Chem 352 - Lecture 9
Photosynthesis

Question for the Day: How is photosynthesis analogous to a combination of gluconeogenesis, the pentose phosphate pathway, and the electron transport chain?

Introduction

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

- It allowed energy to be obtain from an extraterrestrial source.
- This led 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.

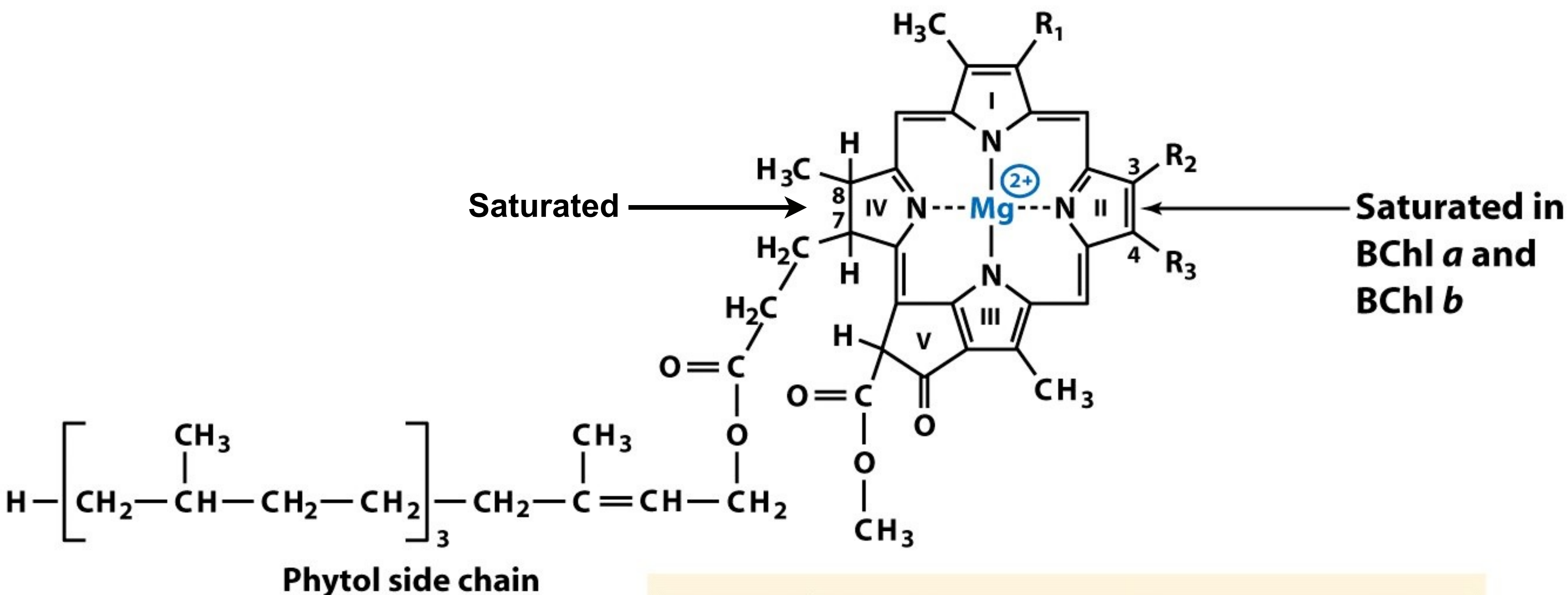
Introduction

- 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*	$-C(=O)-CH_3$	$-CH_3$	$-CH=CH_2$

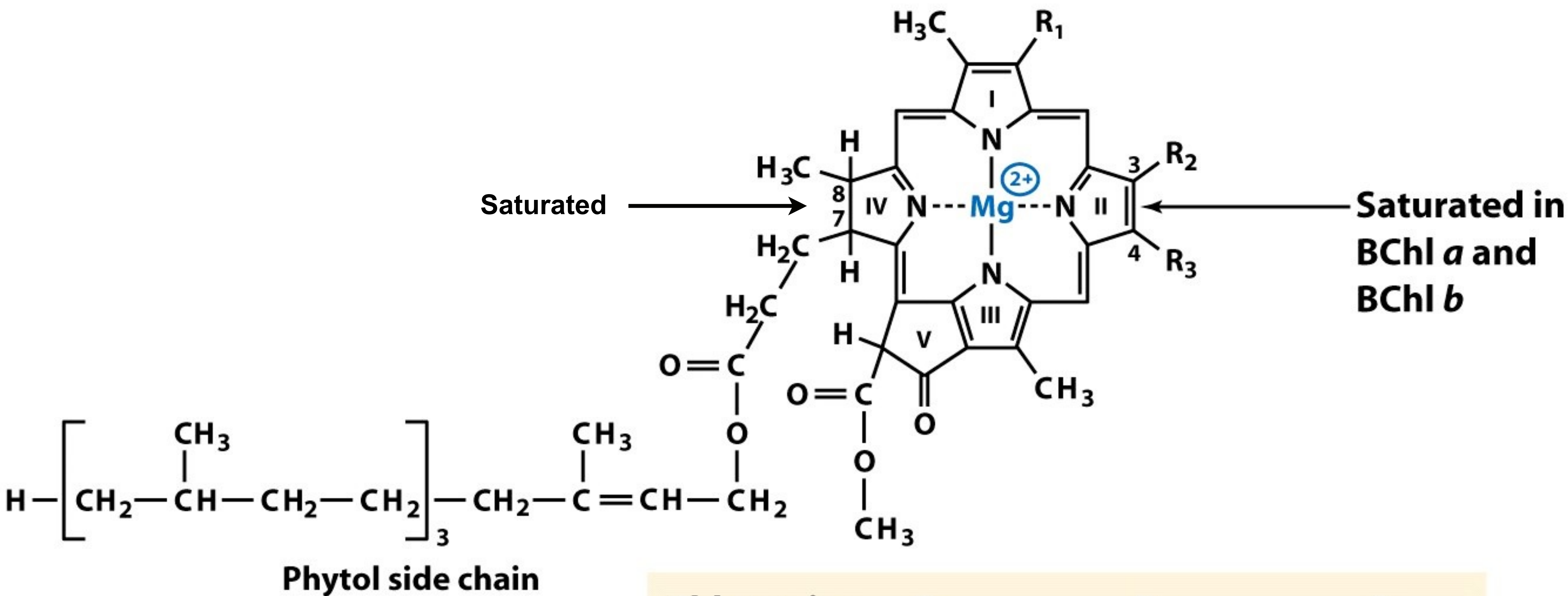
(bacterial)

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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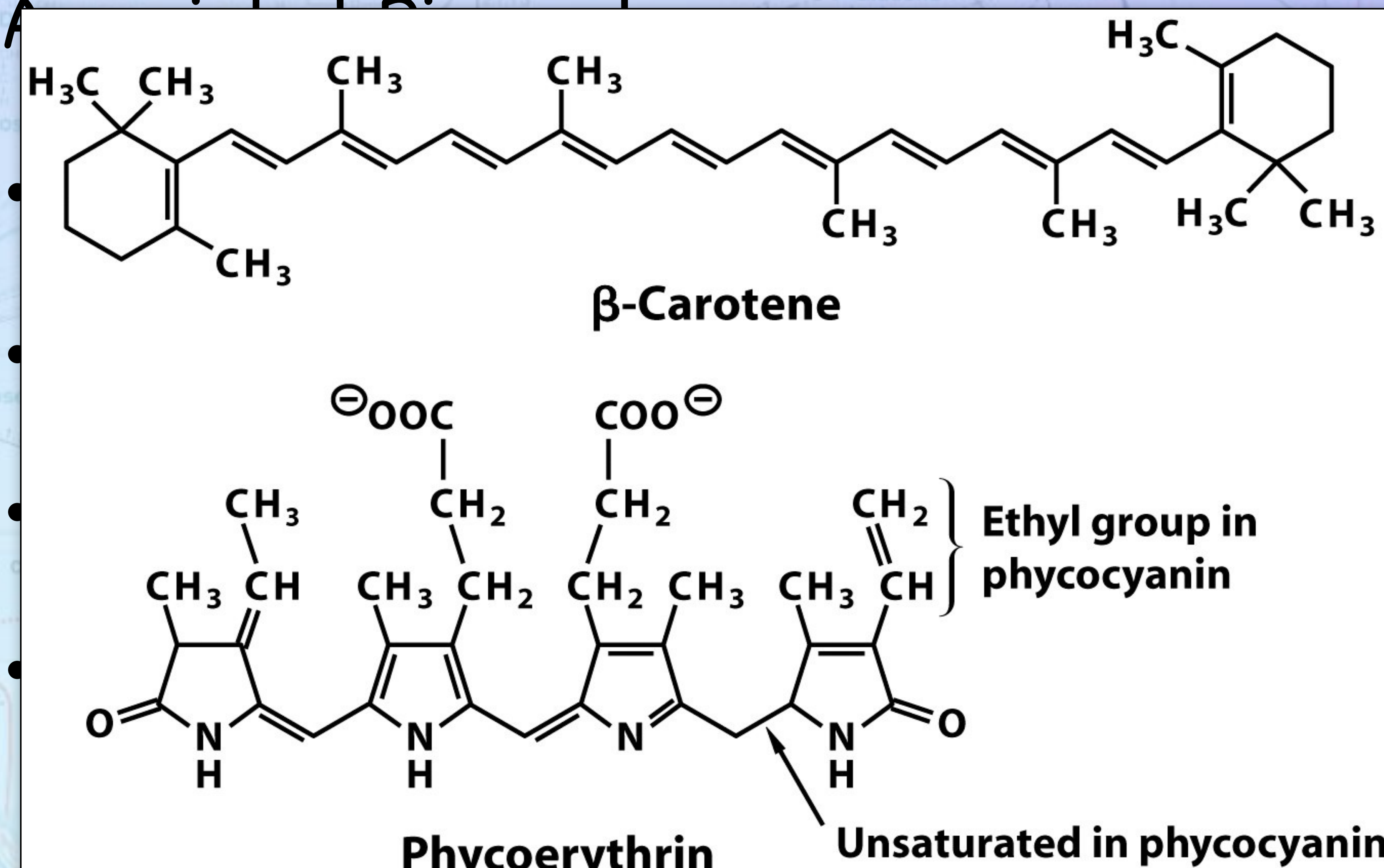

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Light-Harvesting Pigments

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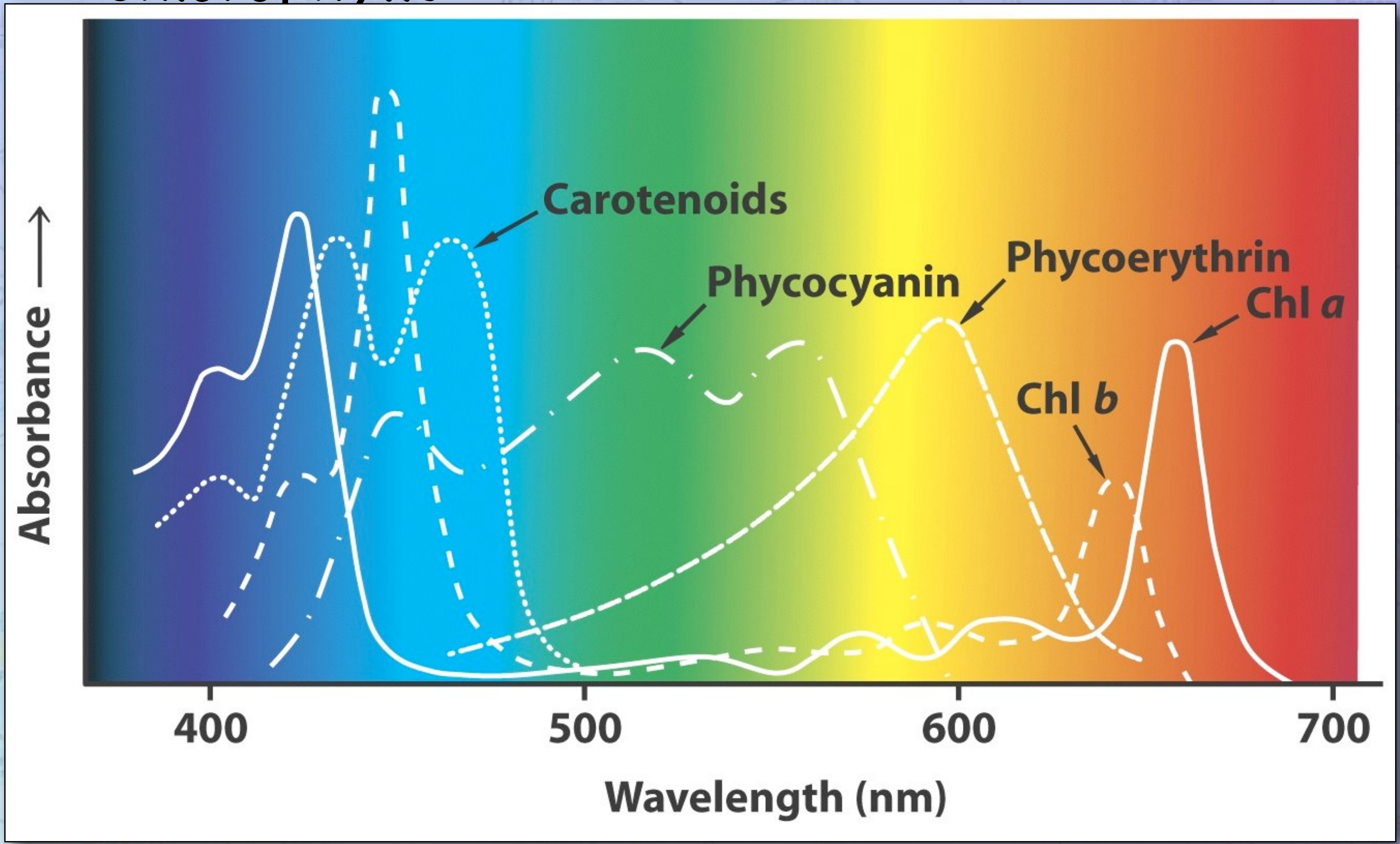

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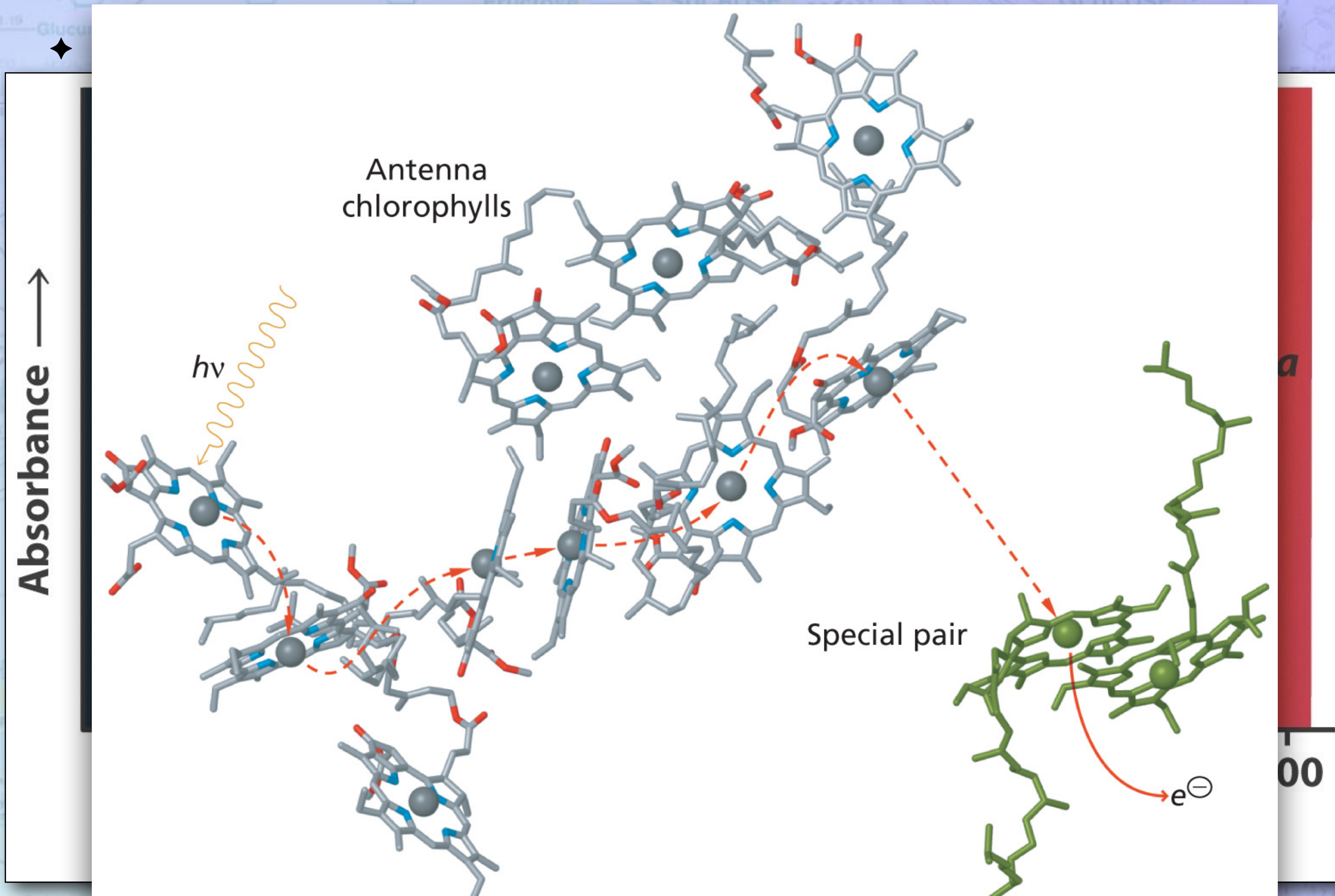

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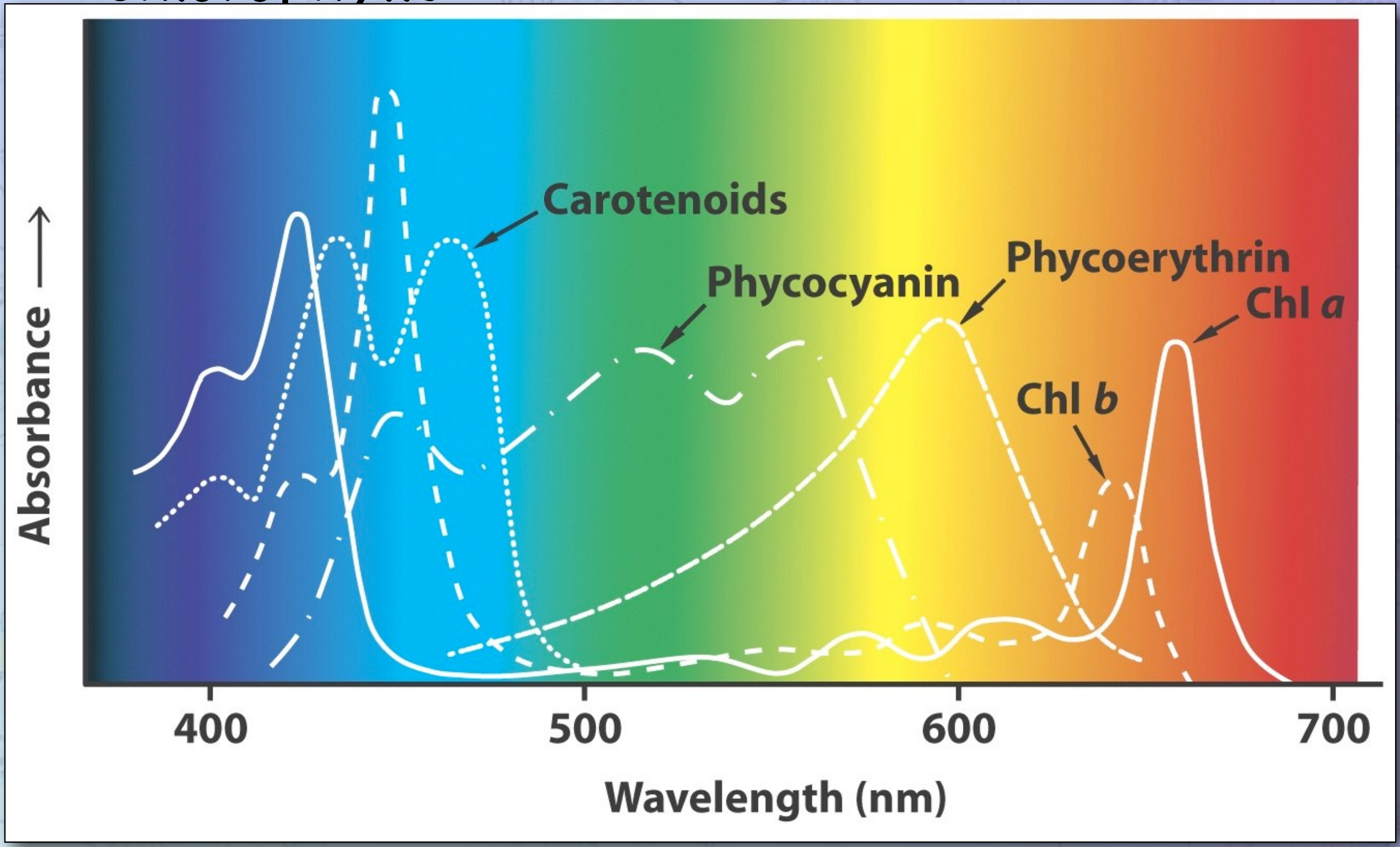

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  - β-carotene
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Light-Harvesting Pigments

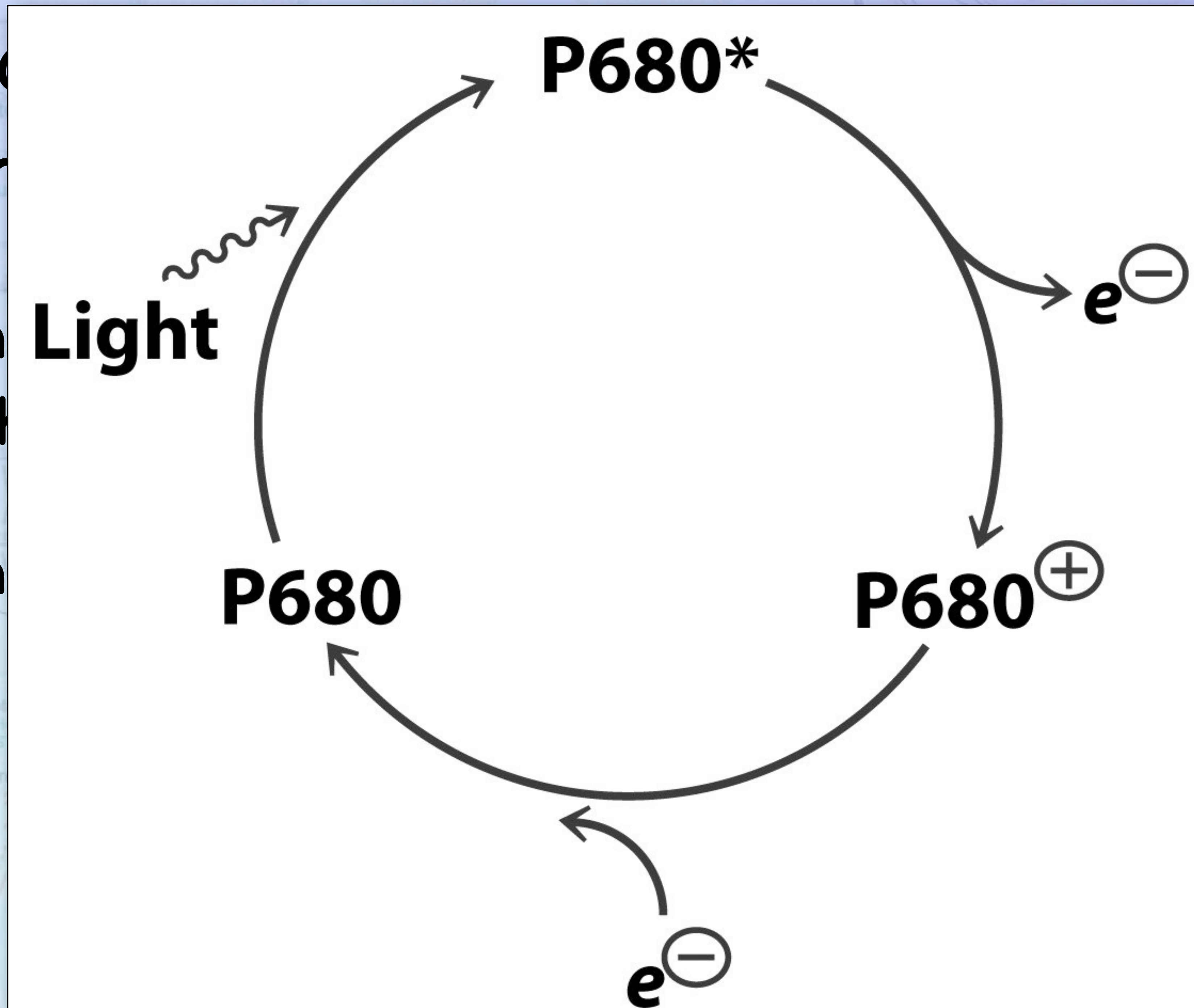
Photosystems have a special pair of chlorophylls called the **special pair**.

