Chemolithotrophy

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Chemolithotrophs

- **Chemolithotrophy** is the oxidation of inorganic chemicals for the generation of energy.
- A chemolithotroph is an organism that is able to use inorganic reduced compounds as a source of energy.
- Each species is rather specific in its preferences for electron donors and acceptors.
- The acceptor is usually O_2, but sulfate and nitrate are also used.
- The most common electron donors are hydrogen, reduced nitrogen compounds, reduced sulfur compounds, and ferrous iron (Fe^{2+}).

… Chemolithotrophs

- Chemolithotrophic bacteria are usually autotrophic and employ the Calvin cycle to fix CO_2 as their carbon source.
- However, some chemolithotrophs can function as heterotrophs if reduced organic compounds are available.
- Incorporation of one CO_2 in the Calvin cycle requires three ATP and two NADPH.
- Moreover, much less energy is available from the oxidation of inorganic molecules than from the complete oxidation of glucose to $CO_{2.}$
- Because the yield of ATP is so low, chemolithotrophs must oxidize a large quantity of inorganic material to grow and reproduce, and this magnifies their ecological impact.

Hydrogen Oxidizing Bacteria

- Several bacterial genera (eg. *Alcaligenes, Hydrogenophaga*, and *Pseudomonas* spp.) can oxidize hydrogen gas to produce energy because they possess a hydrogenase enzyme that catalyzes the oxidation of hydrogen.

$$H_2 \longrightarrow 2H^+ + 2e^-$$

- The electrons are donated either to an electron transport chain or to NAD, depending on the hydrogenase.
- If NADH is produced, it can be used in ATP synthesis by electron transport and oxidative phosphorylation, with O_2 as the terminal electron acceptor.
- These hydrogen-oxidizing microorganisms often will use organic compounds as energy sources when such nutrients are available.

Nitrogen-oxidizing chemolithotrophs

- The best-studied nitrogen-oxidizing chemolithotrophs are the nitrifying bacteria.
- Nitrifying bacteria carryout aerobic biological ammonia oxidation to nitrate in a two step process:
  - Ammonia oxidation to nitrite by ammonia oxidizing bacteria
  - nitrite oxidation to nitrate by nitrite oxidizing bacteria.
- These are soil and aquatic bacteria of considerable ecological significance.
- Ammonia oxidation to nitrate depends on the activity of at least two different genera.
- For example, *Nitrosomonas* and *Nitrosospira* oxidize ammonia to nitrite.

$$NH_4^+ + 1\frac{1}{2}\,O_2 \longrightarrow NO_2^- + H_2O + 2H^+$$

- The nitrite can then be further oxidized by *Nitrobacter and Nitrococcus* to yield nitrate.

$$NO_2^- + \frac{1}{2}\,O_2 \longrightarrow NO_3^-$$

- When two genera work together, ammonia in the soil is oxidized to nitrate in a process called **nitrification.**

... Nitrogen-oxidizing chemolithotrophs

- Energy released upon the oxidation of both ammonia and nitrite is used to make ATP by oxidative phosphorylation.
- However, microorganisms need a source of electrons (reducing power) as well as a source of ATP in order to reduce CO_2 and other molecules.
- Since molecules like ammonia and nitrite have more positive reduction potentials than NAD, they cannot directly donate their electrons to form the required NADH and NADPH.
- This is because electrons spontaneously move only from donors with more negative reduction potentials to acceptors with more positive Potentials.
- Nitrogen oxidizing chemolithotrophs solve this problem by using proton motive force to reverse the flow of electrons in their electron transport chains and reduce NAD with electrons from nitrogen donors.
- **Because** energy is used to generate NADH as well as ATP, the net yield of ATP is fairly low.
- Chemolithotrophs can afford this inefficiency as they have no serious competitors for their unique energy sources.

