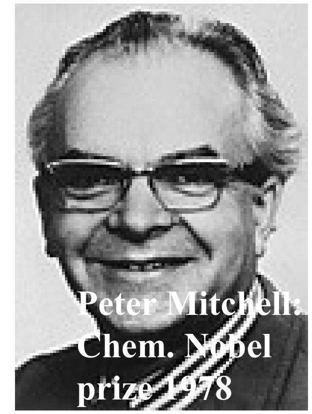
The Resulting Proton Gradient Powers ATP Synthesis = Oxidative Phosphorylation

The Chemiosmotic Hypothesis (proposed by Mitchell 1961):
1.) The free energy of electron transport is conserved by generating a H^+ gradient across the mitochondrial membrane.
2.) The electrochemical potential of this gradient is harnessed to synthesize ATP.


Peter Mitchell: Chem. Nobel prize 1978

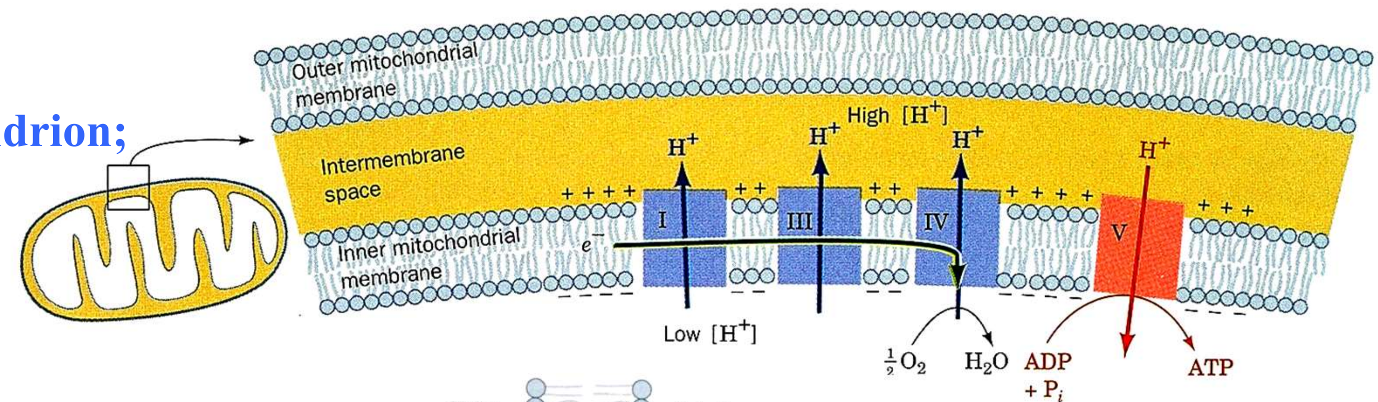
➢ **Evidence:**

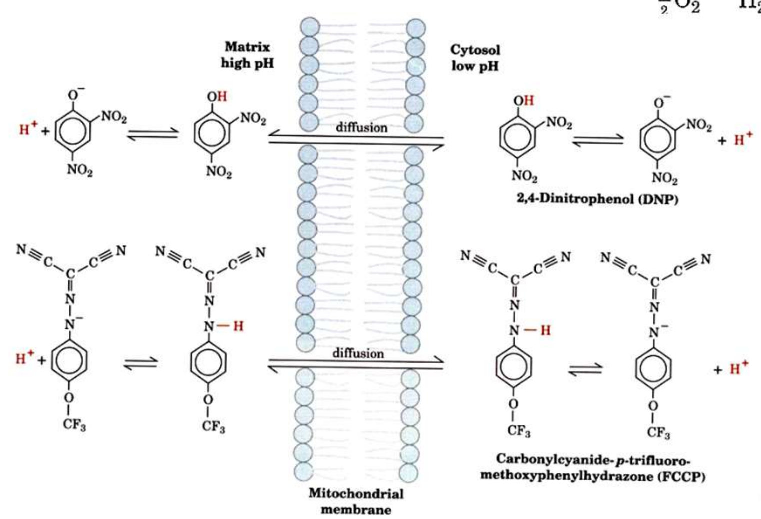
♣ electron transport results in transport of H^+ out of mitochondrion;

