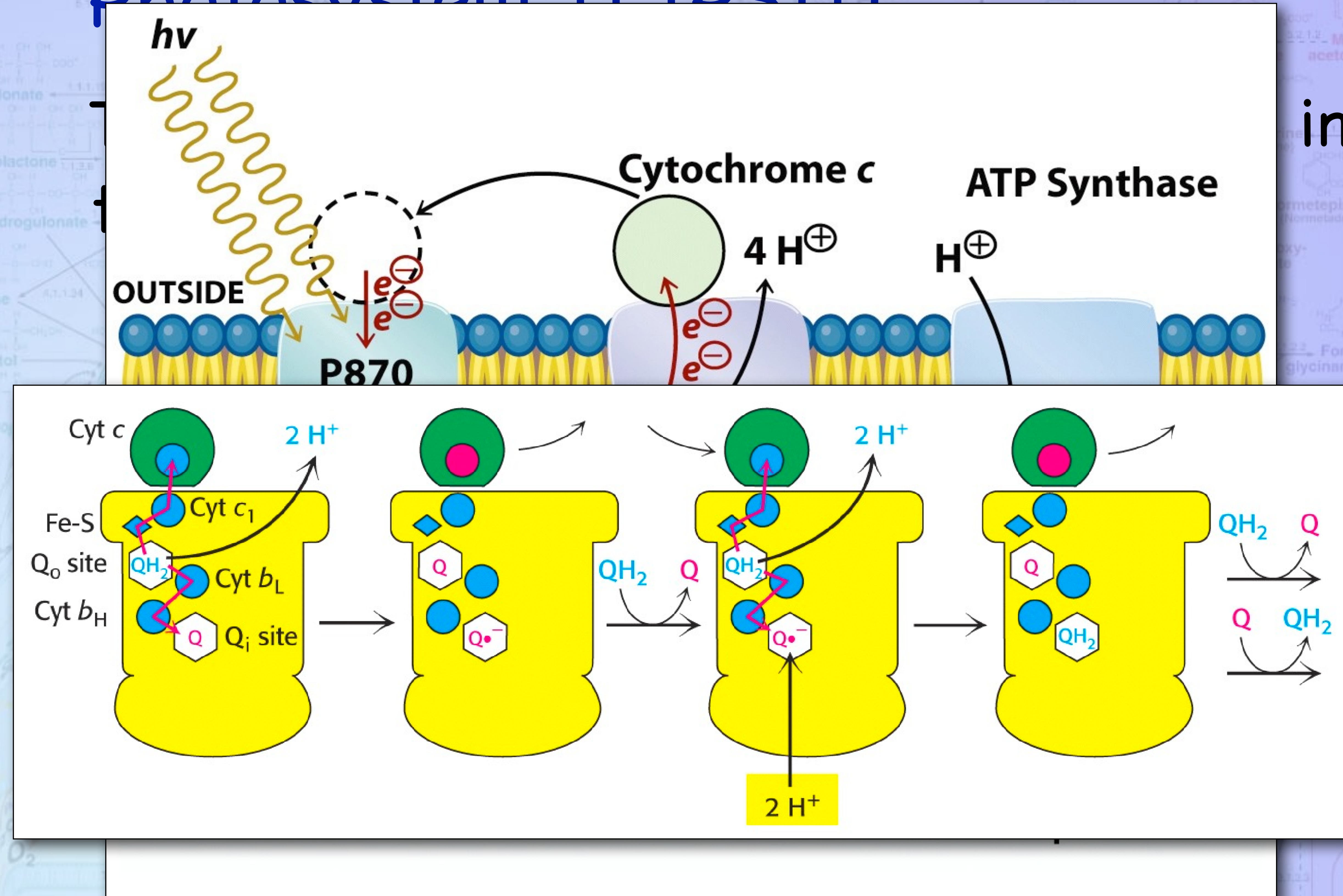

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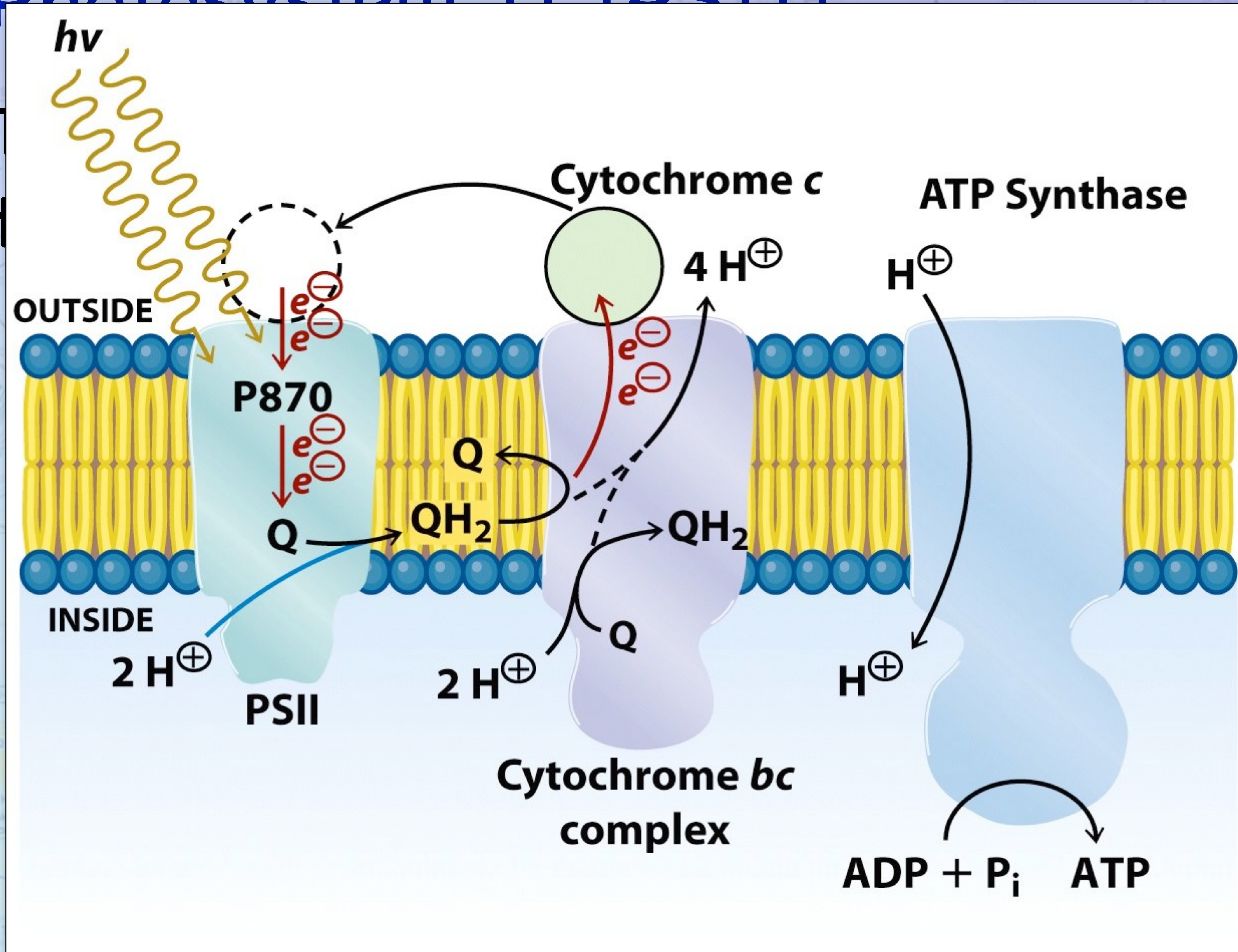

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Table 15.1 Photosystem II reactions

PSII:	$2\ P870 + 2\ \text{photons} \longrightarrow 2\ P870^{\oplus} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
Cyt bc_1:	$2\ QH_2 + 2\ \text{cyt}\ c\ (Fe^{3+}) \longrightarrow 2\ Q + 2\ \text{cyt}\ c\ (Fe^{2+}) + 4\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
PSII:	$2\ \text{cyt}\ c\ (Fe^{2+}) + 2\ P870^{\oplus} \longrightarrow 2\ \text{cyt}\ c\ (Fe^{3+}) + 2\ P870$
Sum:	$2\ \text{photons} + 4\ H^{\oplus}_{in} \longrightarrow 4\ H^{\oplus}_{out}$

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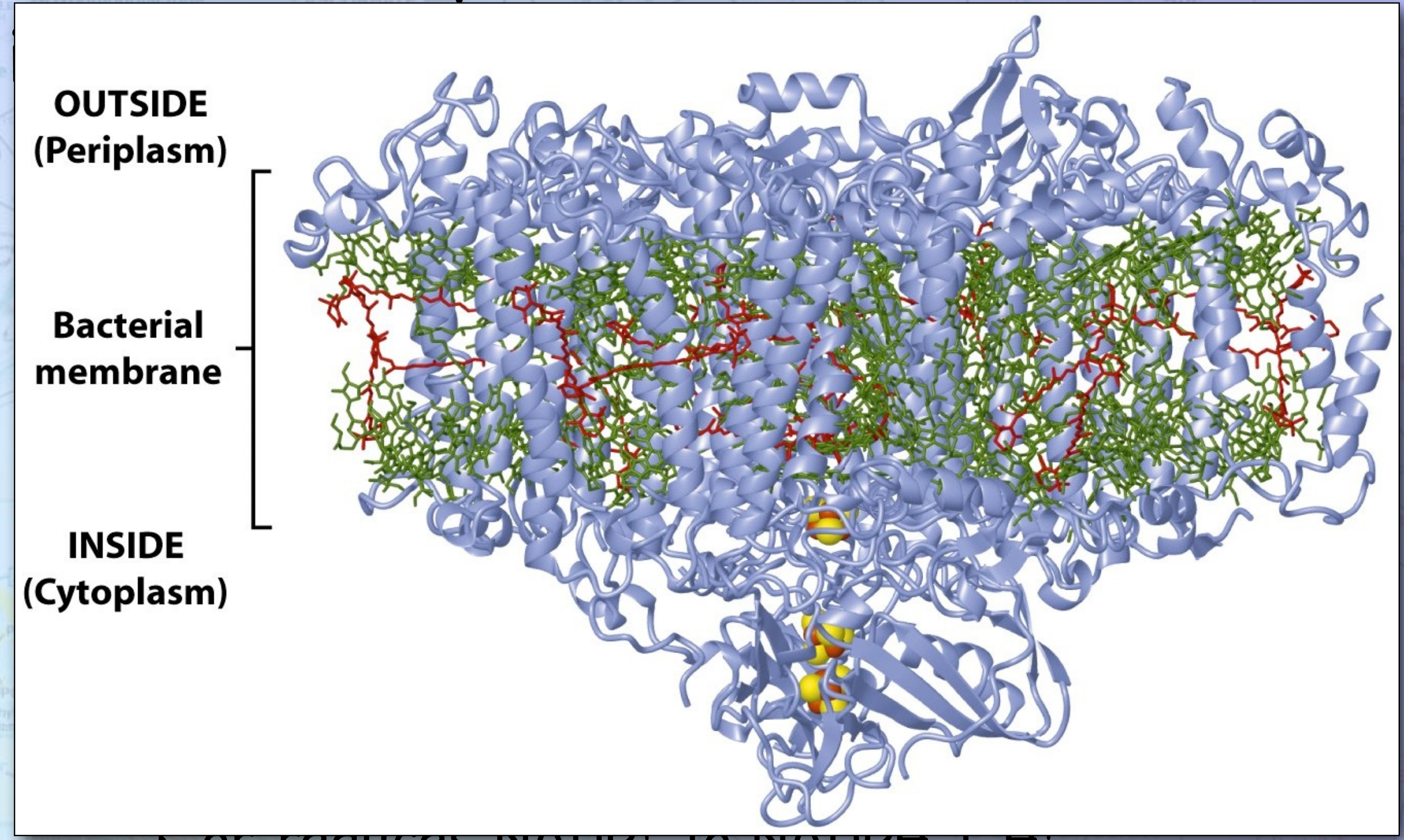
Photosystem I (PSI)

Two related photosystems have evolved in the the last 2 billion years.

- Photosystem I (PSI)
  - Found in
    - Heliobacteria
    - Green sulfur bacteria
  - Combines PSI with cytochrome bc
    - cytochrome bc is complex III from the electron transport chain.
  - Creates either a proton gradient that is used to synthesize ATP.
    - or reduces $NADP^+$ to $NADPH + H^+$.

Photosystem I (PSI)

Two related photosystems have evolved



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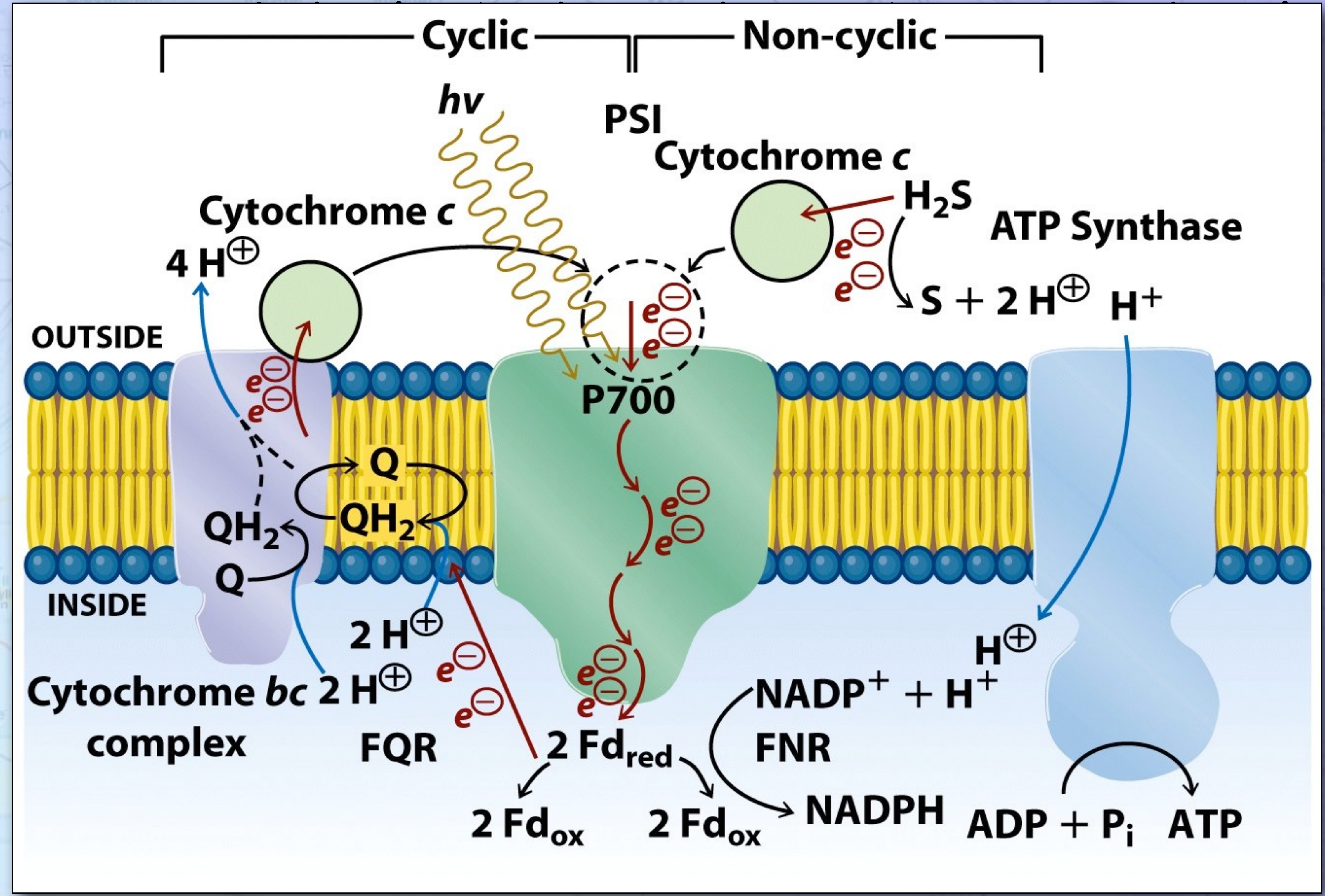

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Photosystem I (PSI)

Two related photosystems have evolved in the the last 2 billion years.