- 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… …of
chlor… …r.

- Th… …move a … .
- Th… …t.



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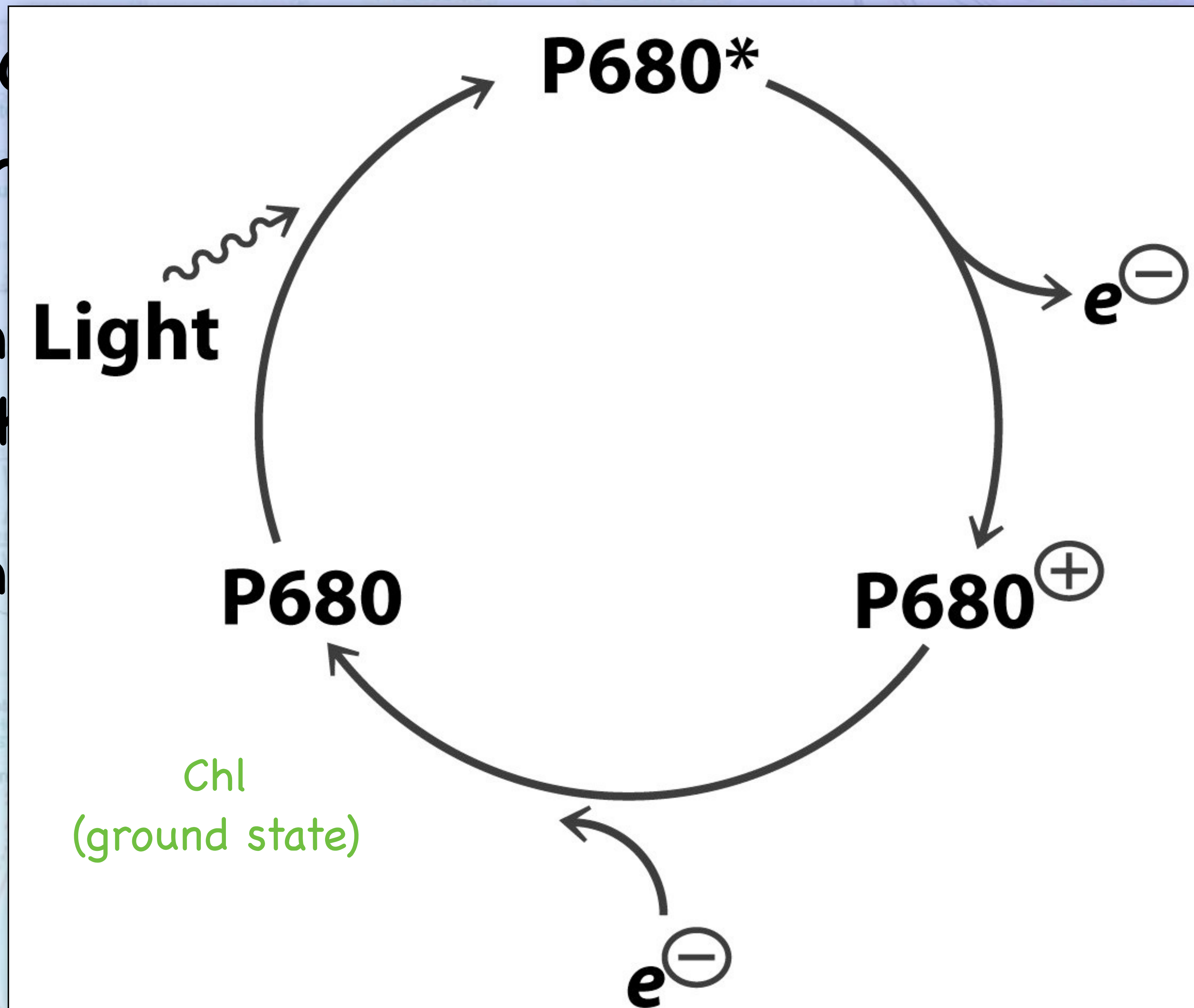

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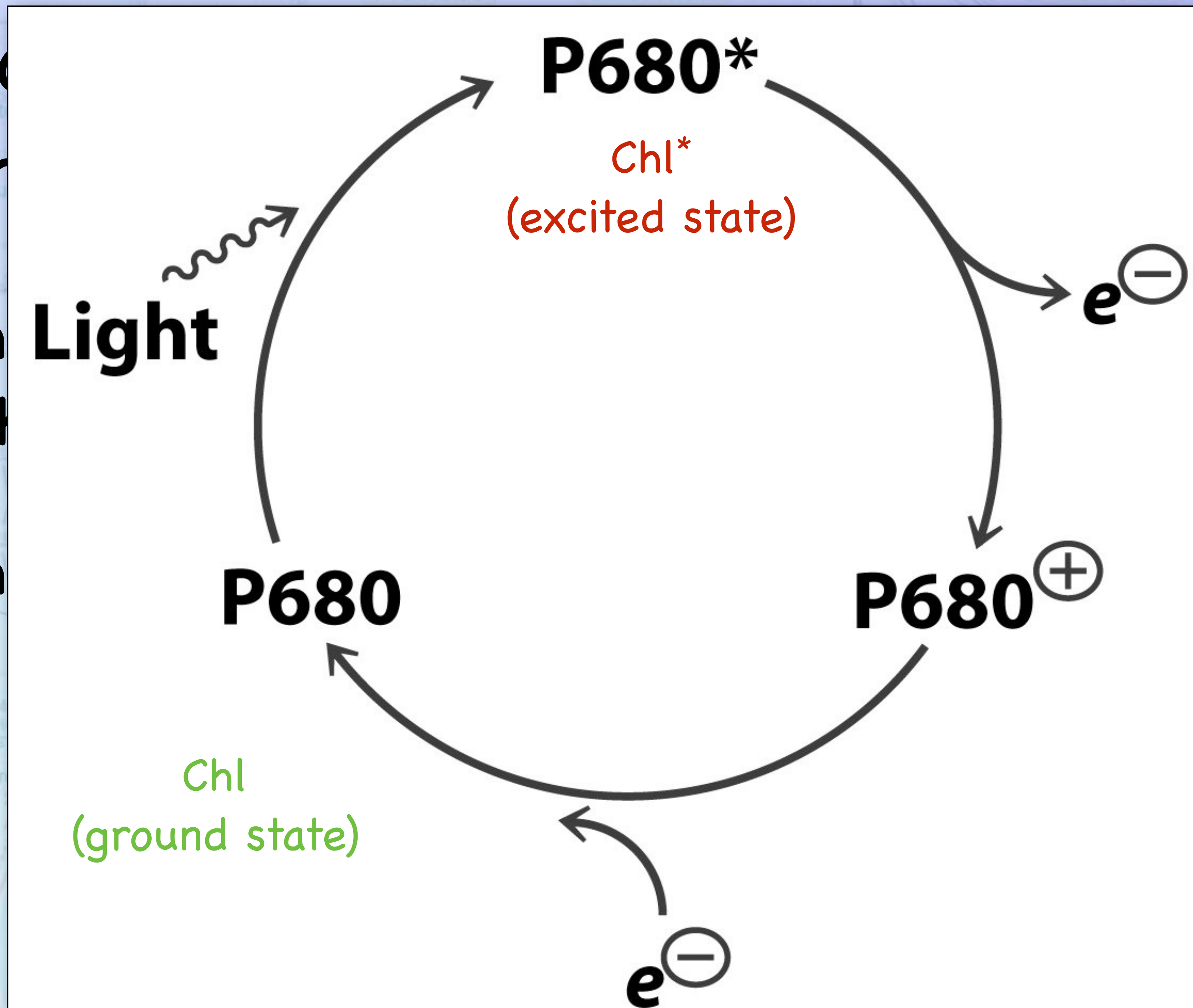

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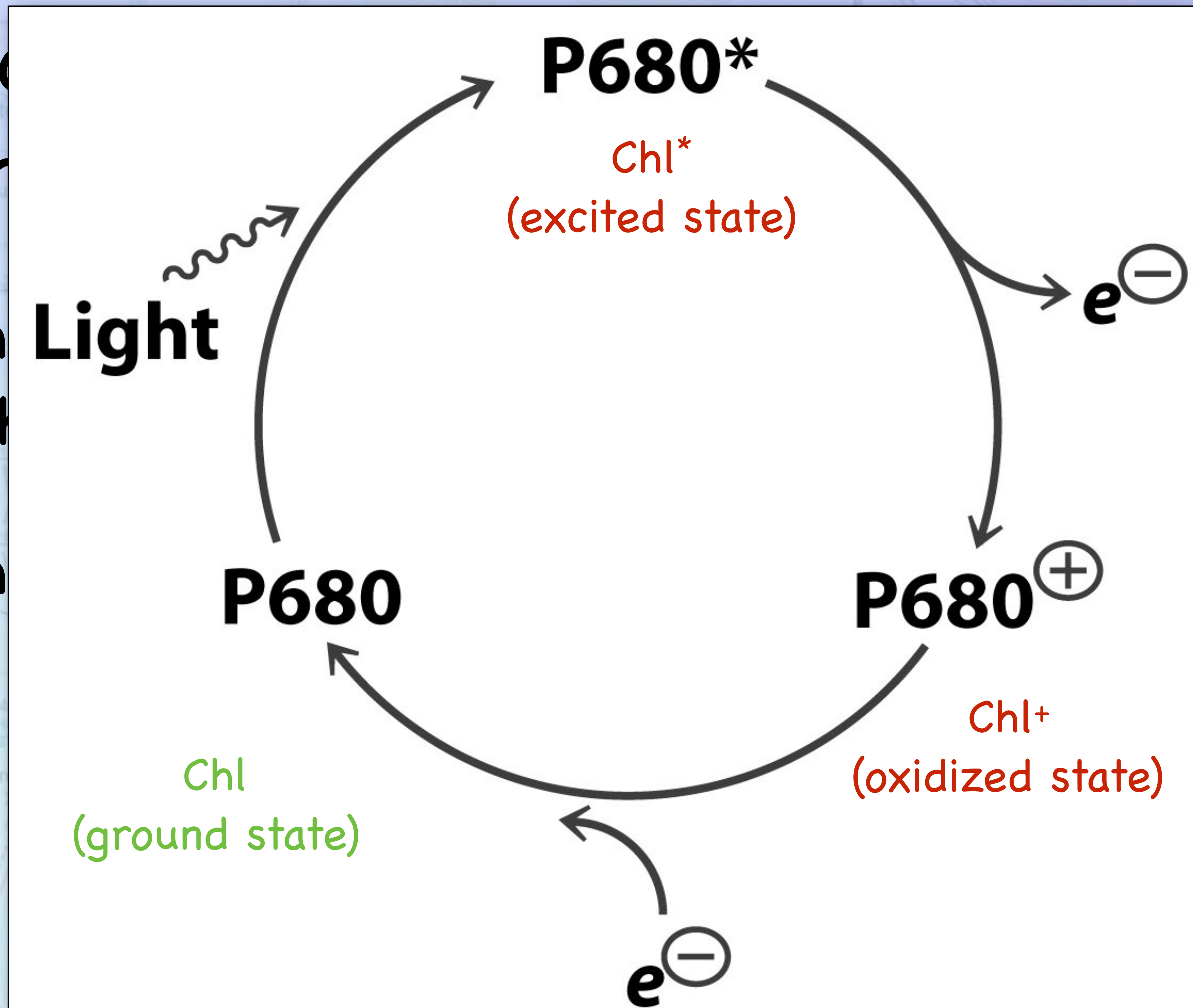

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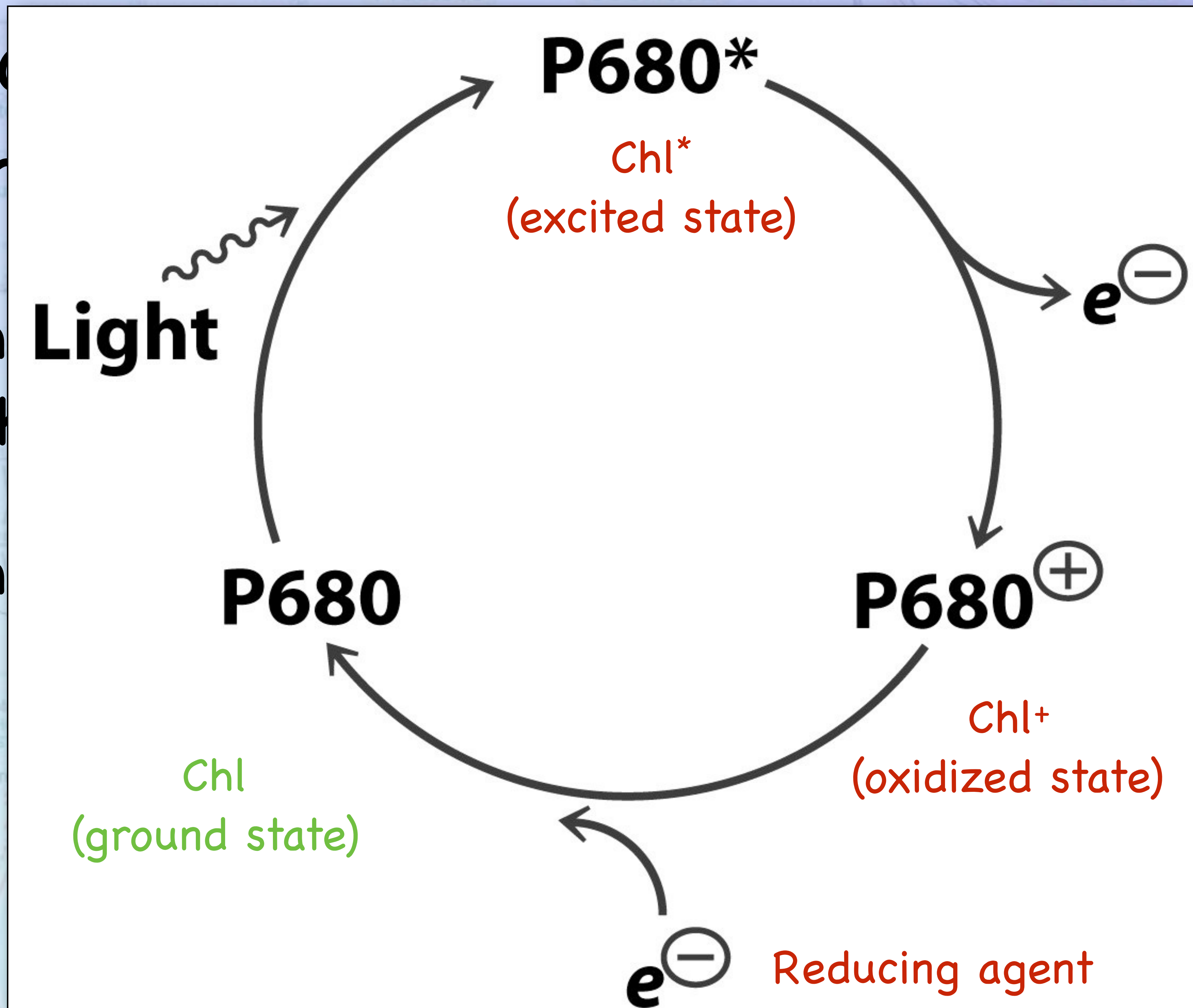

Photosystem II (PSII)

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)

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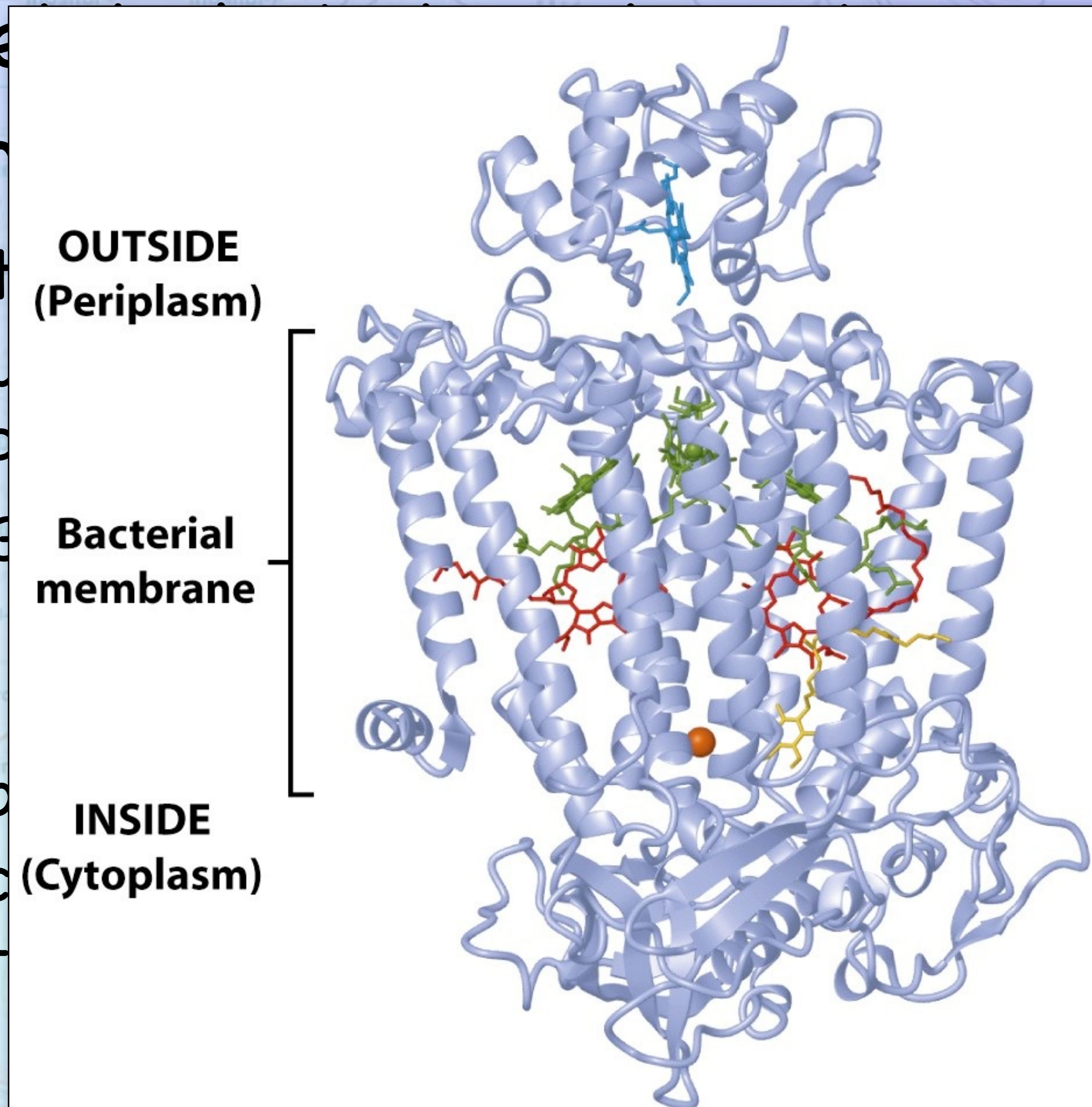

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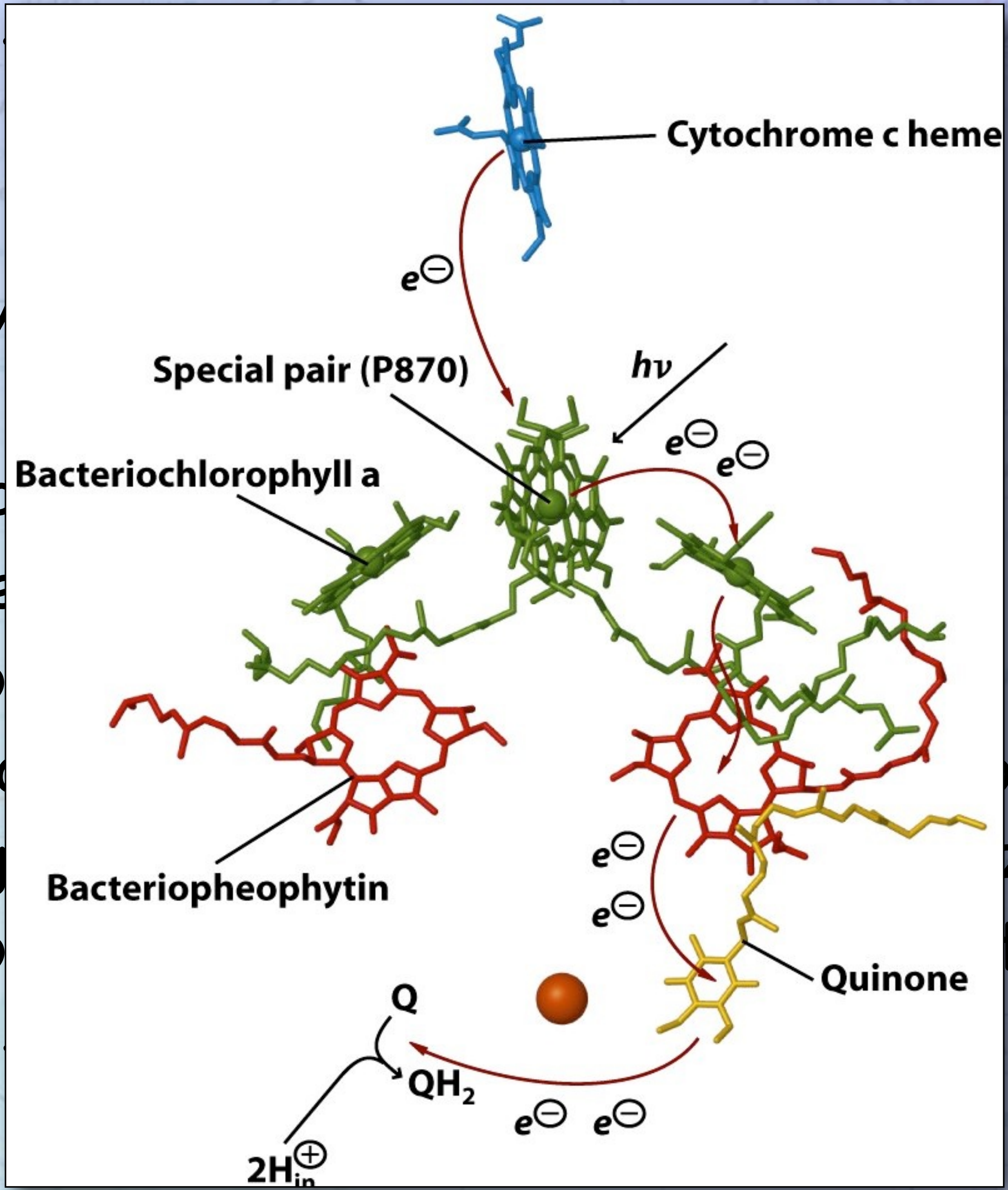

