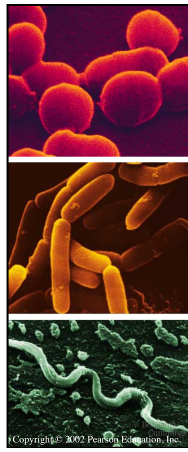
Class announcements

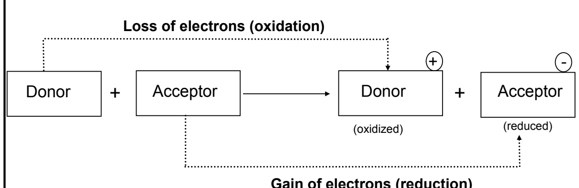
1. Today – we'll use hand clickers, not electronic ones
2. Tuesday – discussion session for reviewing for first mid-term exam @ 9:00-10:30 in Room 1140 Plant Sciences – **bring your questions!**
3. Use the regular meeting time for your study group to prepare for first mid-term exam
4. Wednesday – first mid-term exam



Prokaryotic Bioenergetics II - All That Jazz about Redox Reactions

- Evolutionary origins
- Basic features
- Bacteria – several major groups
- Bacteria - pathogenesis
- Archaea – extremophiles
- Metabolic diversity
- **Bioenergetics – redox reactions**
- Bioenergetics - electron transport chains
- Biogeochemical cycles

Reduction-oxidation (redox) reactions



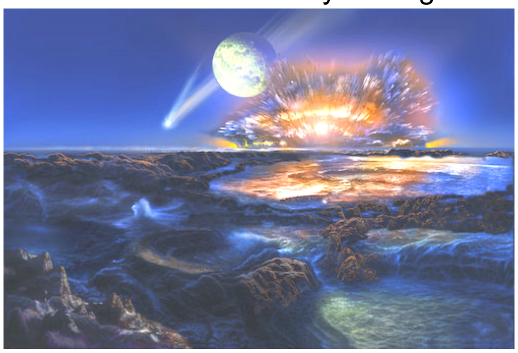
LEO says "GER"

Prokaryotic Bioenergetics: All That Jazz about Reduction-Oxidation (Redox) Reactions

1. Redox reactions transform the physical and chemical energy entering organisms into useful forms of biological energy.
2. Redox reactions are often used to transform the available molecules from the environment into useful metabolites.
3. An integrated biological perspective of redox reactions is:

Biomolecules	Organism	Environment
Catalysts/enzymes ETC's	Nutritional strategies e.g., photoautotrophy, chemolithoautotrophy	Biogeochemical cycles e.g., N and S cycles

Imagine you were the first life form on Earth 4.3 billion years ago



www.cosmographica.com

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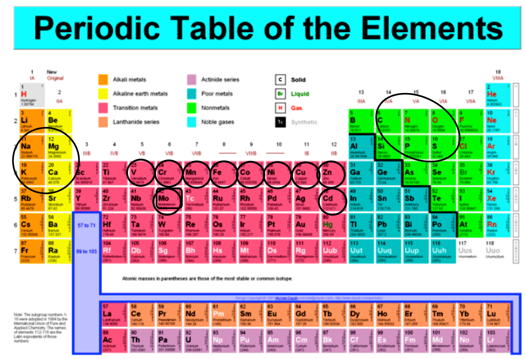

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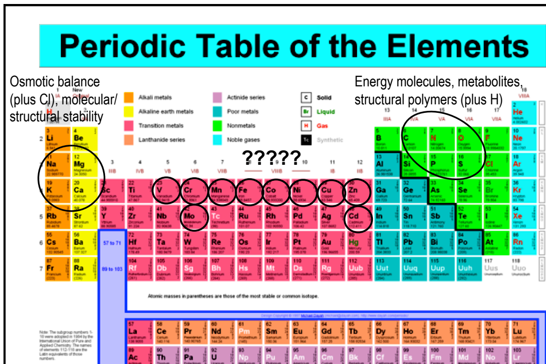


http://www.dayah.com/periodic/Images/periodic%20table.png

Basic Chemistry of Transition Metals

Several or more stable oxidation states
Effective inorganic catalysts
Formation of complex ions composed of more than one atom