Table 15.2 The photosystem I reactions

PSI:	$2\ \text{P700} + 2\ \text{photons} \longrightarrow 2\ \text{P700}^{\oplus} + 2\ e^{\ominus}$
	$2\ \text{Fd}_{ox} + 2\ e^{\ominus} + \longrightarrow 2\ \text{Fd}_{red}$
FNR:	$\text{Fd}_{red} + \text{H}^{\oplus} + \text{FAD} \rightleftharpoons \text{Fd}_{ox} + \text{FADH}\cdot$
	$\text{Fd}_{red} + \text{H}^{\oplus} + \text{FADH}\cdot \rightleftharpoons \text{Fd}_{ox} + \text{FADH}_2$
	$\text{FADH}_2 + \text{NADP}^{\oplus} \rightleftharpoons \text{FAD} + \text{NADPH} + \text{H}^{\oplus}$
Sum:	$2\ \text{P700} + 2\ \text{photons} + \text{NADP}^{\oplus} + \text{H}^{\oplus} \longrightarrow 2\ \text{P700}^{\oplus} + \text{NADPH}$

synthesize ATP.

- or reduces $NADP^+$ to $NADPH + H^+$.

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The Evolution of Photosystems

Cyanobacteria coupled the two systems together.

- An oxygen evolving complex evolved to supply the electrons to PSII
- Cytochrome bf (instead of cytochrome bc) is used to reoxidize plastoquinone (instead of ubiquinone) and reduce the blue copper protein, plastocyanin, or cytochrome c
- Plastocyanin (or cytochrome c) then reduces PSI, which in turn reduces $NADP^+$ to $NADPH + H^+$.

The Evolution of Photosystems

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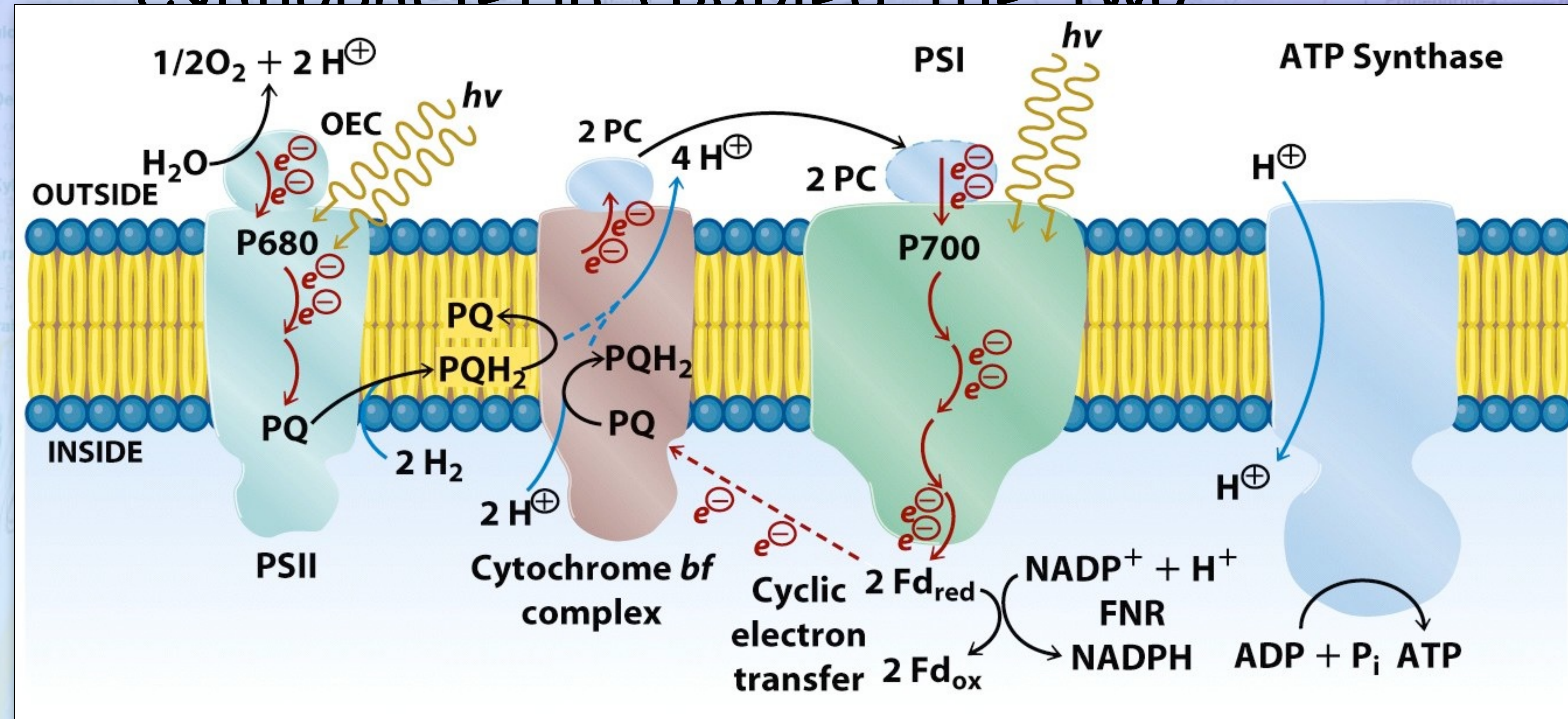

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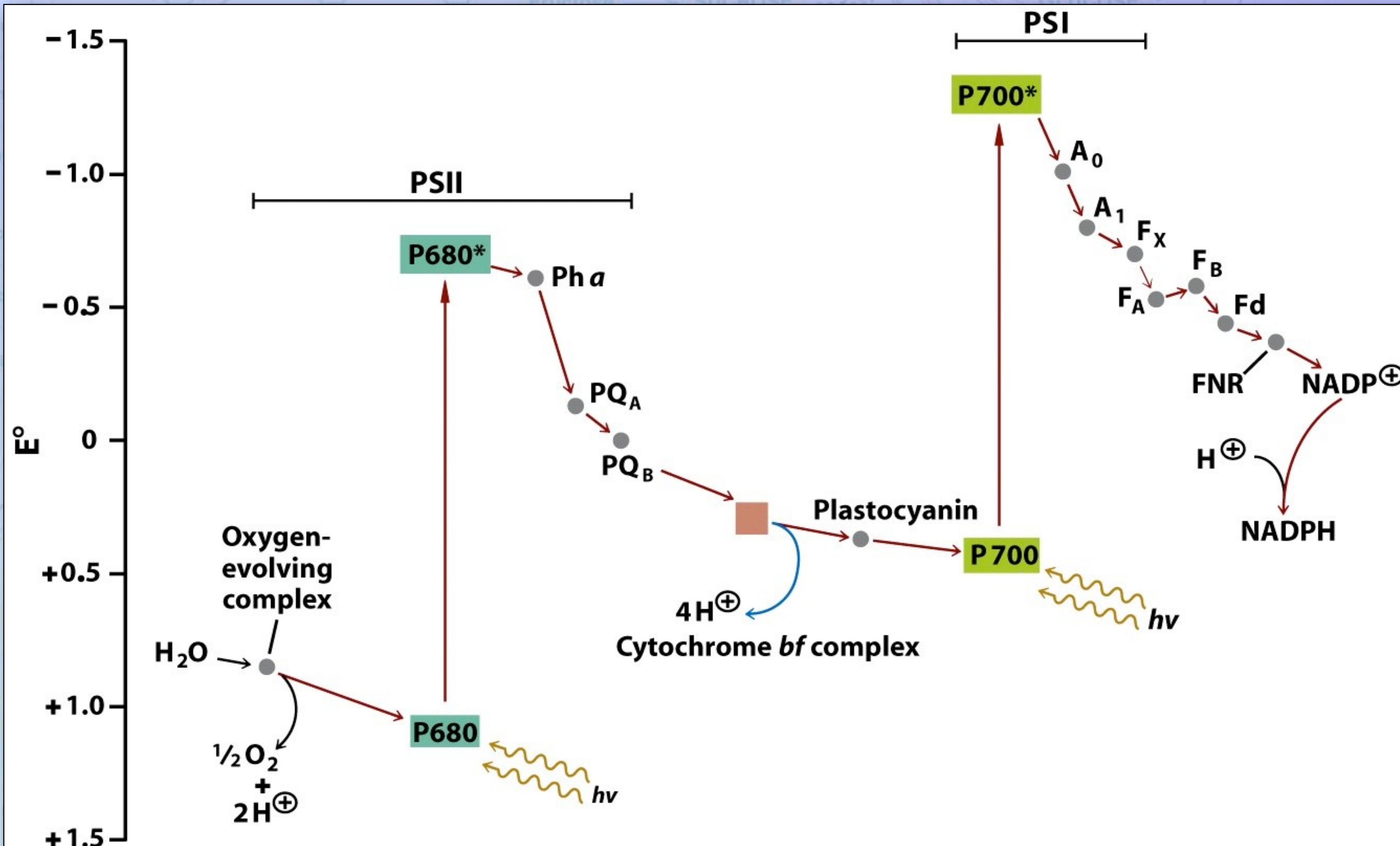
The Evolution of Photosystems



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The Evolution of Photosystems

Cyanobacteria coupled the two

Table 15.3 The photosynthesis reactions in species with both photosystems

PSII:	$2\ P680 + 2\ \text{photons} \longrightarrow 2\ P680^{\oplus} + 2\ e^{\ominus}$
	$PQ + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow PQH_2$
OEC:	$H_2O \longrightarrow \frac{1}{2}O_2 + 2\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$2\ P680^{\oplus} + 2\ e^{\ominus} \longrightarrow 2\ P680$
Cyt *bf*:	$2\ PQH_2 + 2\ \text{plastocyanin}\ (Cu^{2+}) \longrightarrow 2\ PQ + 2\ \text{plastocyanin}\ (Cu^{\oplus}) + 4\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$PQ + 2\ H^{\oplus}_{in} + 2\ e^{\ominus} \longrightarrow PQH_2$
PSI:	$2\ P700 + 2\ \text{photons} \longrightarrow 2\ P700^{\oplus} + 2\ e^{\ominus}$
	$2\ Fd_{ox} + 2\ e^{\ominus} \longrightarrow 2\ Fd_{red}$
	$2\ \text{plastocyanin}\ (Cu^{\oplus}) + 2\ P700^{\oplus} \longrightarrow 2\ \text{plastocyanin}\ (Cu^{2+}) + 2\ P700$
FNR:	$2\ Fd_{red} + H^{\oplus} + NADP^{\oplus} \rightleftharpoons 2\ Fd_{ox} + NADPH$
Sum:	$H_2O + 4\ \text{photons} + 4\ H^{\oplus}_{in} + NADP^{\oplus} + H^{\oplus} \longrightarrow \frac{1}{2}O_2 + 6\ H^{\oplus}_{out} + NADPH$

The Evolution of Photosystems

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The Evolution of Photosystems

By coupling the two systems

- Cyanobacteria are able to produces both ATP and reduced NADPH + H^+.
- Use water as as its source of electrons.

Plant Photosynthesis

Plant photosynthesis takes place in organelles calls chloroplasts.

- The chloroplasts found in photo-synthesizing eukaryotes are believed to have evolved from cyanobacteria, which established a symbiotic relationship with eukaryotes

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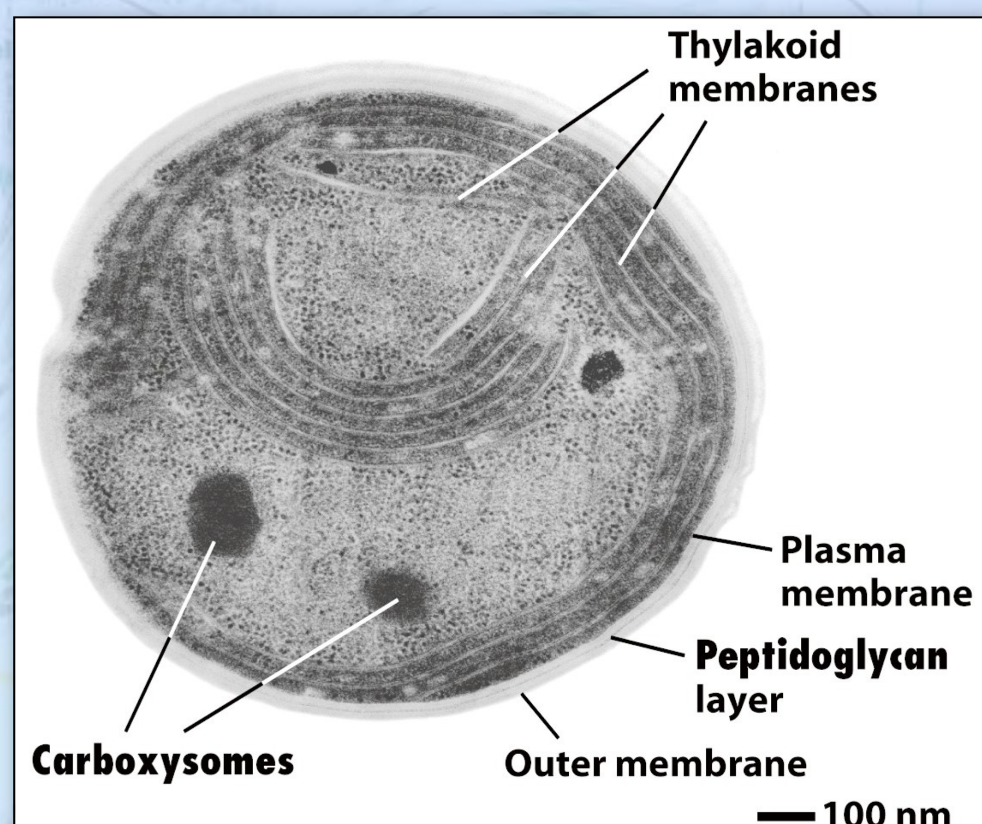

Cyanobacterium

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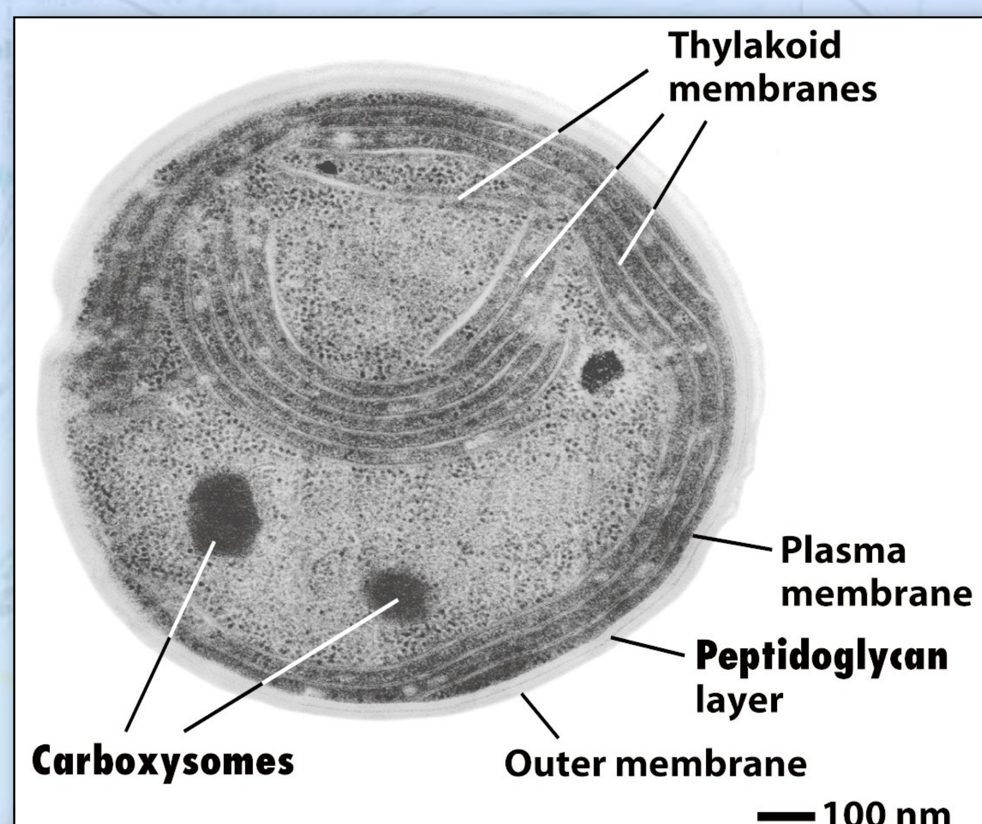
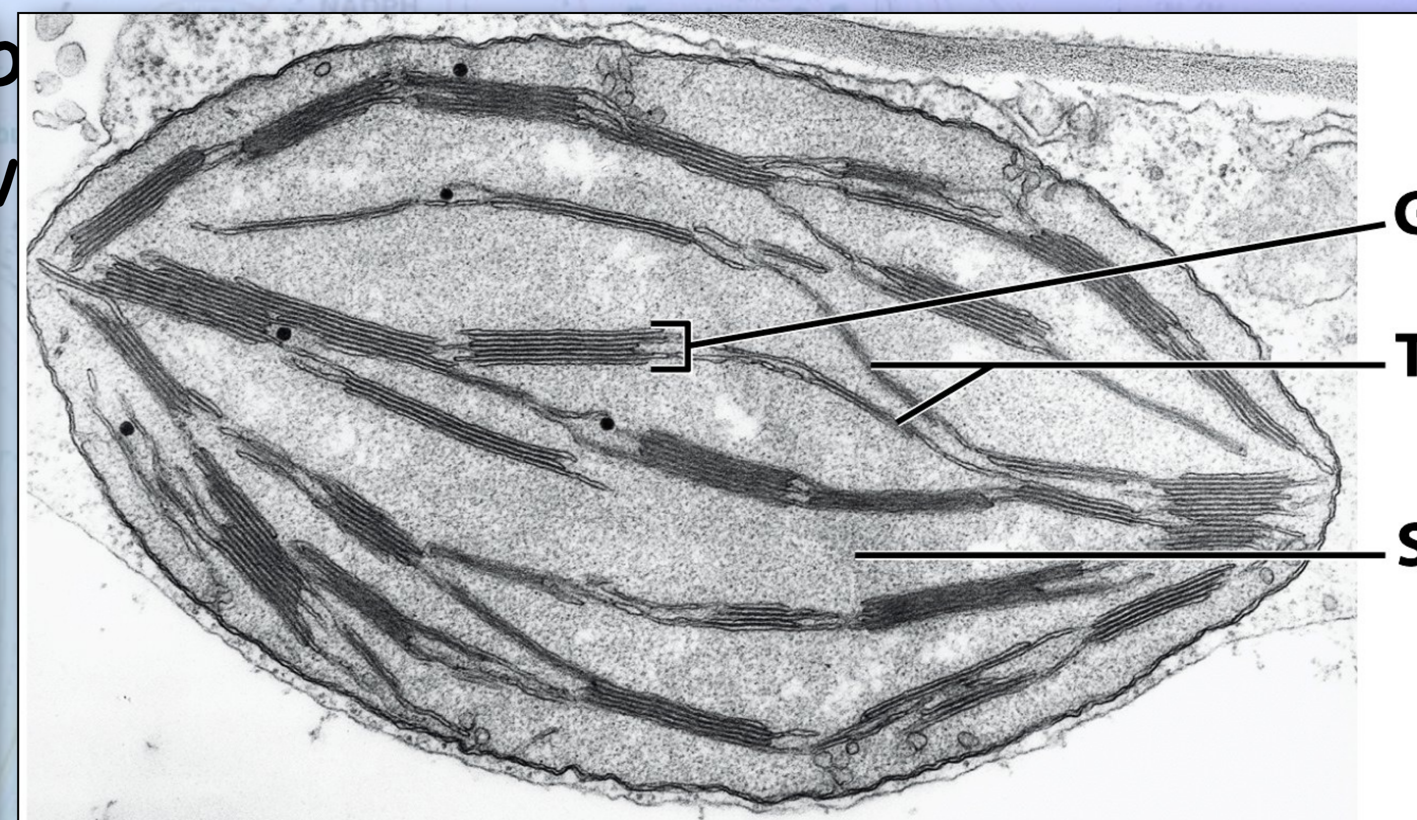