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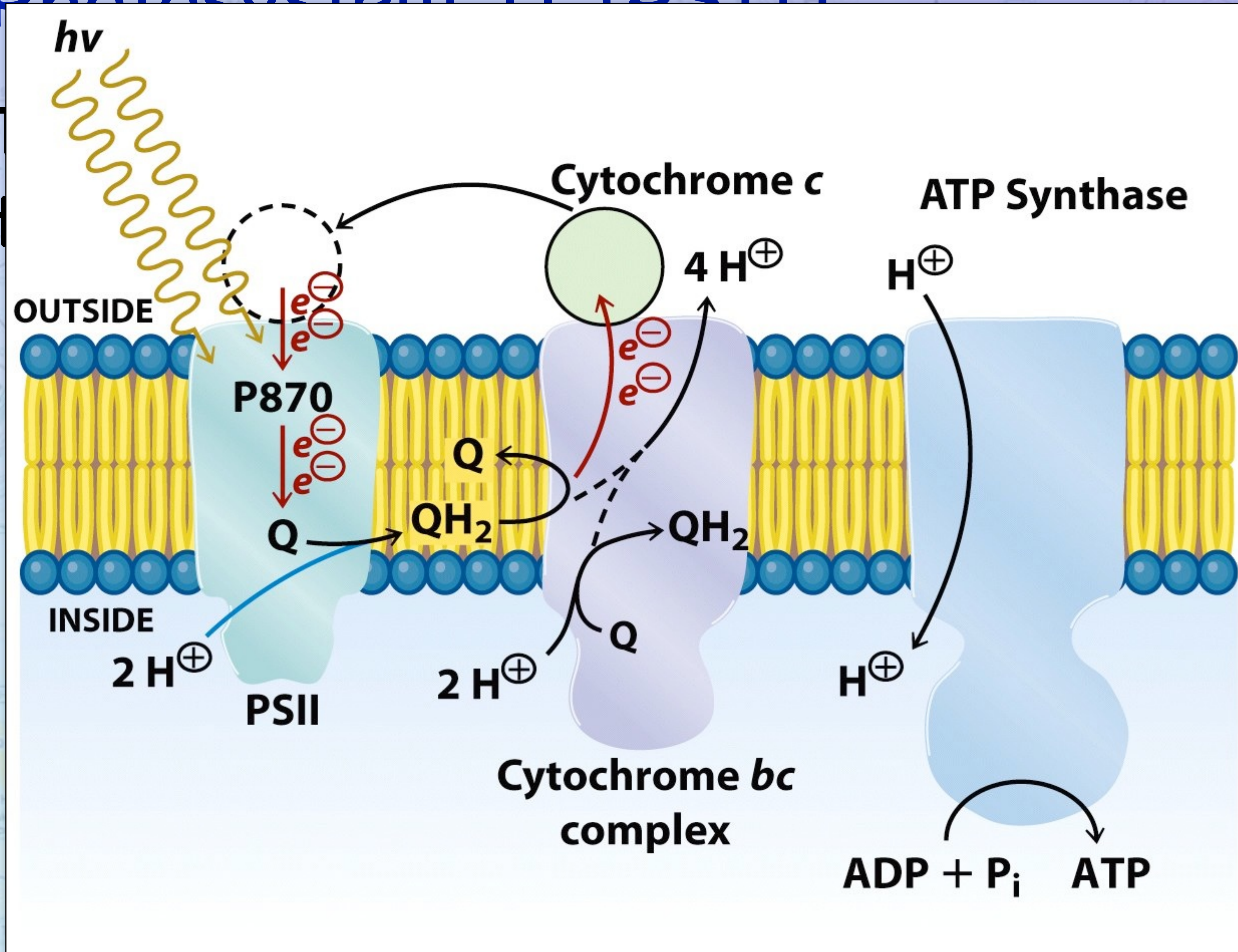

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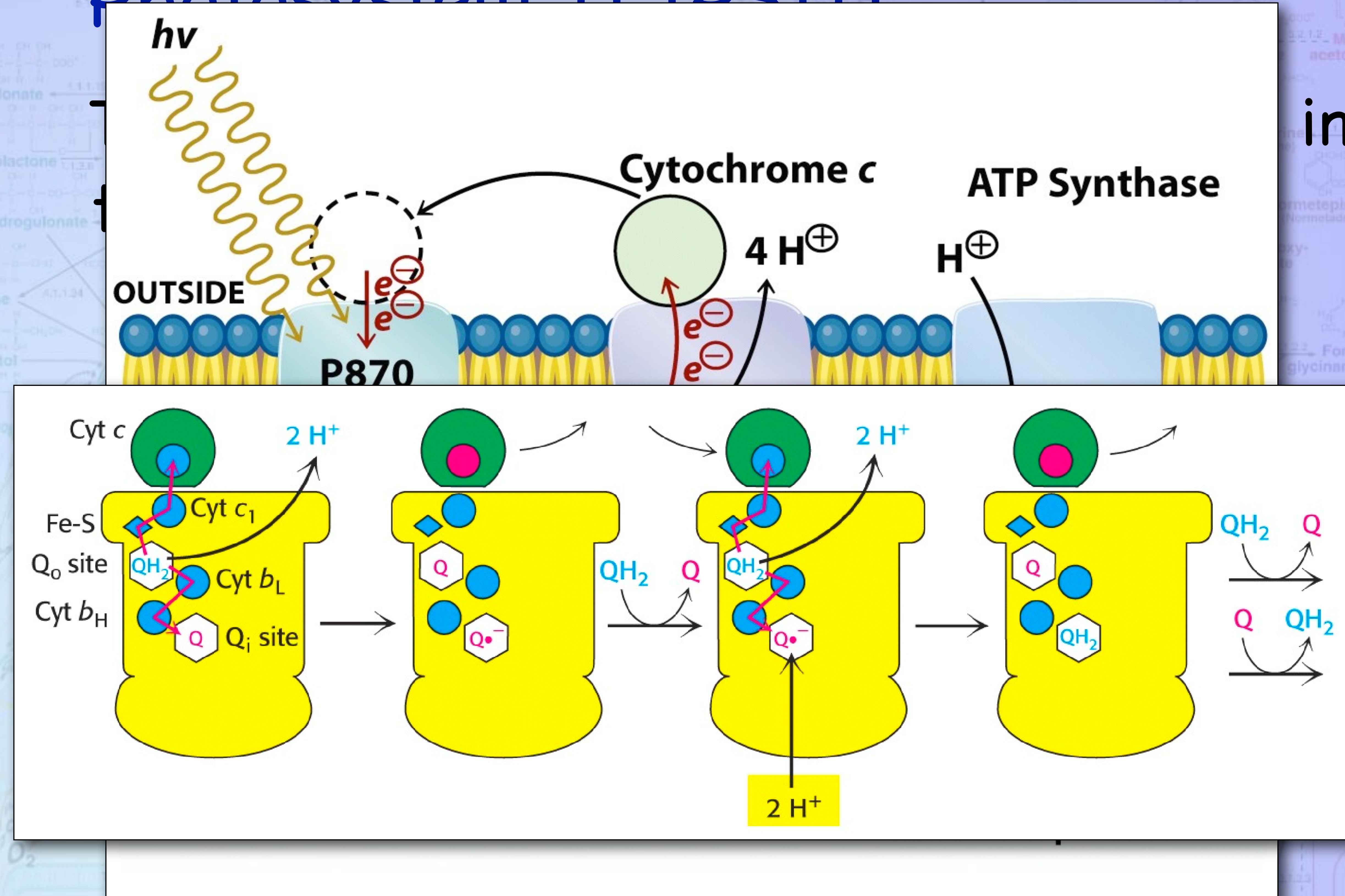

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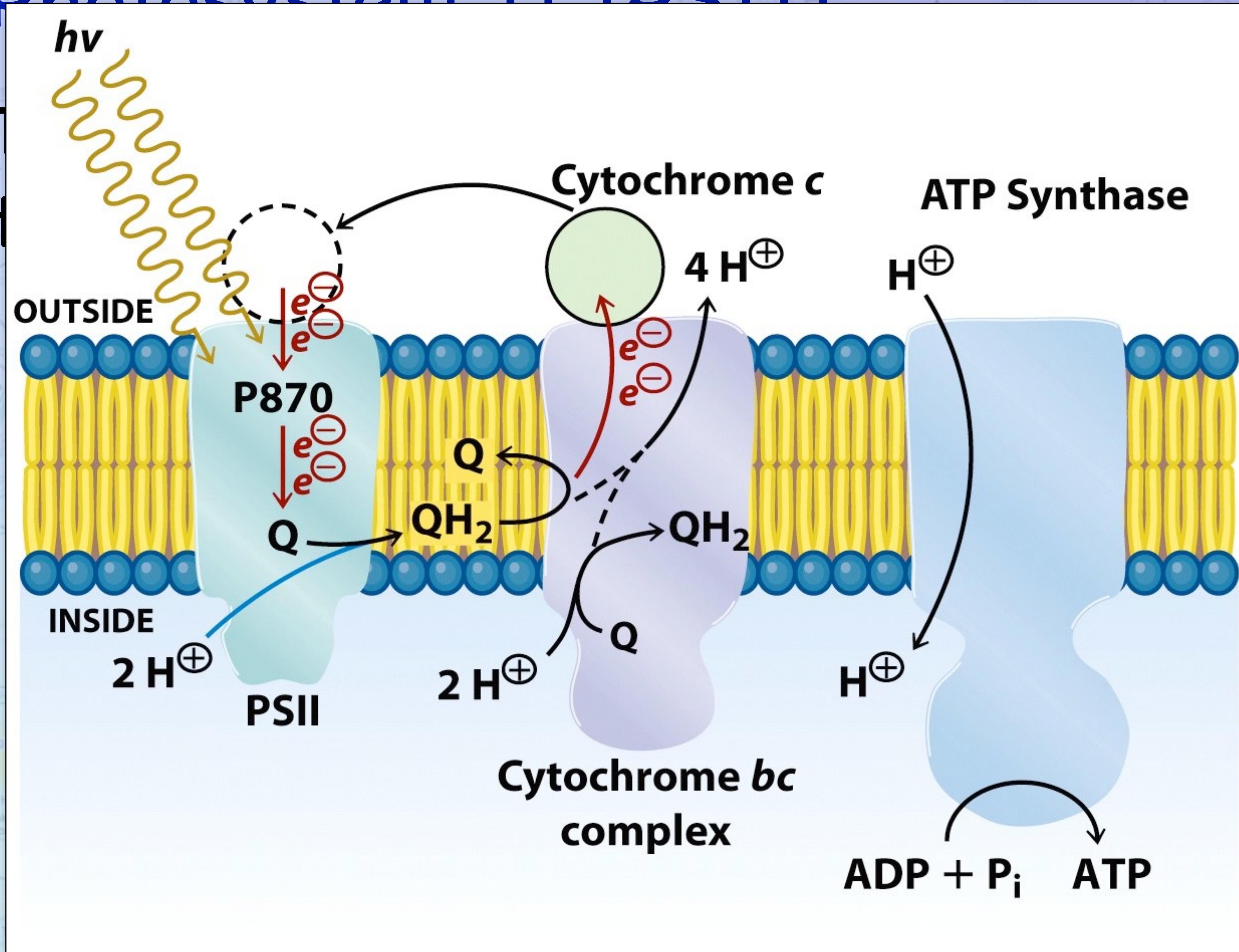

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Table 15.1 Photosystem II reactions

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

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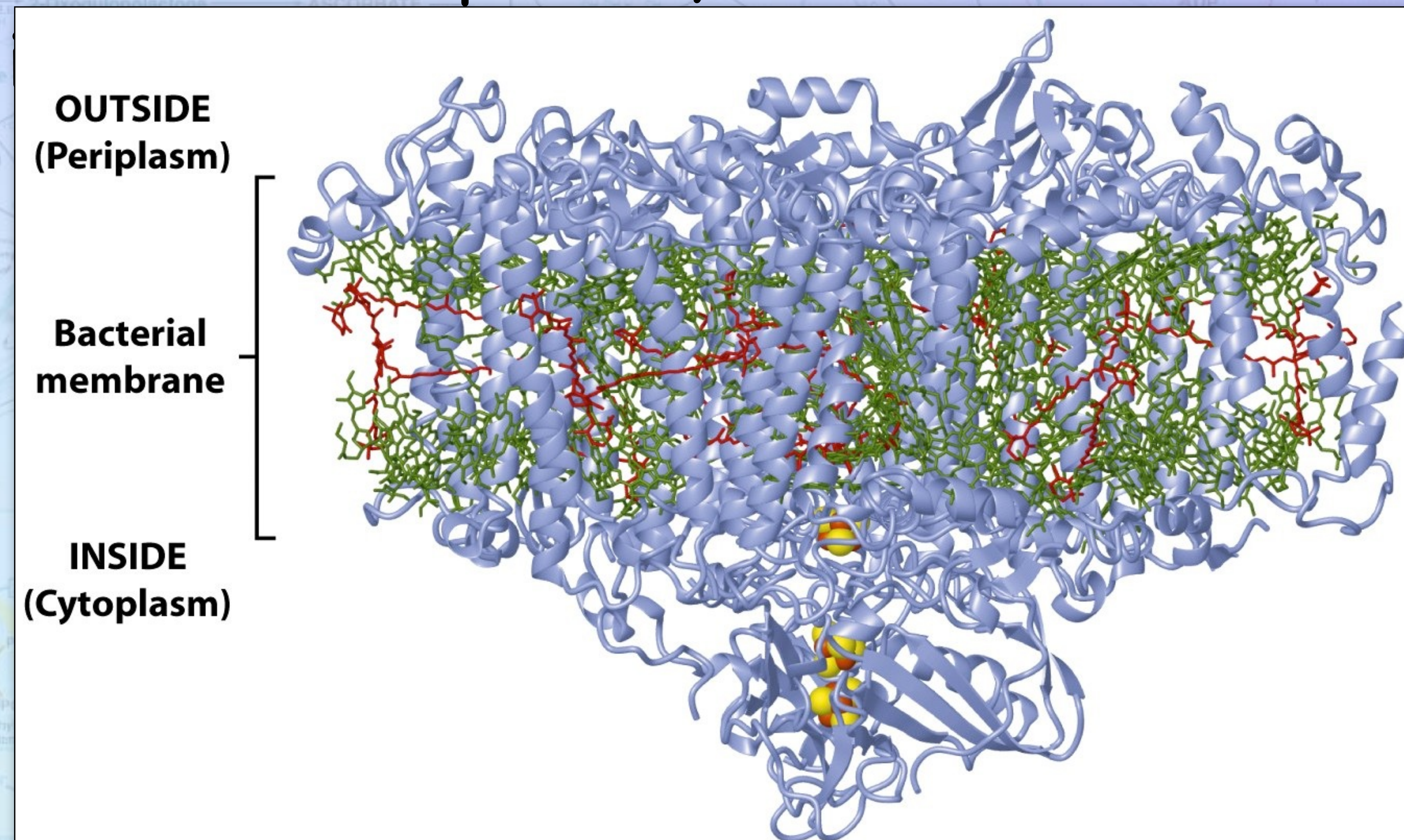
Two related photosystems have evolved



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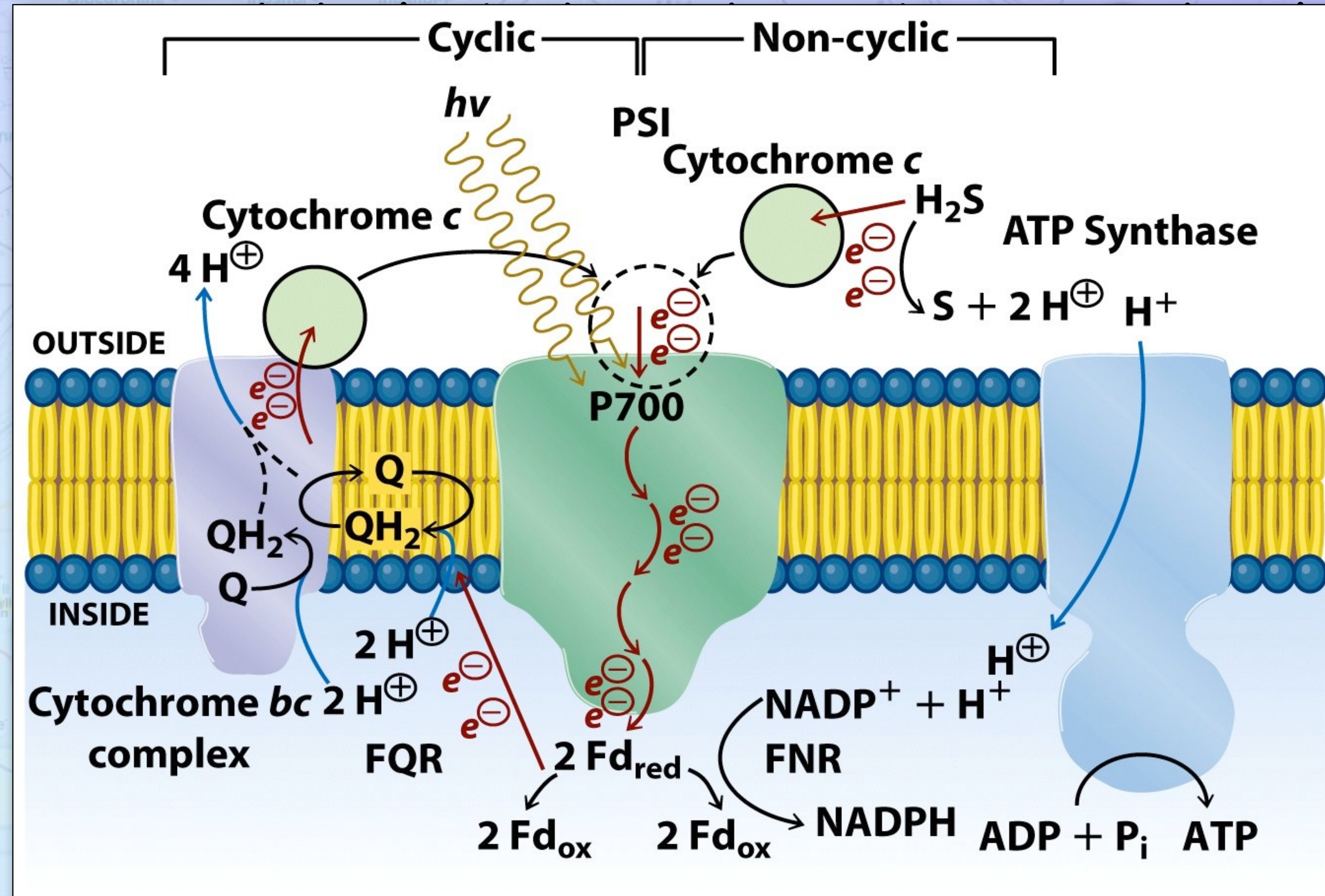
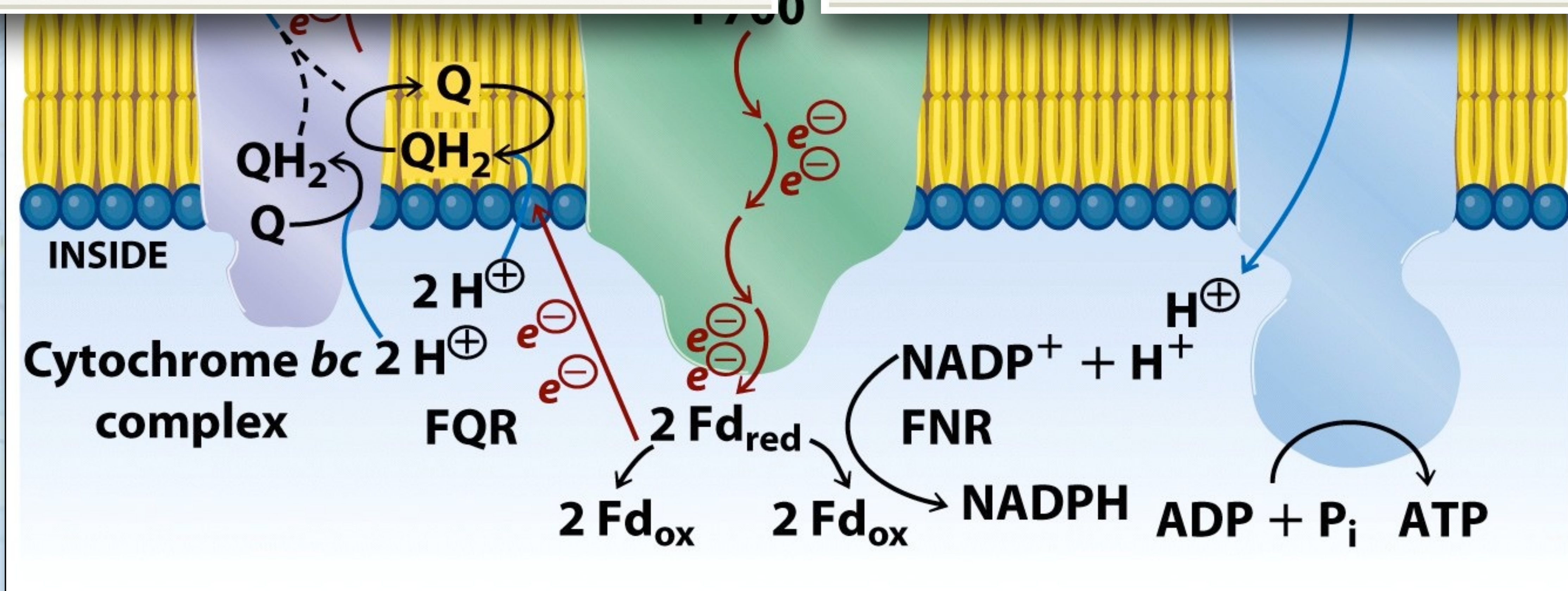


TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
$2\,H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + $2\,H^{\oplus}$ + $2e^{\ominus}$ → NADPH + $H^{\oplus}$	−0.32
$NAD^{\oplus}$ + $2\,H^{\oplus}$ + $2e^{\ominus}$ → NADH + $H^{\oplus}$	−0.32
Lipoic acid + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Dihydrolipoic acid	−0.29
Glutathione (oxidized) + $2\,H^{\oplus}$ + $2e^{\ominus}$ → 2 Glutathione (reduced)	−0.23
FAD + $2\,H^{\oplus}$ + $2e^{\ominus}$ → $FADH_2$	−0.22
FMN + $2\,H^{\oplus}$ + $2e^{\ominus}$ → $FMNH_2$	−0.22
Acetaldehyde + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Ethanol	−0.20
Pyruvate + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Lactate	−0.18
Oxaloacetate + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Malate	−0.17

TABLE 10.4 Standard reduction potentials of some important biological half-reactions

Reduction half-reaction	$E^{\circ\prime}$ (V)
Cytochrome b_5 (microsomal), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.02
Fumarate + $2\,H^{\oplus}$ + $2e^{\ominus}$ → Succinate	0.03
Ubiquinone (Q) + $2\,H^{\oplus}$ + $2e^{\ominus}$ → QH_2	0.04
Cytochrome *b* (mitochondrial), Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.08
Cytochrome c_1, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.22
Cytochrome *c*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.23
Cytochrome *a*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.29
Cytochrome *f*, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.36
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + $2\,H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + $2\,H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1