♣ inner mitochondrial membrane is impermeable to H^+, OH^-, K^+, and Cl^-;

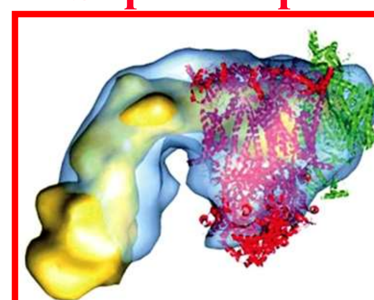
♣ inner mitochondrial membrane needs to be intact;

♣ compounds that increase membrane permeability and dissipate the electrochemical gradient only stop ATP synthesis, i.e., they "uncouple" it from electron transport



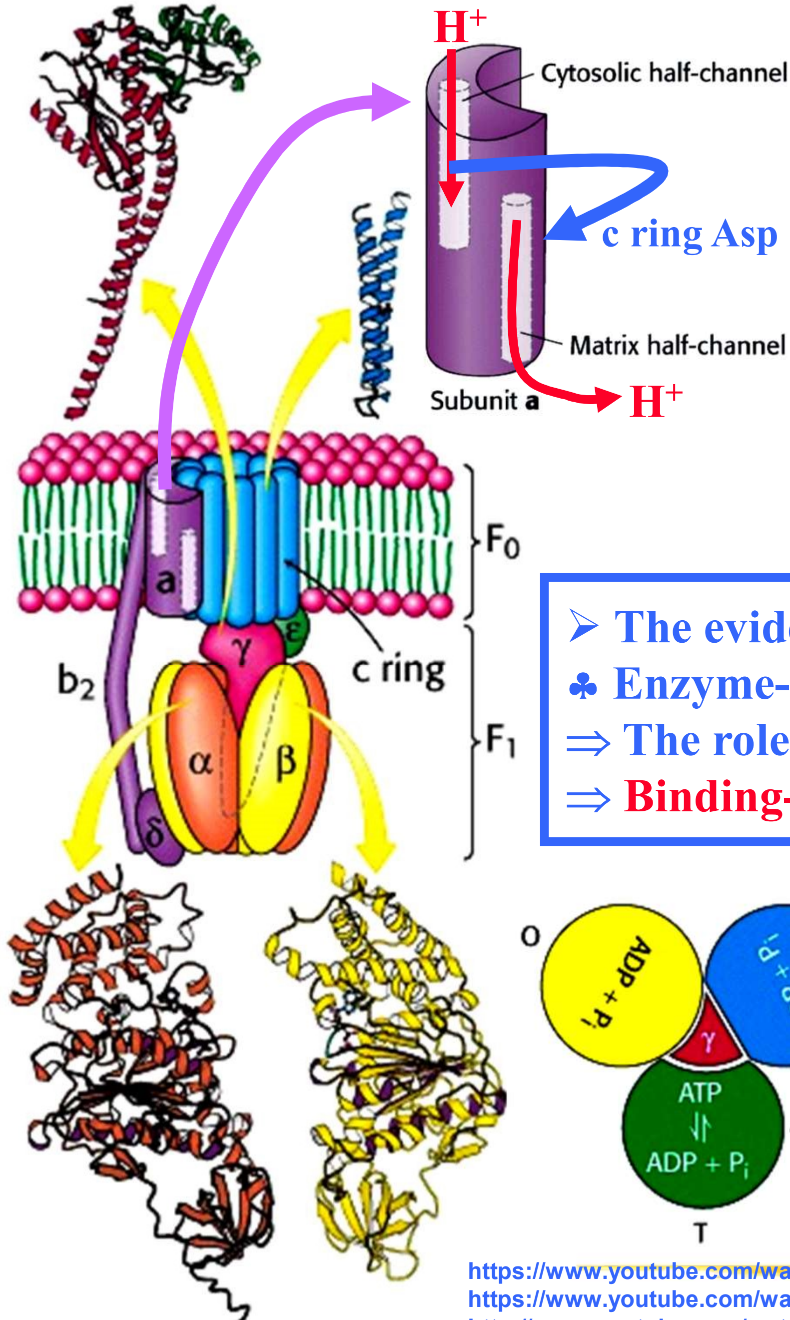


➢ **Supracomplex:**



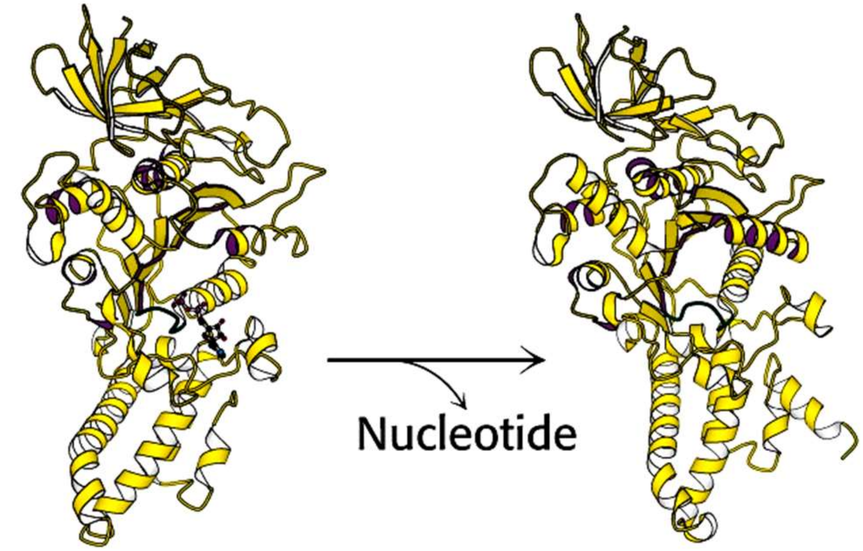
ATP Synthase: The World's Smallest Motor

The engine parts:



c ring has 10 subunits
⇒ Full turn releases 10 H^+, while making 3 ATP
⇒ ~3 H^+/ATP!

Conformational changes accompany ATP release:

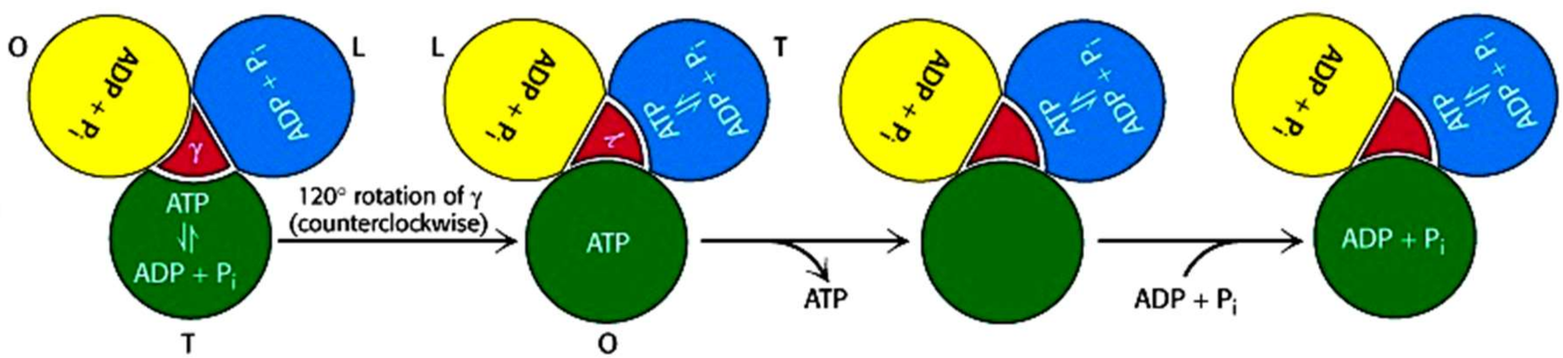


➢ The evidence:

