1

Chem 352 - Lecture 9
Photosynthesis

2

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.

3

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.

4

Introduction

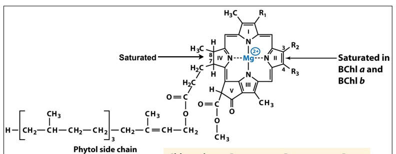
- The light reactions take place in complex structures called **photosystems**.
- Light energy is used to energetically excite electrons, and that energy is then used to make either ATP or reduced NADPH + H^+.

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.

5

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.

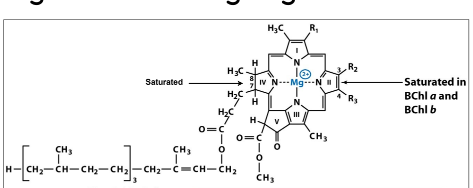
6

Light-Harvesting Pigments

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

7-1

Light-Harvesting Pigments



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

(bacterial)

7-2

7-3

Light-Harvesting Pigments

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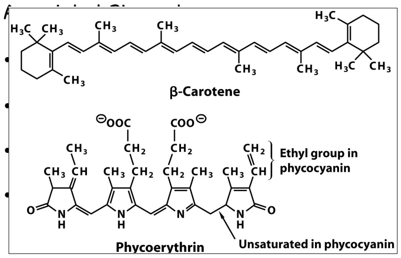
- Associated Pigments
  - β-carotene
  - xanthophylls
  - Phycobilins
  - et al.

7-4

Light-Harvesting Pigments

- Chlorophylls



7-5

Light-Harvesting Pigments

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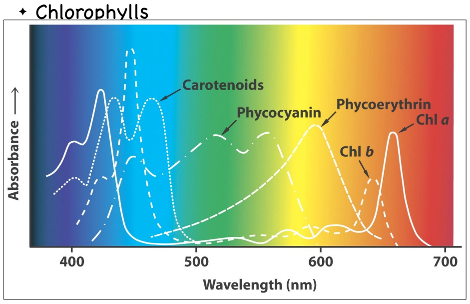
  - et al.

7-6

Light-Harvesting Pigments

- Chlorophylls



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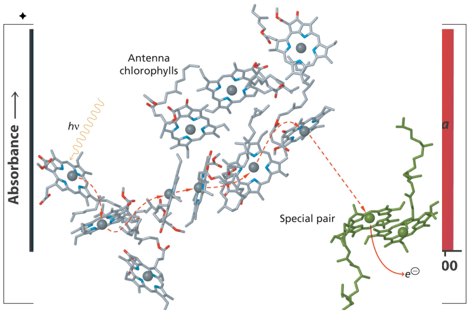
Light-Harvesting Pigments



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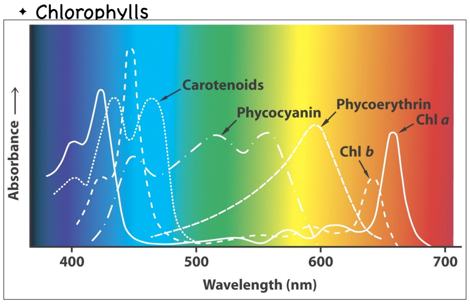
Light-Harvesting Pigments

- Chlorophylls



7-9

Light-Harvesting Pigments

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

8-1

Light-Harvesting Pigments

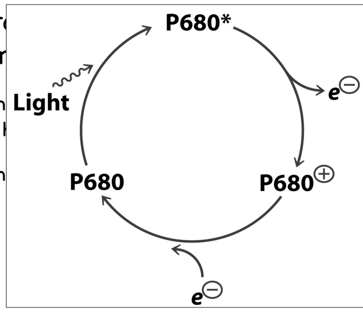
Photosystems have a special pair of chlorophylls called the **special pair**.

- 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
- Th t.