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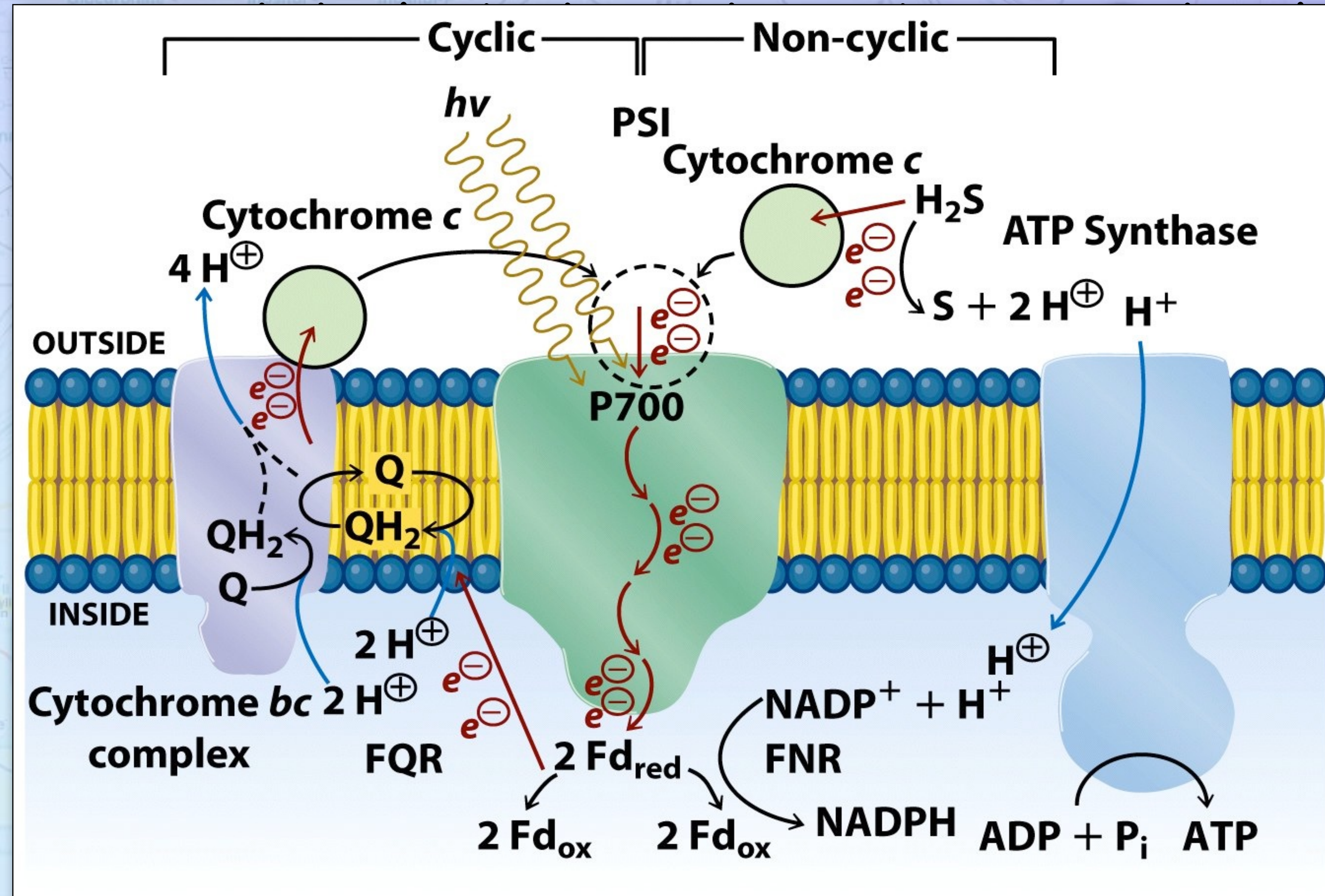

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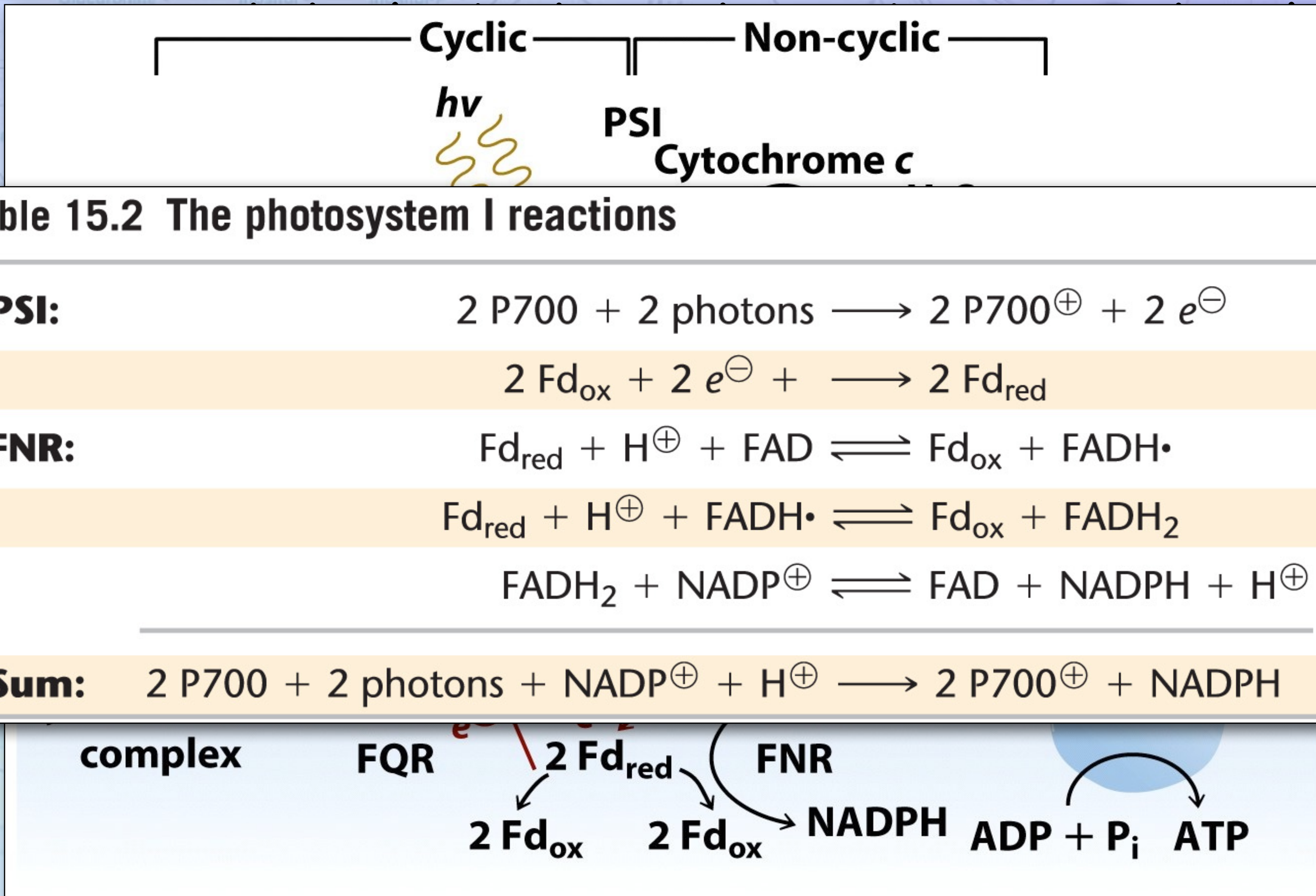
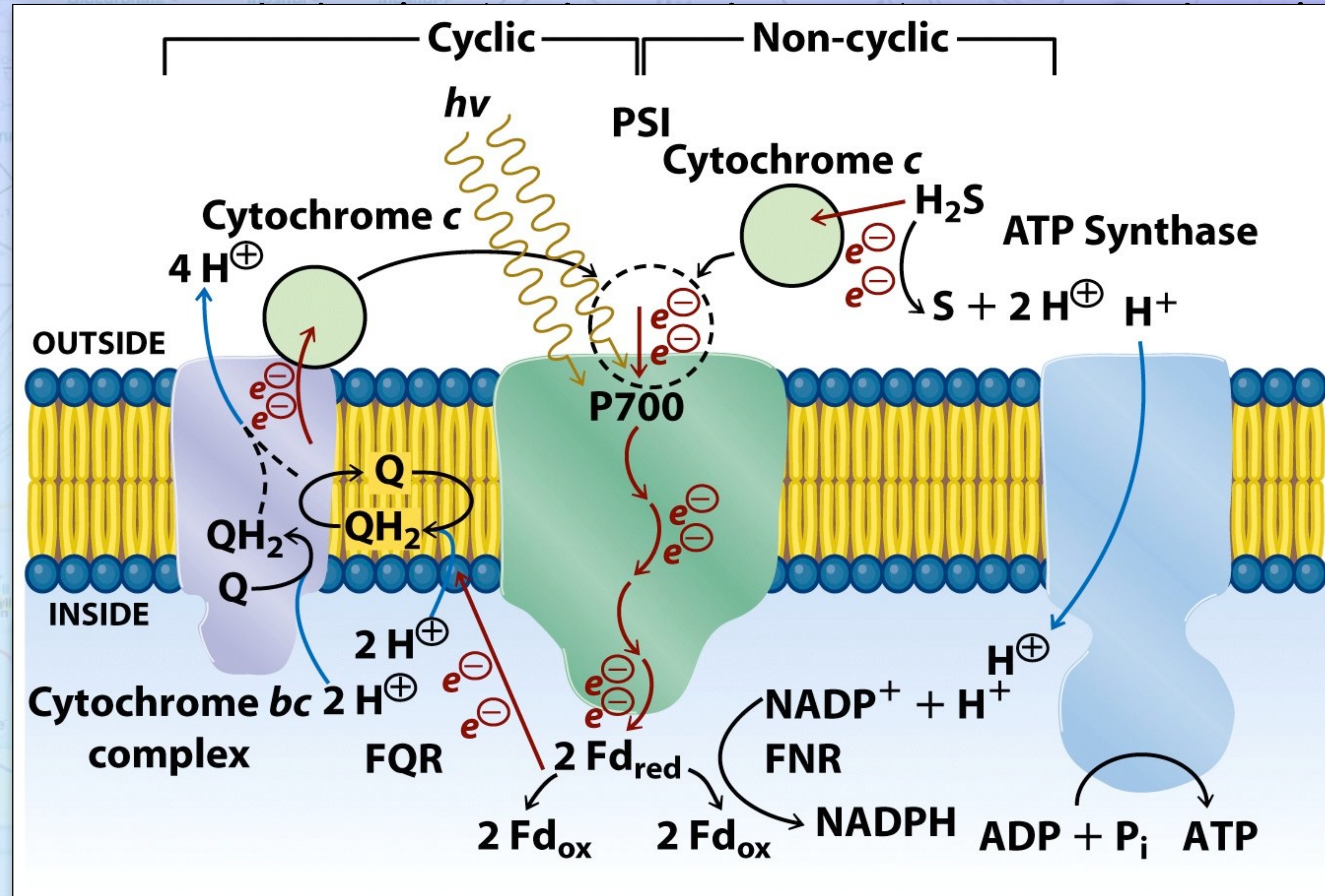


Table 15.2 The photosystem I reactions

PSI:	$2\ P700 + 2\ photons \longrightarrow 2\ P700^{\oplus} + 2\ e^{\ominus}$
	$2\ Fd_{ox} + 2\ e^{\ominus} + \longrightarrow 2\ Fd_{red}$
FNR:	$Fd_{red} + H^{\oplus} + FAD \rightleftharpoons Fd_{ox} + FADH\bullet$
	$Fd_{red} + H^{\oplus} + FADH\bullet \rightleftharpoons Fd_{ox} + FADH_2$
	$FADH_2 + NADP^{\oplus} \rightleftharpoons FAD + NADPH + H^{\oplus}$
Sum:	$2\ P700 + 2\ photons + NADP^{\oplus} + H^{\oplus} \longrightarrow 2\ P700^{\oplus} + NADPH$

Photosystem I (PSI)



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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 $NADPH + H^+$.

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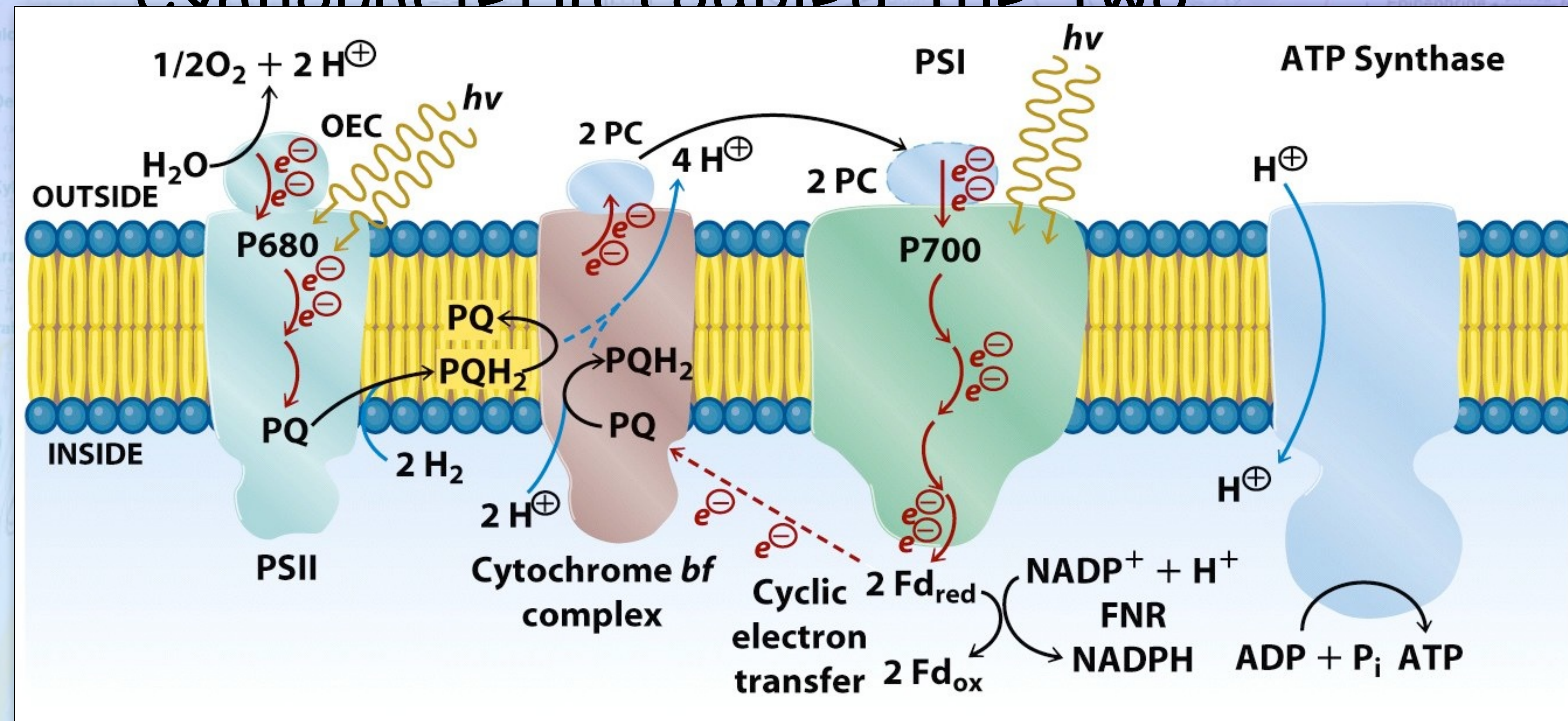

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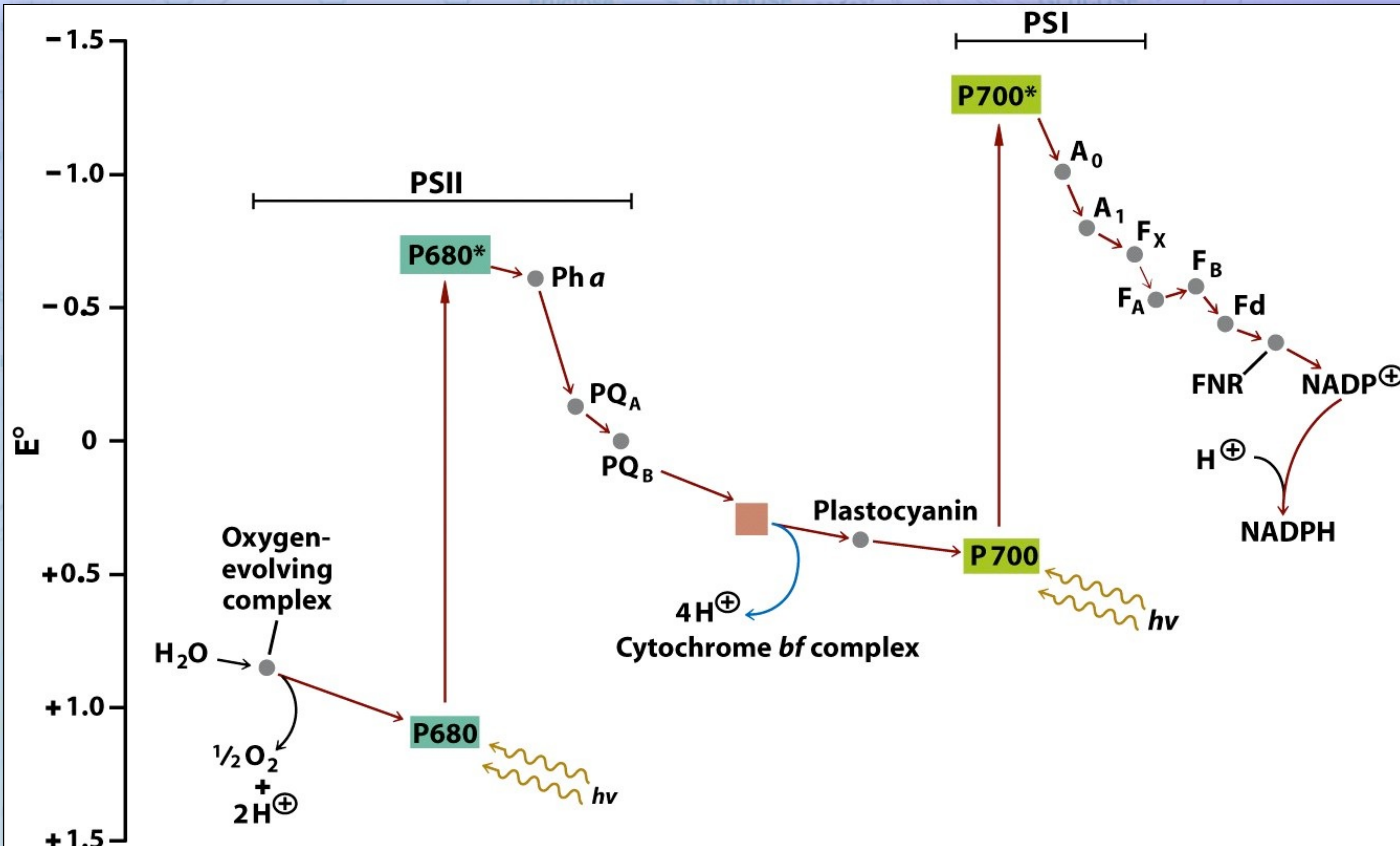

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The Evolution of Photosystems

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:	$H_2O + 4\ \text{photons} + 4\ H^{\oplus}_{in} + NADP^{\oplus} + H^{\oplus} \longrightarrow \frac{1}{2}O_2 + 6\ H^{\oplus}_{out} + NADPH$

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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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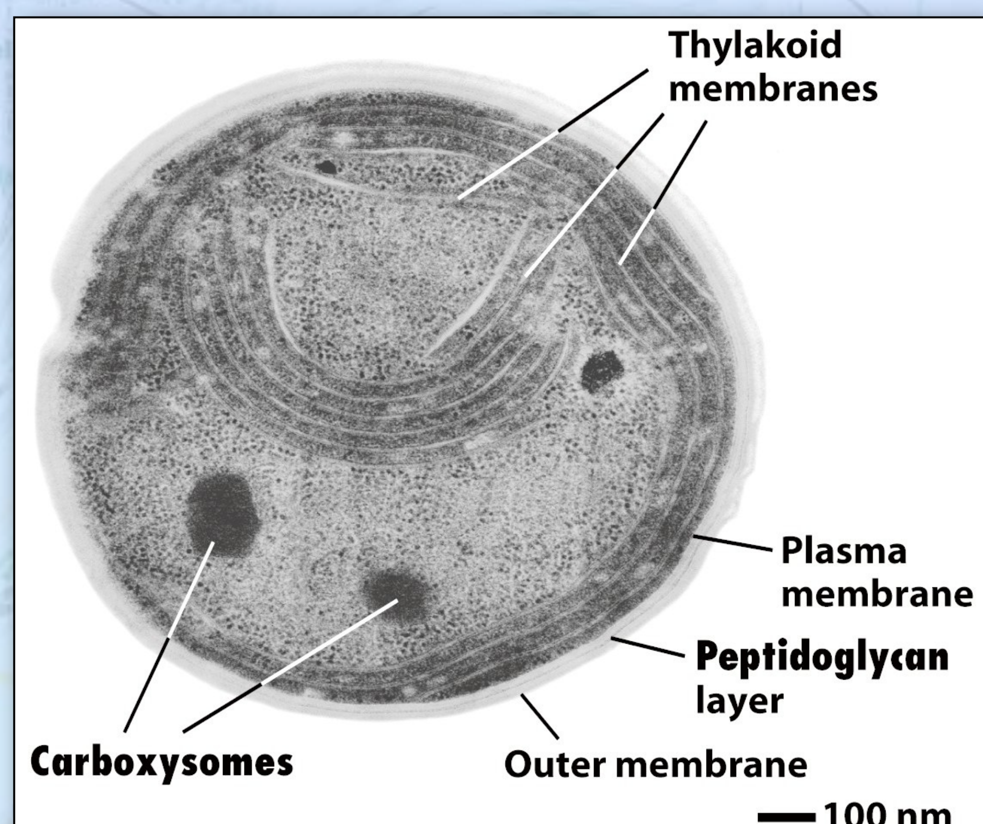

Cyanobacterium

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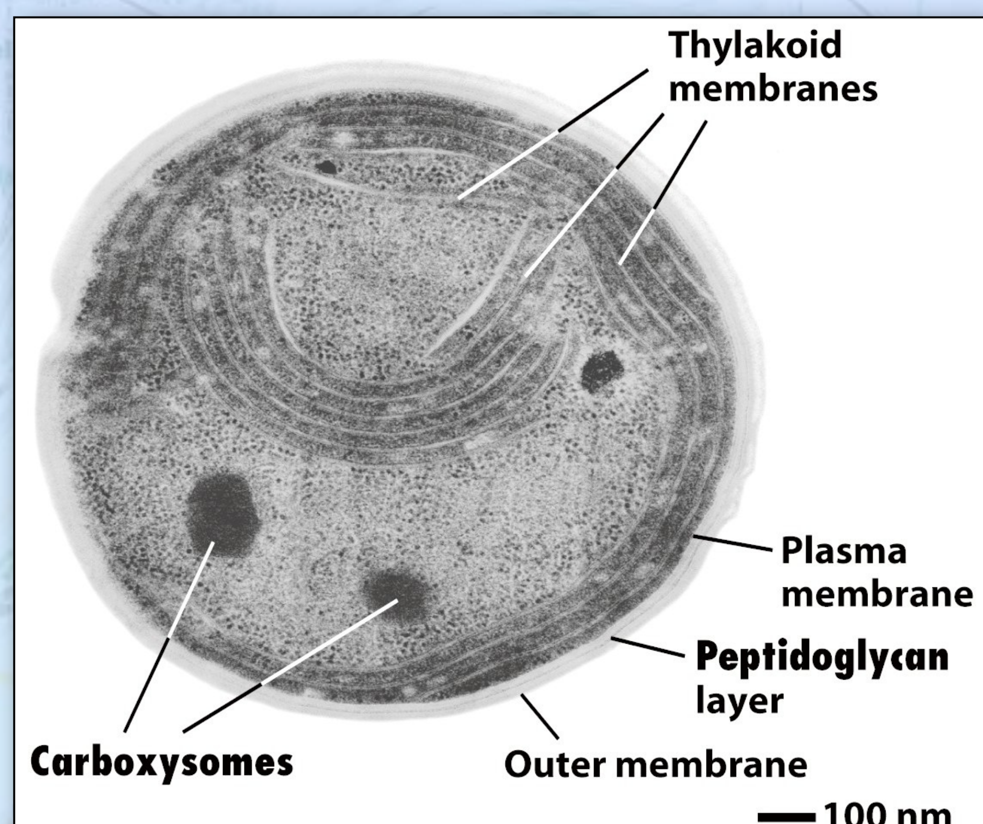