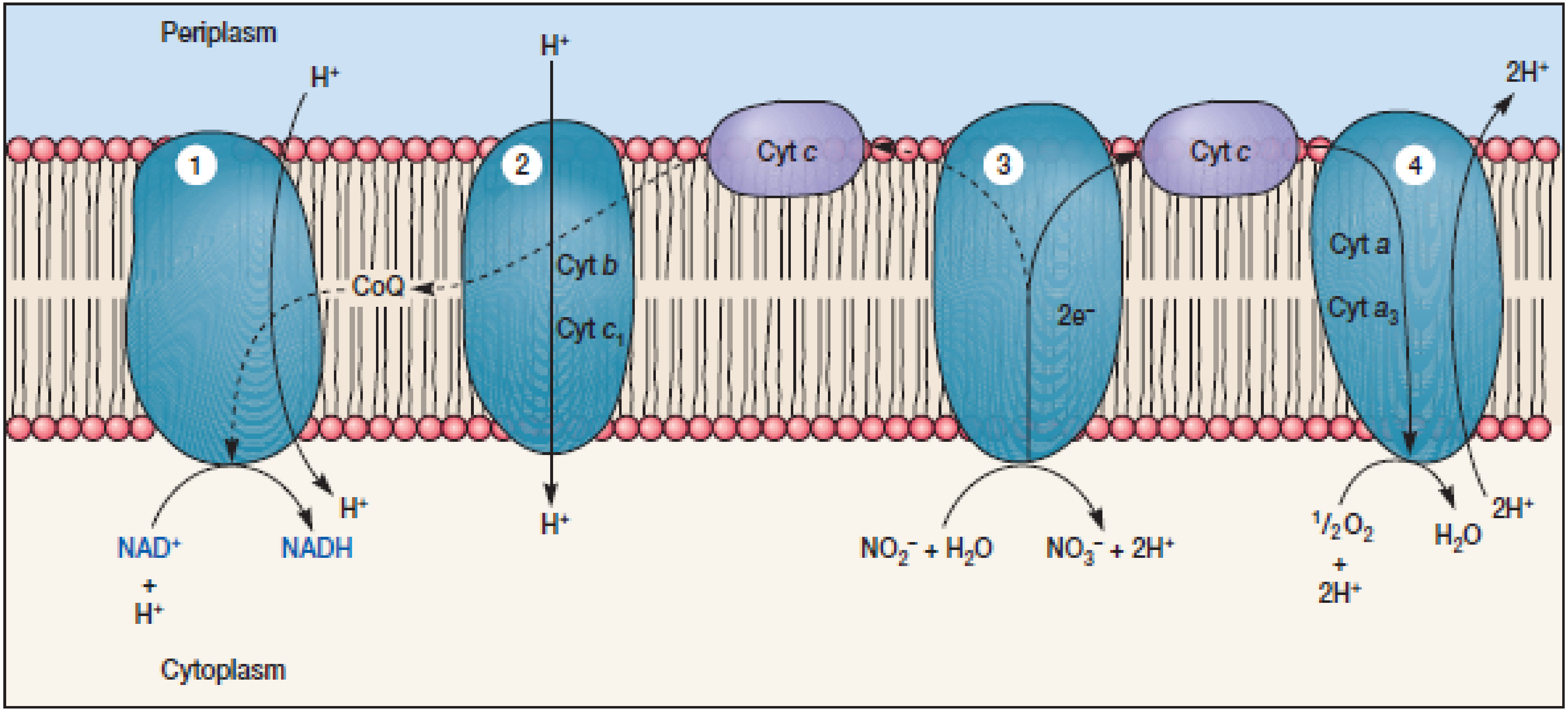


Figure 1. **Electron Flow in *Nitrobacter* Electron Transport Chain.** *Nitrobacter* carries out normal electron transport to generate proton motive force for ATP synthesis. This is the right-hand branch of the diagram. Some of the proton motive force also is used to force electrons to flow up the reduction potential gradient from nitrite to NAD^+ (left-hand branch). Cytochrome *c* and four complexes are involved: NADH-ubiquinone oxidoreductase (1), ubiquinol-cytochrome *c* oxidoreductase (2), nitrite oxidase (3), and cytochrome aa_3 oxidase (4).

Sulfur-oxidizing chemolithotrophs

- The metabolism of *Thiobacillus* has been best studied.
- These bacteria oxidize sulfur (S^0), hydrogen sulfide (H_2S), thiosulfate ($S_2O_3^{2-}$), and other reduced sulfur compounds to sulfuric acid; therefore they have a significant ecological impact.
- Interestingly they generate ATP by both:
  - oxidative phosphorylation: Sulfite can be directly oxidized to provide electrons for electron transport and oxidative phosphorylation. (Fig. 2)

$$SO_3^{2-} \xrightarrow{\text{sulfite oxidase}} SO_4^{2-} + 2e^-$$

  - Substrate-level phosphorylation involving adenosine 5′-phosphosulfate (APS), a high-energy molecule formed from sulfite and adenosine monophosphate (Fig. 3).