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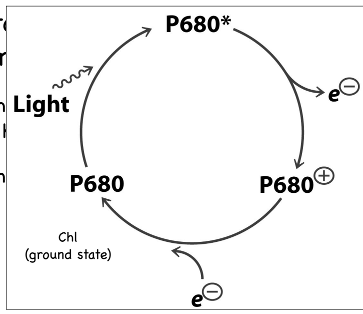
Light-Harvesting Pigments

Phot f
chlor r.

- Th nove
  a
- Th t.



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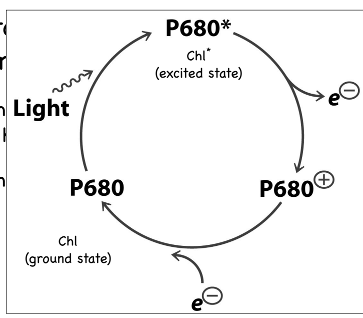
Light-Harvesting Pigments

Phot f
chlor r.

- Th nove
  a
- Th t.



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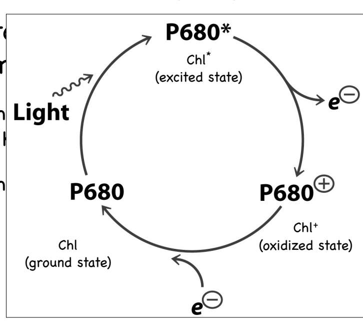
Light-Harvesting Pigments

Phot f
chlor r.

- Th nove
  a
- Th t.

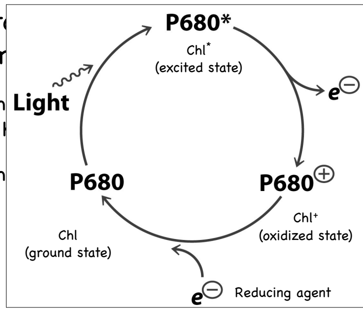


8-5

Light-Harvesting Pigments

Phot... ...f chlor... ...r.

- Th... ...nove a ...
- Th... ...t.



8-6

Photosystem II (PSII)

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

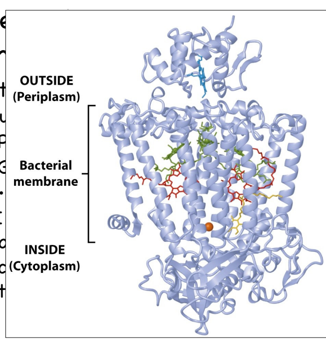
- Photosystem II (PSII)
  - Found in
    - Purple bacteria
    - Green filamentous bacteria
      - both are strict anaerobes
- PSII is combined with cytochrome bc to create a proton gradient that is used to synthesize ATP.
  - cytochrome bc is complex III from the electron transport chain.

9-1

Photosystem II (PSII)

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

- Phot...
  - Fou...
- PSII ... ...reate a proto... ...ATP.
  - c... ...e electron t...



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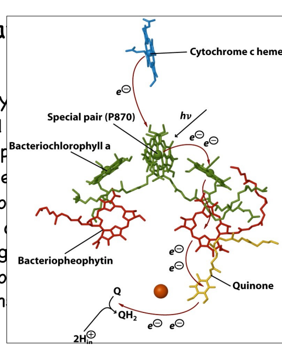
Photosystem II (PSII)

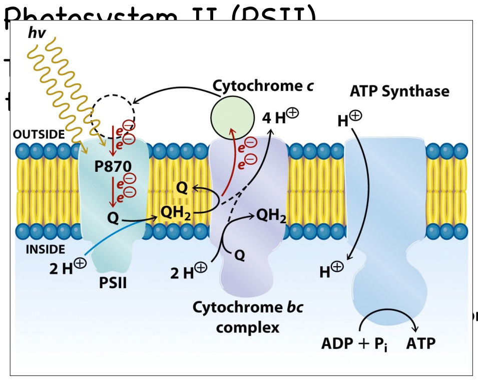
Two rela... ...evolved in the the...