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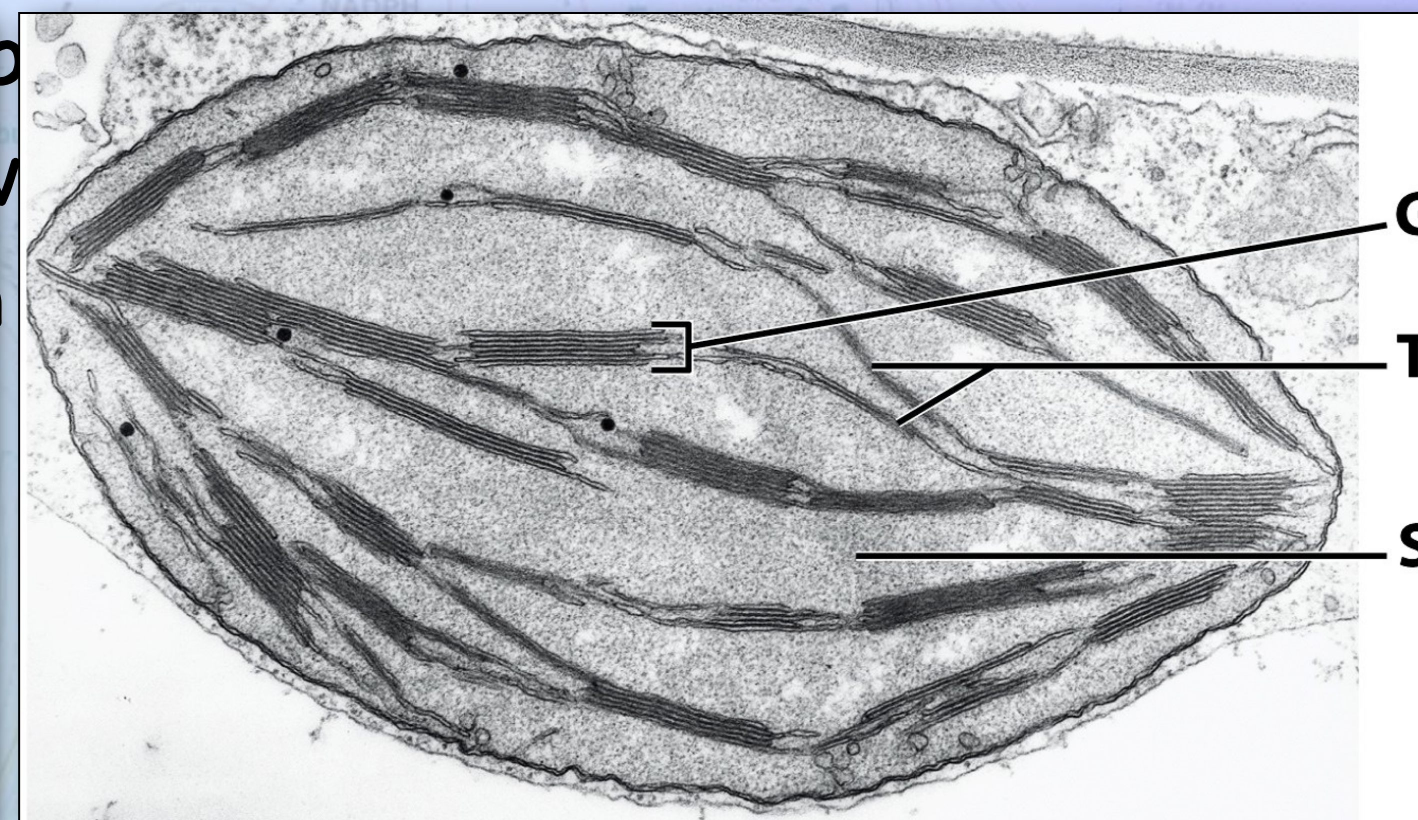

Chloroplast

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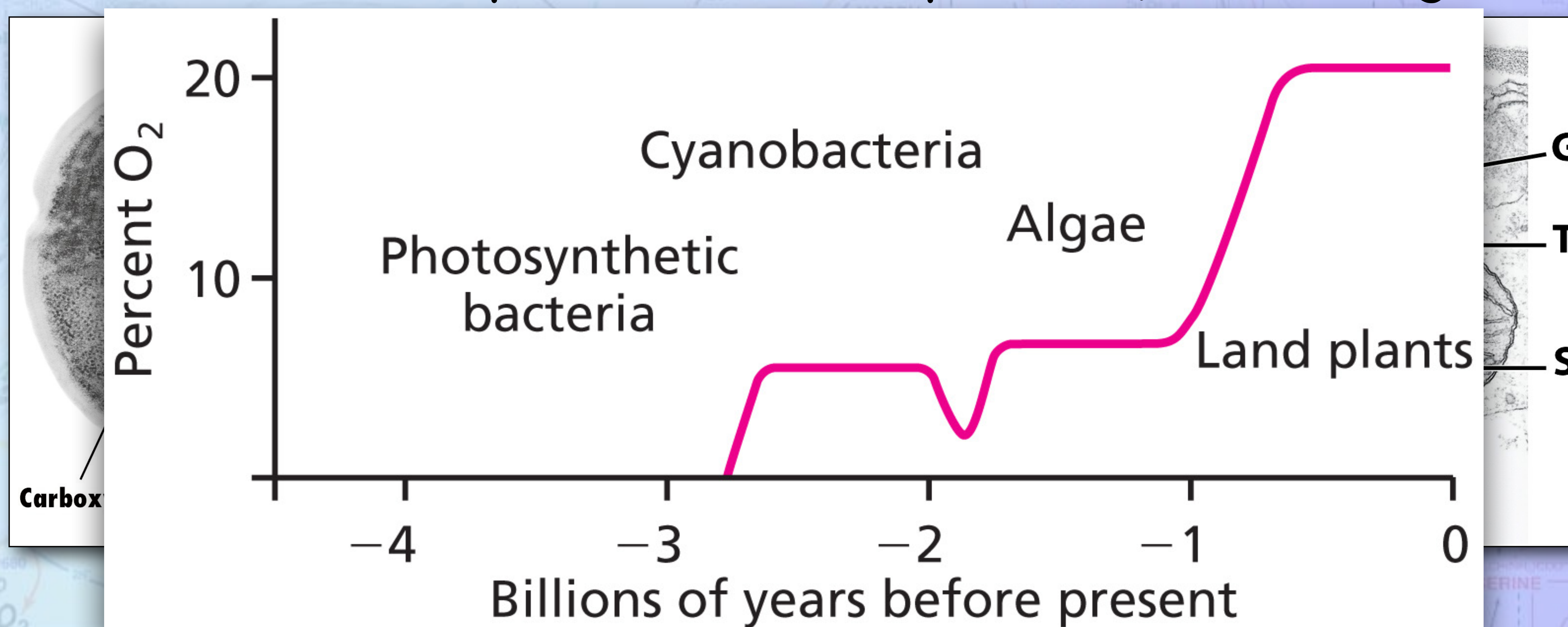

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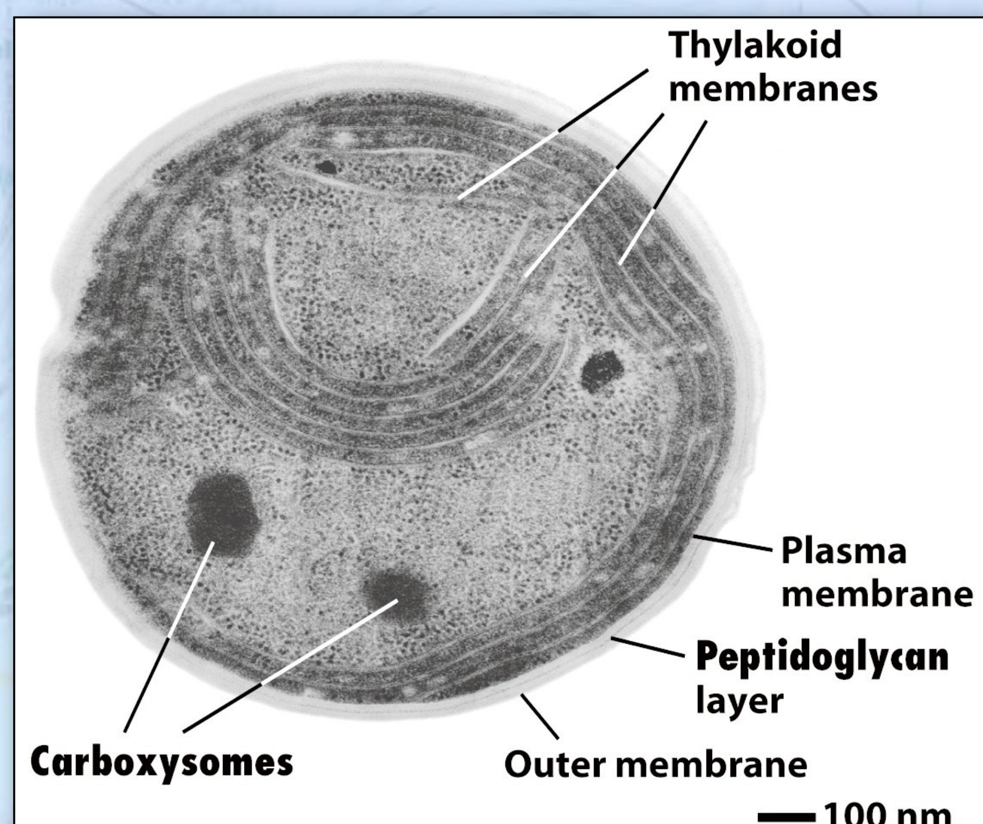

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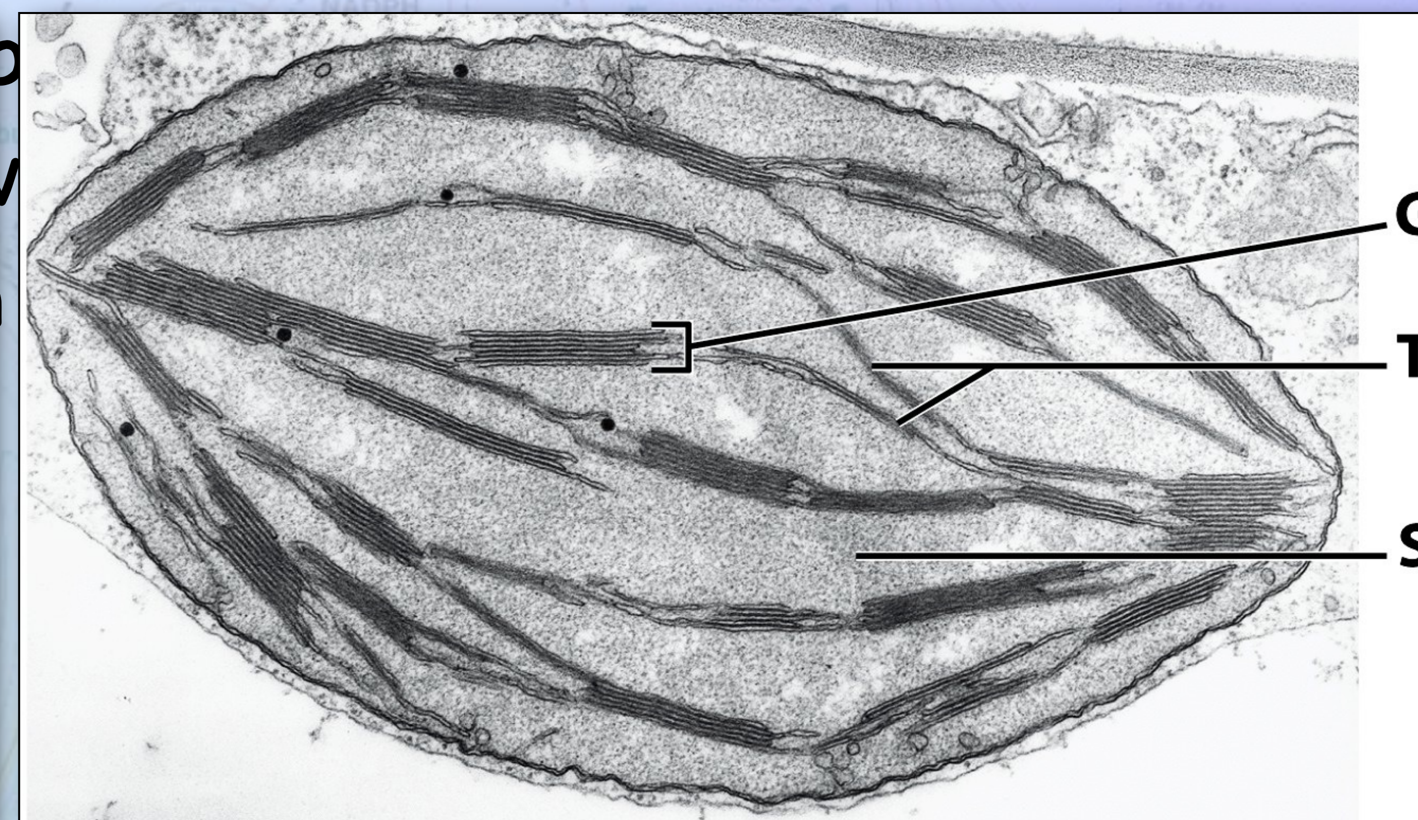

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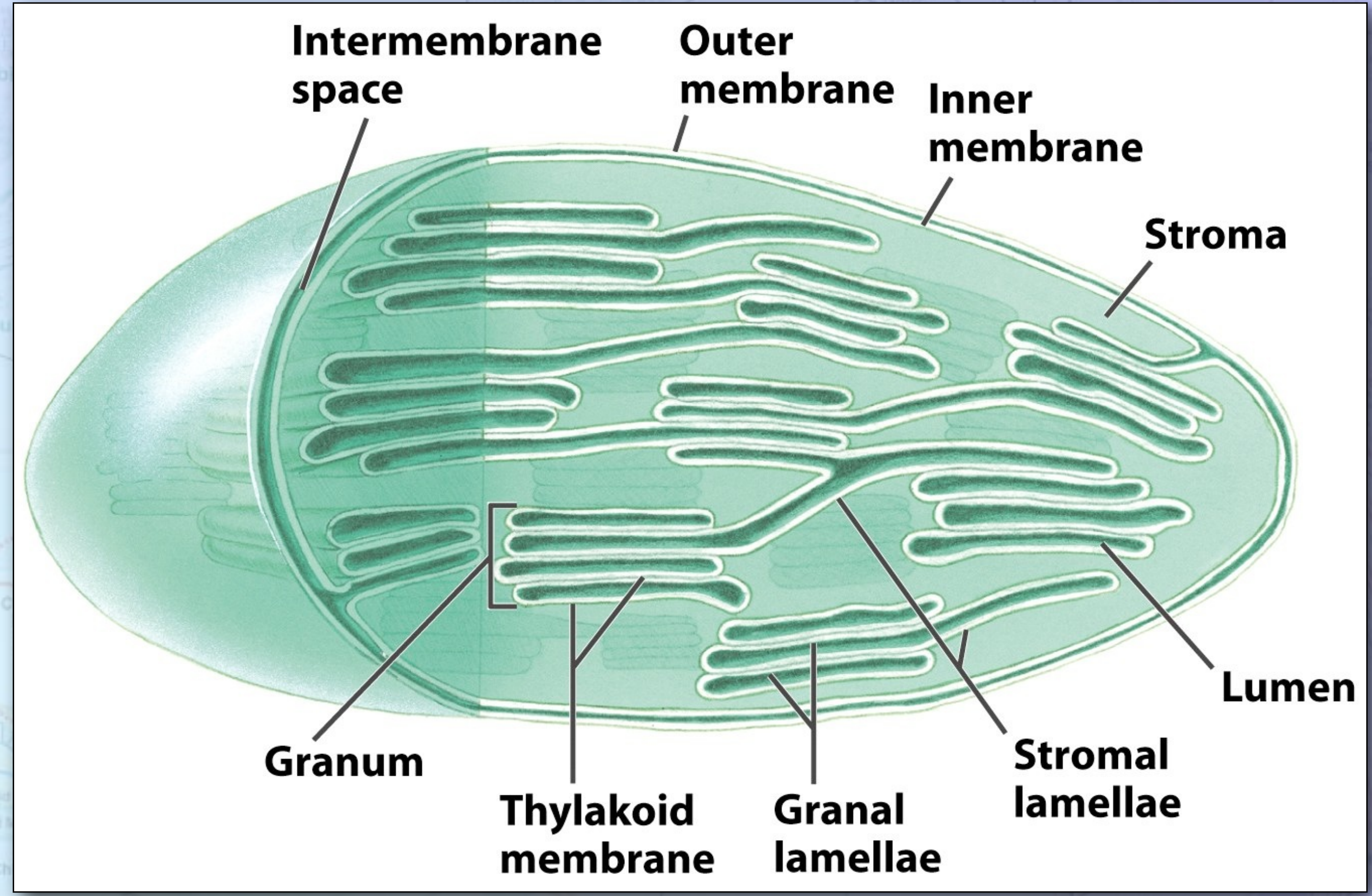

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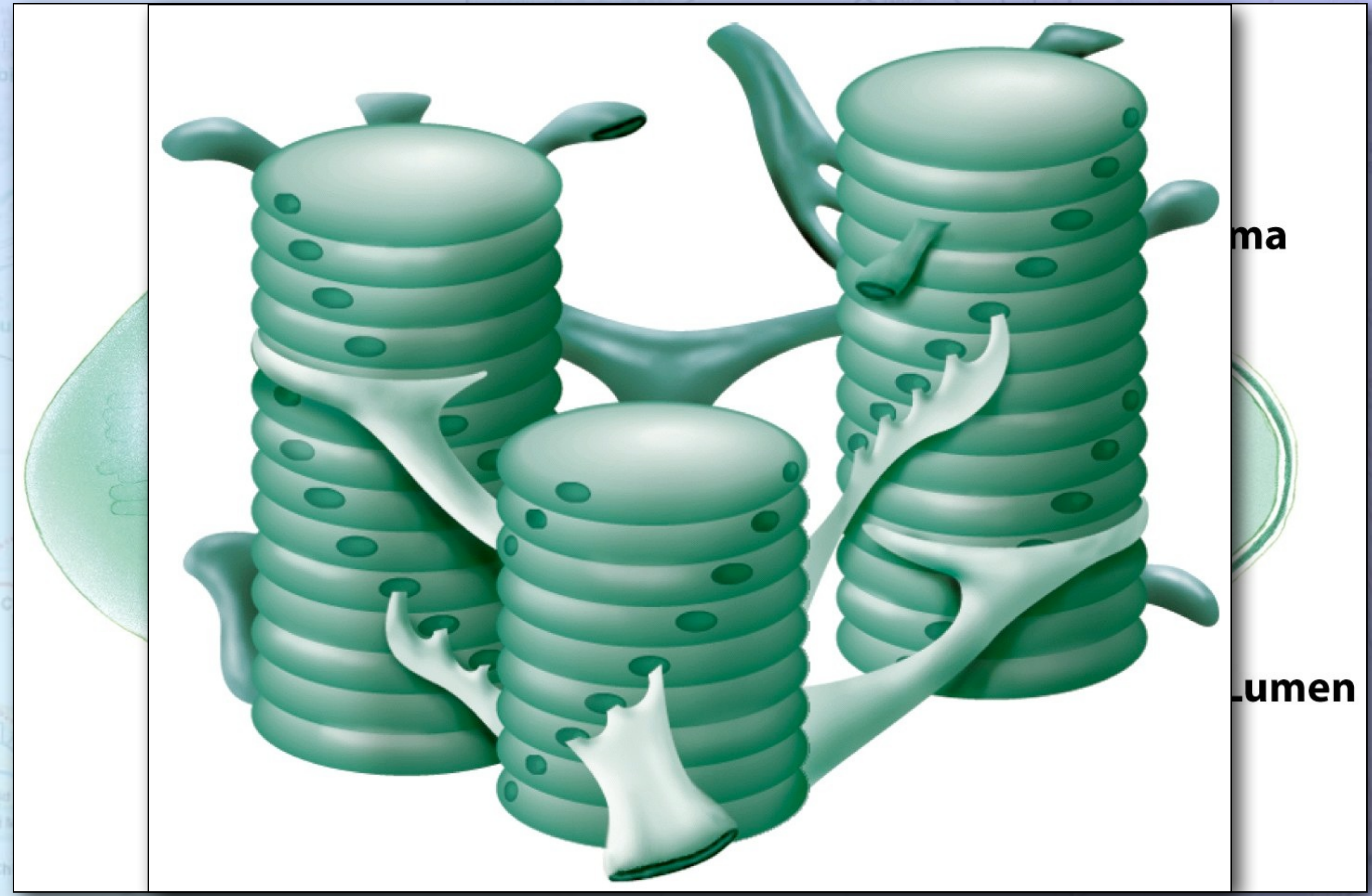
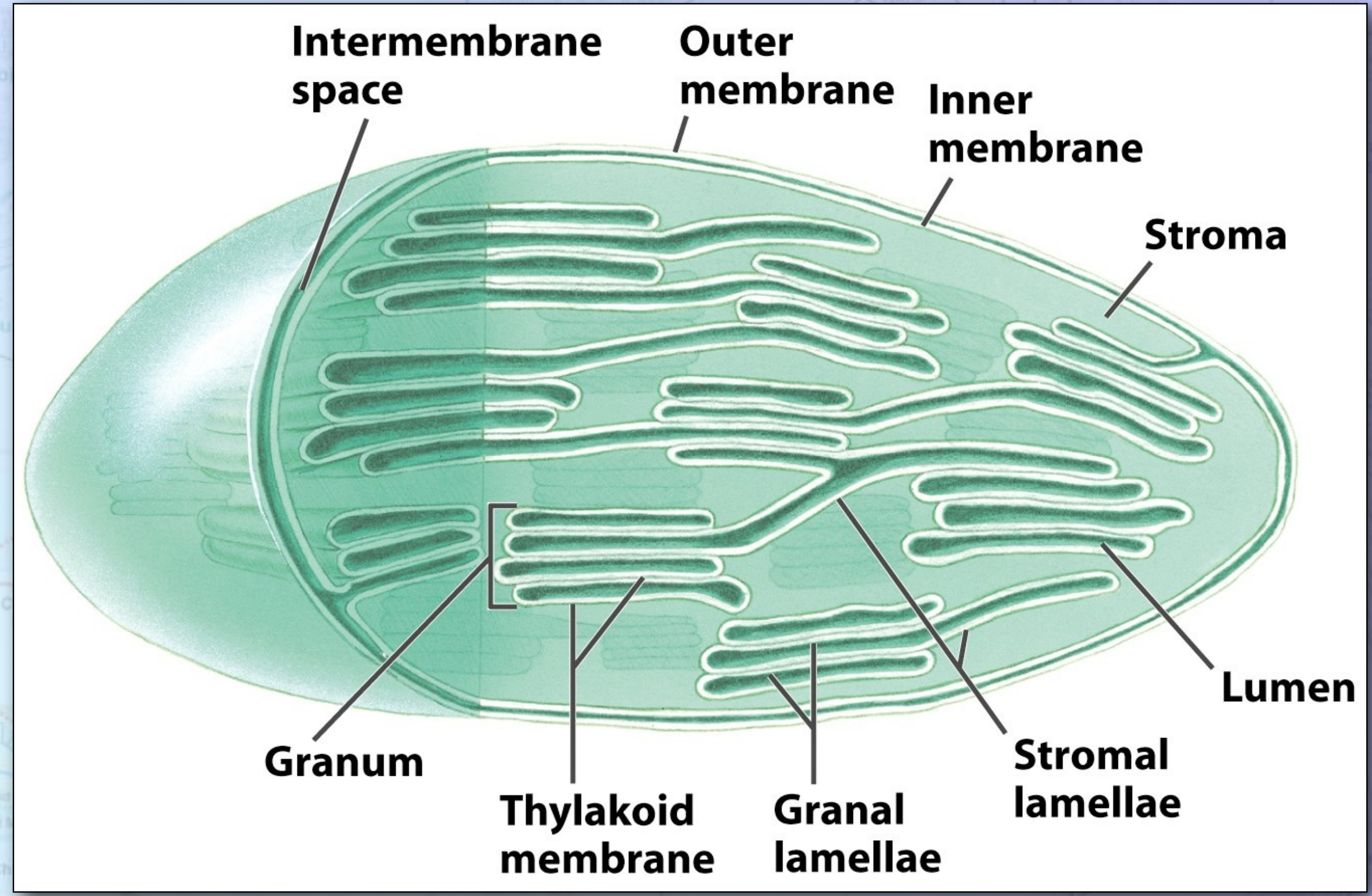


Plant Photosynthesis

- Chloroplasts have double membranes, like mitochondria.