- Reduced sulfur compounds cannot directly donate their electrons to form the required NADH and NADPH because electrons spontaneously move only from donors with more negative reduction potentials to acceptors with more positive potentials.
- Sulfur-oxidizing bacteria solve this problem by using proton motive force to reverse the flow of electrons in their electron transport chains and reduce NAD with electrons from sulfur donors.

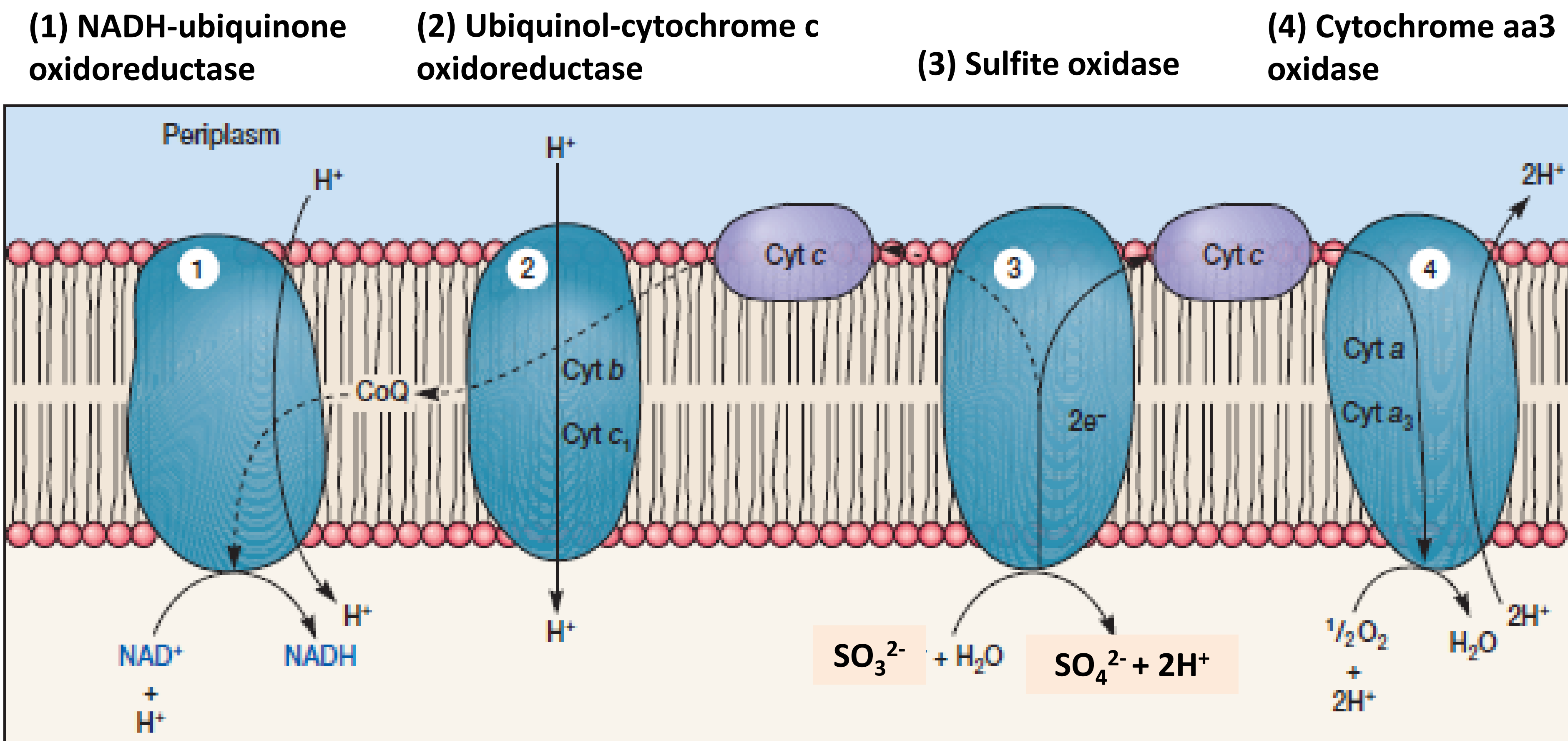


Figure 2.