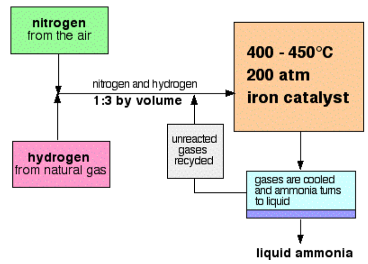
e.g., Fe ions: 2 oxidation states - Fe^{2+}, Fe^{3+}
Mn ions: 7 oxidation states - Mn^{1+}-Mn^{7+}
Mo ions: 8 oxidation states - Mo^{2-}, Mo^{1-}, Mo^{1+}-Mo^{6+}

Some examples of transition metals in biology

Element	Enzyme/protein	Reaction/process
Iron (Fe)	Cytochromes	Electron carrier in ETC's
	Catalase	$2H_2O_2 \longrightarrow 2H_2O + O_2$
	Hemoglobin	Oxygen carrier
Copper (Cu)	Cytochrome oxidase	$4H^+ + 4e^- + O_2 \longrightarrow 2H_2O$
	Hemocyanins	Oxygen carrier
Zinc (Zn)	Carbonic anhydrase	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$
	Alcohol dehydrogenase	$C_2H_5OH \longrightarrow C_2H_4O + 2H^+$
Molybdenum (Mo)	Nitrogenase	$N_2 \longrightarrow 2NH_3 + H_2$
	Nitrate reductase	$2NO_3^- \longrightarrow 2NO_2^-$
Vanadium (V)	Nitrogenase	$N_2 \longrightarrow 2NH_3 + H_2$
Manganese (Mn)	Water-splitting complex	$2H_2O \longrightarrow 4H^+ + 4e^- + O_2$
Cadmium (Cd)	Carbonic anhydrase	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$
Nickel (Ni)	Hydrogenases	$H_2 + X_{ox} \rightleftharpoons 2H^+ + X_{red}$

Haber process (1913) -

How to break the N≡N bond of atmospheric N_2



$N_2 + 3H_2 \text{---> } 2NH_3$

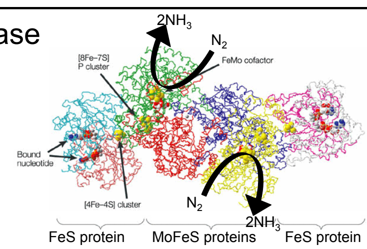
www.chemguide.co.uk/physical/equilibria/haberflow.gif

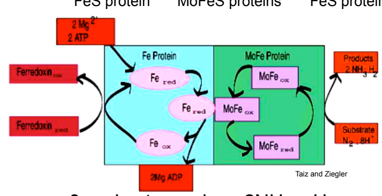
Nitrogenase

- Only physical source of NH_2 groups for amino acid synthesis is lightning strikes.
- Early life evolved the enzyme **nitrogenase** that carries out the reaction called **nitrogen fixation**:

$$N_2 + 8H^+ + 8e^- + 16\text{ ATP ---> } 2NH_3 + H_2 + 16\text{ ADP} + 16\text{ P}_i$$

Nitrogenase





8 cycles to produce $2NH_3 + H_2$

A plausible evolutionary scenario

1. Metal ions were probably used as the catalysts for many metabolic reactions in early protolife.
2. Evolutionary relics: Metallic co-factors at the active sites of many enzymes of ancient origin, e.g.,

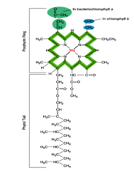
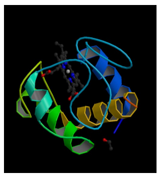


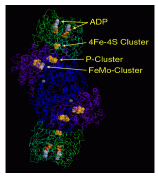
fig.cox.miami.edu/~cmallery/255/255phts/gk6x5.chlorophyll.gif

Chlorophyll *a* - Mg tetrapyrrole (photosynthetic pigment)



www.rcsb.org/pdb/cgi/explore.cgi?pdbId=3CYT

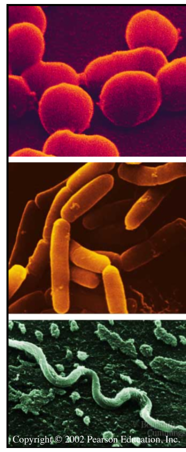
Cytochrome c - Fe heme protein (oxidative phosphorylation)



www.rcsb.org/pdb/molecules/pdb26_3.html

Nitrogenase - MoFeS and FeS metaloproteins (nitrogen fixation)