Plant Photosynthesis

•Chloroplasts have double membranes,
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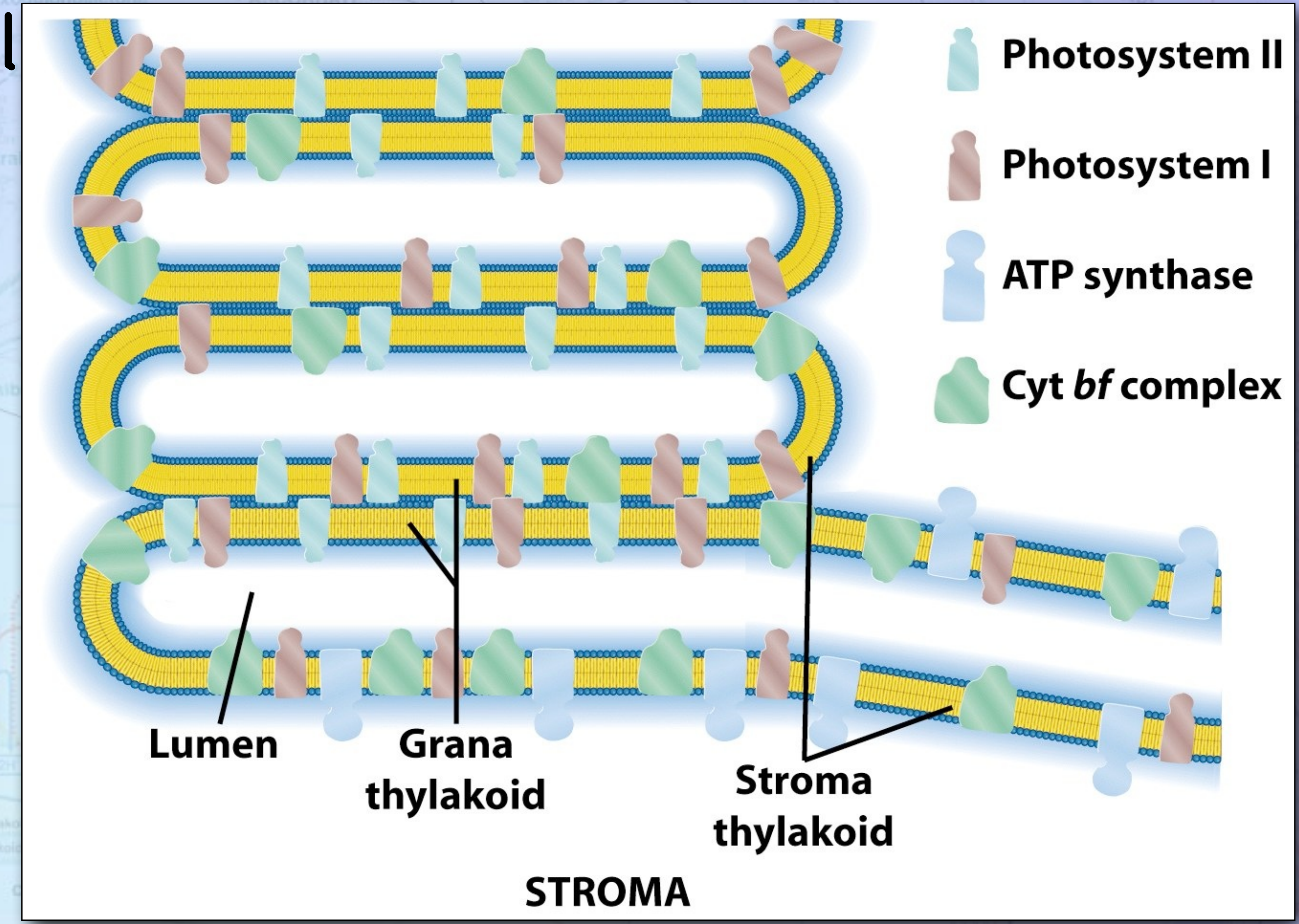

Plant Photosynthesis

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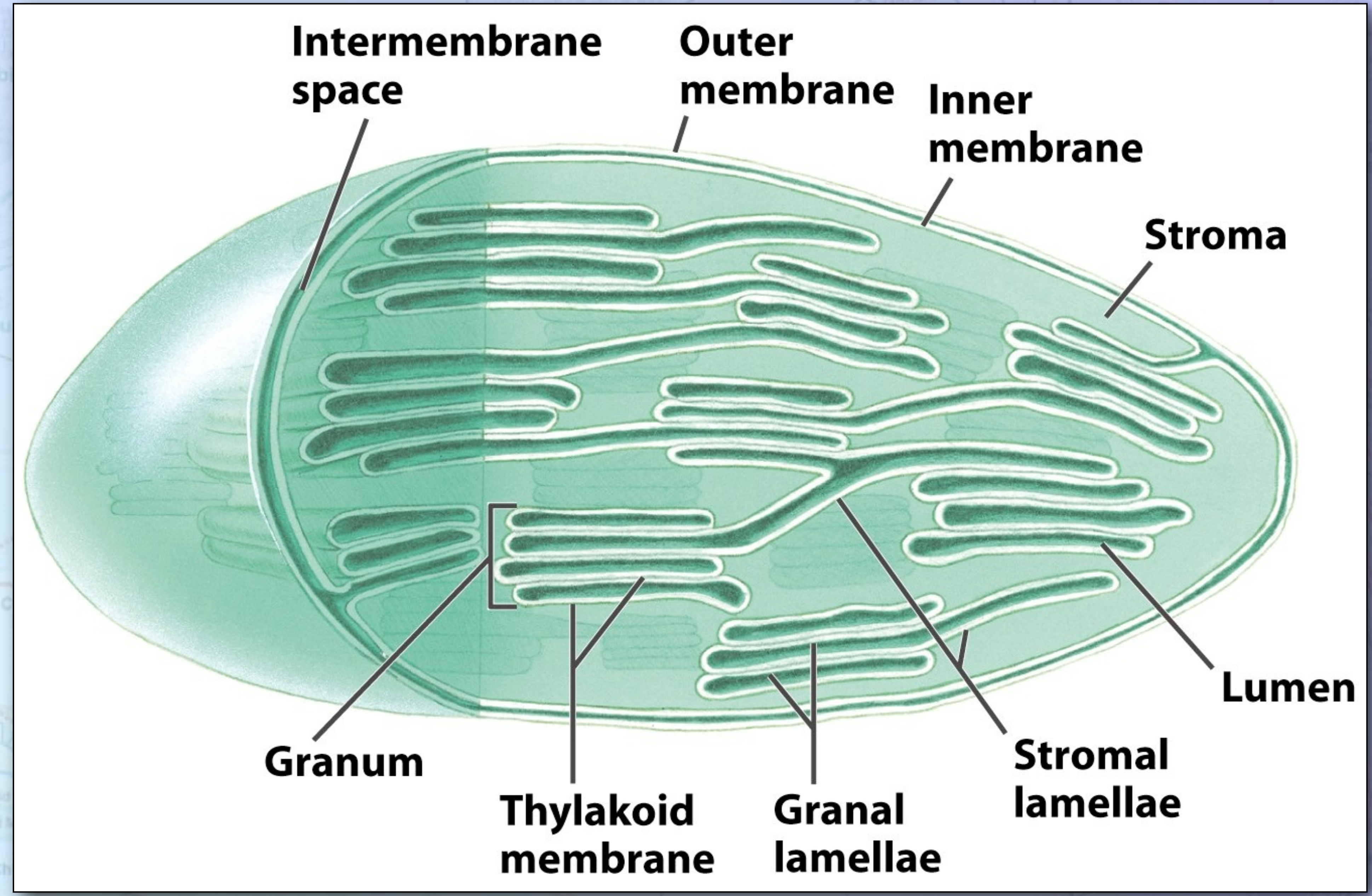


The Dark Reactions

- 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**

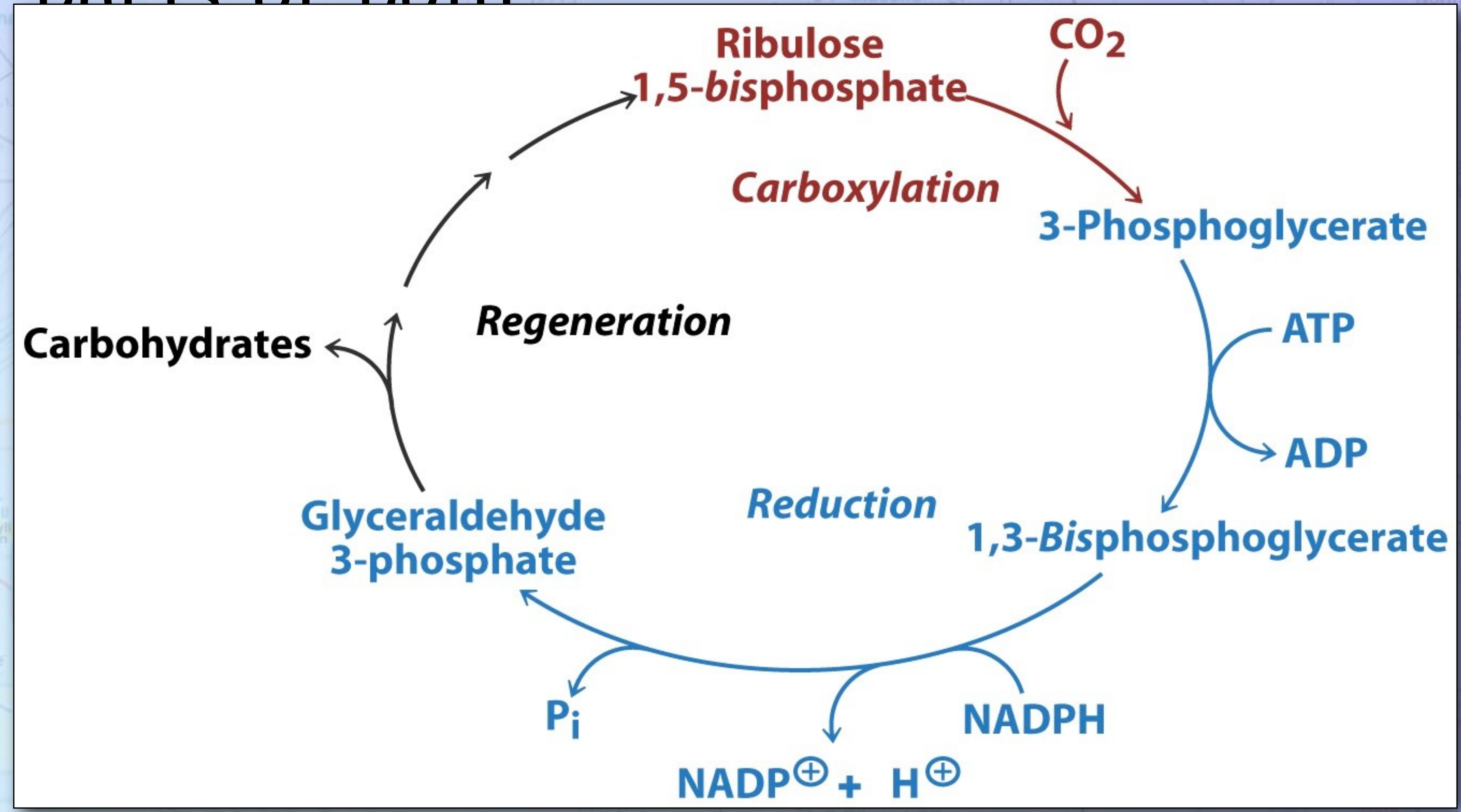
The Dark Reactions

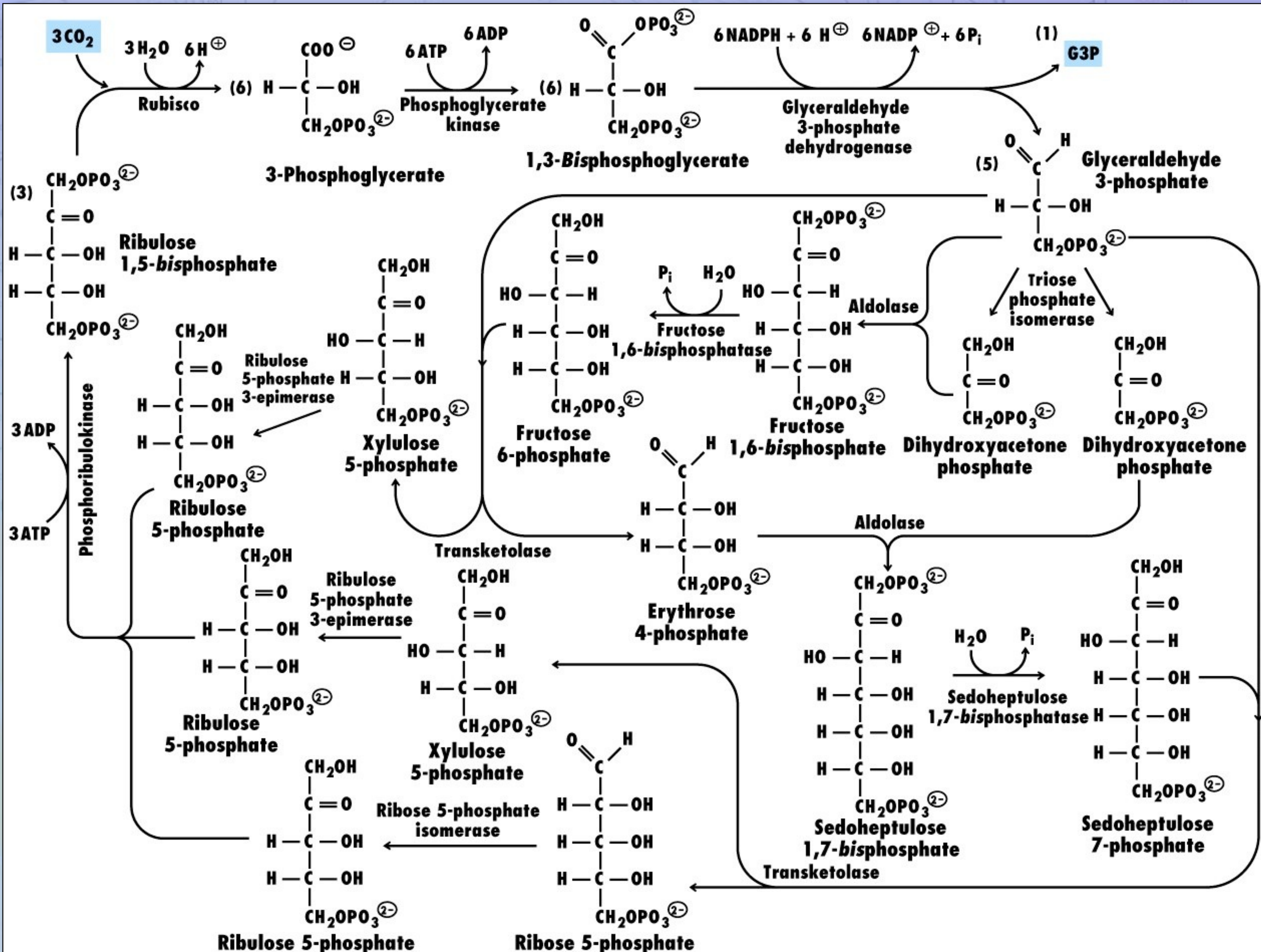
Parts of the Calvin Cycle resembles parts of both

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

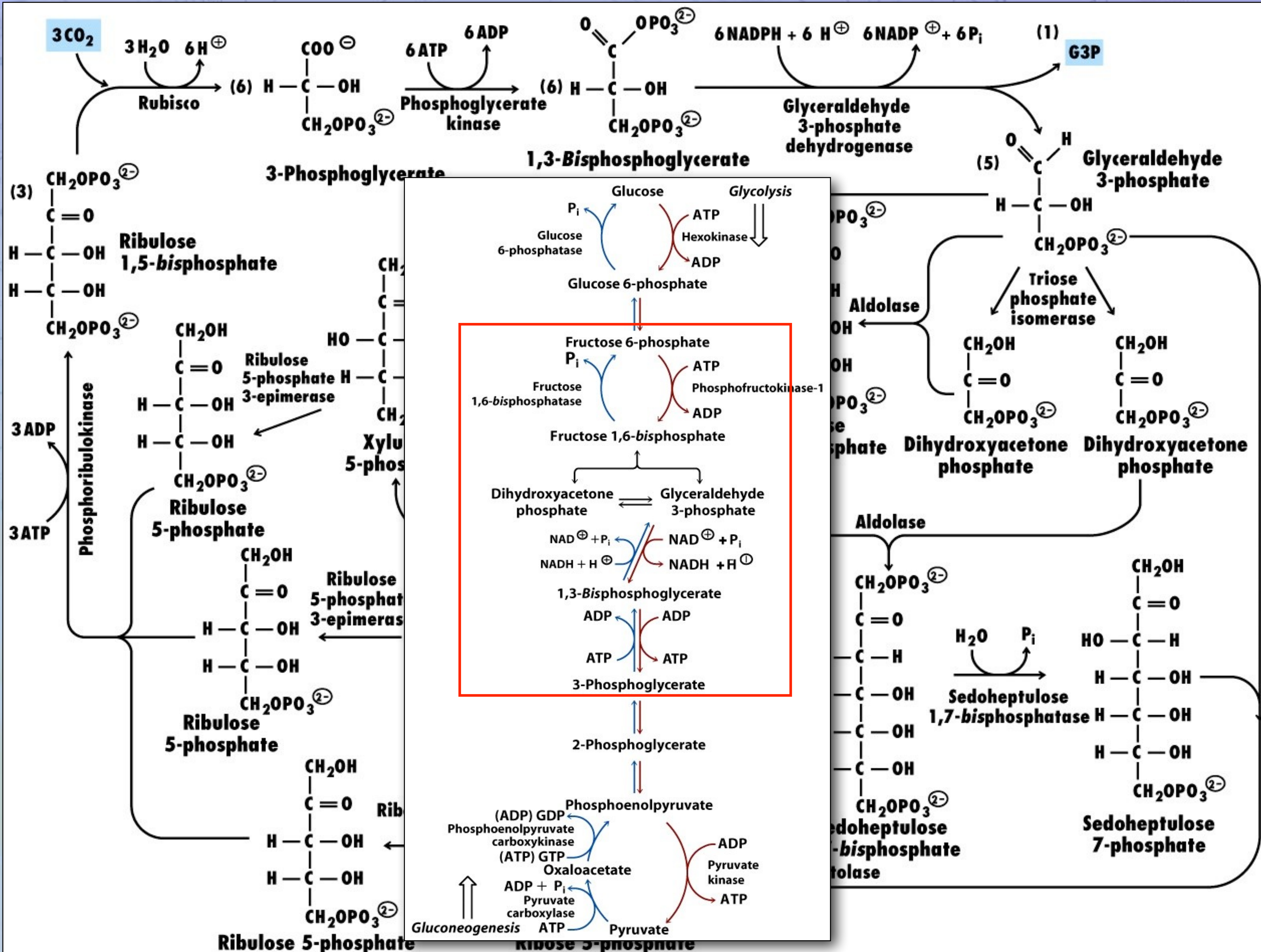
The Dark Reactions

Parts of the Calvin Cycle resembles parts of both





$3CO_2$
$3H_2O$ $6H^{\oplus}$
Rubisco
(6)
3-Phosphoglycerate
6 ATP
6 ADP
Phosphoglycerate kinase
(6)
1,3-*Bis*phosphoglycerate
6 NADPH + 6 $H^{\oplus}$
6 $NADP^{\oplus}$ + 6 P_i
Glyceraldehyde 3-phosphate dehydrogenase
(1)
G3P
(5)
Glyceraldehyde 3-phosphate
(3)
Ribulose 1,5-*bis*phosphate
Triose phosphate isomerase
Aldolase
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
P_i H_2O
Fructose 1,6-*bis*phosphatase
Fructose 1,6-*bis*phosphate
Fructose 6-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-*bis*phosphate
H_2O P_i
Sedoheptulose 1,7-*bis*phosphatase
Sedoheptulose 7-phosphate
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
Xylulose 5-phosphate
Ribose 5-phosphate isomerase
Ribulose 5-phosphate
Ribose 5-phosphate
Transketolase



3 CO_2
3 H_2O 6 $H^{\oplus}$
Rubisco
(6)
$COO^{\ominus}$
$CH_2OPO_3^{2-}$
3-Phosphoglycerate
6 ATP 6 ADP
Phosphoglycerate kinase
OPO_3^{2-}
1,3-*Bis*phosphoglycerate
6 NADPH + 6 $H^{\oplus}$ 6 $NADP^{\oplus}$ + 6 P_i
Glyceraldehyde 3-phosphate dehydrogenase
(1)
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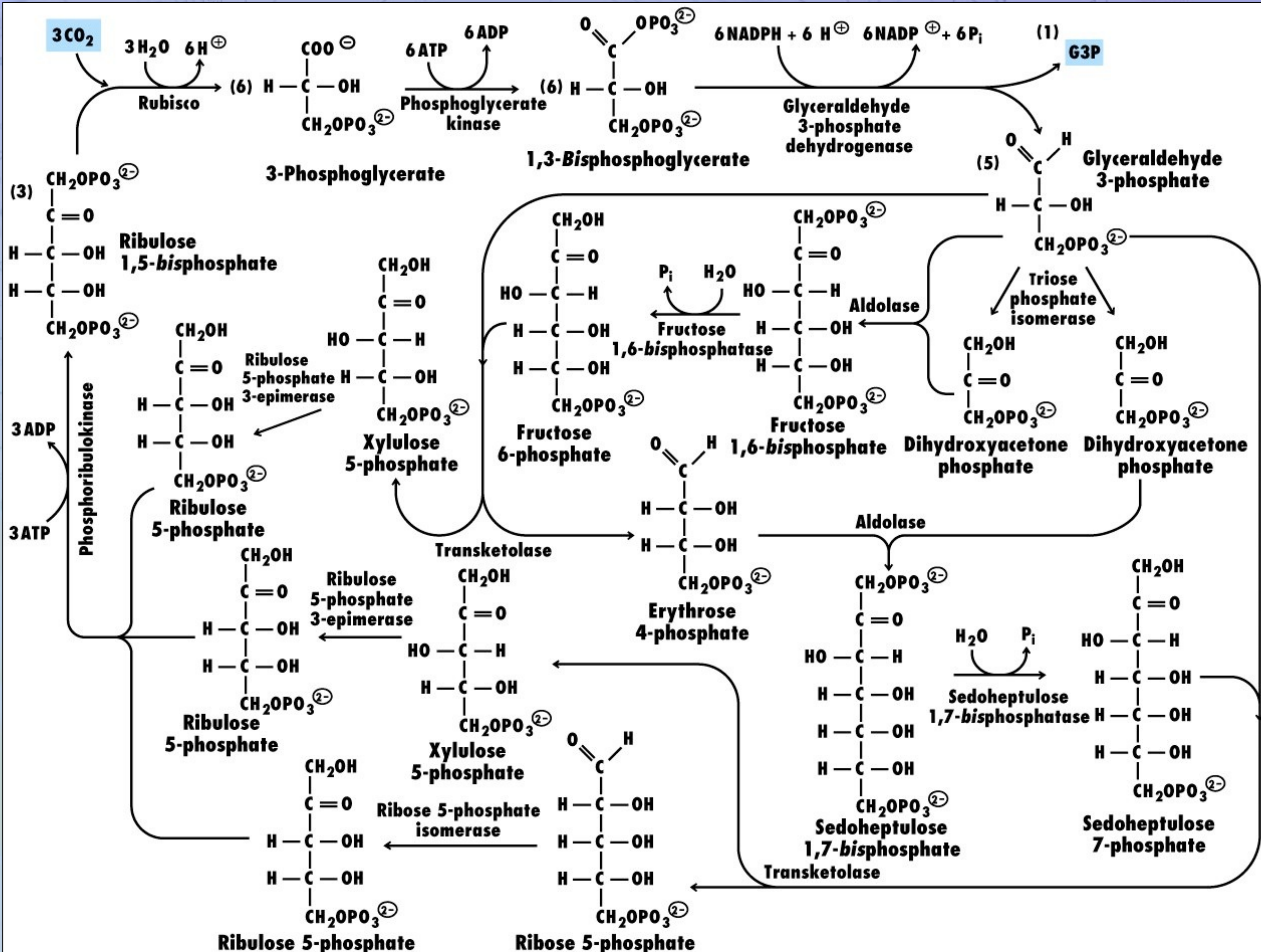
(5)
Glyceraldehyde 3-phosphate
Triose phosphate isomerase
Aldolase
Dihydroxyacetone phosphate
Dihydroxyacetone phosphate
Aldolase
H_2O P_i
Sedoheptulose 1,7-*bis*phosphatase
Sedoheptulose 7-phosphate
(3)
Ribulose 1,5-*bis*phosphate
3 ADP
3 ATP
Phosphoribulokinase
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
Ribulose 5-phosphate
Ribulose 5-phosphate
Glucose
Glycolysis
P_i
Glucose 6-phosphatase
ATP
Hexokinase
ADP
Glucose 6-phosphate
Fructose 6-phosphate
P_i
Fructose 1,6-*bis*phosphatase
ATP
Phosphofructokinase-1
ADP
Fructose 1,6-*bis*phosphate
Dihydroxyacetone phosphate
Glyceraldehyde 3-phosphate
$NAD^{\oplus}$ + P_i
NADH + $H^{\oplus}$
$NAD^{\oplus}$ + P_i
NADH + $H^{\oplus}$
1,3-*Bis*phosphoglycerate
ADP
ADP
ATP
ATP
3-Phosphoglycerate
2-Phosphoglycerate
Phosphoenolpyruvate
(ADP) GDP
Phosphoenolpyruvate carboxykinase
(ATP) GTP
Oxaloacetate
ADP + P_i
Pyruvate carboxylase
ATP
Gluconeogenesis
ADP
Pyruvate kinase
ATP
Pyruvate