♣ Enzyme-bound ATP forms readily in the absence of a proton gradient

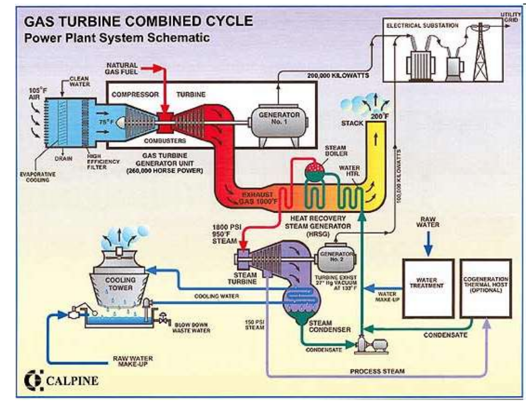
⇒ The role of the proton gradient is to release ATP from the synthase

⇒ **Binding-Change Mechanism**:



https://www.youtube.com/watch?v=RrS2uROUjK4
https://www.youtube.com/watch?v=rdF3mnyS1p0
http://www.youtube.com/watch?v=PjdPTY1wHdQ

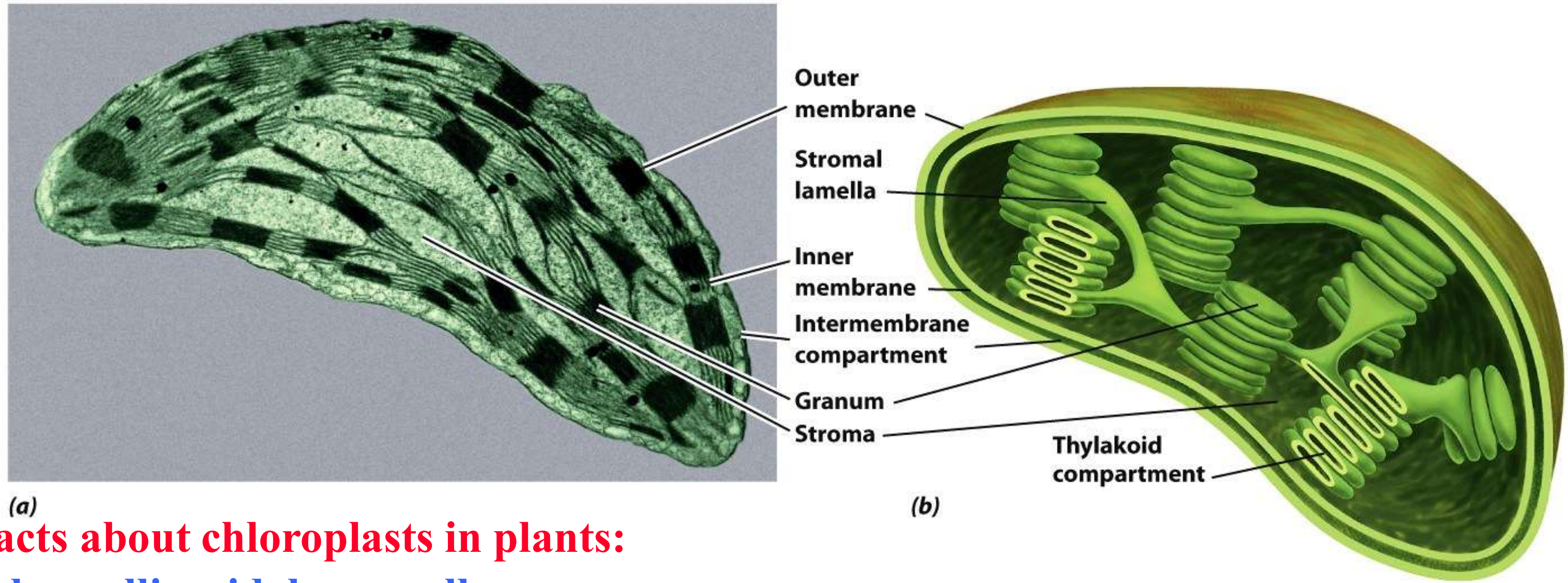
Chapter 22: What have we learned?