3. Typically, enzymes of more recent origin use only amino acids in their active sites.



Prokaryotic Bioenergetics II - All That Jazz about Redox Reactions

- Evolutionary origins
- Basic features
- Bacteria – several major groups
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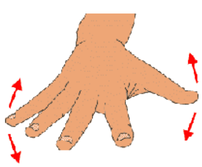
- Metabolic diversity
- Bioenergetics – redox reactions
- **Bioenergetics – electron transport chains**
- Biogeochemical cycles

Fail-safe clicker

False



Don't know/neutral

True

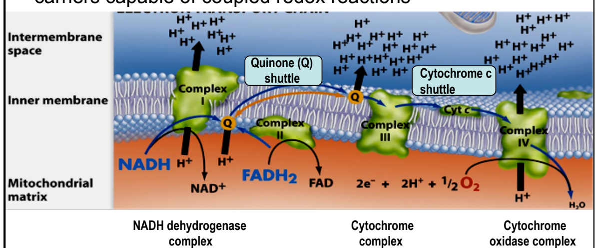
For general clicker assistance, go to: www.clickers.umd.edu

Correctable true-false questions about redox reactions for group discussion

1. Electrons are freely available in aqueous solutions, so that biological molecules can often be reduced without oxidizing another molecule.
2. The energy in a molecule that has acquired an electron (= a reduced molecule) is stored by exciting that electron, i.e., it is placed in an orbital having higher energy.
3. The energy in a molecule that has acquired an electron (= a reduced molecule) is stored as potential energy arising from the repulsion of that electron by other nearby electrons.

Electron transport chains - basic properties

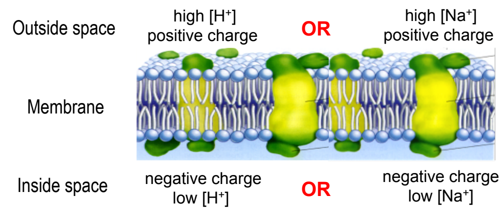
Electron carrier - any molecule capable of redox reactions
Electron transport chain (ETC) - a sequence of electron carriers capable of coupled redox reactions



The products of ETC's are: H^+ electrochemical gradients, reduced compounds (e.g., H_2O), and oxidized compounds (e.g., NAD^+)

F Fig. 9.24

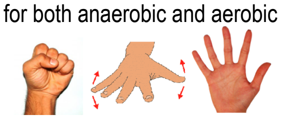
Organisms set up electrochemical gradients across cell membranes to do biological work



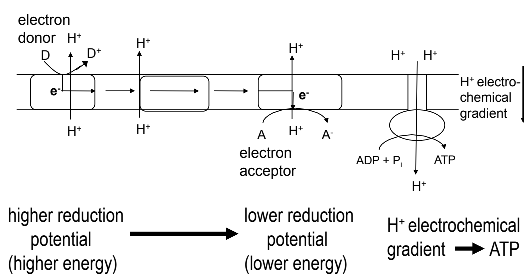
Electrochemical gradient –
a gradient (= difference/distance) of concentration ("- chemical") and charge ("electro-") across the membrane

How are electron transport chains (ETC's) used for carrying out bioenergetics?

1. ETC's are used only for aerobic respiration in aerobic bacteria and mitochondria, and for oxygenic photosynthesis in cyanobacteria and chloroplasts.
3. Prokaryotes use unique ETC's having different carriers for carrying out anaerobic and aerobic processes.
3. Prokaryotes use several homologous electron carriers in their ETC's for both anaerobic and aerobic processes.



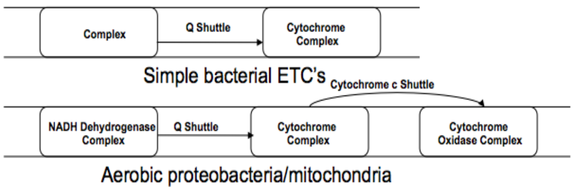
General principles of electron transport chains



Why waste our time on the mitochondrial ETC?

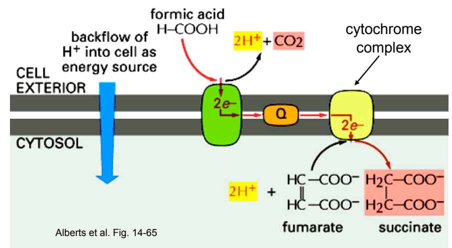
I've learned about it before!