3CO2
3H2O 6H⊕
Rubisco
(6)
3-Phosphoglycerate
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1,3-Bisphosphoglycerate
6NADPH + 6 H⊕ 6NADP⊕ + 6Pi
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Ribulose 5-phosphate
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H2O Pi
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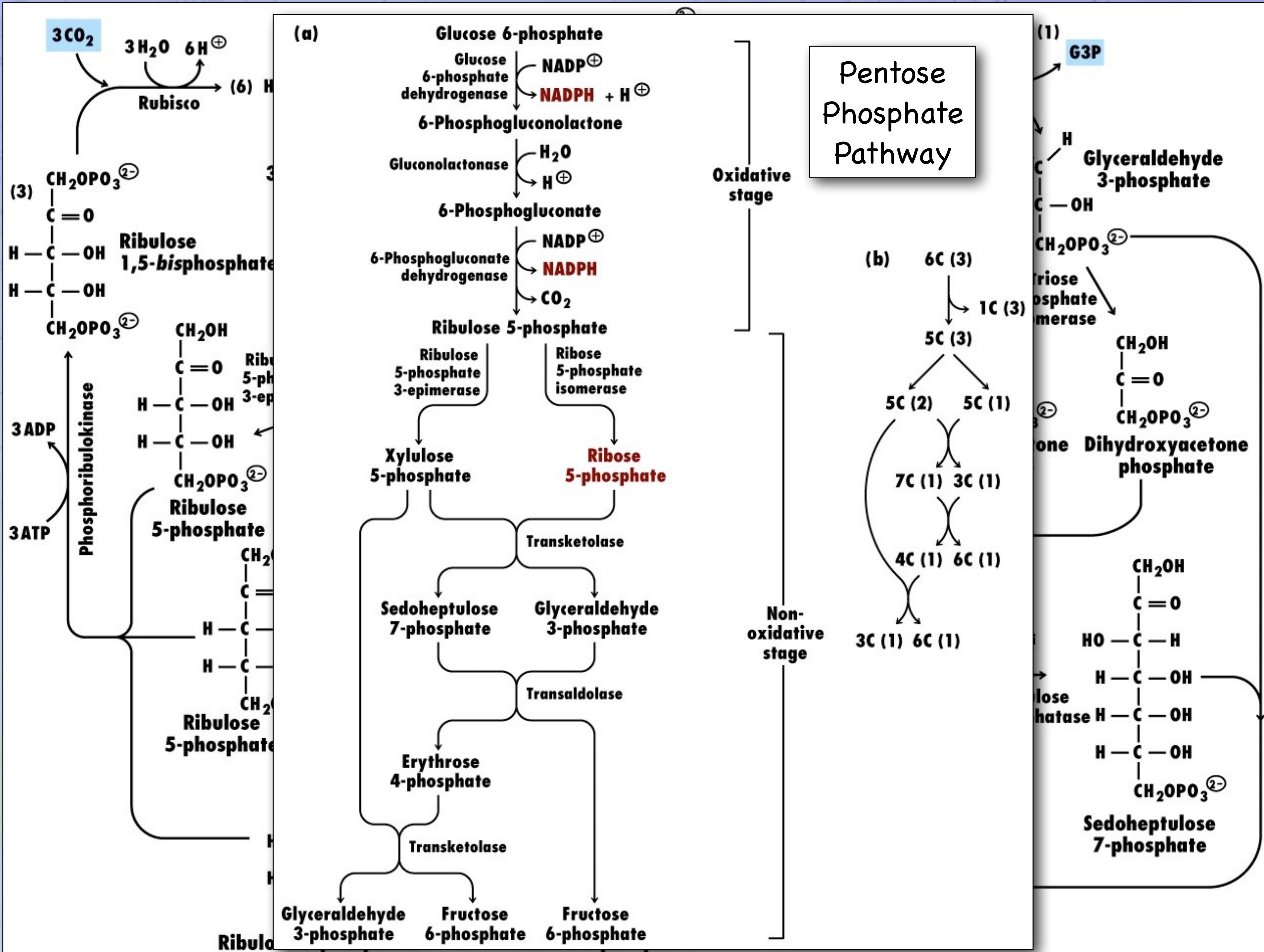
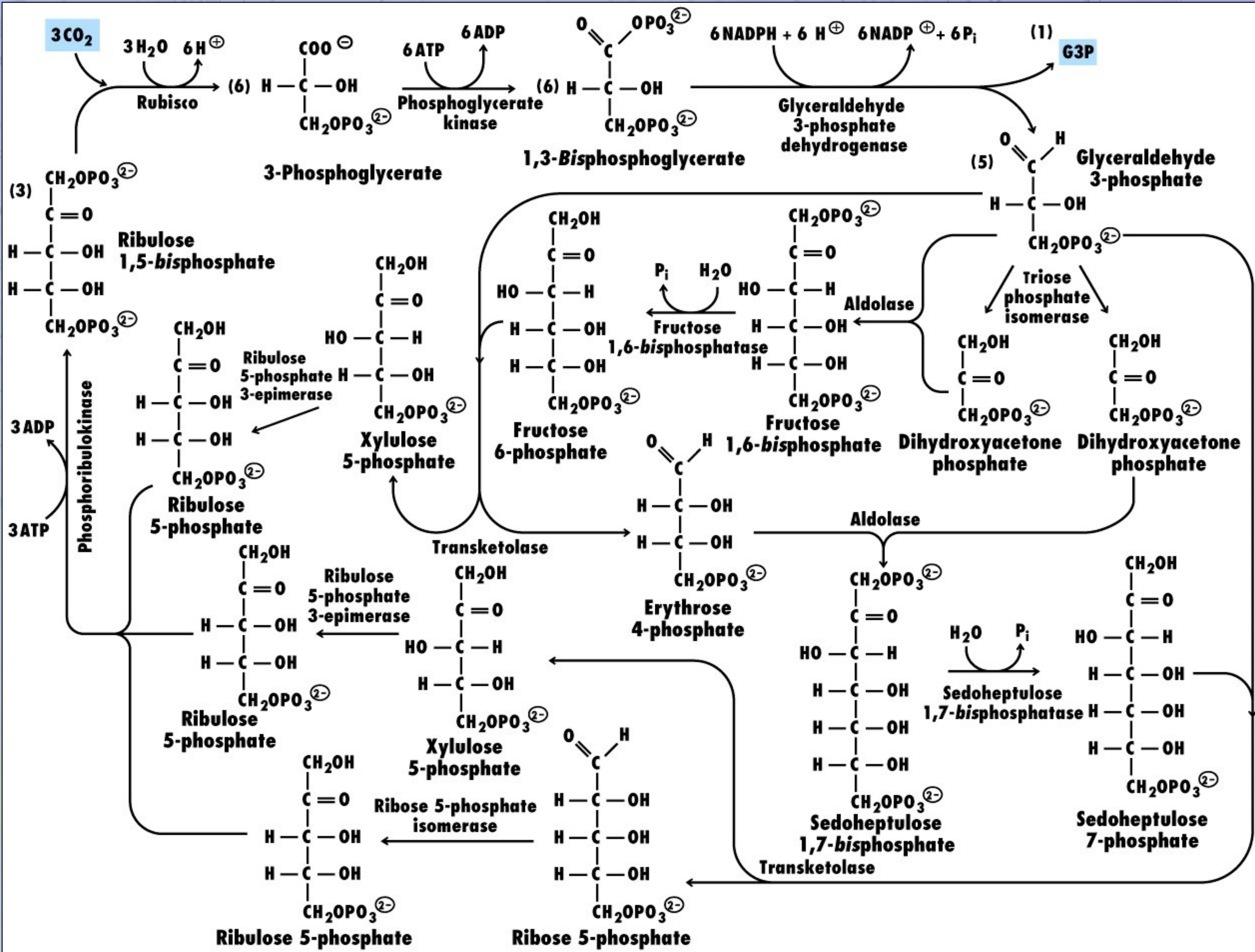
Sedoheptulose 1,7-bisphosphate
Sedoheptulose 7-phosphate
Transketolase
Ribose 5-phosphate isomerase
Ribulose 5-phosphate
Ribose 5-phosphate

Pentose Phosphate Pathway





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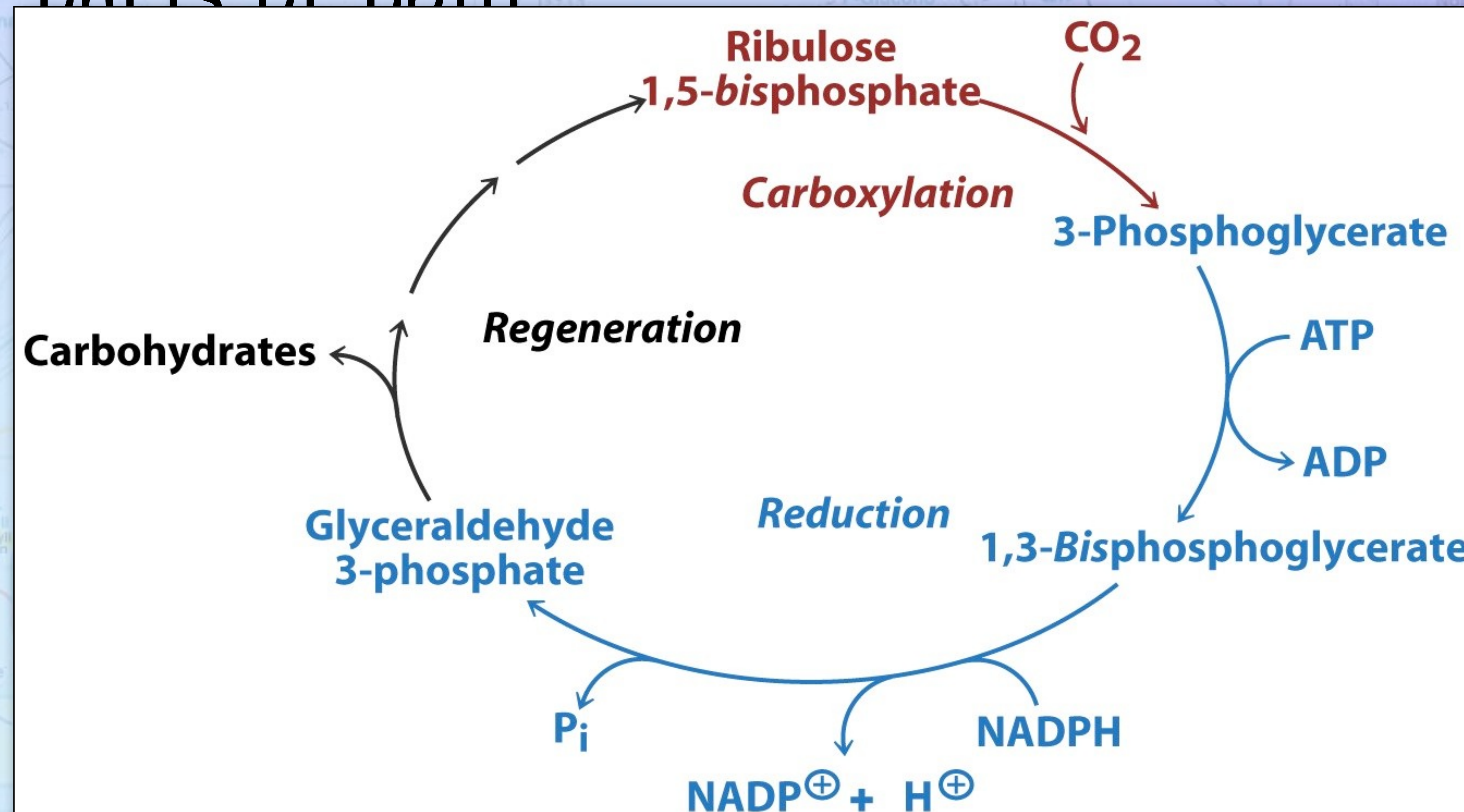
The Dark Reactions

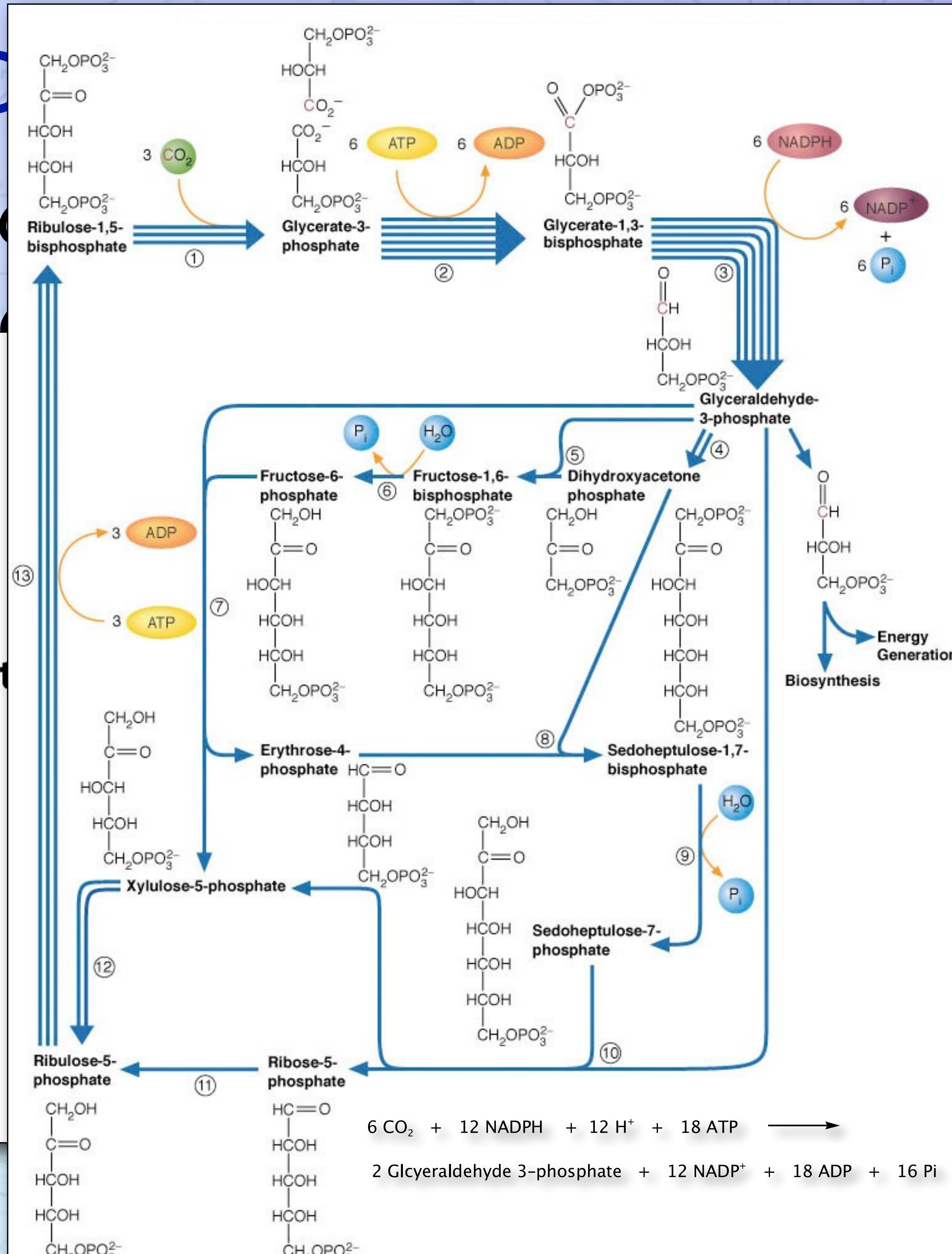
Parts of the Calvin Cycle resembles parts of both



The D

Parts o… les parts …

Carbohydrat



…oglycerate

ATP

ADP

…hoglycerate

The D

Parts o… les
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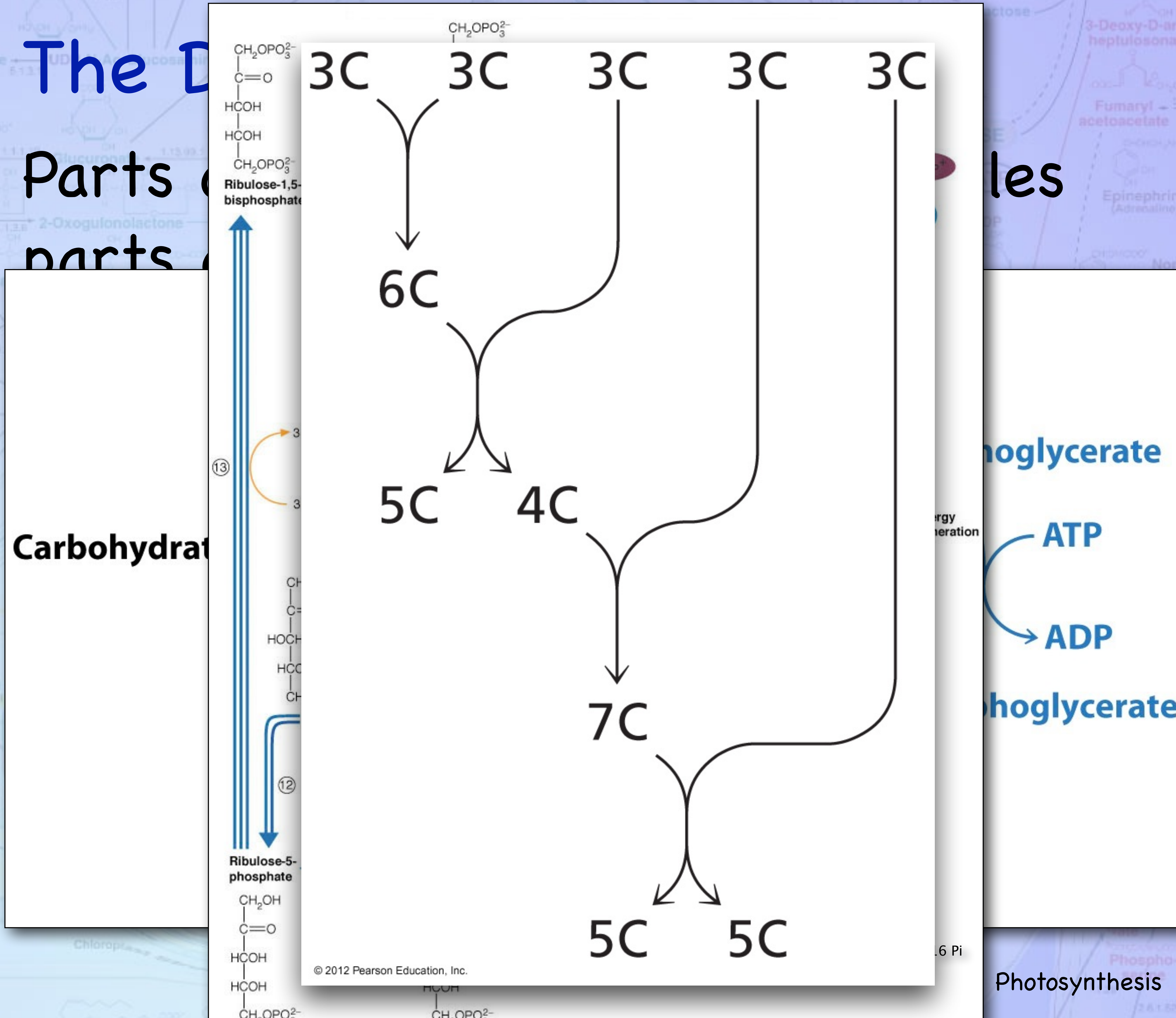


The D

Parts ... les

parts ...