- Photosy...
  - Found...
    - Purp...
    - Gree...
      - bo...
- PSII is ... ...create a proton g... ...ze ATP.
  - cyto... ...the electron tran...



9-3

Photosystem II (PSII)



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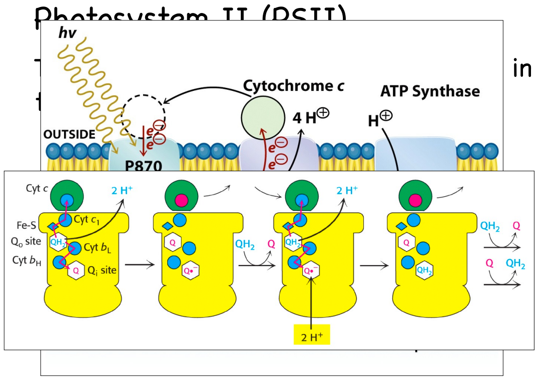
Photosystem II (PSII)



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9-5

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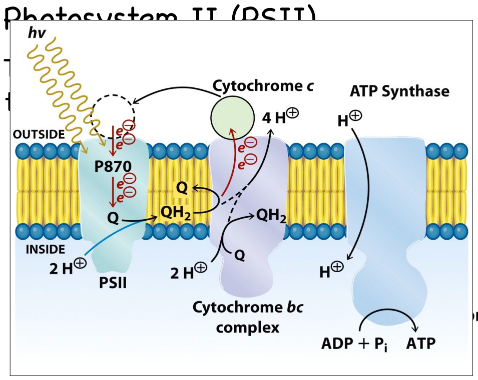

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9-7

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  - Found in

Table 15.1 Photosystem II reactions

PSII:	$2\ P870 + 2\ photons \longrightarrow 2\ P870^{\oplus} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
Cyt *bc*$_1$:	$2\ QH_2 + 2\ cyt\ c\ (Fe^{3+}) \longrightarrow 2\ Q + 2\ cyt\ c\ (Fe^{2+}) + 4\ H^{\oplus}_{out} + 2\ e^{\ominus}$
	$Q + 2\ e^{\ominus} + 2\ H^{\oplus}_{in} \longrightarrow QH_2$
PSII:	$2\ cyt\ c\ (Fe^{2+}) + 2\ P870^{\oplus} \longrightarrow 2\ cyt\ c\ (Fe^{3+}) + 2\ P870$
Sum:	$2\ photons + 4\ H^{\oplus}_{in} \longrightarrow 4\ H^{\oplus}_{out}$

9-8

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9-9

Photosystem I (PSI)

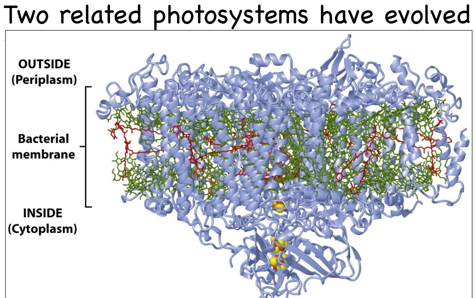
Two related photosystems have evolved in the the last 2 billion years.

- 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 $NADPH + H^+$.

10-1

Photosystem I (PSI)

Two related photosystems have evolved



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

10-2

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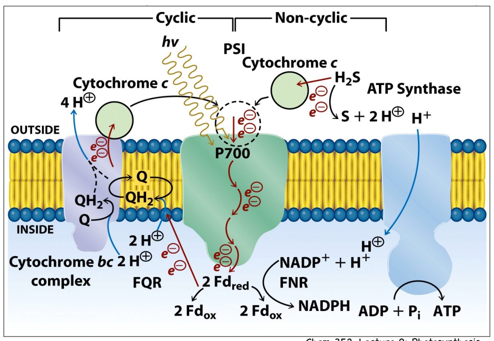
10-3

Photosystem I (PSI)



10-4

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10-5

Photosystem I (PSI)

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

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•
	Fd_{red} + $H^{\oplus}$ + FADH• $\rightleftharpoons$ 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

synthesize ATP.

