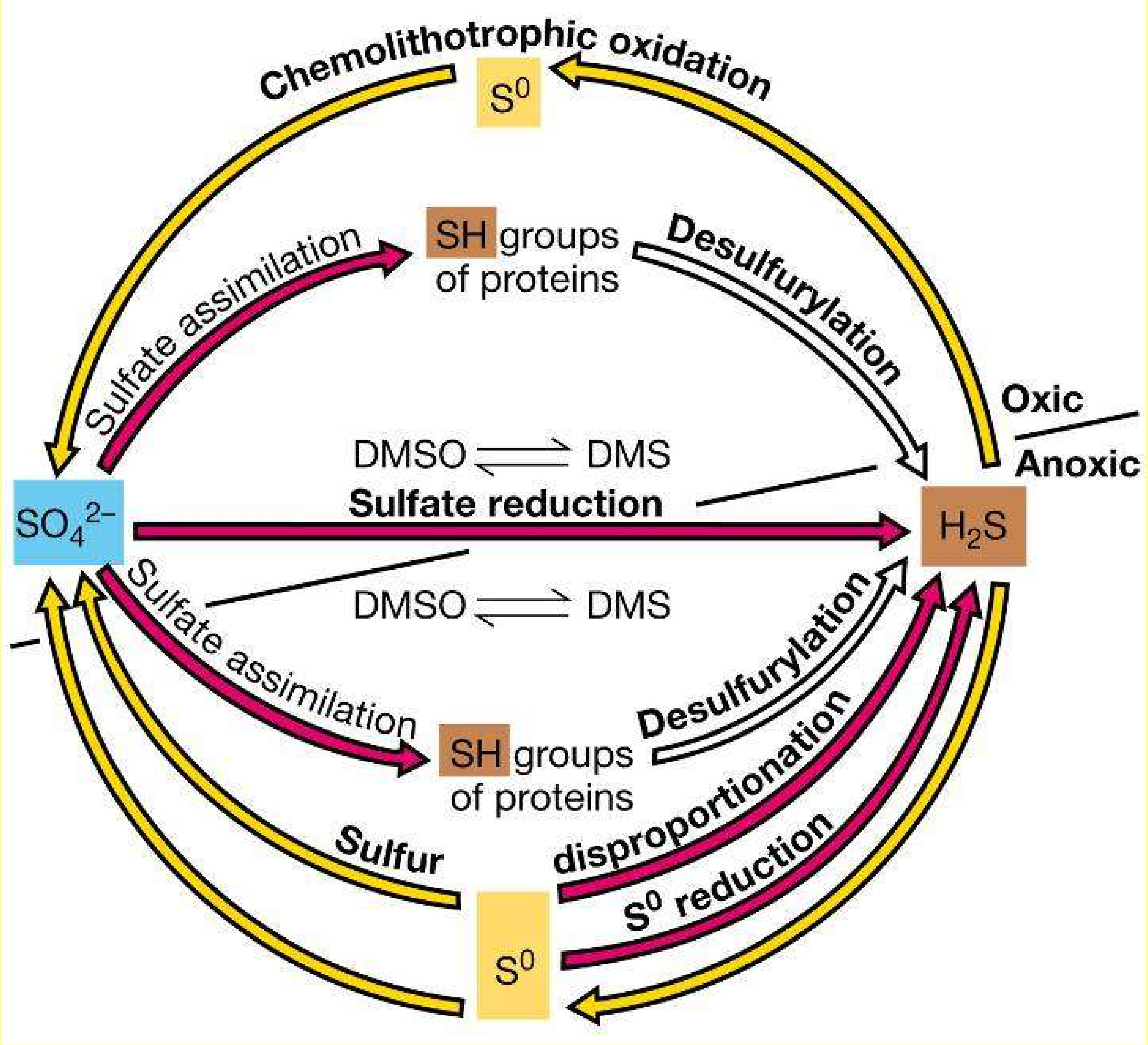
Redox cycle for sulfur From Brock, Fig. 19.30