Cyanobacterium



Chloroplast

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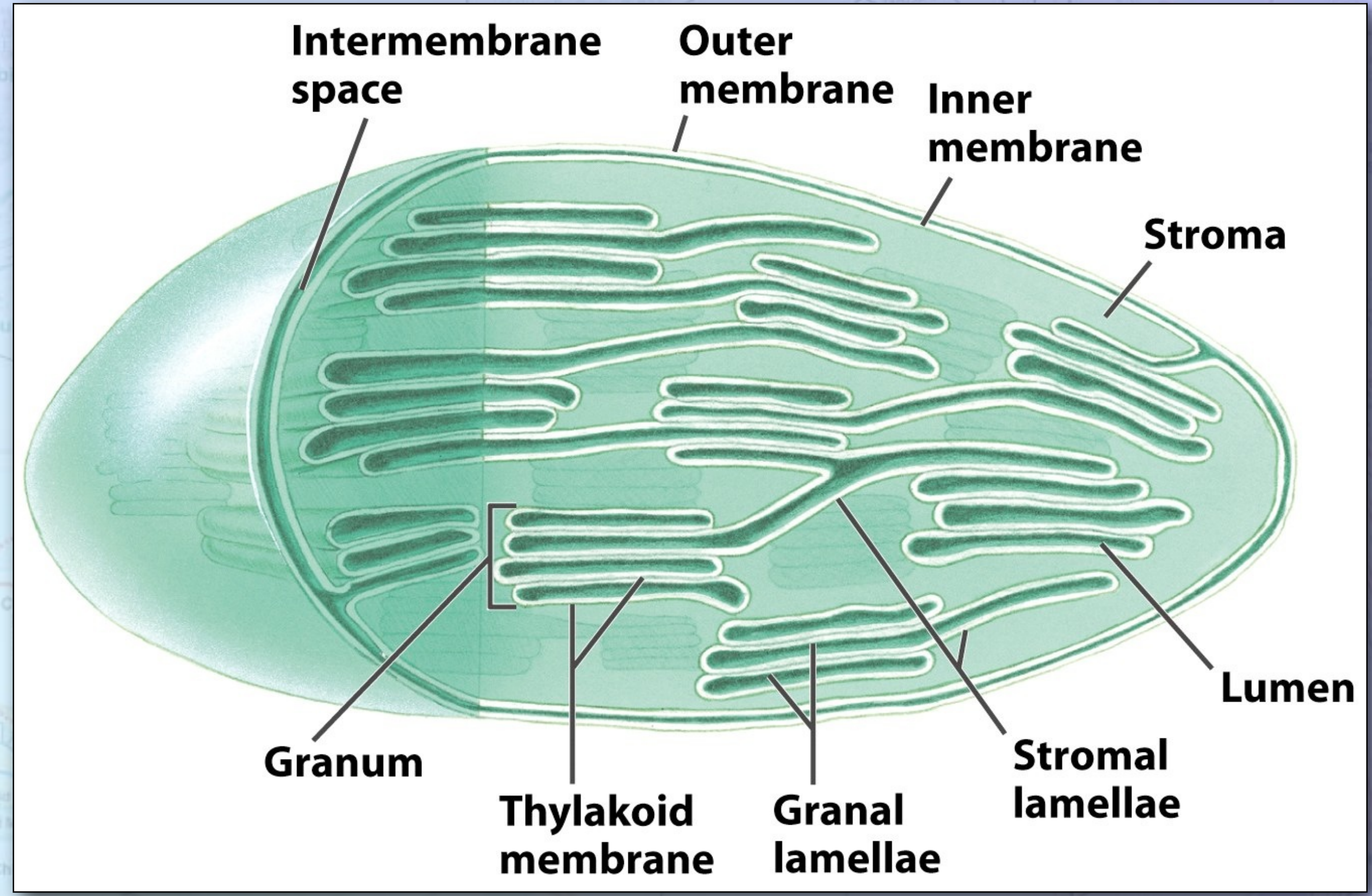
Plant Photosynthesis

- Chloroplasts have double membranes, like mitochondria.



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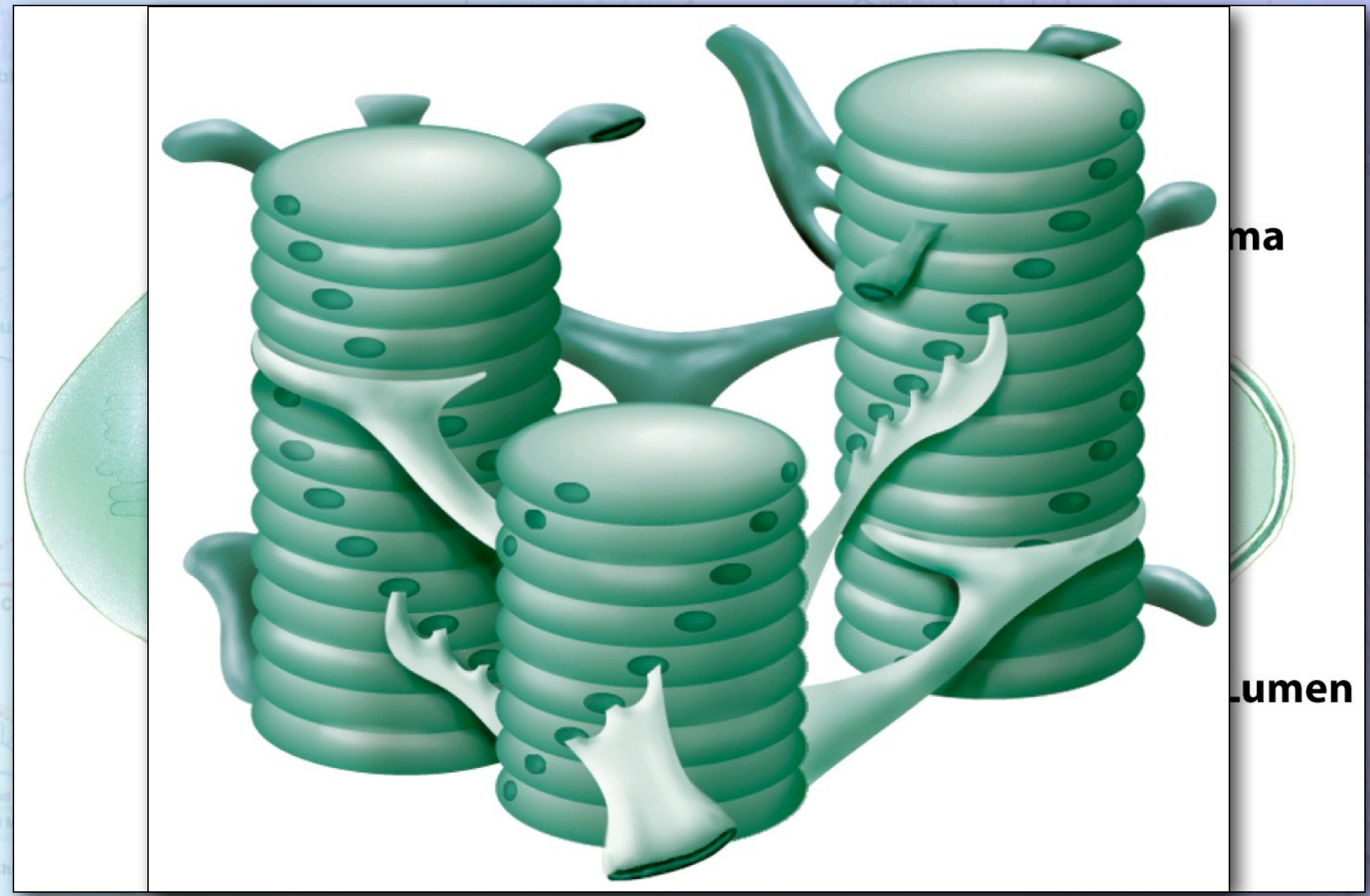

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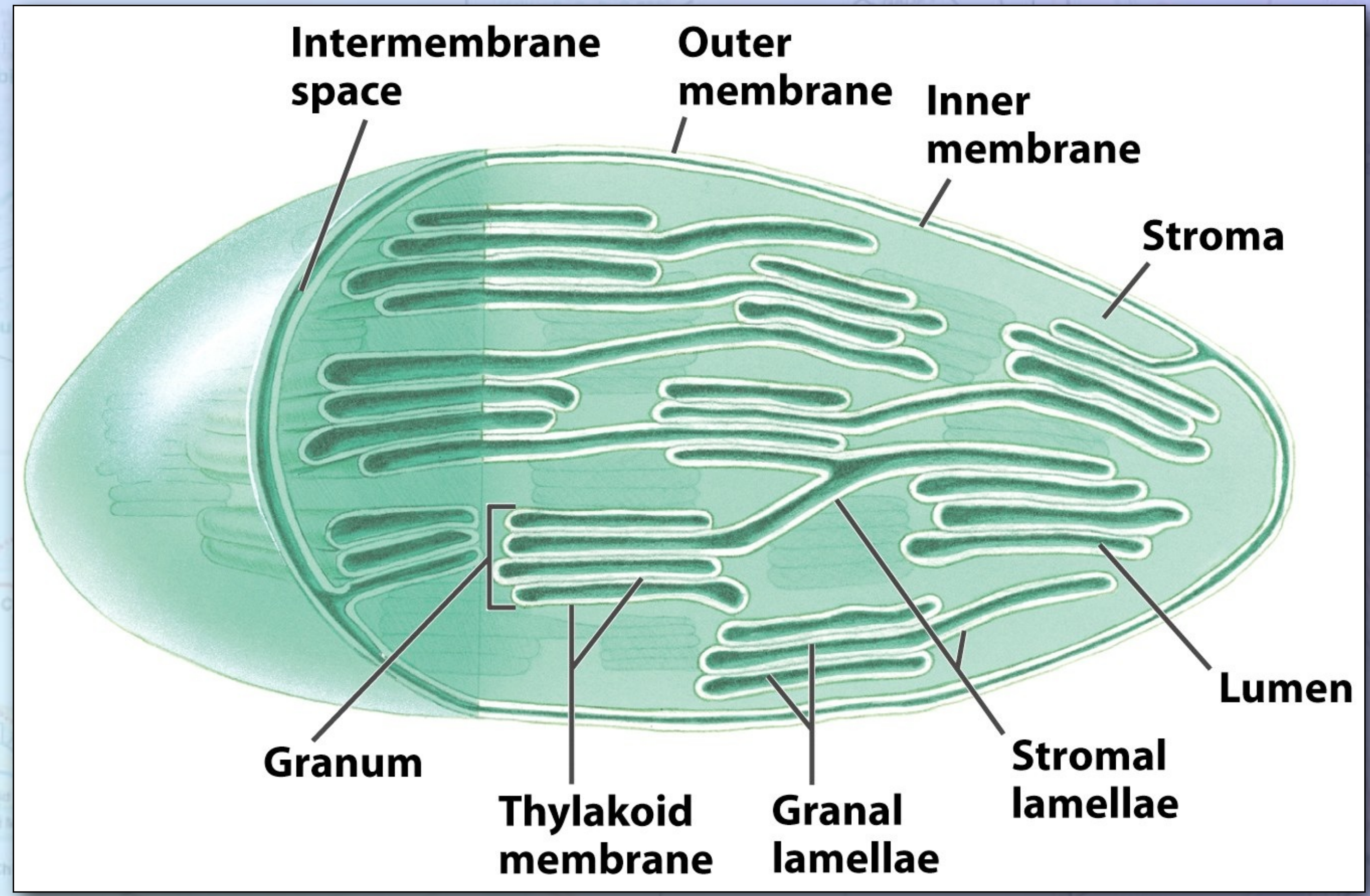

Plant Photosynthesis

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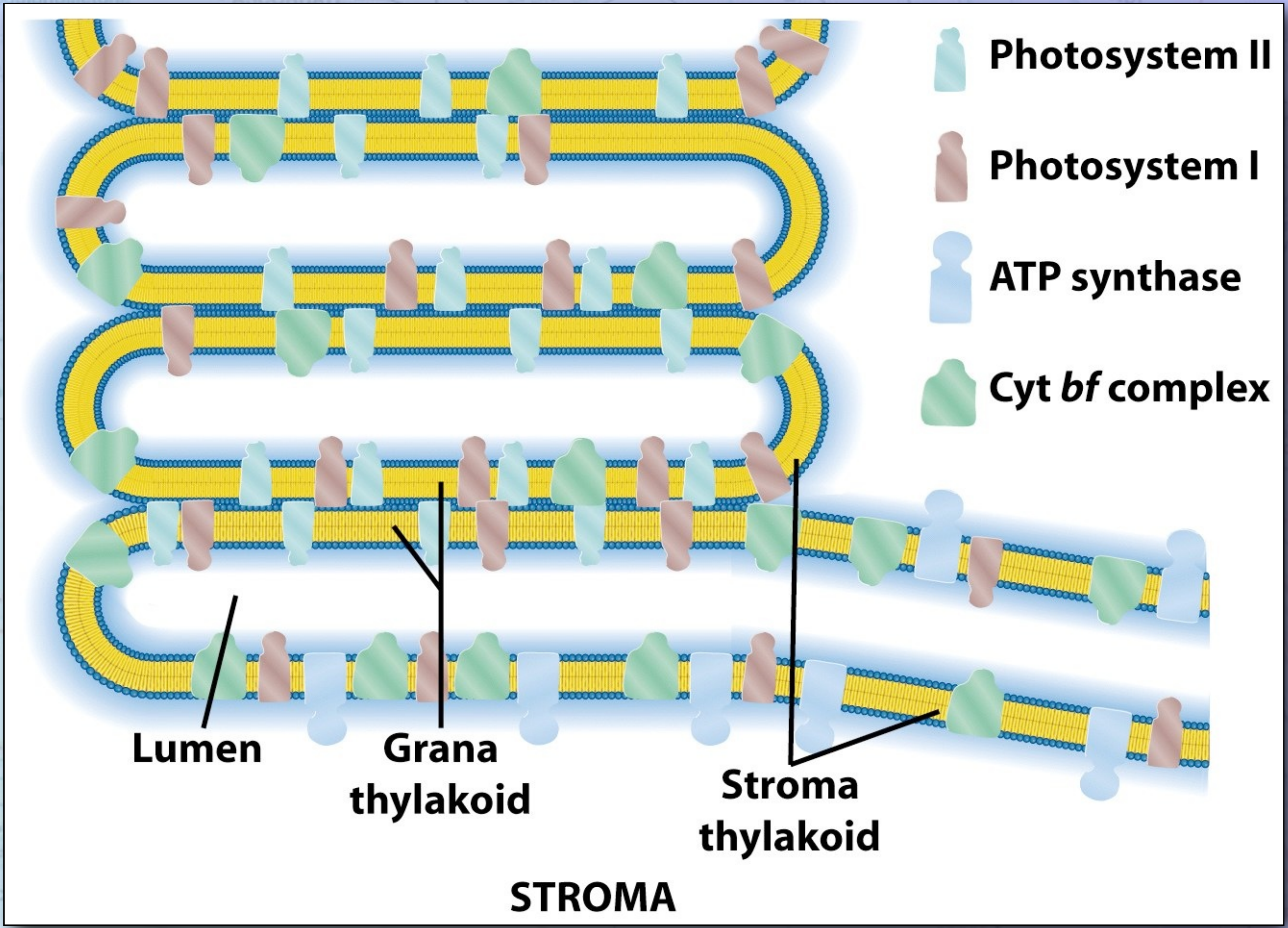