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

10-6

10-7

Photosystem I (PSI)

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11-1

The Evolution of Photosystems

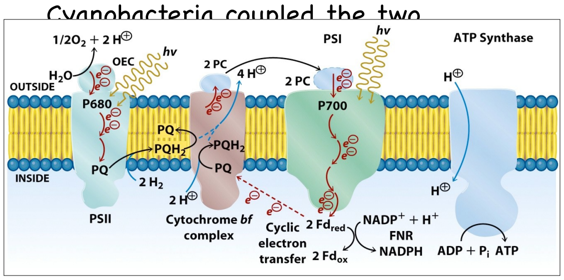
Cyanobacteria coupled the two systems together.

- 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^+.

11-2

The Evolution of Photosystems

Cyanobacteria coupled the two



11-3

The Evolution of Photosystems

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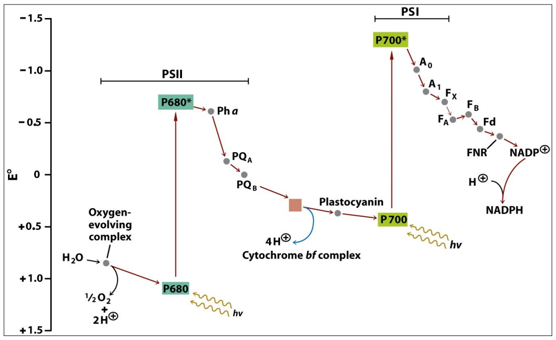
The Evolution of Photosystems



11-4

The Evolution of Photosystems

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11-5

The Evolution of Photosystems

Cyanobacteria coupled the two

Table 15.3 The photosynthesis reactions in species with both photosystems

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

11-6

The Evolution of Photosystems

Cyanobacteria coupled the two systems together.

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- 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^+.

11-7

12

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.

13-1

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

13-2

Plant Photosynthesis

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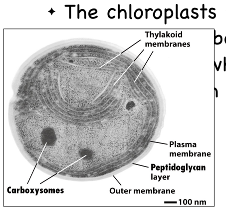


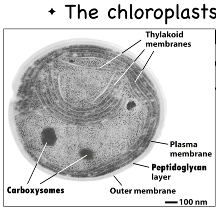
Cyanobacterium

13-3

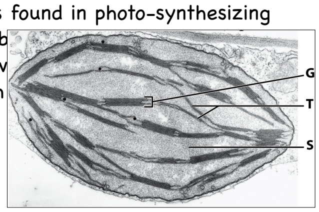
Plant Photosynthesis

Plant photosynthesis takes place in organelles calls chloroplasts.

- The chloroplasts found in photo-synthesizing



Cyanobacterium



Chloroplast

Plant Photosynthesis

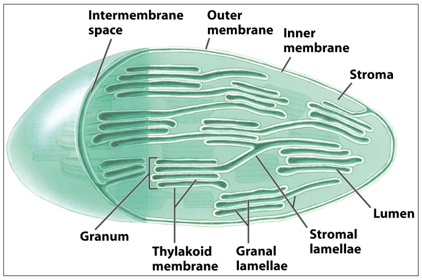
Plant photosynthesis takes place in organelles calls chloroplasts.

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

13-4

Plant Photosynthesis

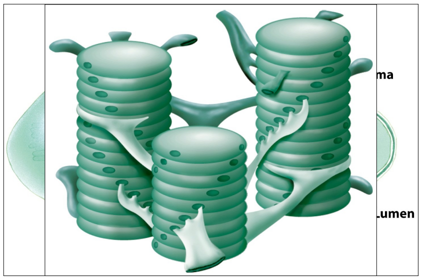
- Chloroplasts have double membranes, like mitochondria.