Telegraphing the punch – typical prokaryotic ETC's



Evolutionary conservation: certain e^- carriers, overall organization
Evolutionary variation: other e^- carriers, donor/acceptor pairs

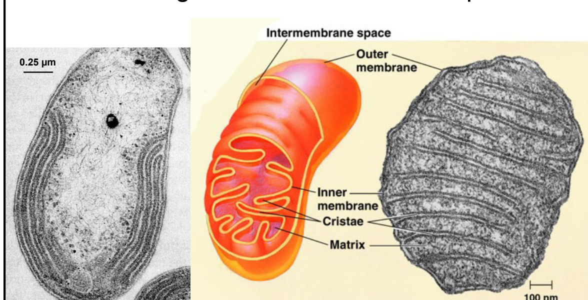
Simple ETC's - organic acid oxidation in some modern bacteria



Alberts et al. Fig. 14-65

- Simple ETC composed of 2 complexes of several electron carriers and 1 lipid-soluble shuttle (Q = quinone)
- H^+ generation on the outside and H^+ consumption on the inside ---> H^+ electrochemical gradient

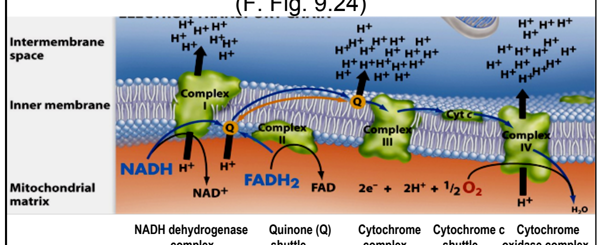
ETC-bearing structures - aerobic respiration



C & R Fig. 27.8 C & R Fig. 7.17

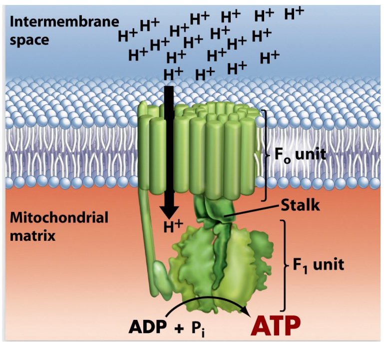
α-proteobacterium mitochondrion

Aerobic respiration - electron transport chain (F. Fig. 9.24)



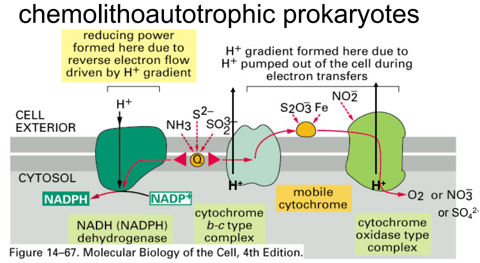
- Electron transport chains (ETC) are typically organized into 2 - 4 large complexes composed of several electron carriers, plus other carriers acting as shuttles. Homologous ETC core!
- The products of ETC's are H^+ electrochem. gradients, reduced compounds (e.g., H_2O), and oxidized compounds (e.g., NAD^+)

Aerobic respiration - ATP synthesis (F. Fig. 9.25)



ATP synthase converts the H^+ gradient into ATP

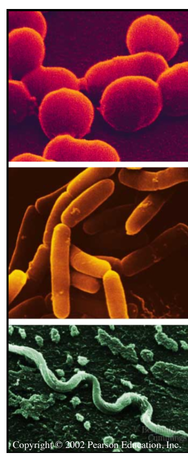
Anaerobic respiration: ETC's of chemolithoautotrophic prokaryotes



- Same ETC organization - 3 complexes and 2 shuttles
- Different donor and acceptor molecules in different bacteria
- Positive e^- flow (to the right) generates H^+ gradient for ATP synthesis
- H^+ gradient can also drive reversed e^- flow (to the left) for synthesizing high energy NADH/NADPH

Complex ETC's composed of three complexes and two shuttles

- Very different processes
  - aerobic respiration – NADH oxidation and O_2 reduction
  - anaerobic respiration - different initial e^- donors and terminal e^- acceptors (e.g., NO_3^- reduction)
- Homologous carriers -> common evolutionary origin
- Unique complexes and/or unique carriers for specialized functions
- Same end product - H^+ gradient for ATP synthesis