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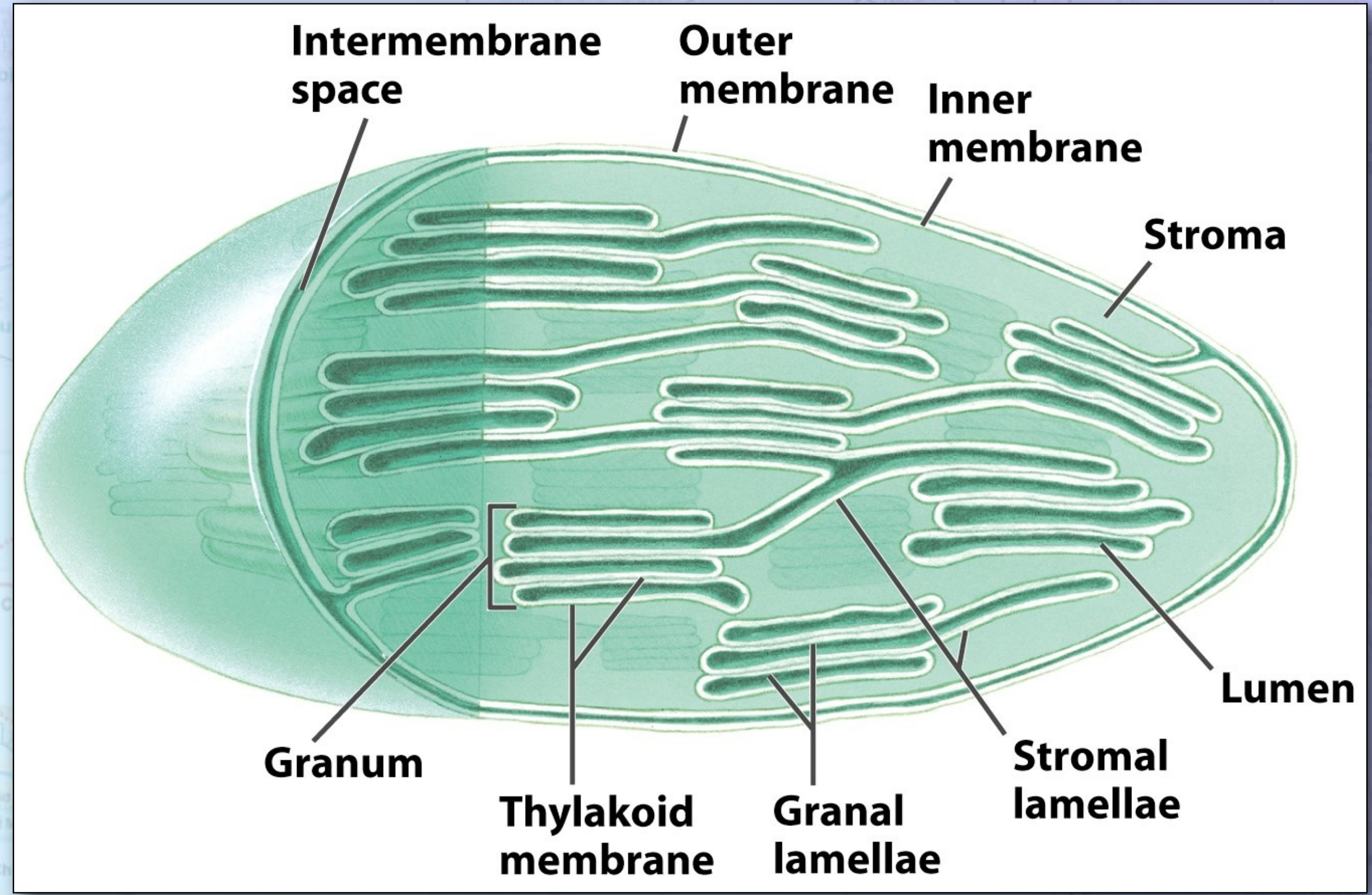


The Dark Reactions

- The **dark reactions** of photosynthesis use the ATP and reduced NADPH + H^+ from the light reactions to convert CO_2 and H_2O into glycolytic intermediates.

- Called the **Calvin Cycle**

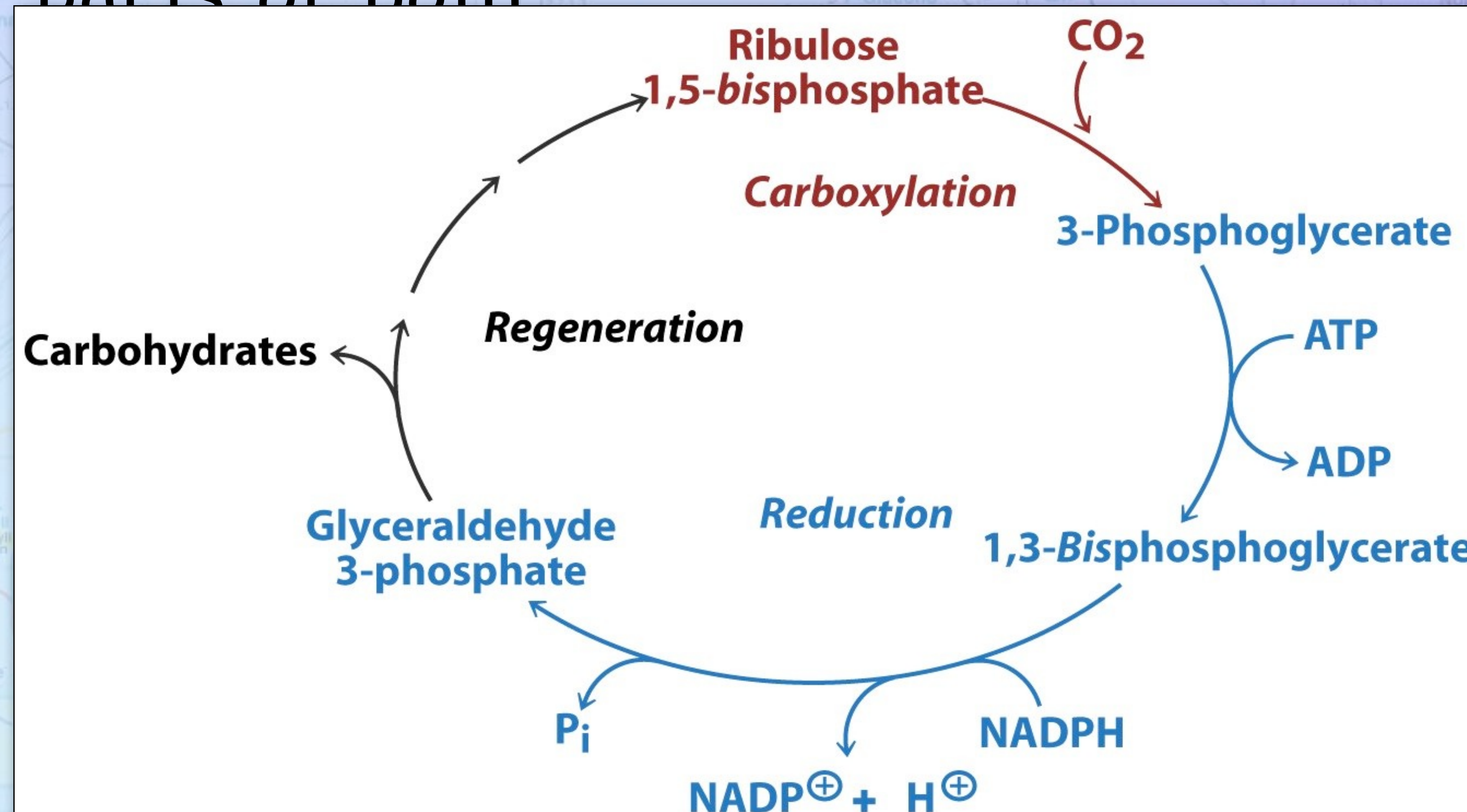
The Dark Reactions

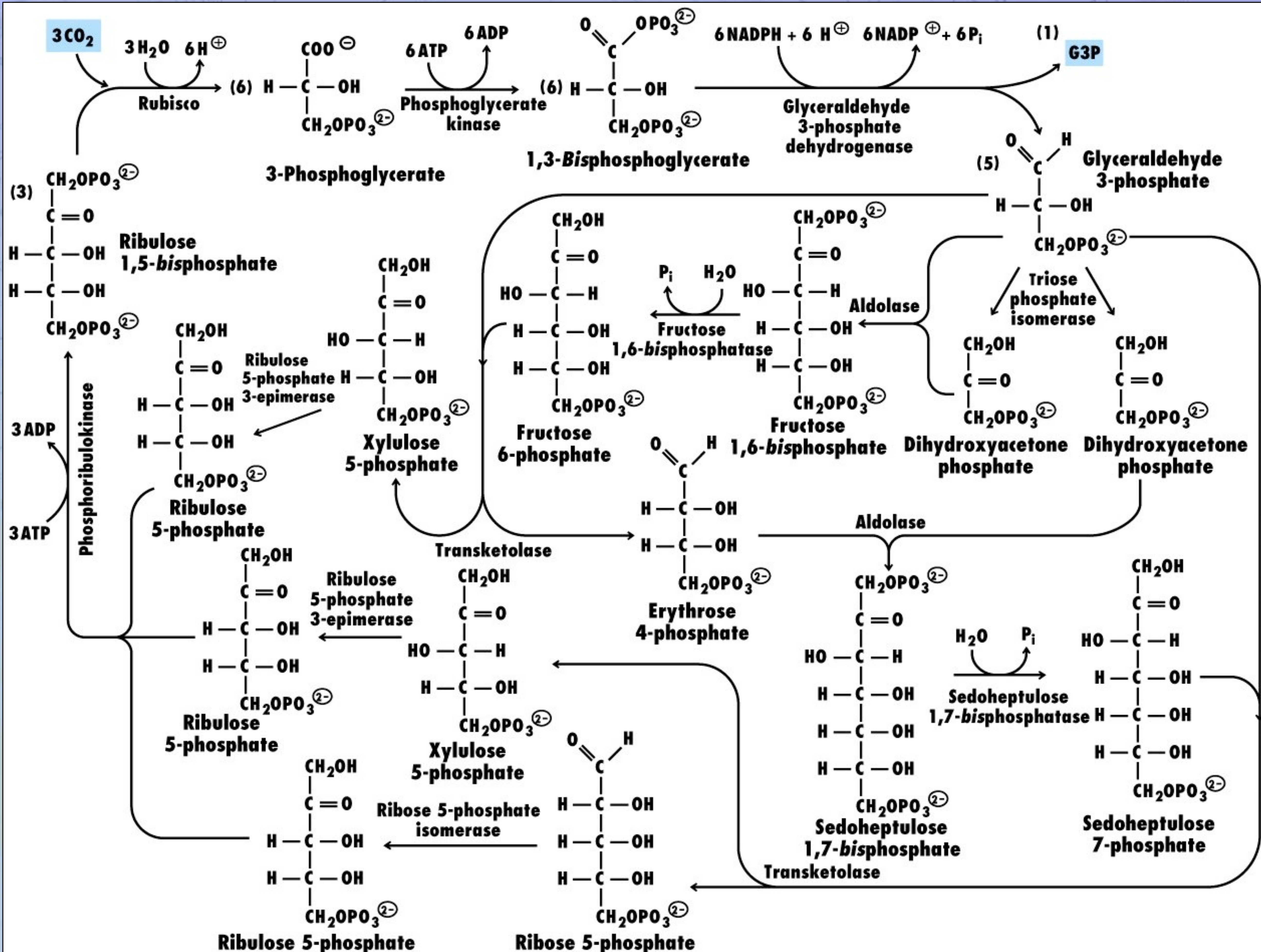
Parts of the Calvin Cycle resembles parts of both

- Gluconeogenesis (Reduction)
- Nonoxidative phase of the Pentose Phosphate Pathway (Regeneration)