14-1

Plant Photosynthesis

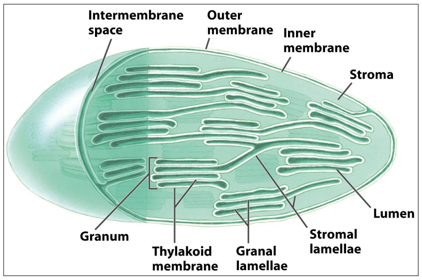
- Chloroplasts have double membranes, like mitochondria.



14-2

Plant Photosynthesis

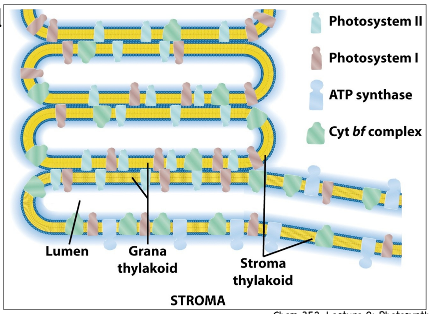
- Chloroplasts have double membranes, like mitochondria.



14-3

Plant Photosynthesis

- Chloroplasts have double membranes,
l



14-4

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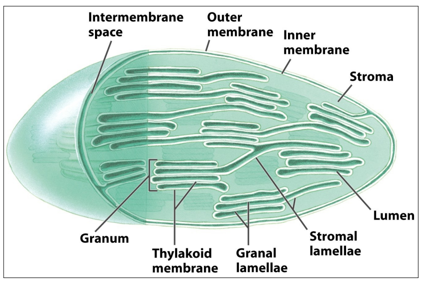


14-5

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**

15

The Dark Reactions

Parts of the Calvin Cycle resembles parts of both

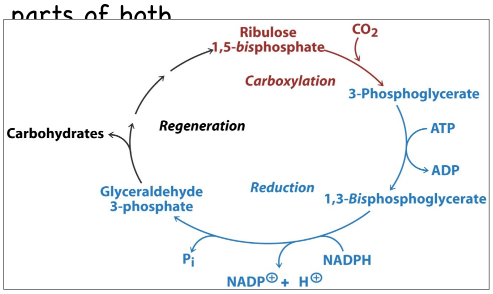
- Gluconeogenesis (Reduction)
- Nonoxidative phase of the Pentose Phosphate Pathway (Regeneration)

16-1

16-2

The Dark Reactions

Parts of the Calvin Cycle resembles parts of both



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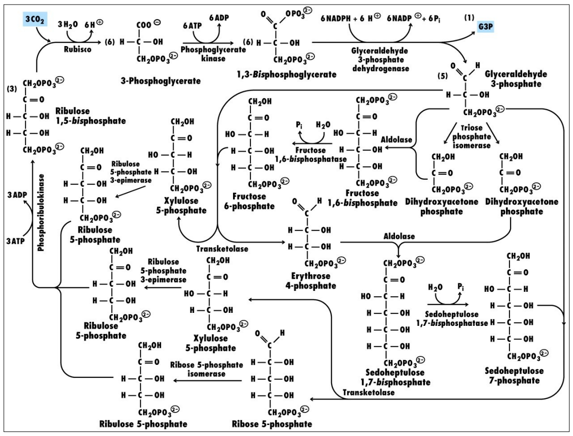

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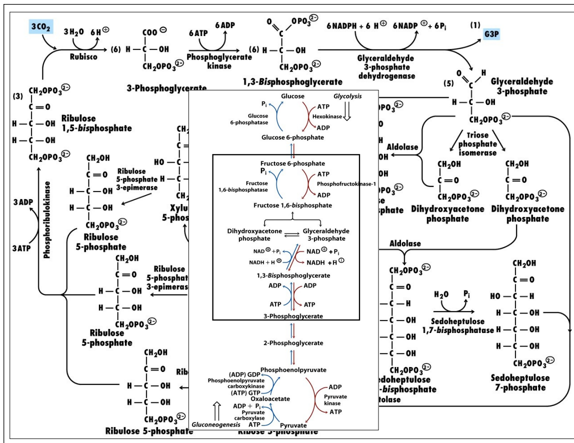