Figure 3.

- (a) Sulfite can also be oxidized and converted to APS.
- This route produces electrons for use in electron transport and ATP by substrate-level phosphorylation with APS.
- (b) The structure of adenosine 5′-phosphosulfate.

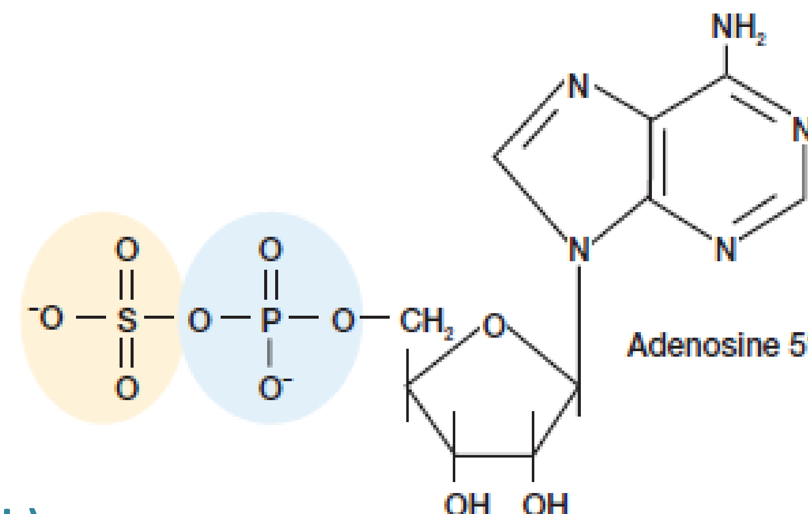
(a) Formation of adenosine 5′-phosphosulfate

$$2SO_3^{2-} + 2AMP \longrightarrow 2APS + 4e^-$$

$$2APS + 2P_i \longrightarrow 2ADP + 2SO_4^{2-}$$

$$2ADP \longrightarrow AMP + ATP$$

$$2SO_3^{2-} + AMP + 2P_i \longrightarrow 2SO_4^{2-} + ATP + 4e^-$$



Adenosine 5′-phosphosulfate

(b)

… **Sulfur-oxidizing chemolithotrophs**

- Some of these procaryotes are extraordinarily flexible metabolically.
- For example, *Sulfolobus brierleyi* and a few other species can grow aerobically as sulfur-oxidizing bacteria; in the absence of O_2, they carry out anaerobic respiration with molecular sulfur as an electron acceptor.
- Sulfur-oxidizing bacteria, like other chemolithotrophs, can use CO_2 as their carbon source.
- Many will grow heterotrophically if they are supplied with reduced organic carbon sources like glucose or amino acids.

Iron Oxidizing Chemolithotrophs

- These organisms **oxidize** ferrous **iron** (Fe^{2+}) to ferric **iron** (Fe^{3+}).
- Since Fe^{2+} has such a positive standard reduction potential, the bioenergetics are not extremely favorable, even using oxygen as a final electron acceptor.
- Ferrous iron is a soluble form of iron that is stable at extremely low pH or under anaerobic conditions.
- Under aerobic, moderate pH conditions ferrous iron is oxidized spontaneously to the ferric (Fe^{3+}) form and is hydrolyzed abiotically to insoluble ferric hydroxide [$Fe(OH)_3$].
- There are three distinct types of ferrous iron-oxidizing microbes.
  - The first are acidophiles, such as the bacteria *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, as well as the archaeon *Ferroplasma*.
    - These microbes oxidize iron in environments that have a very low pH and are important in acid mine drainage.
  - The second type of microbes oxidizes ferrous iron at circum-neutral pH. These micro-organisms (for example *Gallionella ferruginea* or *Leptothrix ochracea*) live at the oxic-anoxic interfaces and are microaerophiles.
  - The third type of iron-oxidizing microbes is anaerobic photosynthetic bacteria such as *Rhodopseudomonas*, which use ferrous iron to produce NADH for autotrophic carbon dioxide fixation.

... **Iron Oxidizing Chemolithotrophs**

- Biochemically, aerobic iron oxidation is a very energetically poor process which therefore requires large amounts of iron to be oxidized by the enzyme rusticyanin to facilitate the formation of proton motive force.
- Like sulfur oxidation, reverse electron flow must be used to form the NADH used for carbon dioxide fixation via the Calvin cycle (Figure 4).