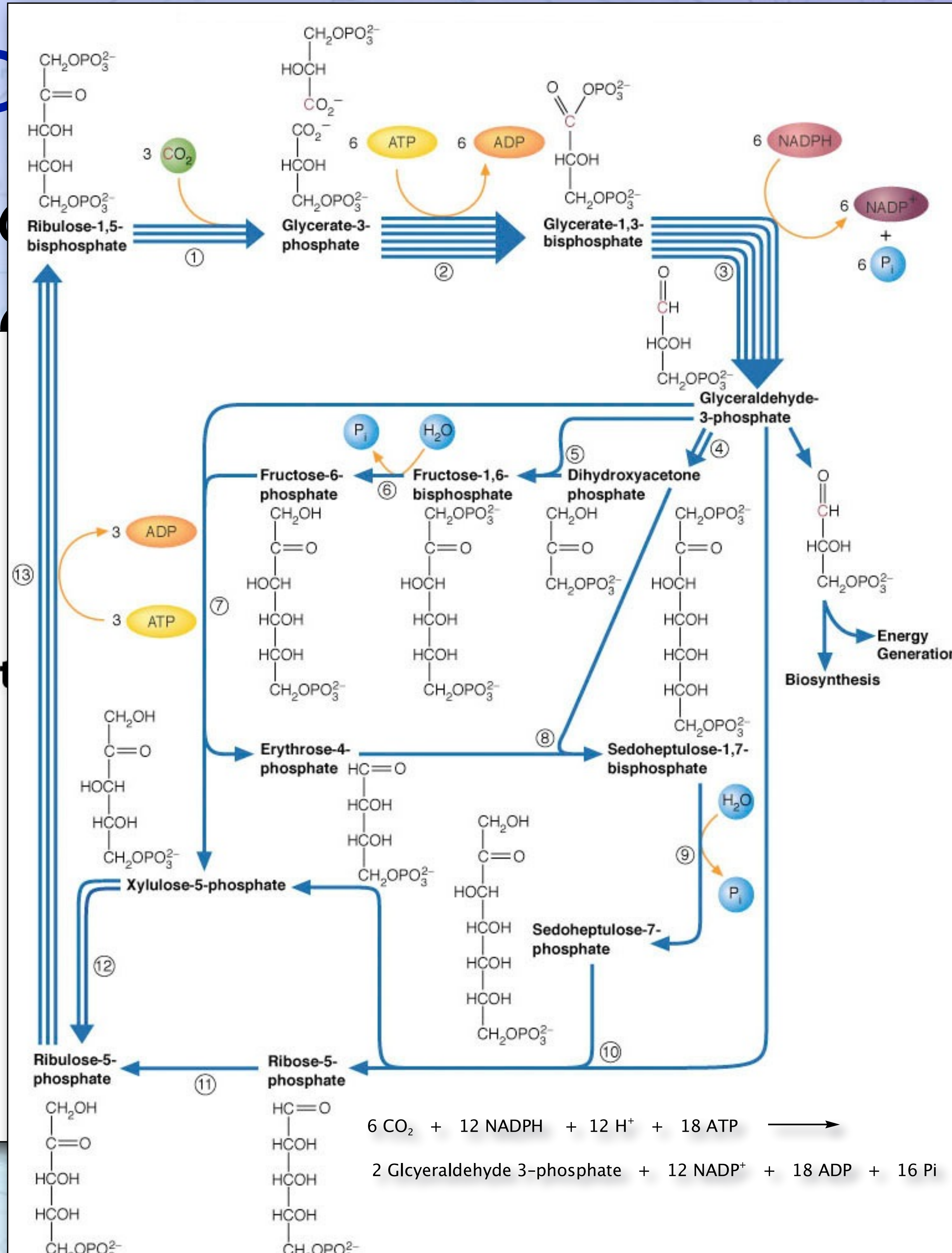
Carbohydrat

...oglycerate

ATP

ADP

...hoglycerate



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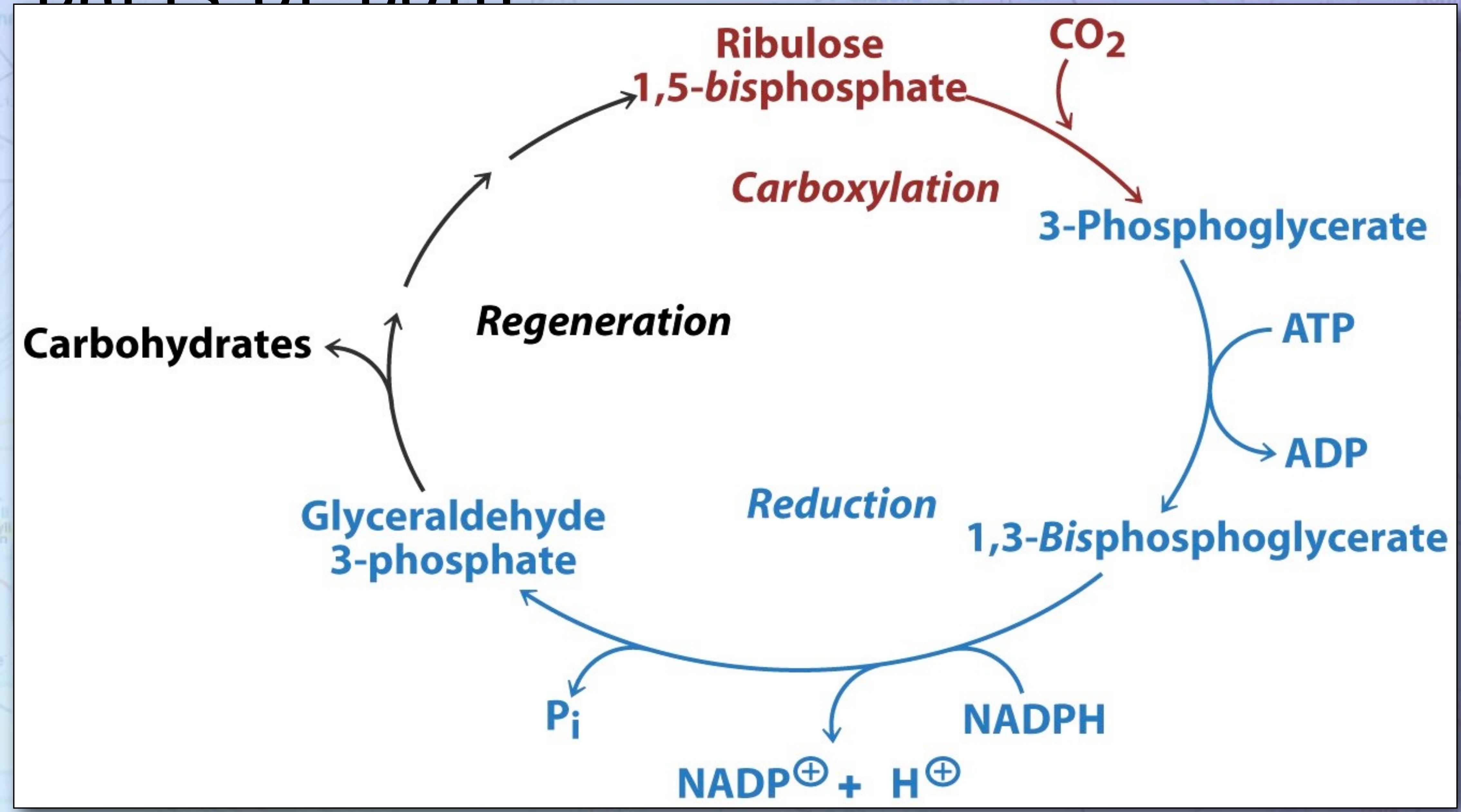


The Dark Reactions

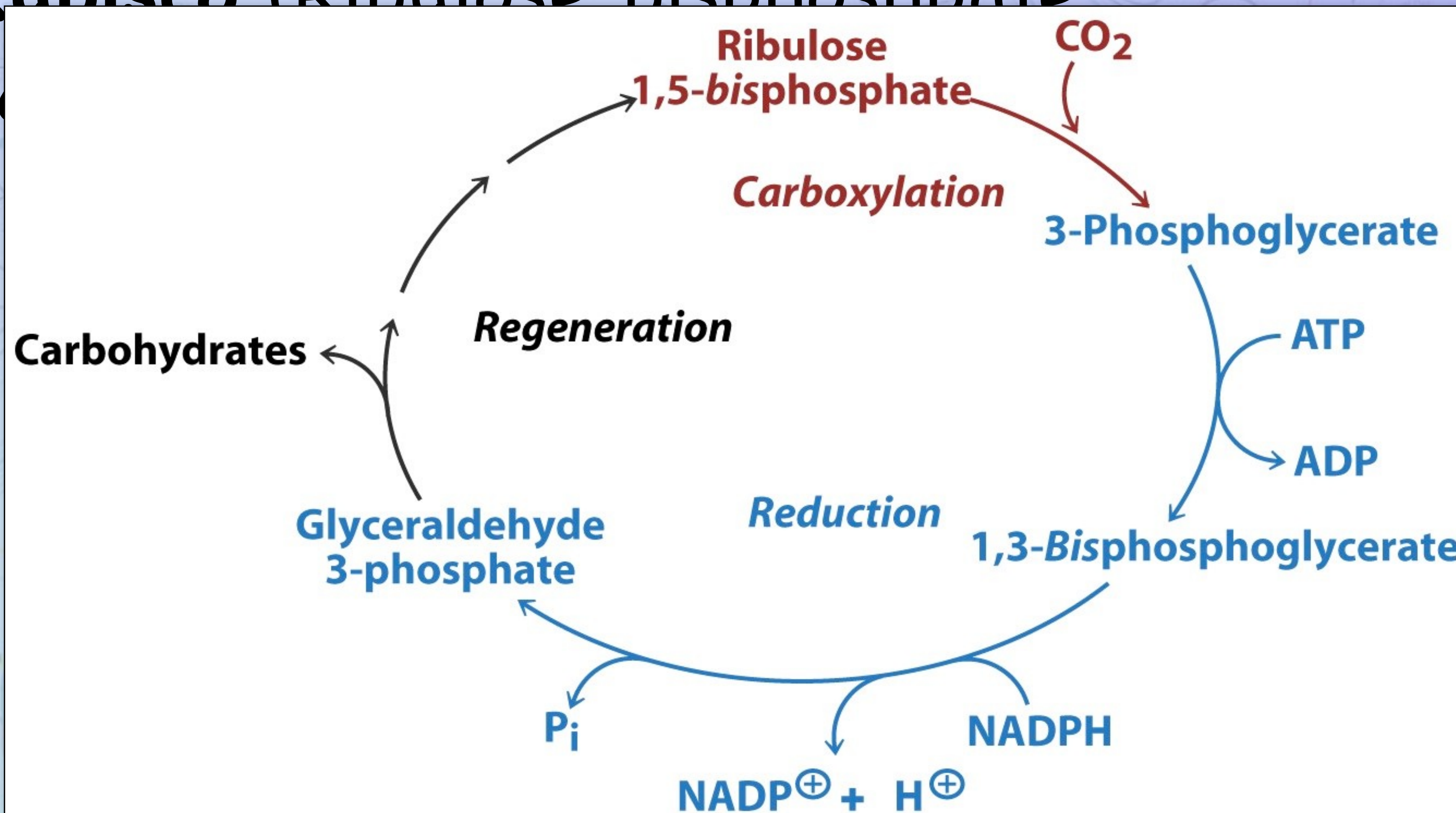
Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

- 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



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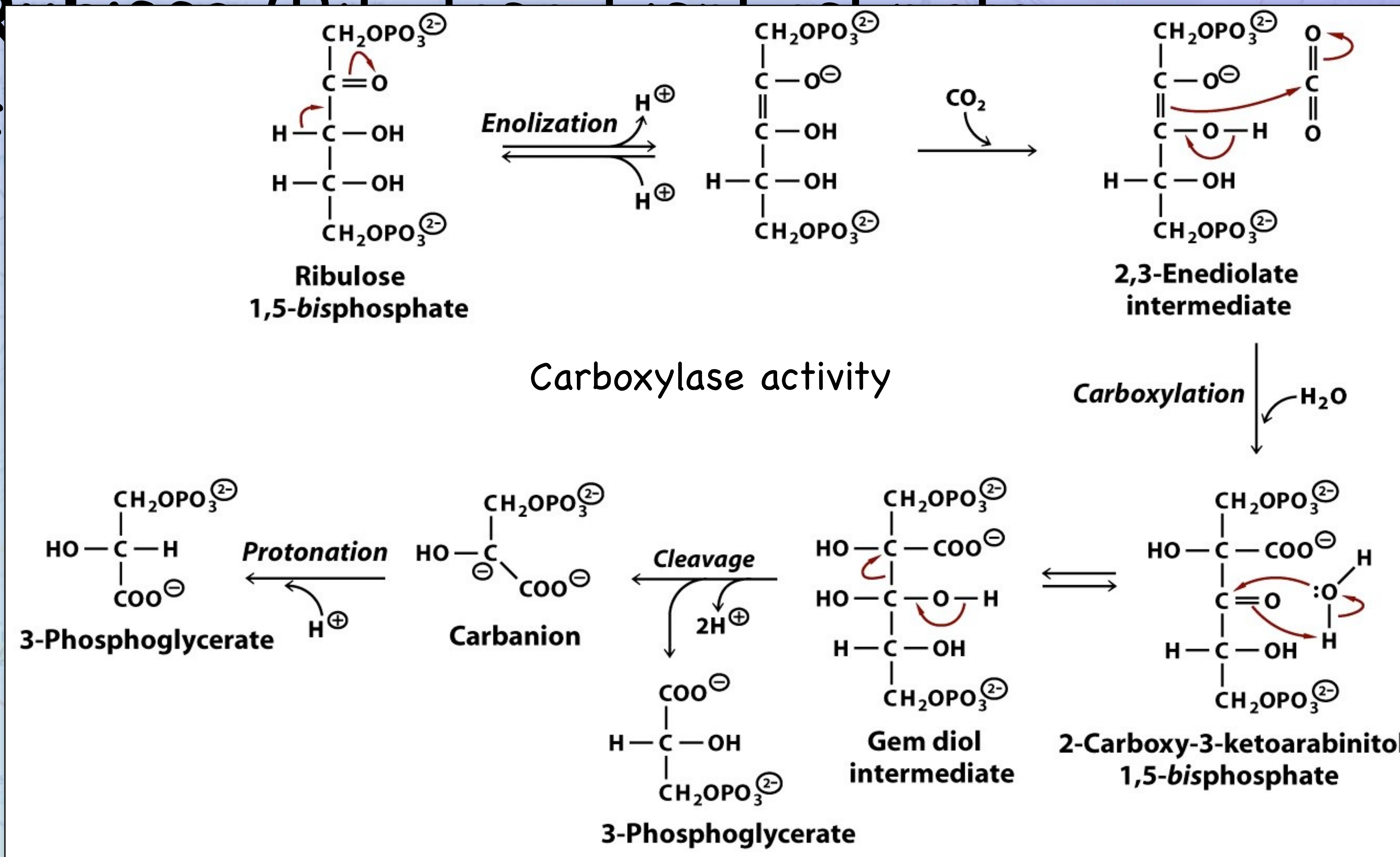

The Dark Reactions

R

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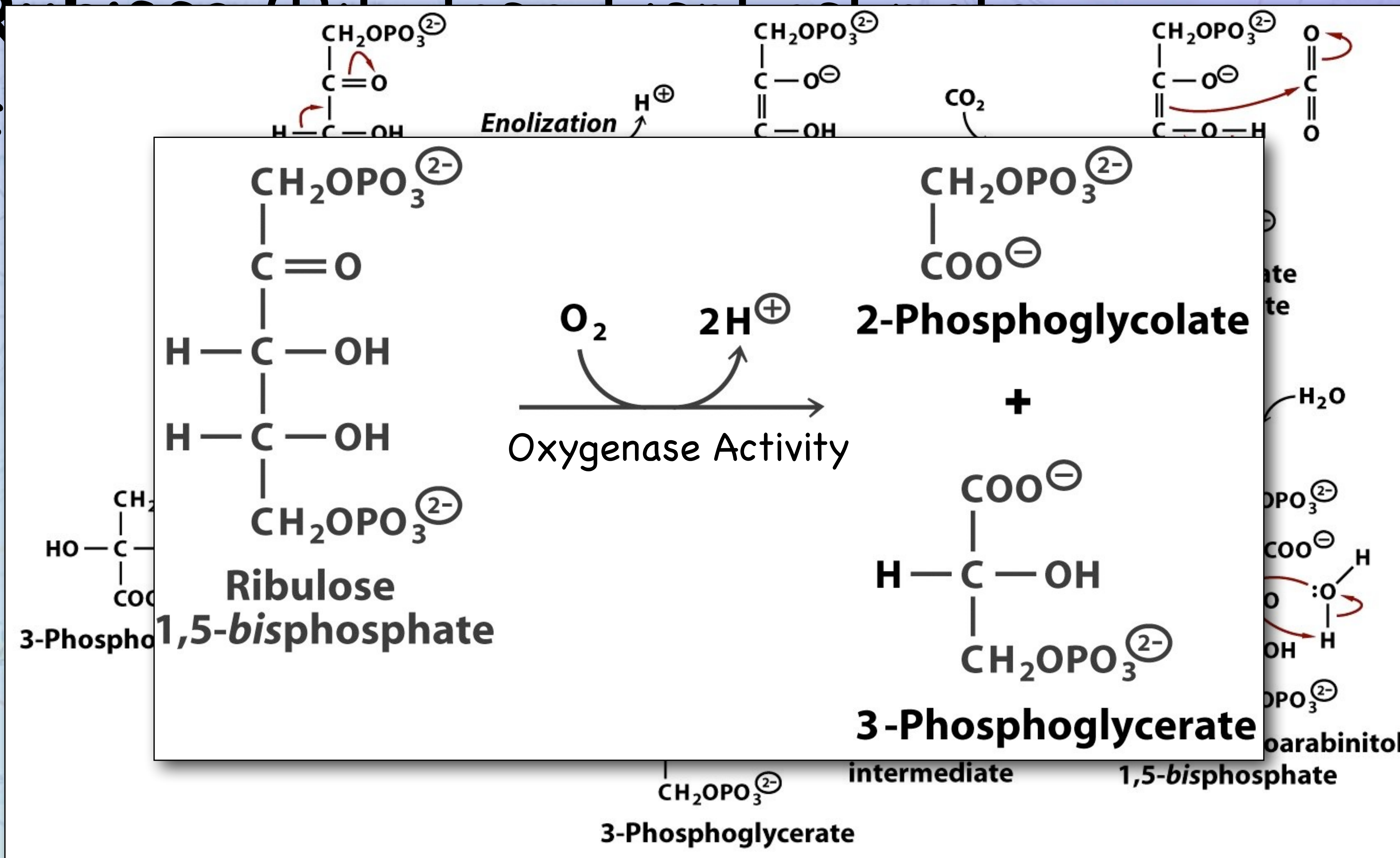

The Dark Reactions

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

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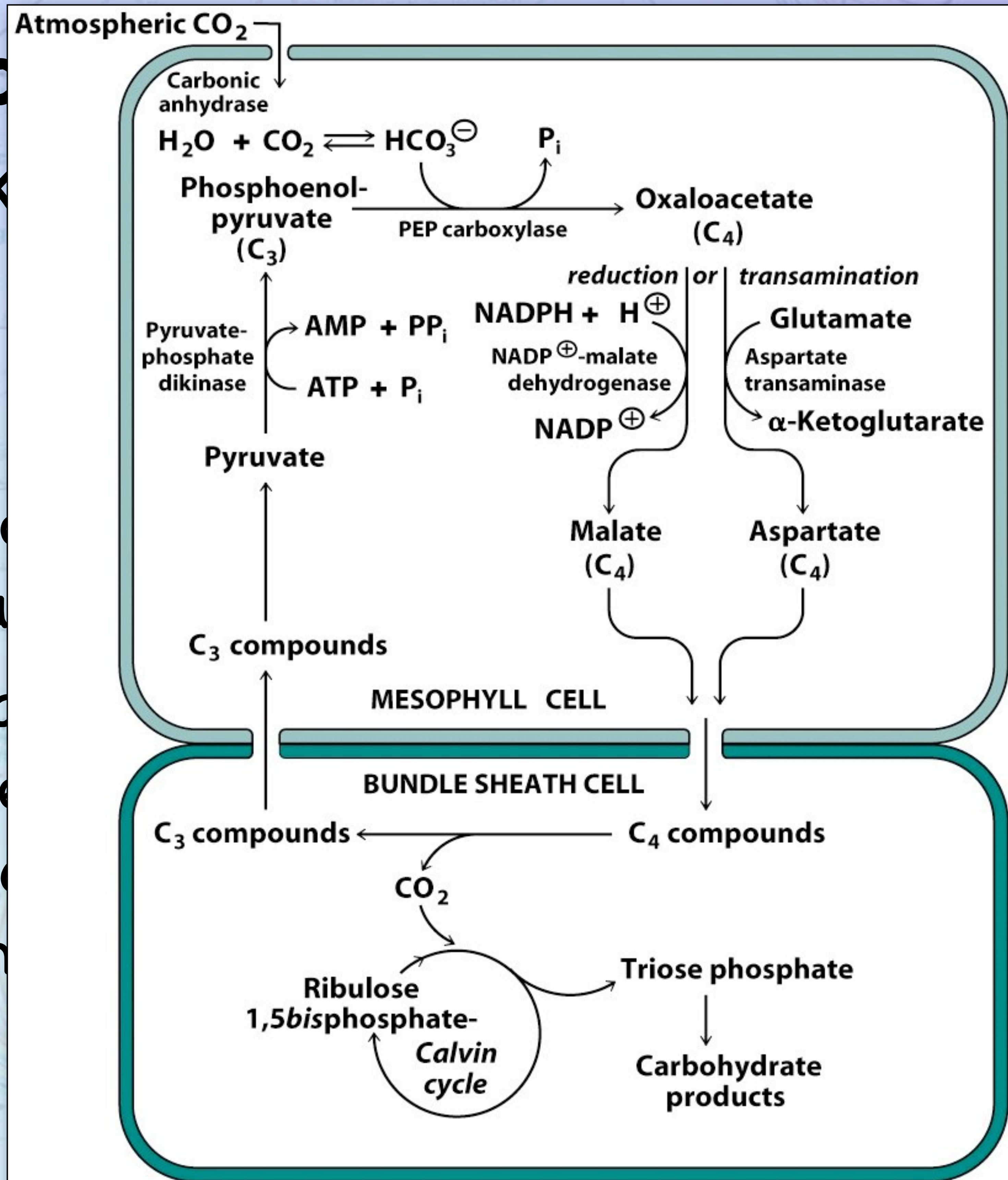

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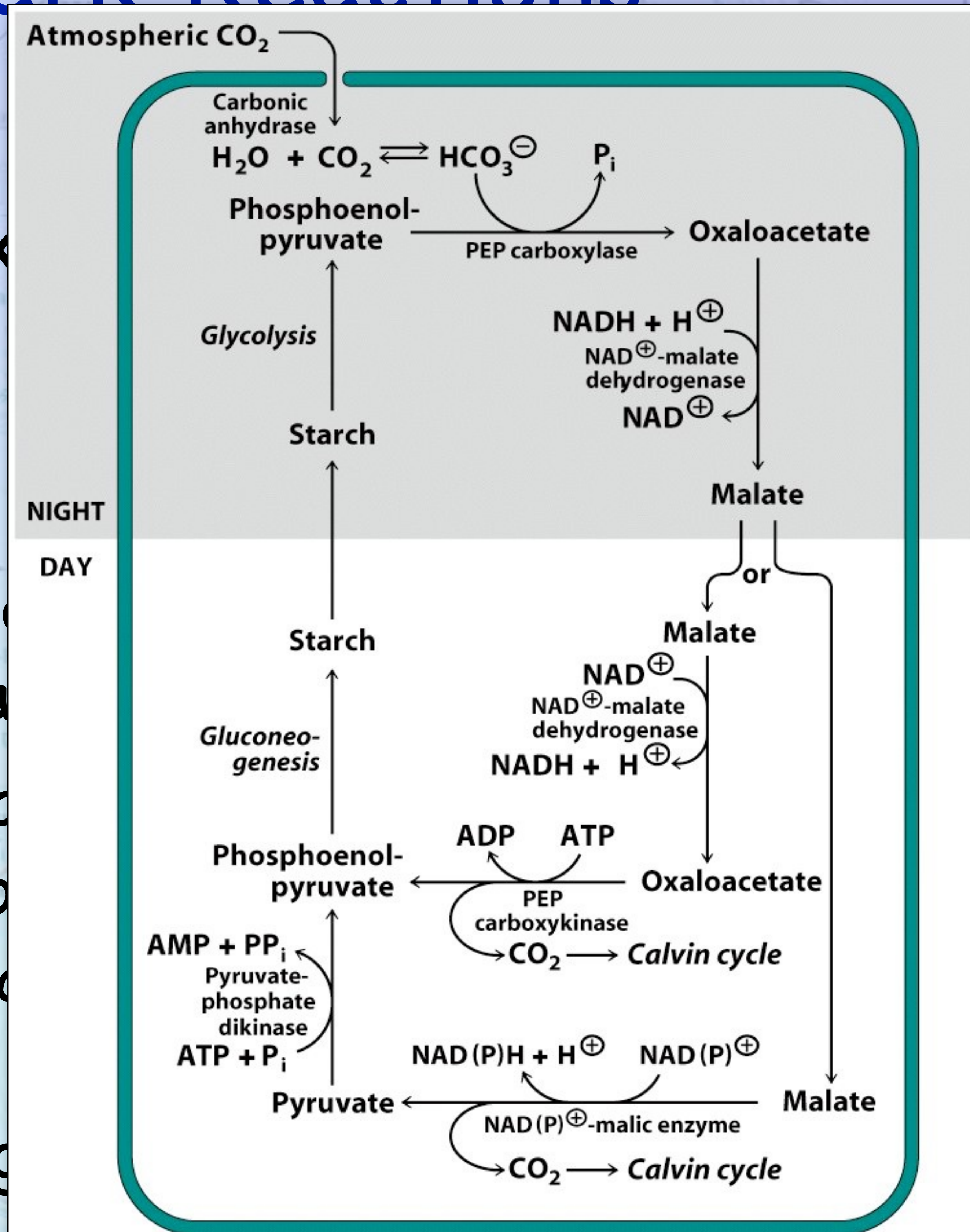
The Dark Reactions

- **Rubis**… …e
  carbox…
  - The … …t
    - It … …+
    - It …
    - Th… …glycerate
      lea…
  - Is ca…
  - Xero… …nd
    pinea… …uring the
    day … …night
    using…



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Next Up

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