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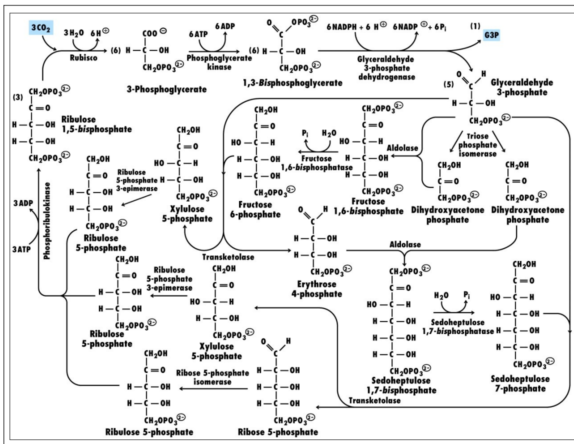

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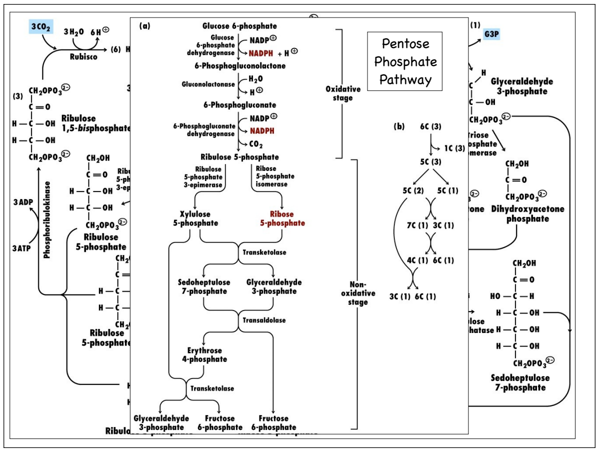

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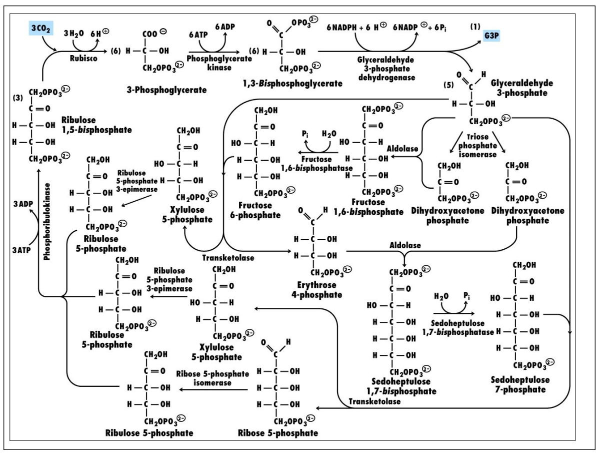
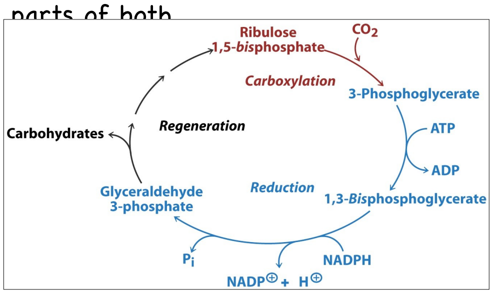