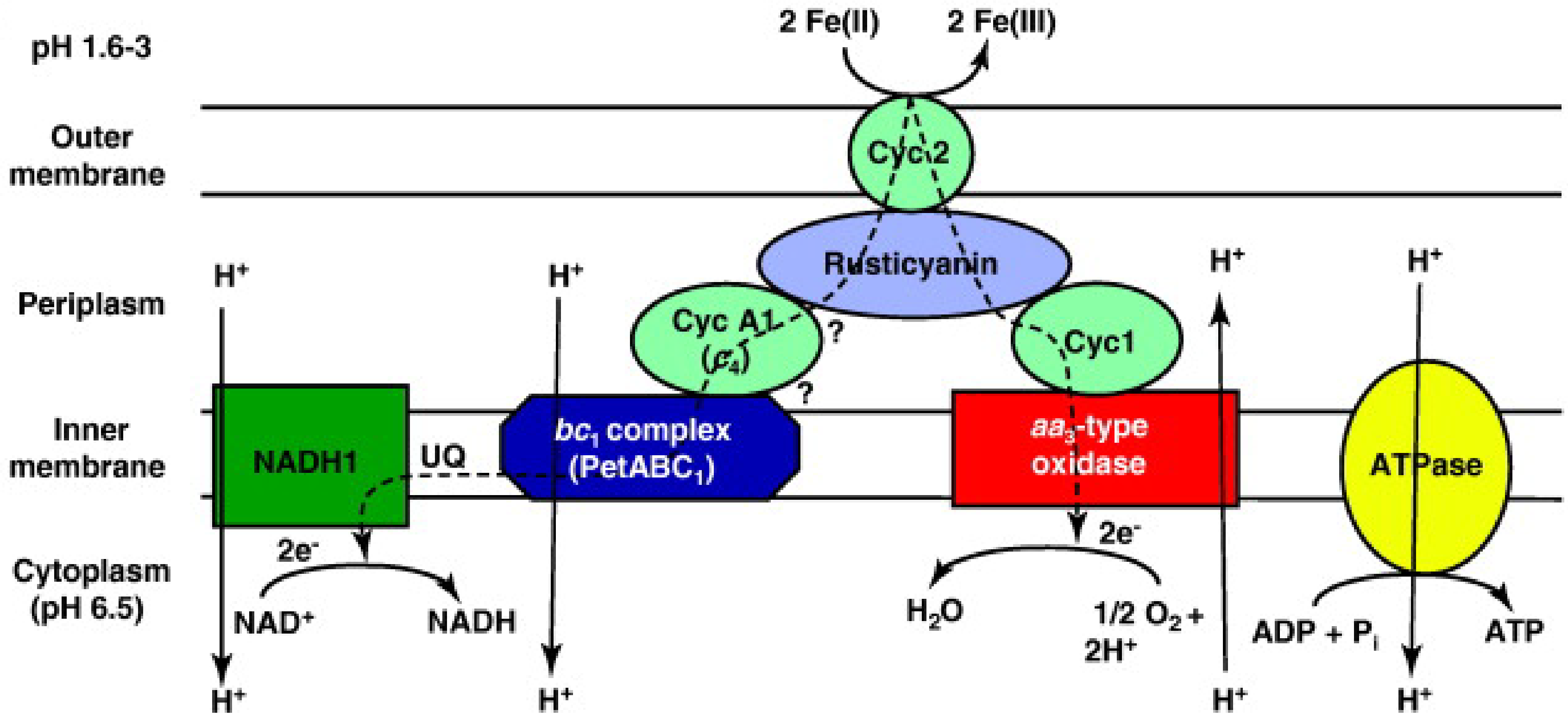


Figure 4. Model of Fe(II) oxidation in *Acidithiobacillus ferrooxidans.*

Questions

- Write short notes on chemolithotrphs.
- What is chemolithotrophy? How do sulfur oxidizing chemolithotrophs obtain their ATP to fix carbon dioxide?
- Write an essay on Nitrogen oxidizing chemolithotrophs. How they generate NADH and ATP required for anabolic processes?
- Write short note on hydrogen oxidizing chemolithotrophs.
- Briefly discuss Fe oxidizing chemolithotrophs.