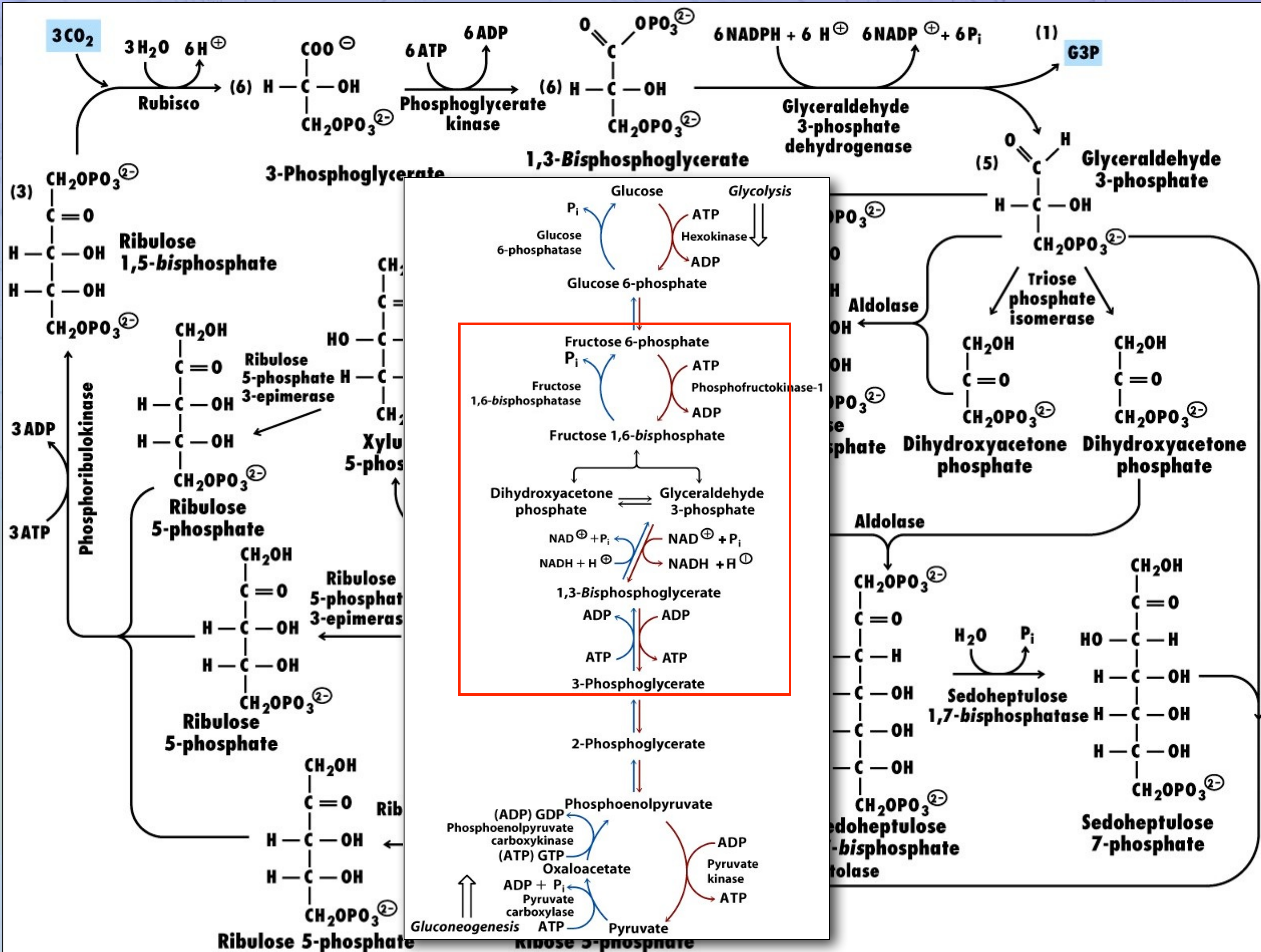
The Dark Reactions

Parts of the Calvin Cycle resembles parts of both

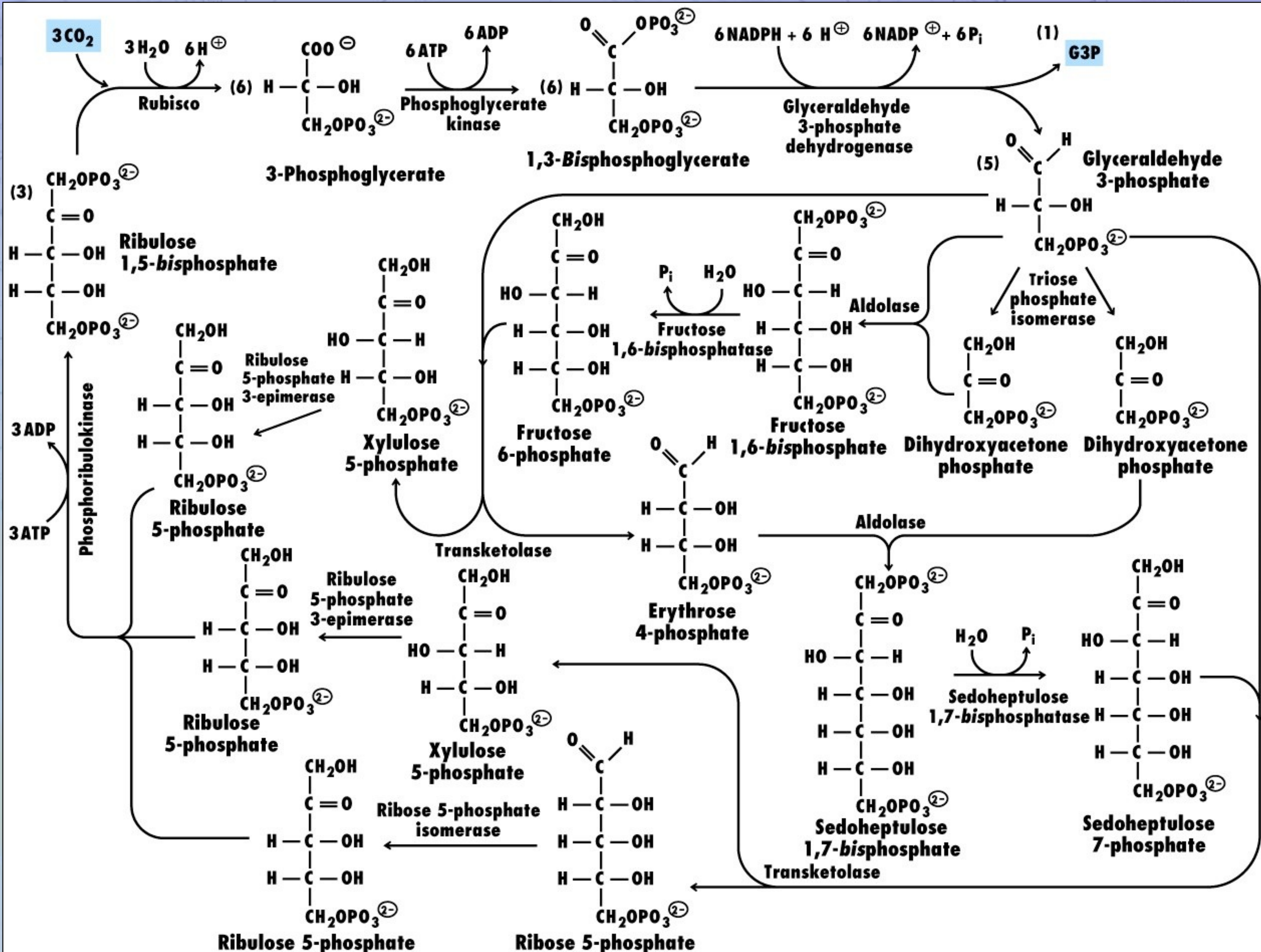




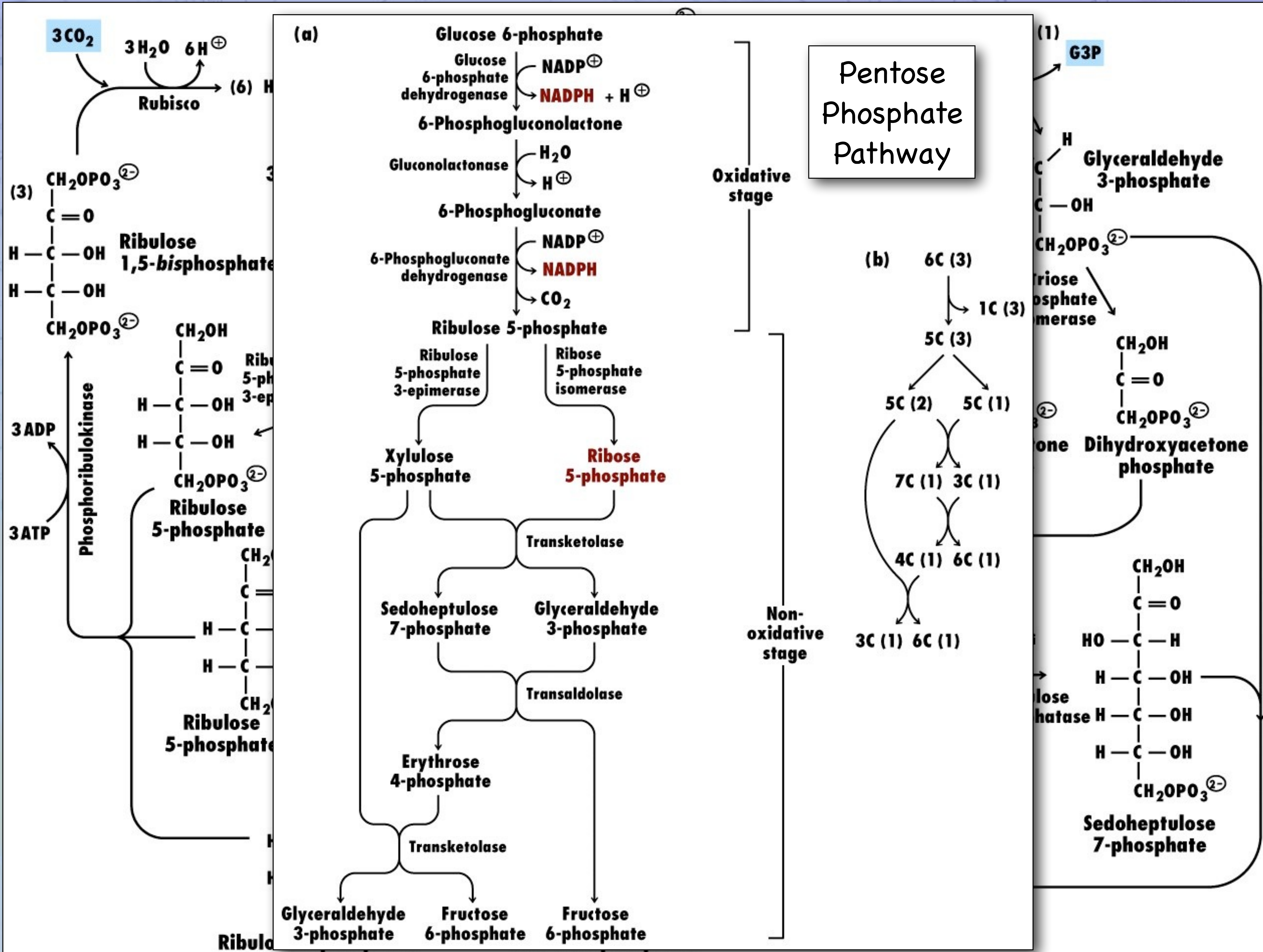
3CO2
3H2O
6H⊕
Rubisco
(6)
COO⊖
3-Phosphoglycerate
6ATP
6ADP
Phosphoglycerate kinase
(6)
1,3-Bisphosphoglycerate
6NADPH + 6 H⊕
6NADP⊕ + 6Pi
Glyceraldehyde 3-phosphate dehydrogenase
(1)
G3P
(5)
Glyceraldehyde 3-phosphate
(3)
Ribulose 1,5-bisphosphate
3ADP
3ATP
Phosphoribulokinase
Ribulose 5-phosphate 3-epimerase
Xylulose 5-phosphate
Ribulose 5-phosphate
Fructose 6-phosphate
Pi
H2O
Fructose 1,6-bisphosphatase
Aldolase
Fructose 1,6-bisphosphate
Triose phosphate isomerase
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
Erythrose 4-phosphate
Aldolase
Transketolase
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
Xylulose 5-phosphate
H2O
Pi
Sedoheptulose 1,7-bisphosphatase
Sedoheptulose 1,7-bisphosphate
Sedoheptulose 7-phosphate
Transketolase
Ribose 5-phosphate isomerase
Ribulose 5-phosphate
Ribose 5-phosphate

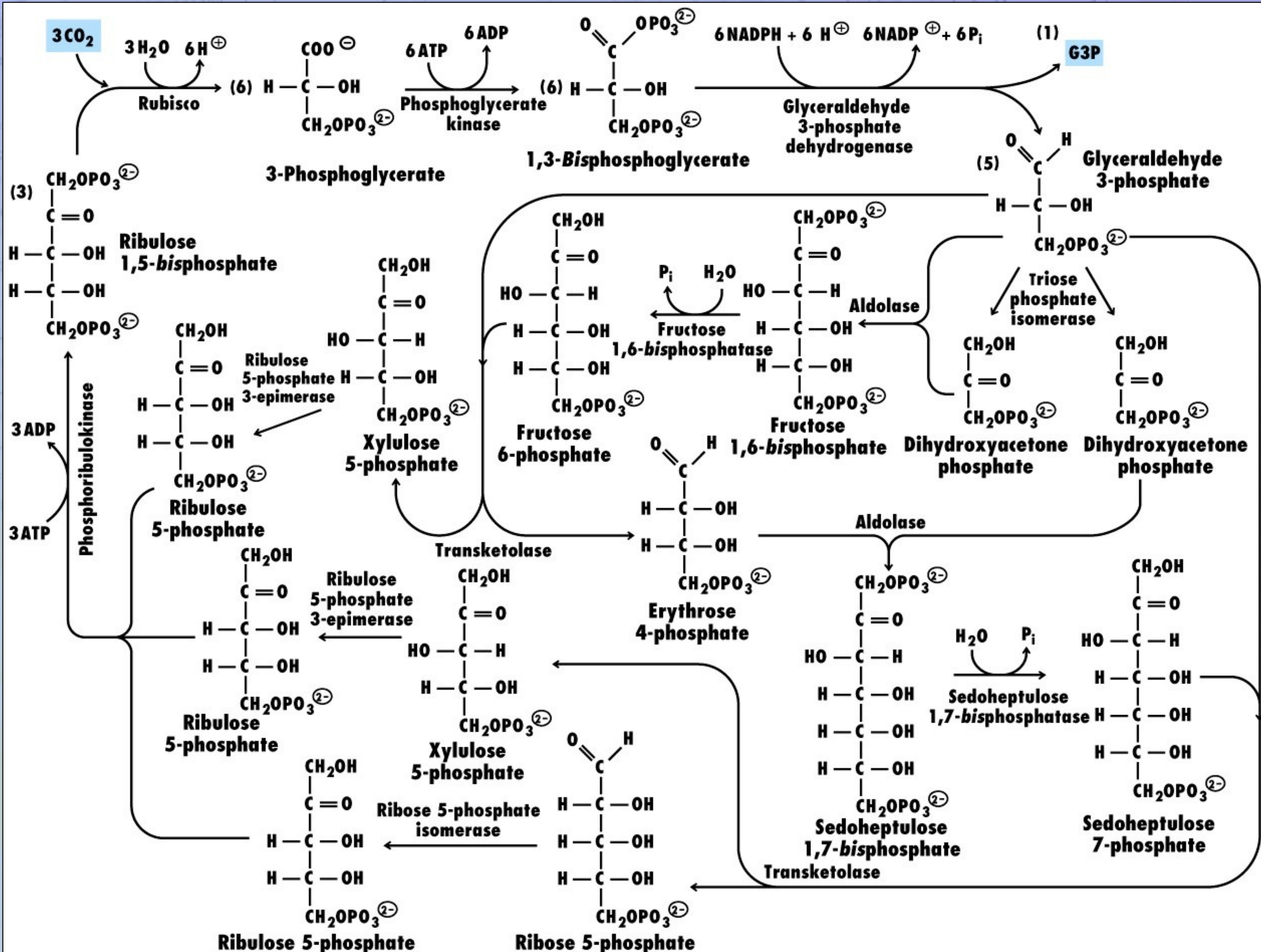


3CO2
3H2O 6H⊕
Rubisco
(6)
3-Phosphoglycerate
6ATP 6ADP
Phosphoglycerate kinase
1,3-Bisphosphoglycerate
6NADPH + 6 H⊕ 6NADP⊕ + 6Pi
Glyceraldehyde 3-phosphate dehydrogenase
(1)
G3P
(5)
Glyceraldehyde 3-phosphate
Triose phosphate isomerase
Aldolase
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
Aldolase
H2O Pi
Sedoheptulose 1,7-bisphosphatase
Sedoheptulose 7-phosphate
(3)
Ribulose 1,5-bisphosphate
3 ADP
3 ATP
Phosphoribulokinase
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
Ribulose 5-phosphate
Ribulose 5-phosphate
Glucose
Glycolysis
Pi
Glucose 6-phosphatase
ATP
Hexokinase
ADP
Glucose 6-phosphate
Fructose 6-phosphate
Pi
Fructose 1,6-bisphosphatase
ATP
Phosphofructokinase-1
ADP
Fructose 1,6-bisphosphate
Dihydroxyacetone phosphate
Glyceraldehyde 3-phosphate
NAD⊕ + Pi
NADH + H⊕
NAD⊕ + Pi
NADH + H⊕
1,3-Bisphosphoglycerate
ADP
ADP
ATP
ATP
3-Phosphoglycerate
2-Phosphoglycerate
Phosphoenolpyruvate
(ADP) GDP
Phosphoenolpyruvate carboxykinase
(ATP) GTP
Oxaloacetate
ADP + Pi
Pyruvate carboxylase
ATP
Gluconeogenesis
Pyruvate
ADP
Pyruvate kinase
ATP


3CO2
3H2O 6H⊕
Rubisco
6ATP 6ADP
Phosphoglycerate kinase
3-Phosphoglycerate
1,3-Bisphosphoglycerate
6NADPH + 6 H⊕ 6NADP⊕+ 6Pi
Glyceraldehyde 3-phosphate dehydrogenase
(1) G3P
(5) Glyceraldehyde 3-phosphate
(3) Ribulose 1,5-bisphosphate
Triose phosphate isomerase
Aldolase
Pi H2O
Fructose 1,6-bisphosphatase
Fructose 6-phosphate
Fructose 1,6-bisphosphate
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
Xylulose 5-phosphate
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
3 ADP
3 ATP
Phosphoribulokinase
Transketolase
Erythrose 4-phosphate
Aldolase
Sedoheptulose 1,7-bisphosphate
H2O Pi
Sedoheptulose 1,7-bisphosphatase
Sedoheptulose 7-phosphate
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
Xylulose 5-phosphate
Ribose 5-phosphate isomerase
Transketolase
Ribulose 5-phosphate
Ribose 5-phosphate