- Anatomy of mitochondria
- ATP/ADP, Ca^{2+}, and NADH transport across the largely impermeable inner mitochondrial membrane
- The thermodynamics and sequence of electron transport
- The P/O ratio
- 3 classes of redox players: Fe-S clusters, quinones, cytochromes
- What is known about Complexes I, III, and IV of the electron transport chain
- Evidence for and mechanism of ATP synthesis by the proton gradient across the inner mitochondrial membrane

Photosynthesis

Voet & Voet, Chapter 24



➢ **The facts about chloroplasts in plants:**

♣ ~5 μm long ellipsoidal organelles

♣ 1 to 1,000 per plant cell

♣ highly permeable outer membrane, separated by a narrow intermembrane space from a nearly impermeable inner membrane

♣ inner membrane encloses stroma = concentrated enzyme solution that also contains DNA, RNA, and ribosomes involved in the synthesis of several chloroplast proteins

♣ stroma, in turn, surrounds a third membraneous compartment, the thylalkoid (greek: pouch), a single vesicle highly folded into 10 to 100 stacks of disclike sacs = grana, interconnected by unstacked stroma lamellae

♣ thylalkoid membrane has distinctive lipid composition with ~80% uncharged mono- and digalactosyl diacylglycerols, ~10% sulfated galactosyl diacylglycerols, and ~10% phospholipids

⇒ **(1) Highly resemble mitochondria ⇒ probably also endosymbiotic in origin**

⇒ **(2) Compartmentalization allows two new sets of reactions: light and dark reactions**

An Overview: Light and Dark Reactions

Overall photosynthesis - Fixation of CO_2 by light:

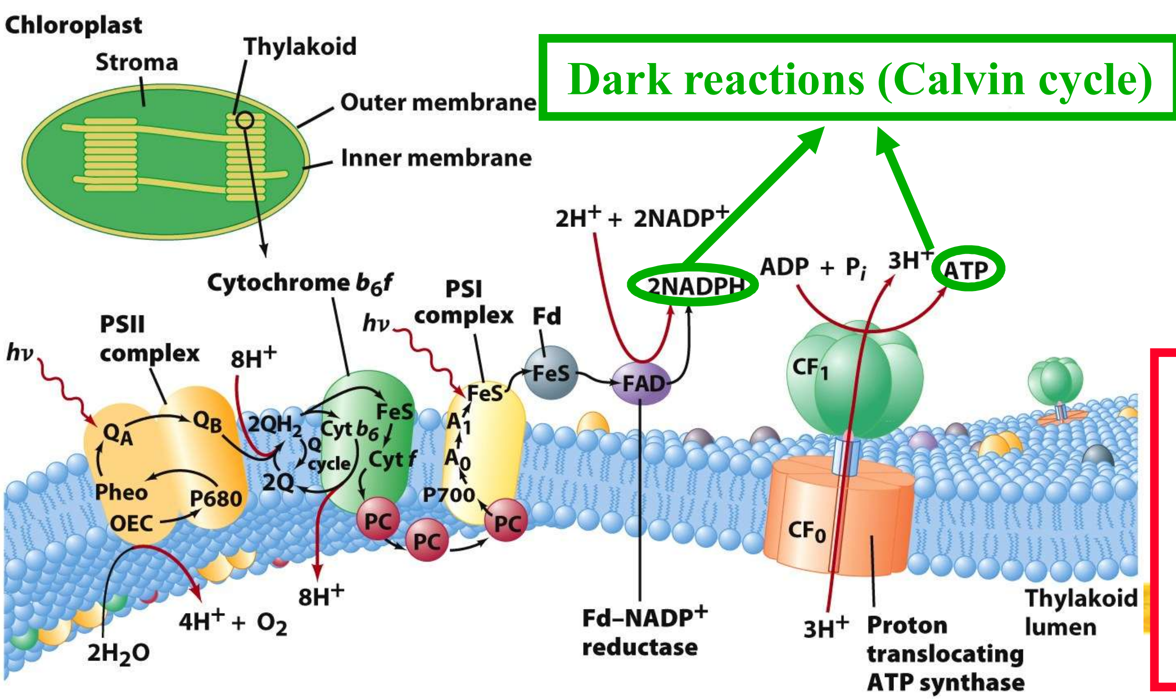
$$CO_2 + H_2O \xrightarrow{\text{light}} (CH_2O) + O_2$$