Prokaryotic Bioenergetics: All That Jazz about Redox Reactions

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- Bioenergetics – redox reactions
- Bioenergetics – respiratory electron transport chains
- **Biogeochemical cycles**

ETC's of chemoautotrophic bacteria

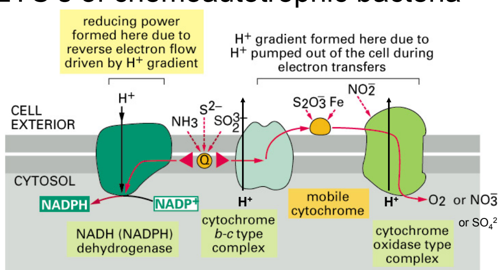
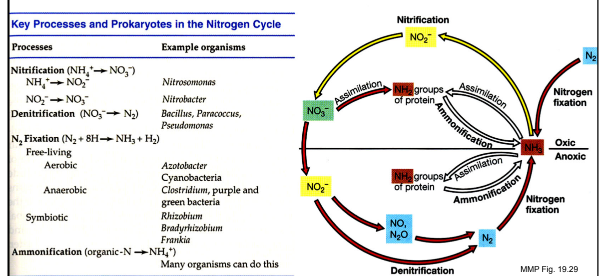


Figure 14–67. Molecular Biology of the Cell, 4th Edition.

Biogeochemical cycles (especially N and S cycles) - ecological consequences of the molecular activities of prokaryotic ETC's

Biological nitrogen cycle



Nitrification - oxidation of N compounds from NH_3 to NO_3^-
Denitrification - reduction of N compounds from NO_3^- to N_2
Fixation - the conversion of N_2 to NH_3 by nitrogenase

Biological sulfur cycle

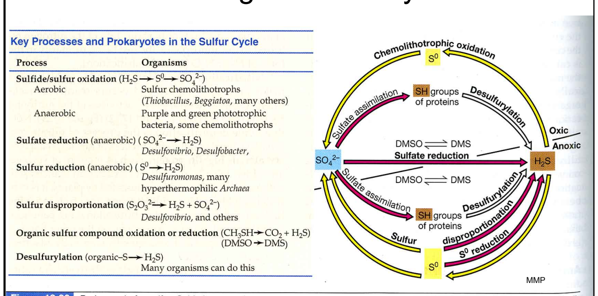


Figure 19.30 Redox cycle for sulfur. Oxidations are shown in yellow arrows and reductions in red. DMSO, dimethylsulfoxide; DMS, dimethylsulfide.

Oxidation: H_2S ---> S° ---> SO_4^{-2}
Reduction: SO_4^{-2} ---> HS^{-1} or S° ---> H_2S

Summary - geobiochemical cycles

1. Prokaryotes use the redox reactions of ETC's plus other enzymatic reactions to obtain energy from the inorganic and organic compounds available in their environments.

2. At least one prokaryote group can metabolize any form of the essential elements (H, C, O, N, S, and P).

3. One prokaryote's waste product is another prokaryote's food.

4. Consequently, these elements must necessarily cycle in, through, out of, and back into the biological world.

Study questions for prokaryotic bioenergetics

1. Define the six classes of prokaryotic nutritional strategies (e.g., photoautotrophs, etc.) in terms of their energy and organic compound sources.
2. Describe the energy source, chemolithotrophic prokaryotes, and other organisms in the deep-sea hydrothermal vent communities.
3. Assemble the evidence needed to evaluate whether Darwin's "warm little pond" or a deep-sea hydrothermal vent seem a more likely site for the origin of early life.
4. How does the chemistry of transition metals make them appropriate cofactors for biological redox reactions?
5. Make plausible predictions about the evolution of metallic complexes as the catalysts for biological metabolism and energetics.
6. Describe the fundamental organization of the complex bacterial electron transport chain. (Hint: how are the three complexes, the Q shuttle, and a soluble shuttle organized to form a functional ETC?)
7. How has this fundamental ETC evolved to carry out aerobic respiration in aerobic bacteria and mitochondria, and B) anaerobic respiration in chemoautotrophic prokaryotes.
8. What are the products of ETC's, and what are their roles in biological energy flow?
9. Using one real example, describe the relationship between prokaryotic electron transport chains and the biogeochemical cycle of either nitrogen or sulfur.