Pentose Phosphate Pathway

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3H2O 6H⊕
Rubisco
(6)
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6NADPH + 6 H⊕ 6NADP⊕ + 6Pi
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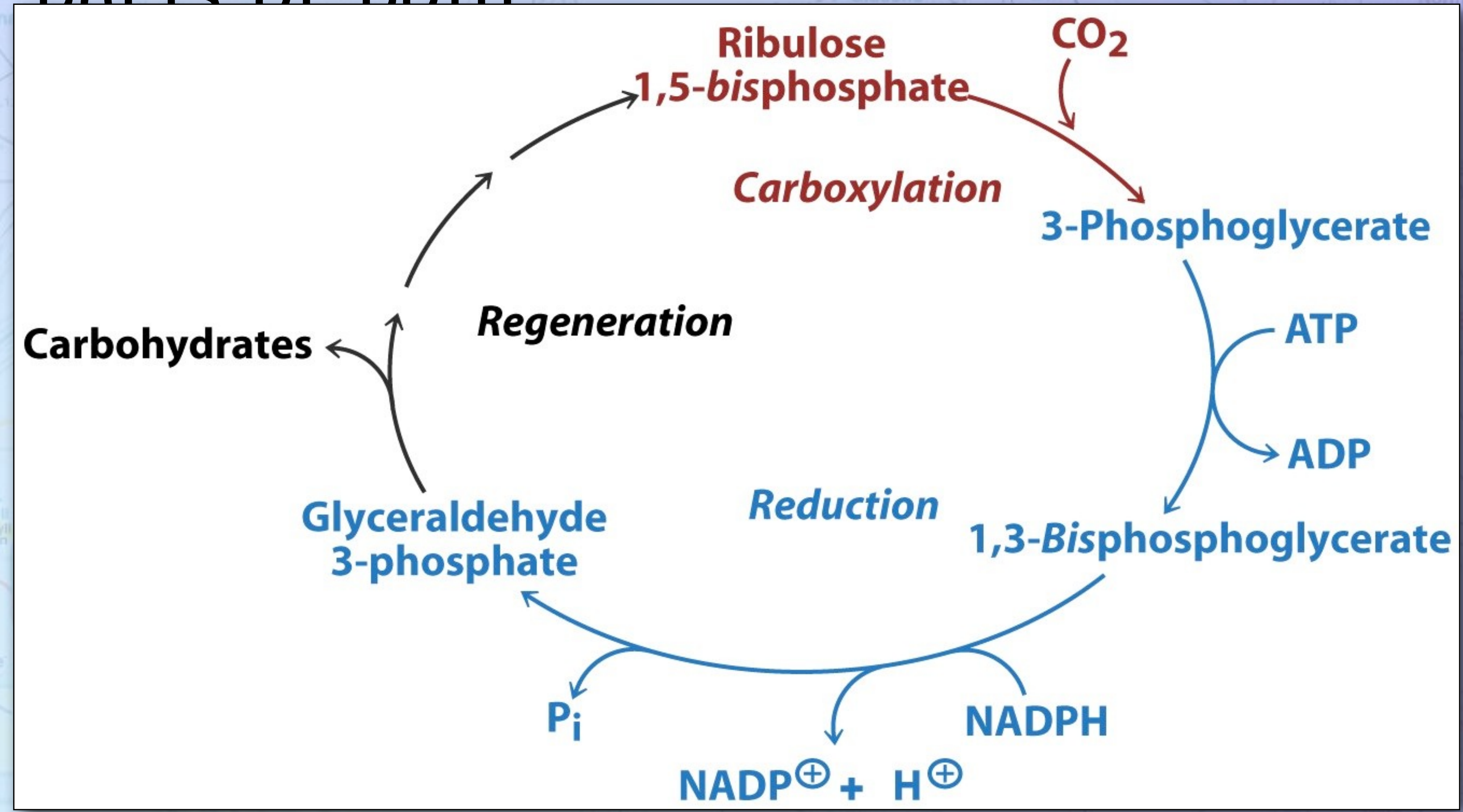
Phosphoribulokinase
3ATP
3ADP
(3)
Ribulose 1,5-bisphosphate

The Dark Reactions

Parts of the Calvin Cycle resembles parts of both



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Parts … les

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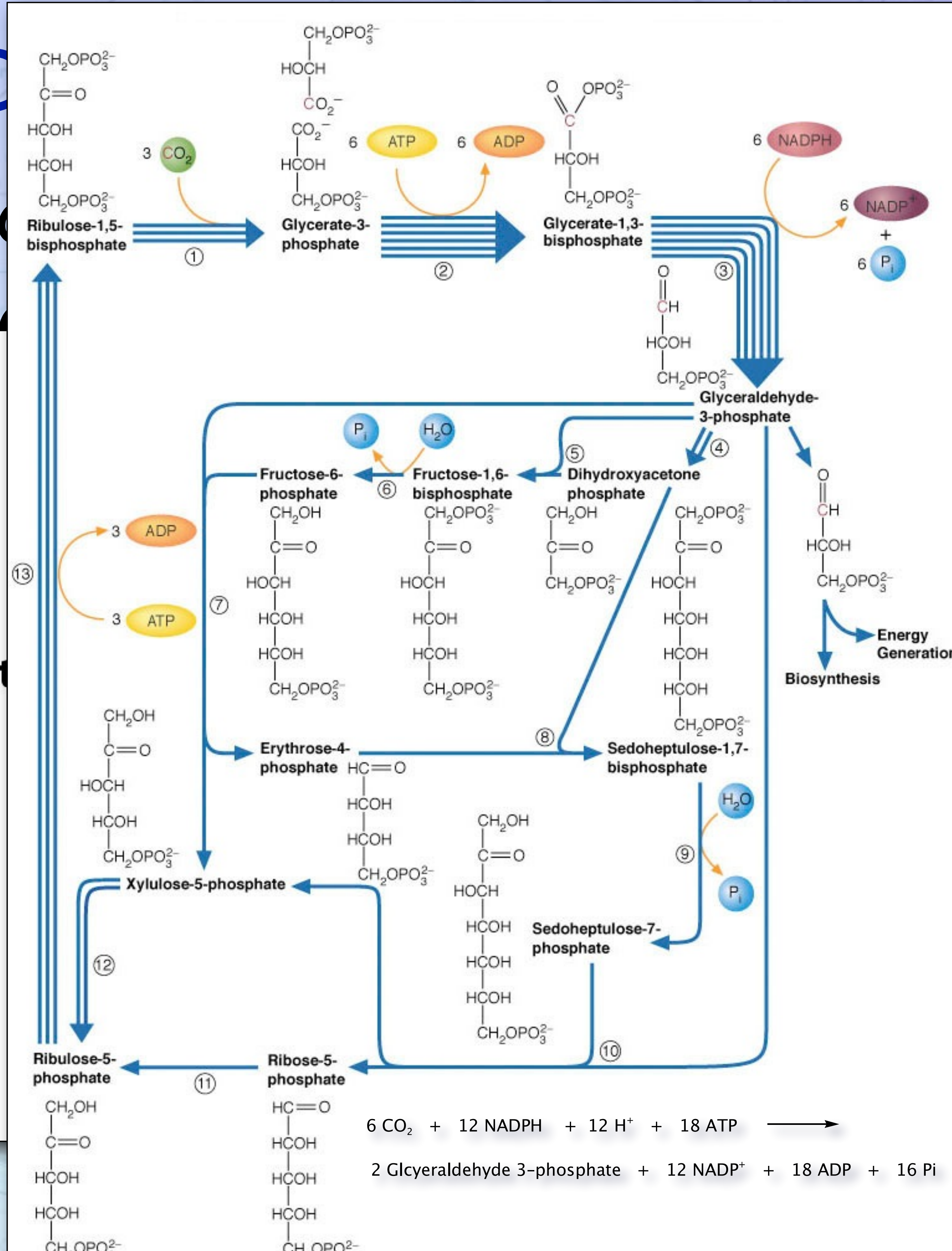

Carbohydrat

…oglycerate

ATP

ADP

…hoglycerate

The D

Parts o les
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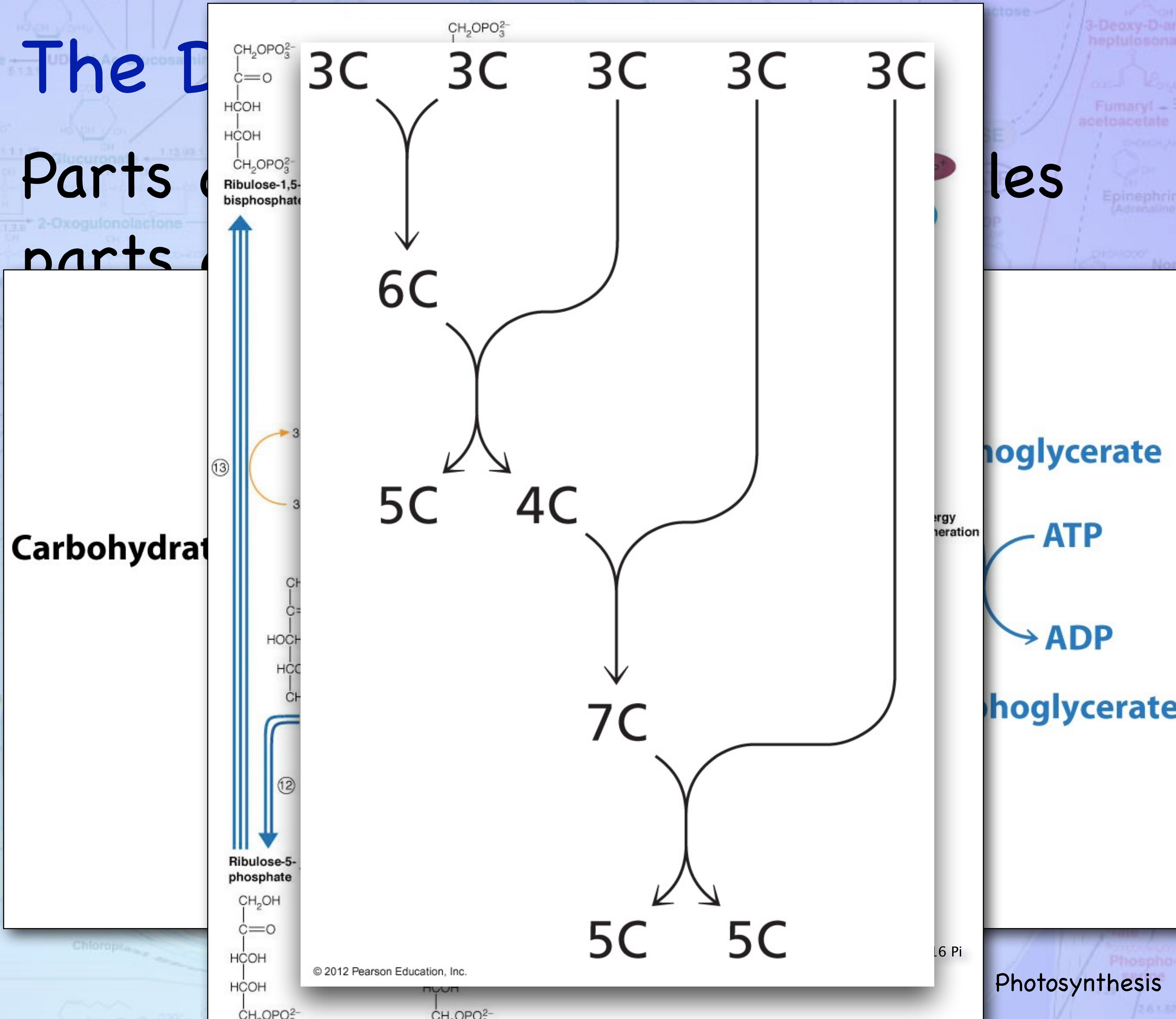

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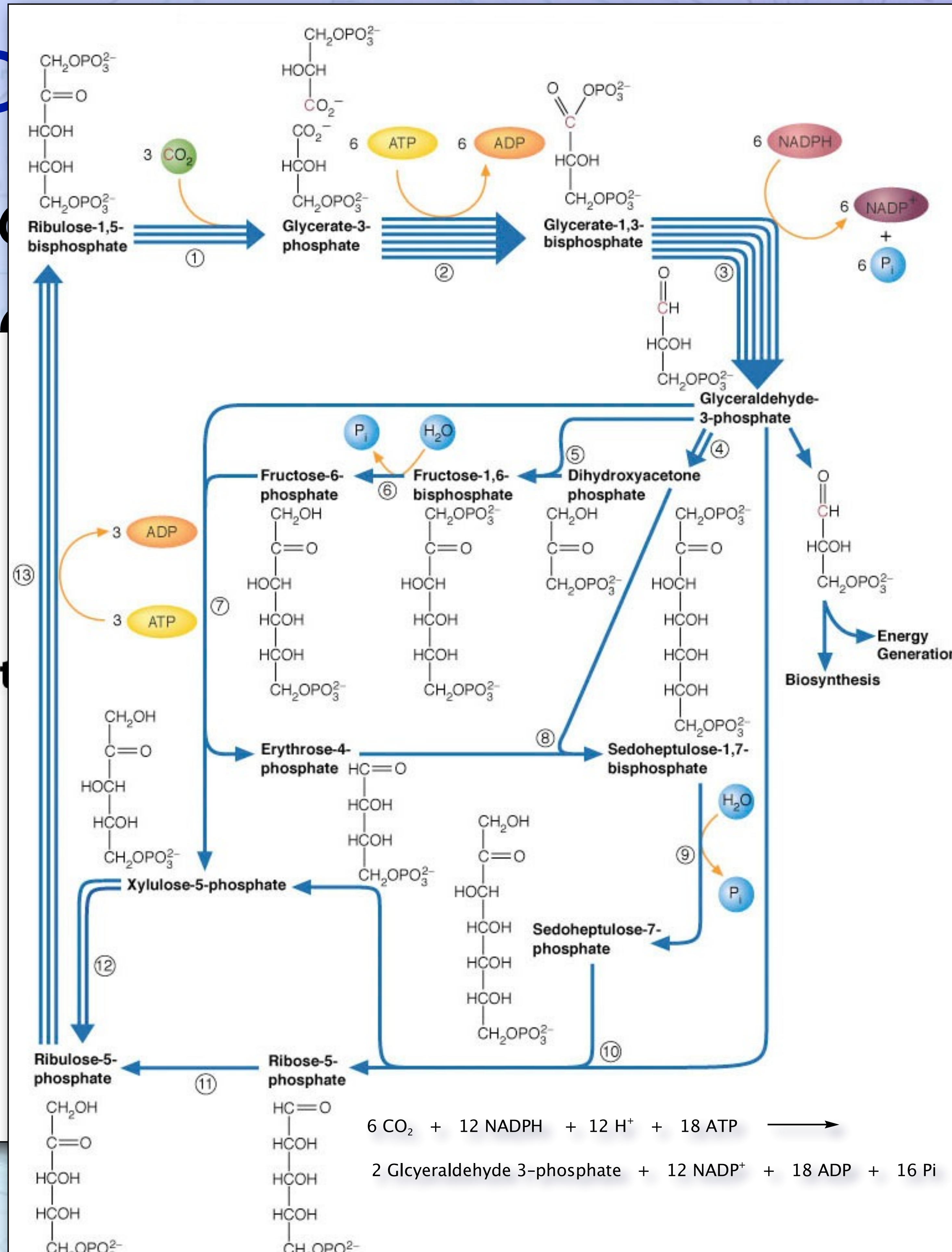