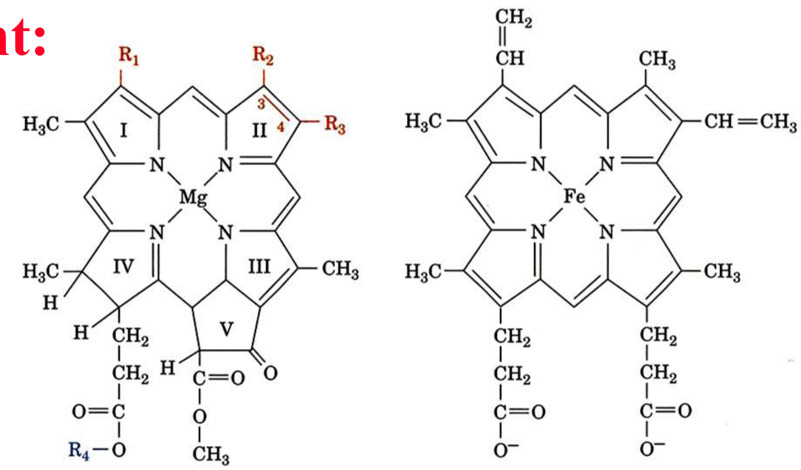
- 10^{11} tons CO_2/year fixed = 10^{18} kJ of energy
- fossil fuels = coal, oil, gas are evidence that this process has occurred over eons
- BUT in anaerobic green photosynthetic bacteria:

$$CO_2 + 2H_2S \xrightarrow{\text{light}} (CH_2O) + 2S + H_2O$$

- AND :

$$CO_2 + H_2{}^{18}O \xrightarrow{\text{light}} (CH_2O) + {}^{18}O_2$$



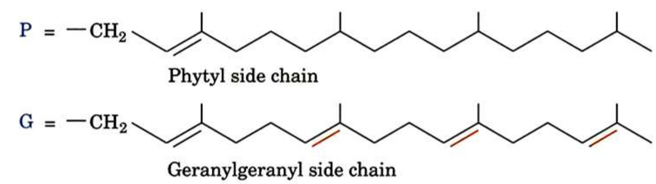


Chlorophyll

Iron-protoporphyrin IX

	R_1	R_2	R_3	R_4
Chlorophyll *a*	$-CH{=}CH_2$	$-CH_3$	$-CH_2-CH_3$	P
Chlorophyll *b*	$-CH{=}CH_2$	$-\overset{O}{\overset{\Vert}{C}}-H$	$-CH_2-CH_3$	P
Bacteriochlorophyll *a*	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	$-CH_3{}^{a}$	$-CH_2-CH_3{}^{a}$	P or G
Bacteriochlorophyll *b*	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	$-CH_3{}^{a}$	$=CH-CH_3{}^{a}$	P

[a] No double bond between positions C3 and C4.



- **The start: Light-absorbing chlorophylls:**

♣ porphyrine systems with a central Mg^{2+} (not iron!)

♣ modifications fine-tune electronic properties

♣ isoprenoid tails increase solubility in nonpolar media