16-8

The Dark Reactions

Parts of the Calvin Cycle resembles parts of both



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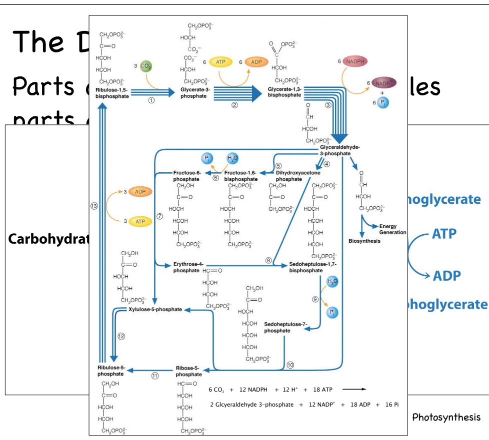
Parts ... les

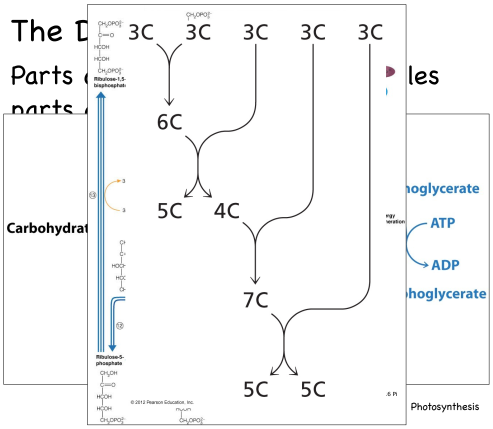


16-10

The D

Parts ... les

parts



16-11

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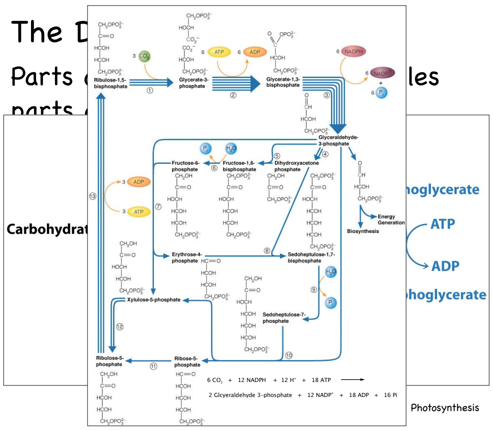
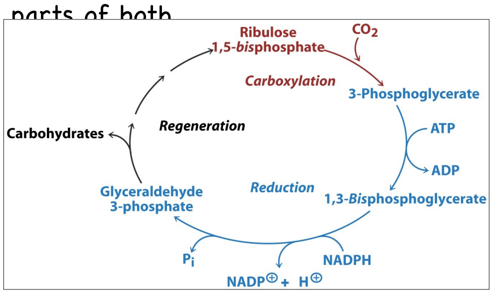


16-12

The Dark Reactions

Parts of the Calvin Cycle resembles

parts of both



17-1

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

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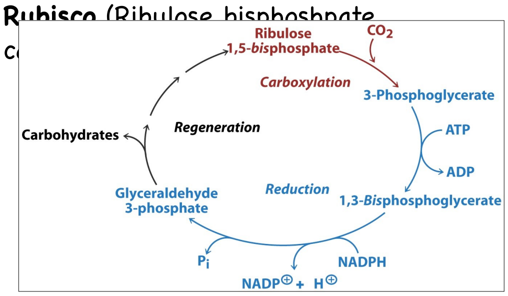

17-2

The Dark Reactions

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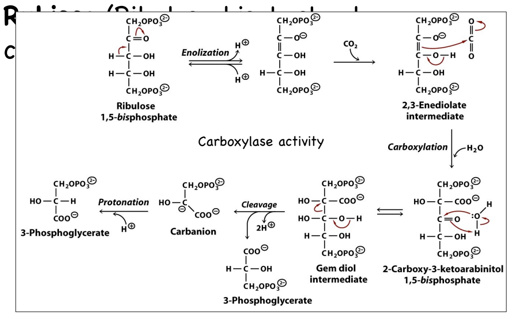