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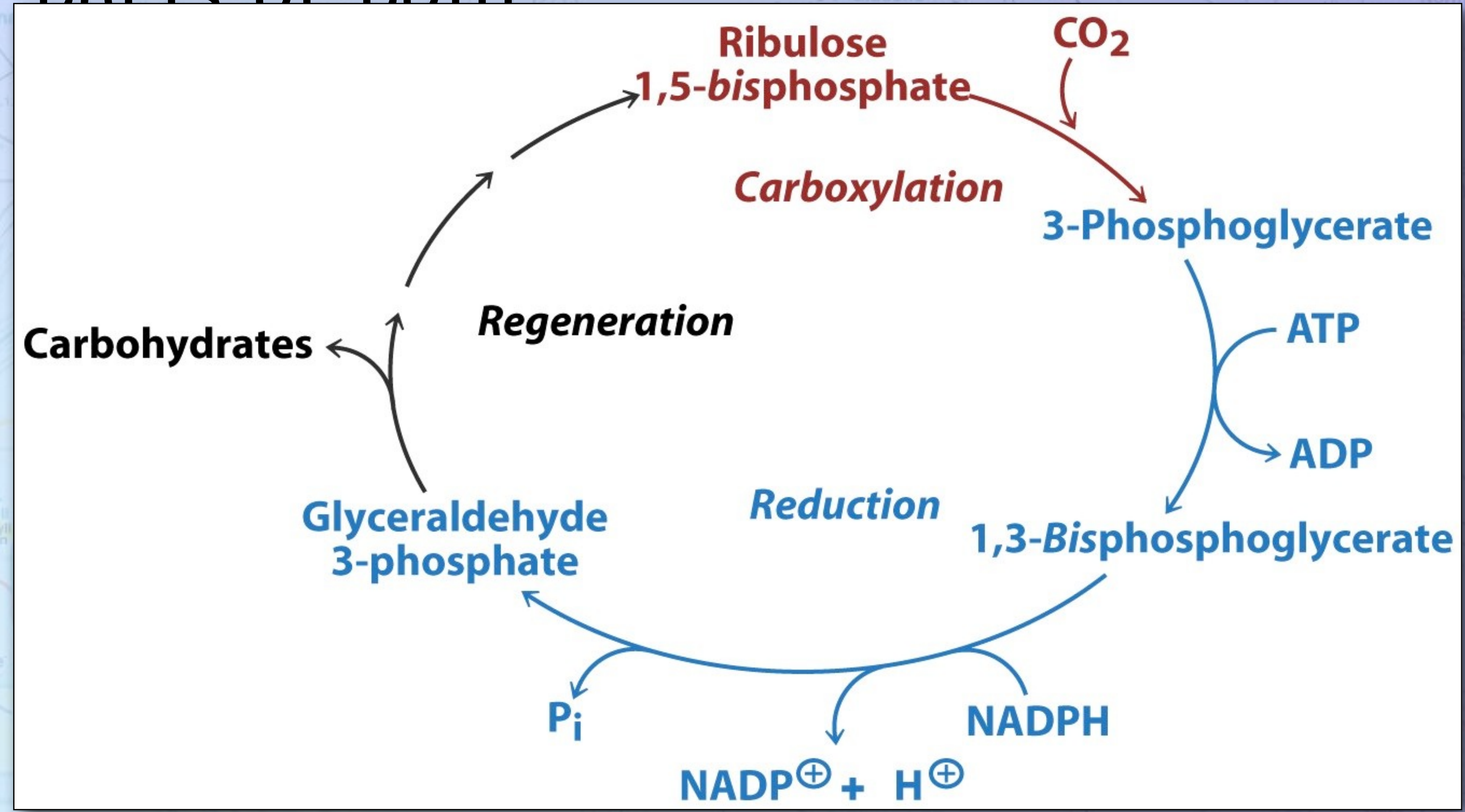


The Dark Reactions

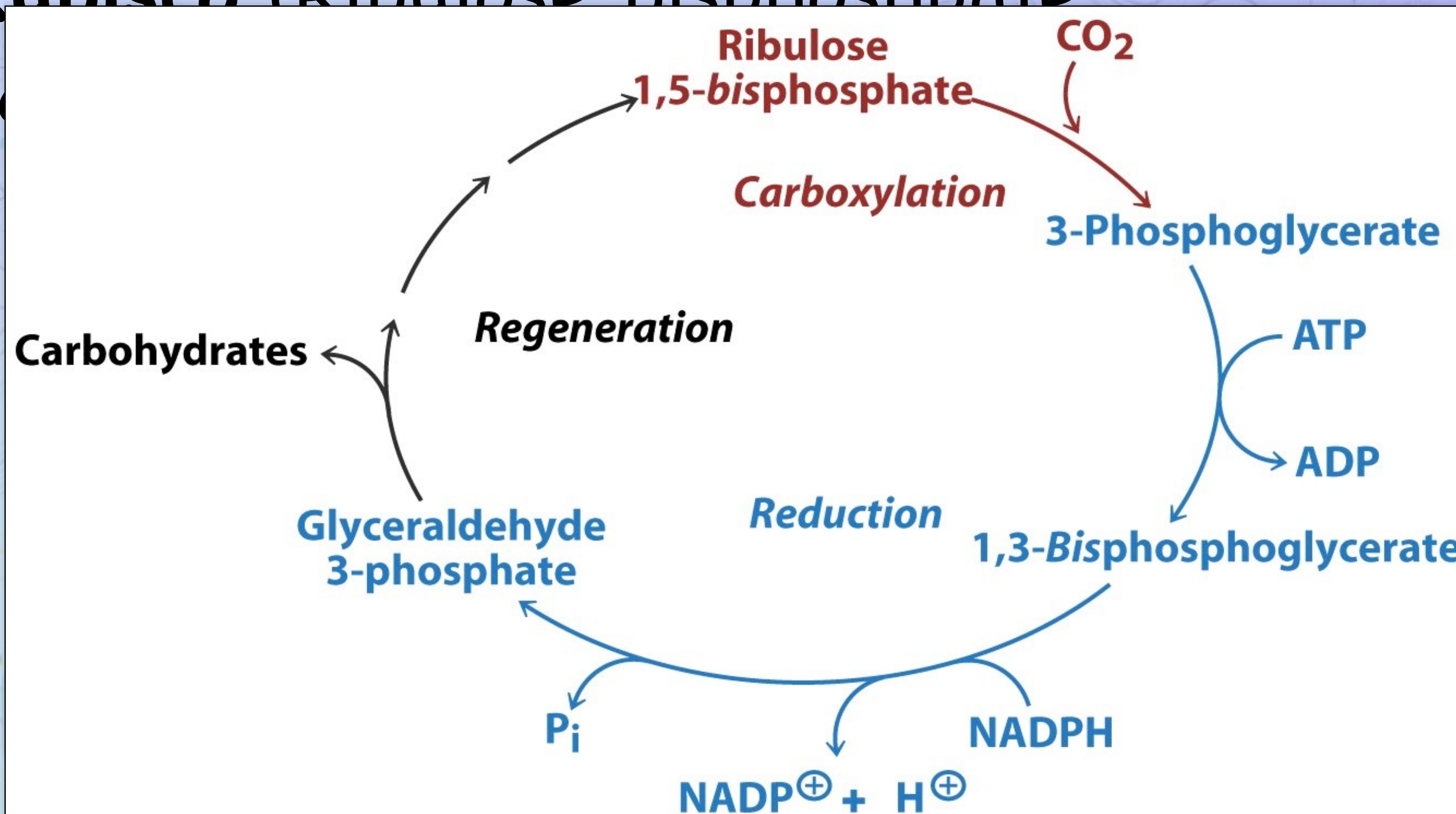
Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

- 50% of soluble protein in leaves is rubisco
- Very inefficient ($k_{cat} \approx 3\ s^{-1}$)
- Nearly every organic-based carbon on earth has passed through the active site of this enzyme.

The Dark Reactions

Rubisco (Ribulose bisphoshpate

c



The Dark Reactions

R

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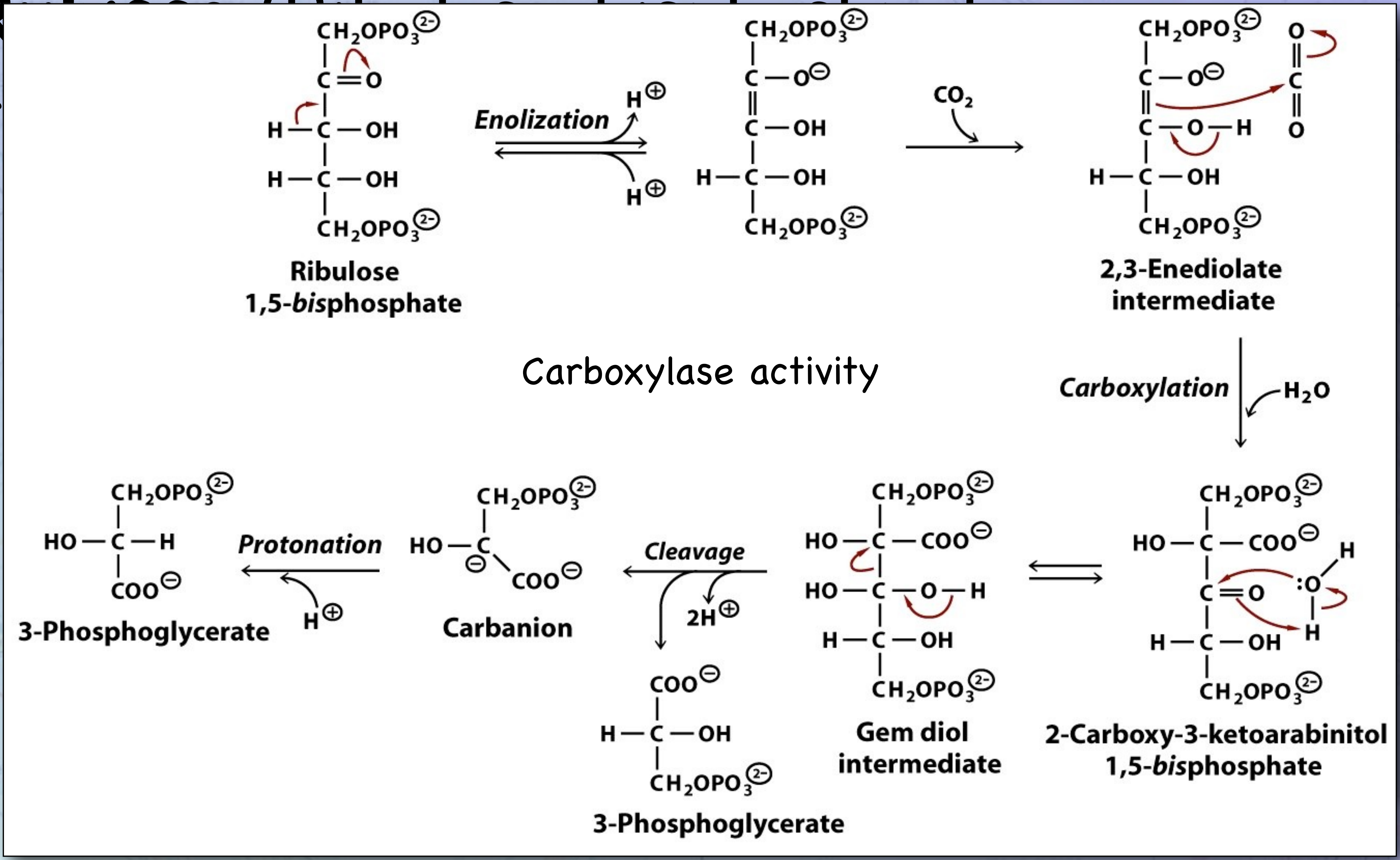
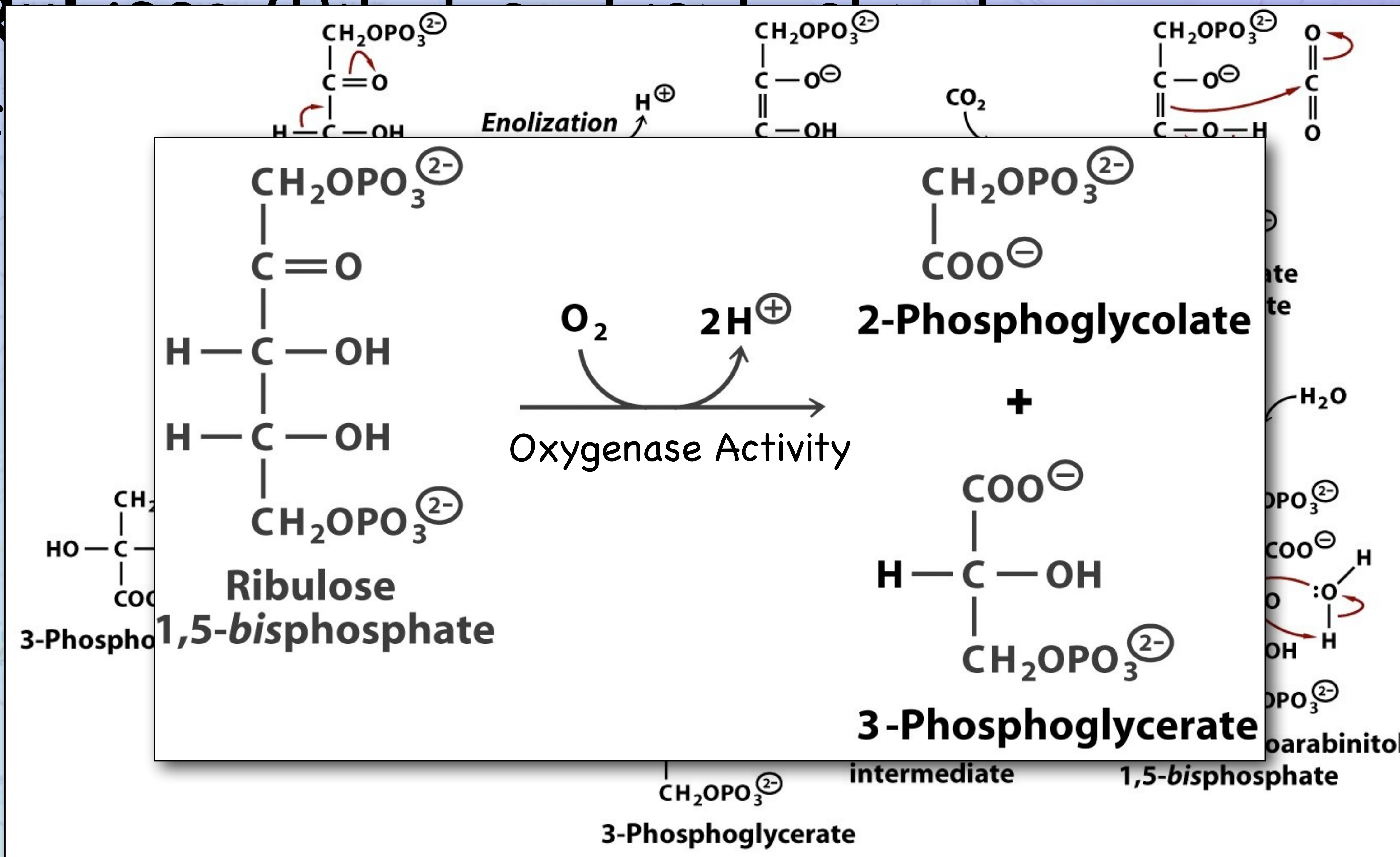


The Dark Reactions



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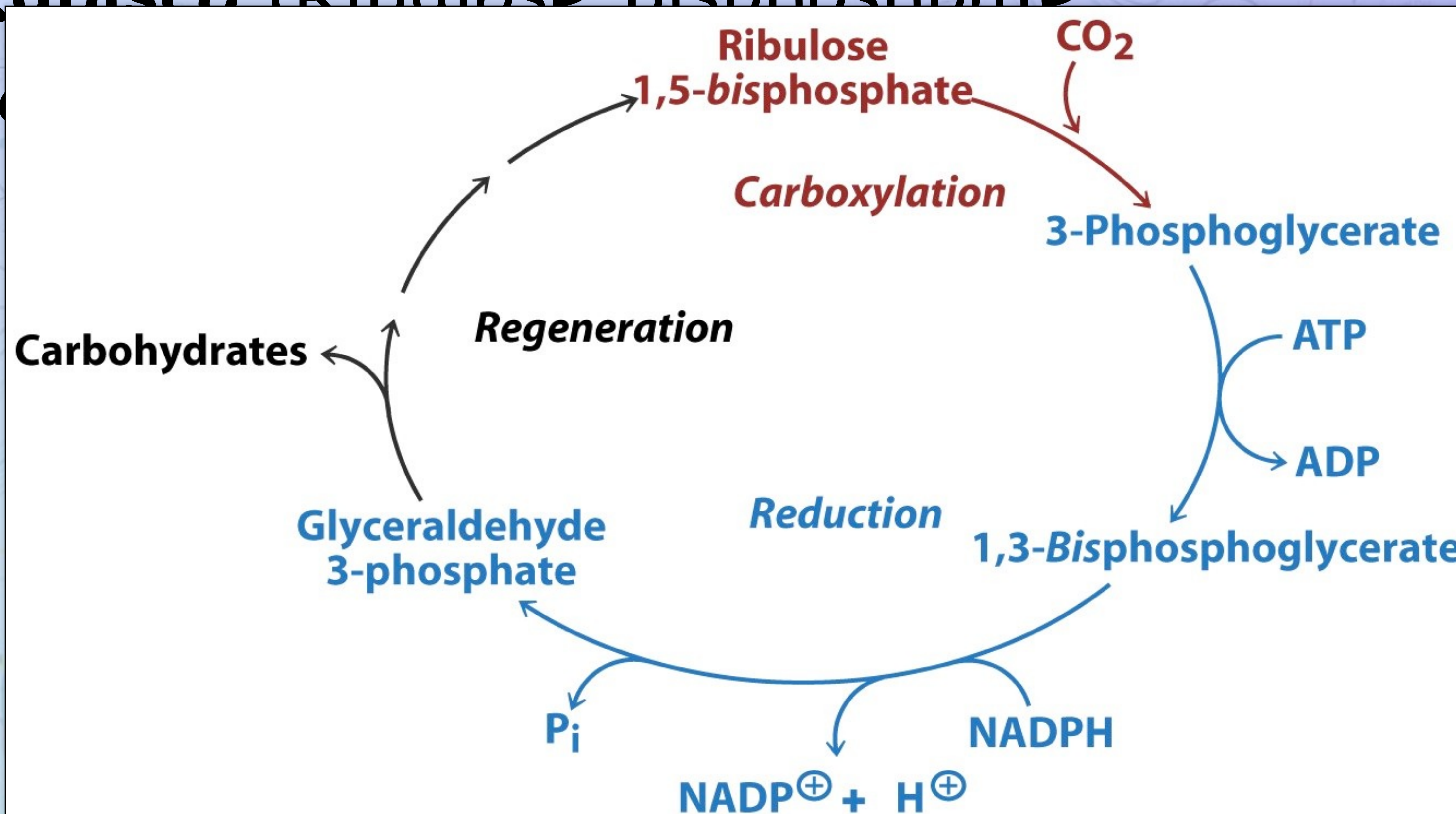

