- I. Photoreaction and Carbon Reaction
- 1. Types
- Photoreaction: Refer to a photochemical reaction that can occur only in light and is induced by light. It is taken on thylakoid membranes;
- Carbon reaction: Refer to a reaction taken inside the stroma of chloroplast in a dark place (or under light) under the catalysis of a number of enzymes.
- 2. Steps
- Absorption, transfer and conversion processes of optical energy (primary reaction)
- Process of conversion from electric energy into active chemical energy (electron transport and photosynthetic phosphorylation)
- Process of conversion from active chemical energy into stable chemical energy (carbon assimilation)



- **II.** Primary Reaction
- 1. <u>Photosynthetic unit</u> = LHP system + reaction center.
- 2. Light harvesting pigment (LHP) and its effect: Most pigments are LHPs. They don't have photochemical activity and only have an effect of collecting and transferring optical energy, also known as "antenna pigment".
- 3. Energy transfer method: Energy is transferred by method of induced resonance. The speed and efficiency are high. The transfer sequence is: carotenoid  $\rightarrow$ chlorophyll  $b \rightarrow$  chlorophyll  $a \rightarrow$  special chlorophyll a pair.

- 4. The reaction center at least includes in reaction center pigment molecules for conversion of optical energy, primary electron receptors and primary electron donors.
  - Reaction center pigment: Refer to the most fundamental chromoprotein structure for primary reaction of photosynthesis conducted on thylakoid. A minority of chl *a* pair molecules in a special state are this type of pigment molecules, have photochemical activity and are both "catchers" and "converters";
  - 2 Primary electron receptors: Refer to objects, which directly receive electrons transported from reaction center pigment molecules;
  - ③ Primary electron donors: Refer to objects directly donating electrons to reaction center pigment molecules.
- 5. Reaction in the photo<u>reaction center</u>: D·Chl·A $\xrightarrow{h\nu}$ D·Chl\*·A $\rightarrow$ D·Chl+·A<sup>-</sup> $\rightarrow$ D+·Chl·A<sup>-</sup>
- 6. The ultimate electron donor of higher plants is water, and the ultimate electron receptor is NADP<sup>+</sup>.



A schematic diagram of harvest, transport, and transformation of light.

- III. Optical System
- 1. Quantum yield: Number of  $O_2$  molecules given out or  $CO_2$  molecules fixed after absorption of one light quantum.
- 2. **Red drop**: Refer to the phenomenon of abrupt drop of quantum yield when light wavelength is greater than 685 nm regardless of mass absorption by chlorophyll.
- 3. Enhancement effect (Emerson effect): Refer to the phenomenon that red light and far-red light of two wavelengths act synergistically to enhance photosynthetic efficiency.
- 4. Discovery of optical system

PSI: Small particles, 11 nm, located in the non-overlapping part;

PSII: Large particles, 17.5 nm, located in the overlapping part. DCMU can inhibit the photochemical reaction of this system.

Red drop effect. The quantum yield of photosynthesis (black curve) falls off drastically for far-red light of wavelengths greater than 680 nm, indicating that far-red light alone is

inefficient in driving photosynthesis. The slight dip near 500 nm reflects the somewhat lower efficiency of photosynthesis using light absorbed by accessory pigments, carotenoids.



Enhancement effect. The rate of photosynthesis when red and far-red light are given together is greater than the sum of the rates when they are given apart. The enhancement effect provided essential evidence in favor of the concept that photosynthesis is carried out by two photochemical systems working in tandem but with slightly different wavelength optima.



# IV. Photosynthetic Electron Transfersome and Its Function

# (I) Photosynthetic chain

Refer to a general track where electron transfersomes between PSII and PSI on a thylakoid membrane are closely arranged in order of redox potential to complete electron transport.



# (II) PSII

1. Composition

PSII reaction center, light -harvesting complex II and oxygen-evolving complex;

2. Function

Use optical energy to oxidize water and reduce plasmid quinone: oxidize water on the side of thylakoid cavity to release protons, and reduce plasmid quinone on the side of chloroplast stroma.

- 3. Hydrolysis and oxygen evolution of PSII
- (1) Hill reaction:  $4Fe^{3+}+2H_2O \xrightarrow{hv} 4Fe^{2+}+O_2+4H^++4e^-$
- ② Overall reaction:  $2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^-$
- Oxygen-evolving complex: Composed of polypeptides (33 kD, 23 kD and 18 kD), Mn compounds relevant with oxygen evolution, Cl<sup>-</sup> and Ca<sup>2+</sup>;
- ④ Primary electron receptor pheo (pheophytin), primary electron donor Tyr;

**Structural model** of the PSII reaction center, a schematic representation showing the structure dominated by the two **PSII** reaction center protein D1 and D2.



Electron transport direction:  $H_2O \rightarrow MSP \rightarrow Z \rightarrow P680$ 

2.4

# 5 Flash dynamics:

The release of oxygen is accompanied with periodic swing of four flashes. In the first flash, no  $O_2$  is generated; in the second flash, little  $O_2$  is generated; in the third flash, the most  $O_2$  is generated; in the fourth flash, the amount of released  $O_2$  is the second most, then gradually falls to a constant value.