17-3

The Dark Reactions

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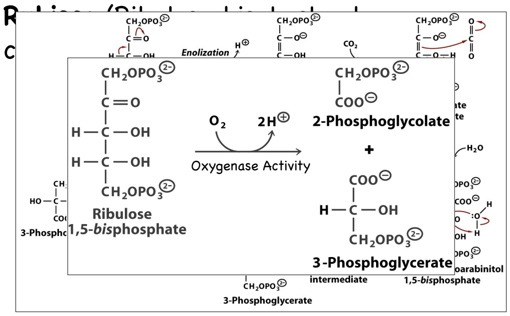


17-4

The Dark Reactions

Rubisco (Ribulose bisphoshpate carboxylase/oxygenase

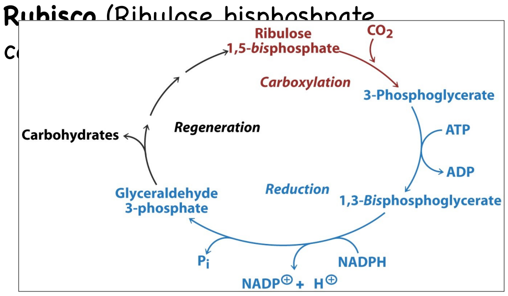
- 50% of soluble protein in leaves is rubisco
- Very inefficient ($k_{cat} \approx 3\ s^{-1}$)
- Nearly every organic-based carbon on earth has passed through the active site of this enzyme.

18-1

18-2

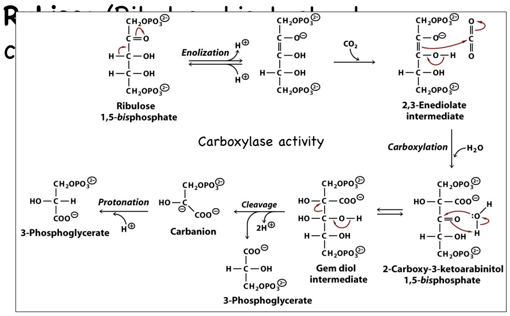
The Dark Reactions

Rubisco (Ribulose bisphoshpate



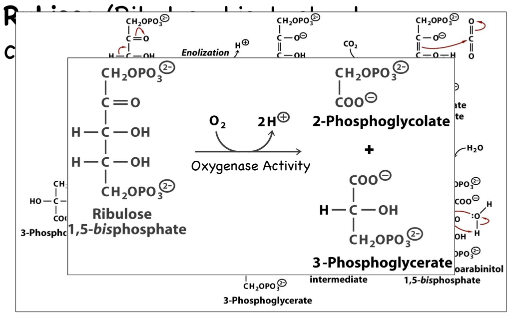
18-3

The Dark Reactions



18-4

The Dark Reactions



19-1

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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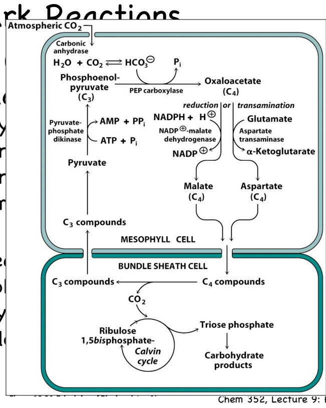

19-2

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.

19-3

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**
  - Xerophilic plants, such as cactus and pineapples, reduce their H_2O loss during the day by storing up CO_2 during the night using the CAM pathway.

20-1

The Dark Reactions

- **Rubis** ... e
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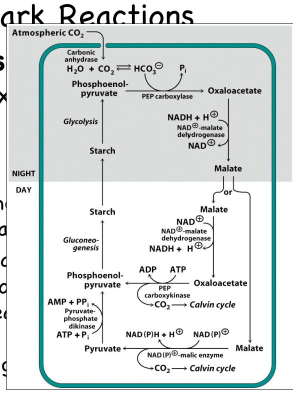

20-2

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**
  - Xerophilic plants, such as cactus and pineapples, reduce their H_2O loss during the day by storing up CO_2 during the night using the CAM pathway.

20-3

Next Up

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

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