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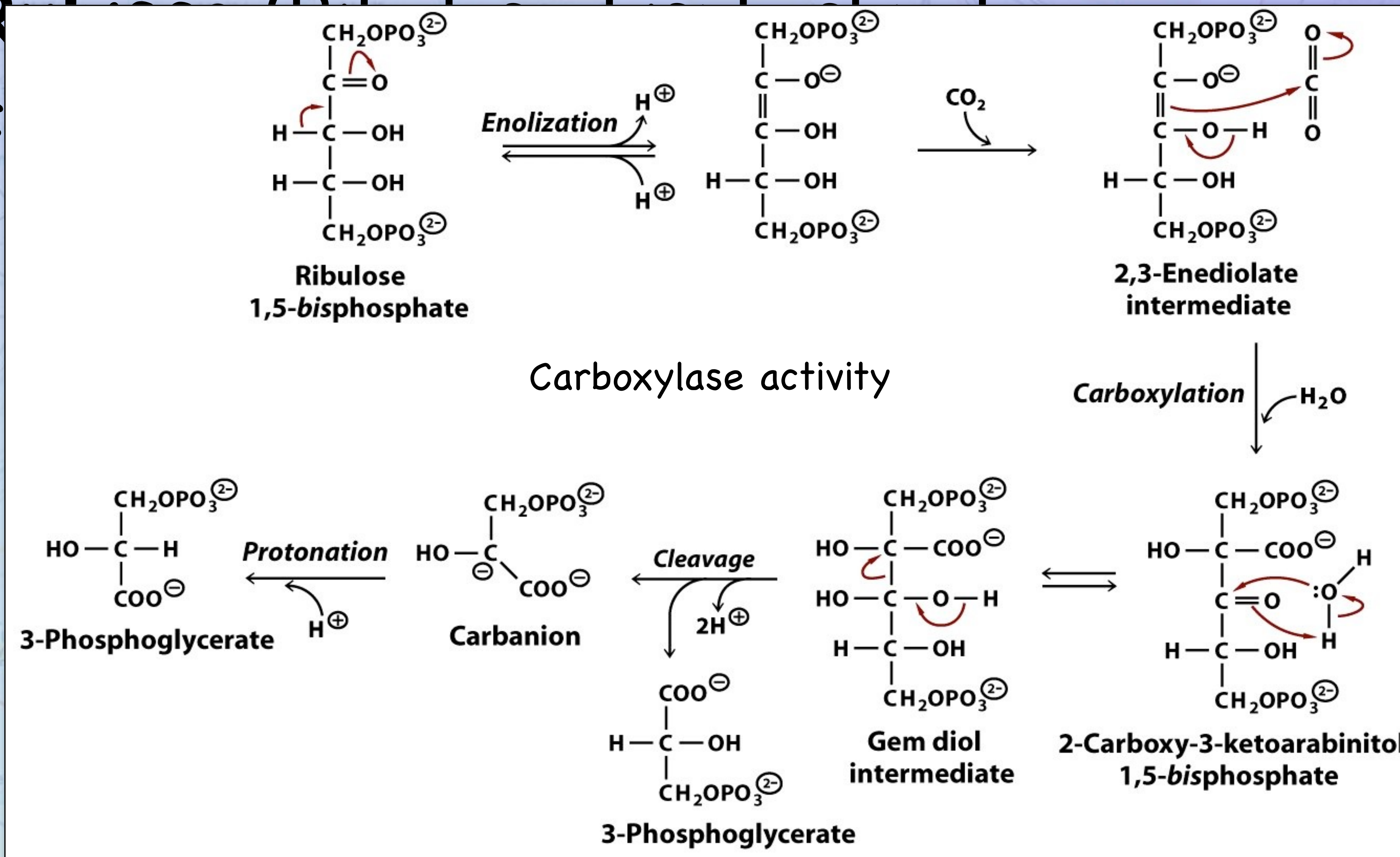
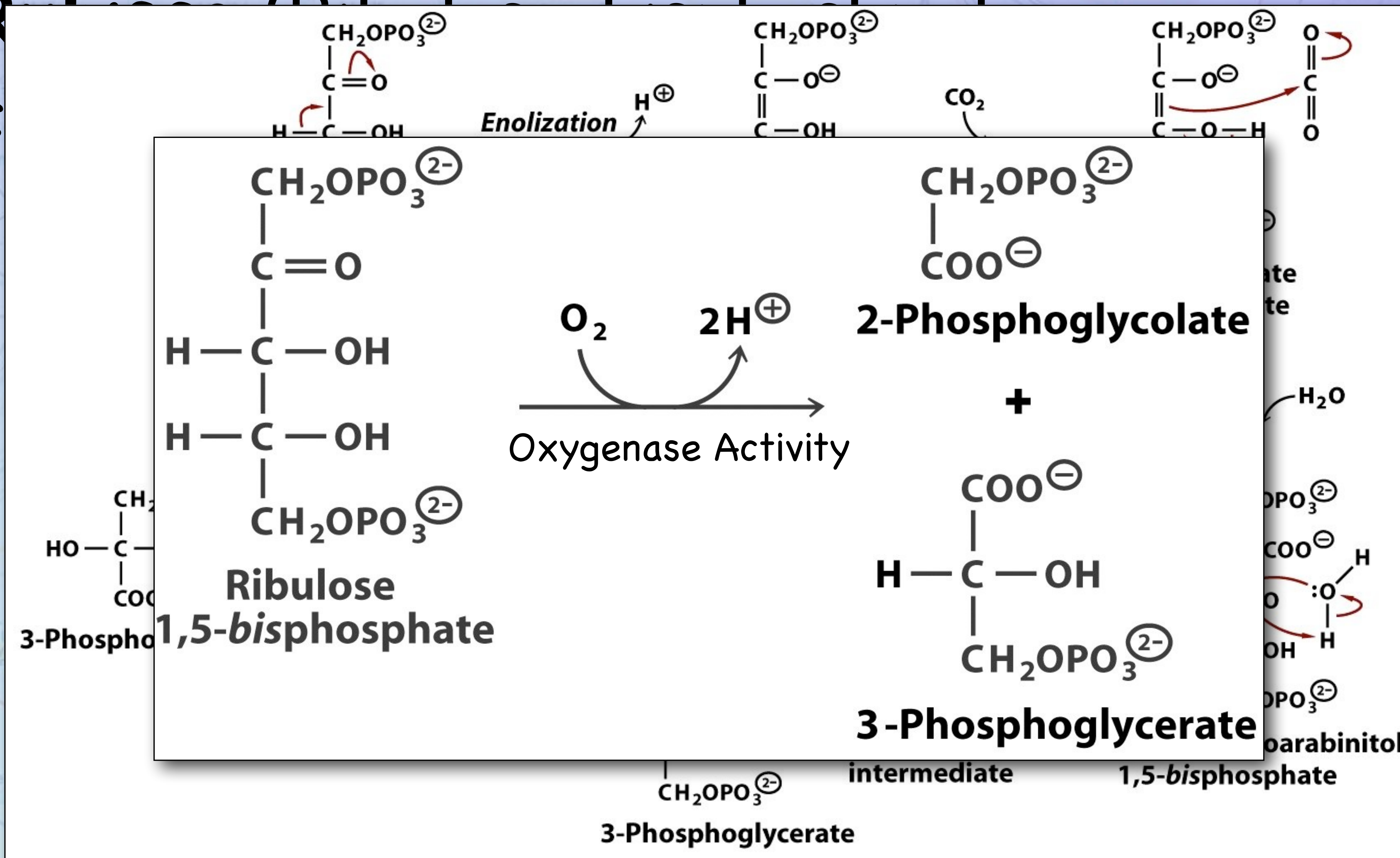


The Dark Reactions



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Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

- The oxygenase activity is inefficient
  - It consumes ATP and NADPH + H^+
  - It consumes O_2
  - The metabolism of the 2-Phosphoglycerate leads to the release of CO_2
- Is called **photorespiration**
- Some plants, called C_4 plants, can counteract the oxygenase activity by concentrating CO_2 in the leaf cells.

The Dark Reactions

Rubisco (
carboxyl

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  - It con
  - It con
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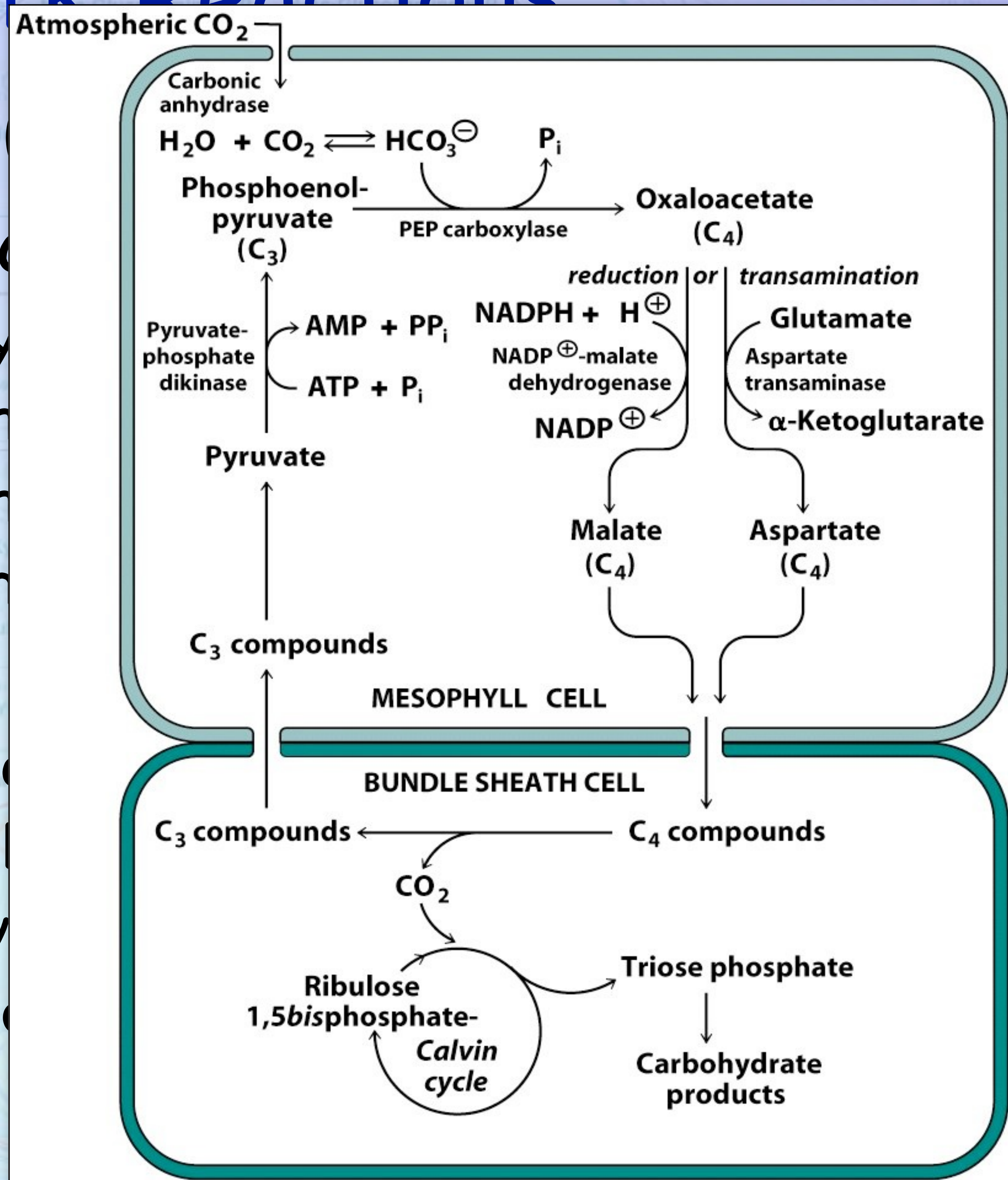
  the oxy CO_2
  in the l



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The Dark Reactions

- **Rubis** ... e
  carbox ...
  - The ... t
    - It ... +
    - It
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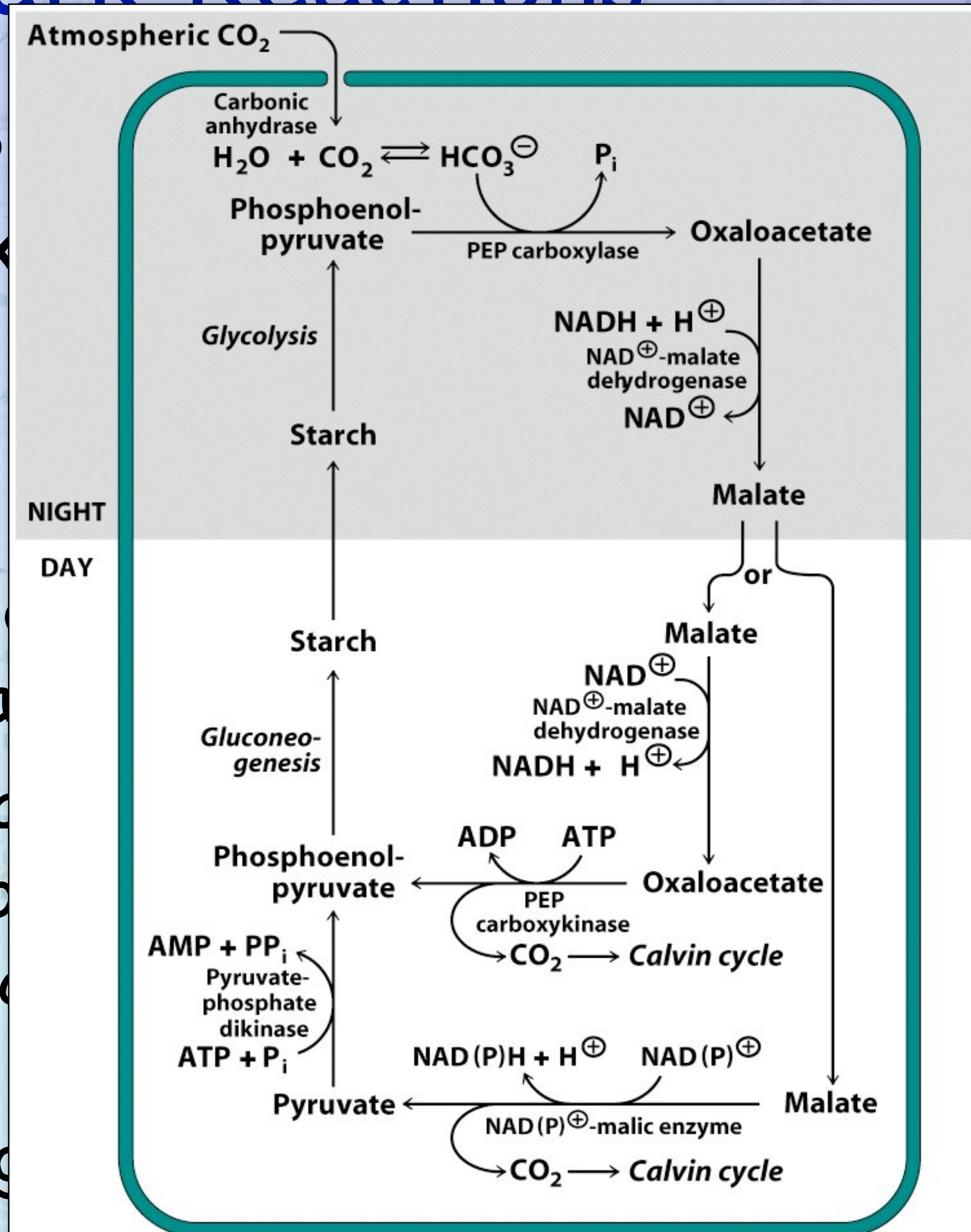
  - Is c ...
  - Xer ... nd
    pine ... uring the
    day ... night
    using ...



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Next Up

- Lecture 10 – Lipid Metabolism (Moran et al., Chapter 16)