- 4. Electron transport in PSII
- 1 Composition of PSII reaction center: 6 kinds of polypeptides,  $D_1$  and  $D_2$ proteins are basic components. Primary electron donor Z, center pigment P680, primary electron donors Pheo,  $Q_A$  and  $Q_B$  are above them;
- ② Electron transport direction: Electrons are transported to chloroplast stroma direction
  Stroma

 $P680 \xrightarrow{H^{+}} P680^{*} \rightarrow pheo \rightarrow Q_{A} \rightarrow Q_{B} \rightarrow PQH_{2} \rightarrow PQ$  Cavity  $H^{+}$ 

# (III) Cytochrome $b_6 f$ complex

1. Composition

Multiple polypeptides: A Cytf, 2 Cyt $b_6$ , 1 Rieske Fe-S protein, 2 quinone redox locations, etc.

2. Function

Transport electrons in PQH<sub>2</sub> to PC and release H<sup>+</sup> to thylakoid cavity.

3. Electron transport pathway





# **Organization of the protein subunits of the cytochrome** $b_6 f$ **complex.**



# (IV) PSI

1. <u>Composition</u> of core complex

Reaction center pigment P700, electron receptor and PSI light harvesting complex.

2. Function

Transport electrons to ferredoxin from PC.

3. Electron transport pathway

Non-cyclic electron transport

```
P700 \rightarrow A_0(Chl a) \rightarrow A_1(Leaf quinone) \rightarrow Fe-S \rightarrow Fdx \rightarrow NADP^+
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 $\underline{PC} \leftarrow Cytf \leftarrow Cytb_6 \leftarrow PQH_2 \leftarrow \dot{P}Q$ 

Cyclic electron transport

**Structure model of** the PSI reaction center, a schematic representation showing the organization of the two major proteins in this complex, the psaA and psaB subunits, designated here as A and B.



**Mechanism of** cyclic electron transport in chloroplasts. The pathway involves **PSI**, a putative ferredoxinplastoquinone oxidoreductase, and the cytochrome *b*<sub>6</sub>*f* complex.





DBMIB, an inhibitor of the Cyt  $b_6 f$  complex



Paraquat (methyl viologen), an inhibitor of PSI

(V) Photosynthetic electron transport inhibitor (VI) DCMU: Resist reduction of  $Q_A$  in PSII Paraquat: Resist reduction of Fd in PSI DBMIB: Compete against PQ, and stop electrons from being transported to Cytb<sub>6</sub>f

⇐ Chemical structures three inhibitors of the photsynthetic electron transport chain.

Paraquat

# Sites of action for the inhibitors.



- V. Photosynthetic Phosphorylation
- (I) Definition

A process in which organic phosphor and ADP are synthesized into ATP by using the proton motive force stored across thylakoid membrane.

(II) Type

- (1) Non-cyclic photosynthetic phosphorylation (on granum thylakoid membrane)  $2ADP+2Pi+2NADP++2H_2O \xrightarrow{hv} 2ATP+2NADPH+2H++O_2$
- (2) Cyclic photosynthetic phosphorylation (on stromal thylakoid membrane)  $ADP+Pi \xrightarrow{hv} ATP$

# (III) <u>ATP</u> synthase (or coupling factor)

1. Position

In the non-stacking area located in stromal lamellae or grana lamellae and adjacent to PSI, also known as coupling factor.

#### 2. Composition

- The head  $(CF_1)$  is on the surface of thylakoid. There are 5 types of polypeptides (3: 3: 1: 1):
- α—55 kD—catalysis
- β—54 kD—catalysis
- $\gamma$ —36 kD—proton entrance
- δ—20 kD—connecting peptide
- ε—15 kD—inhibit ATP enzyme activity

The handle (CF<sub>0</sub>) sticks into thylakoid . There are 4 types of polypeptides (1: 1: 12: 1): I—17 kD—connecting peptide II—16 kD—connecting peptide III—8 kD—proton translocation IV—27 kD—connecting peptide

**Model for the ATP** synthase complex. The subunit structure of the ATP synthase indicates two major regions in the protein: an integral membrane protein portion  $(CF_0)$ , and an extrinsic portion (**CF**<sub>1</sub>).



(IV) Mechanism of photosynthetic phosphorylation
 Chemiosmotic theory (P. Mitchell):
 Light →hydrolysis→ retain protons in the thylakoid cavity
 Electrons →PQ→discharge protons into the cavity
 H<sup>+</sup> outside the membrane Transport electrons to PC

-Concentration and potential difference

between inside and outside the cavity  $\uparrow$ 

← $[H^+]_{internal}$ ,  $[H^+]_{external}$ 

H<sup>+</sup> is returned to stroma $\rightarrow$ ATP synase activity  $\uparrow \rightarrow$ ATP  $\uparrow$ 

# Summary of the experiment carried out by Jagendorf and coworkers.



# Binding change mechanism of ATP synthesis by the CF<sub>0</sub>-CF<sub>1</sub> complex.



(V) Working mechanism of ATP synase: combined with the change mechanism, i.e.:  $O \rightarrow L \rightarrow T \rightarrow O$ 

Membrane organization of the Z-scheme. The components of the chloroplast electron transport chain and the ATP-synthesizing apparatus are illustrated in the thylakoid membrane.





**Organization of the** thylakoid membrane showing relative positions of antenna complexes, photosystems, and protein complexes. **Proteins of** photosystems within the thylakoid membrane pump hydrogen ions from the stroma into the thylakoid space (lumen). When hydrogen ions flow back out of the thylakoid into the stroma through the **ATP synthase complex**, **ATP** is produced.