Important sulfur-containing compounds for synthesis and degradation

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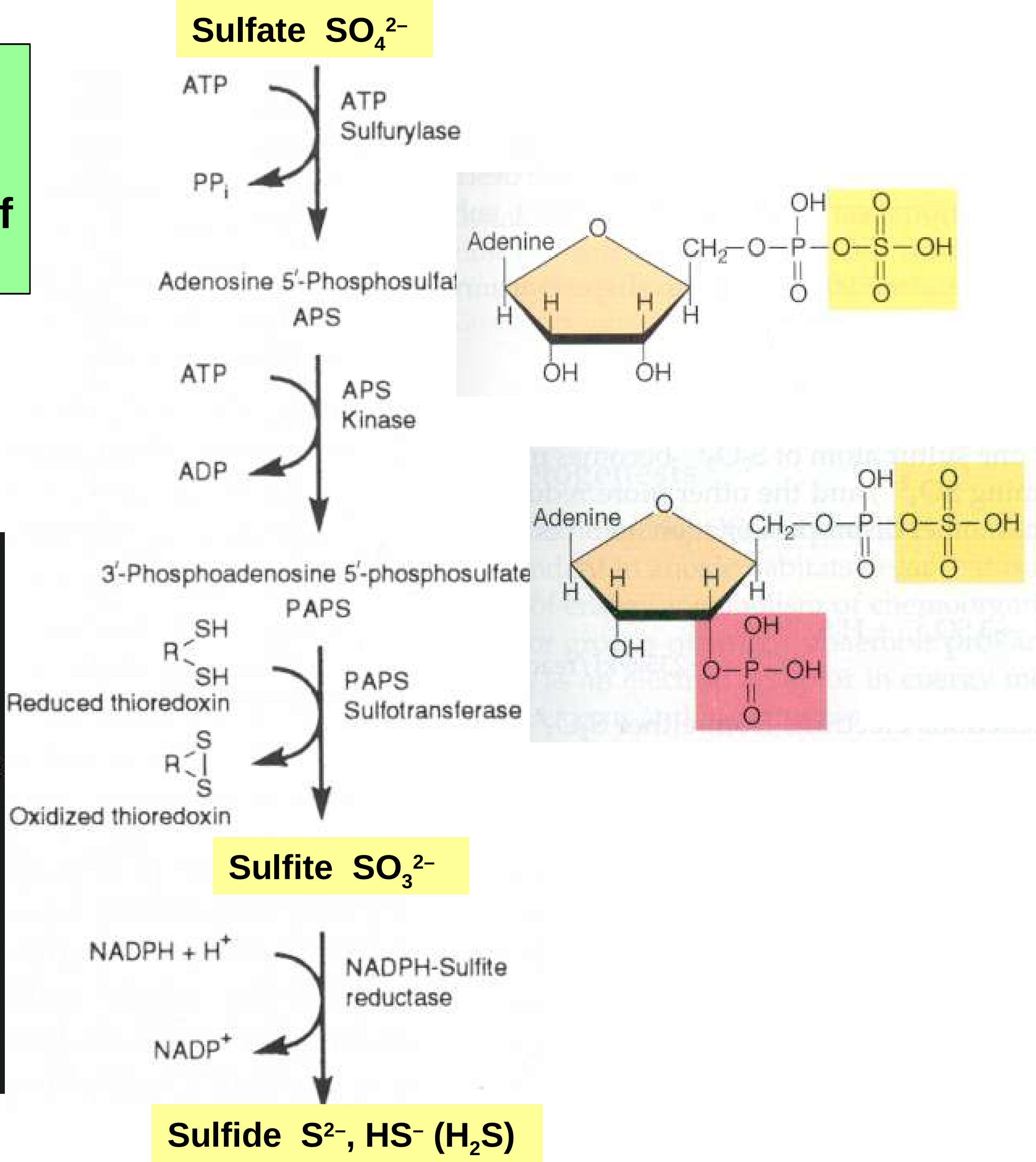
- **Cysteine, methionine, proteins, peptides (*e.g.* glutathione: -Glu-Cys-Gly)**
- **Iron-sulfur clusters: 2Fe:2S, 3Fe:3S, 3Fe:4S, 4Fe:4S, P-cluster + FeMo-cluster in nitrogenase**
- **Thiouracil in certain tRNAs**
- **Cofactors: pantothenic acid in CoA and ACP, CoM + CoB (in methanogens), ThPP, lipoic acid, biotin, molybdopterin, SAM**
- **Secondary metabolites, *e.g.* taurine, penicillin**

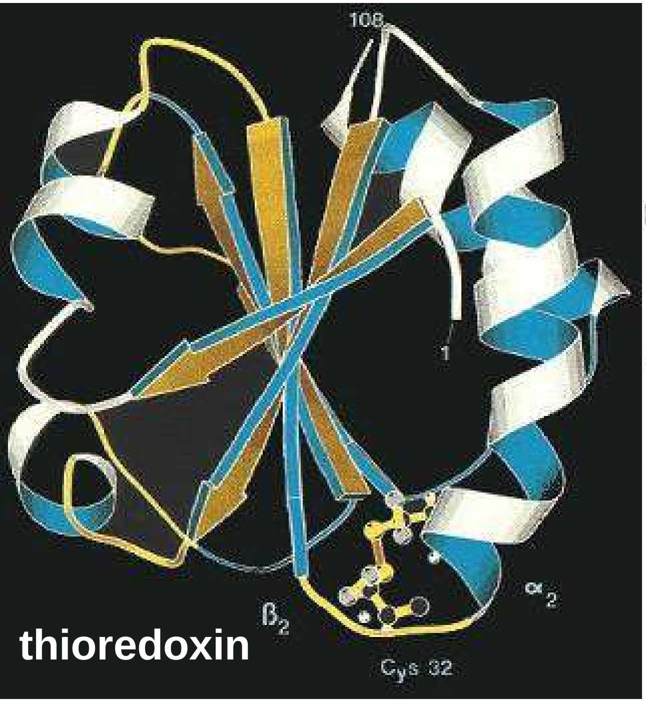
Release of hydrogen sulfide from organic compounds by desulfurylation

$$R_1\text{-}\underset{\substack{| \\ R_3}}{\overset{\substack{R_2 \\ |}}{C}}\text{-}SH + H_2O \longrightarrow R_1\text{-}\underset{\substack{| \\ R_3}}{\overset{\substack{R_2 \\ |}}{C}}\text{-}OH + H_2S$$

Bacterial sulfur assimilation

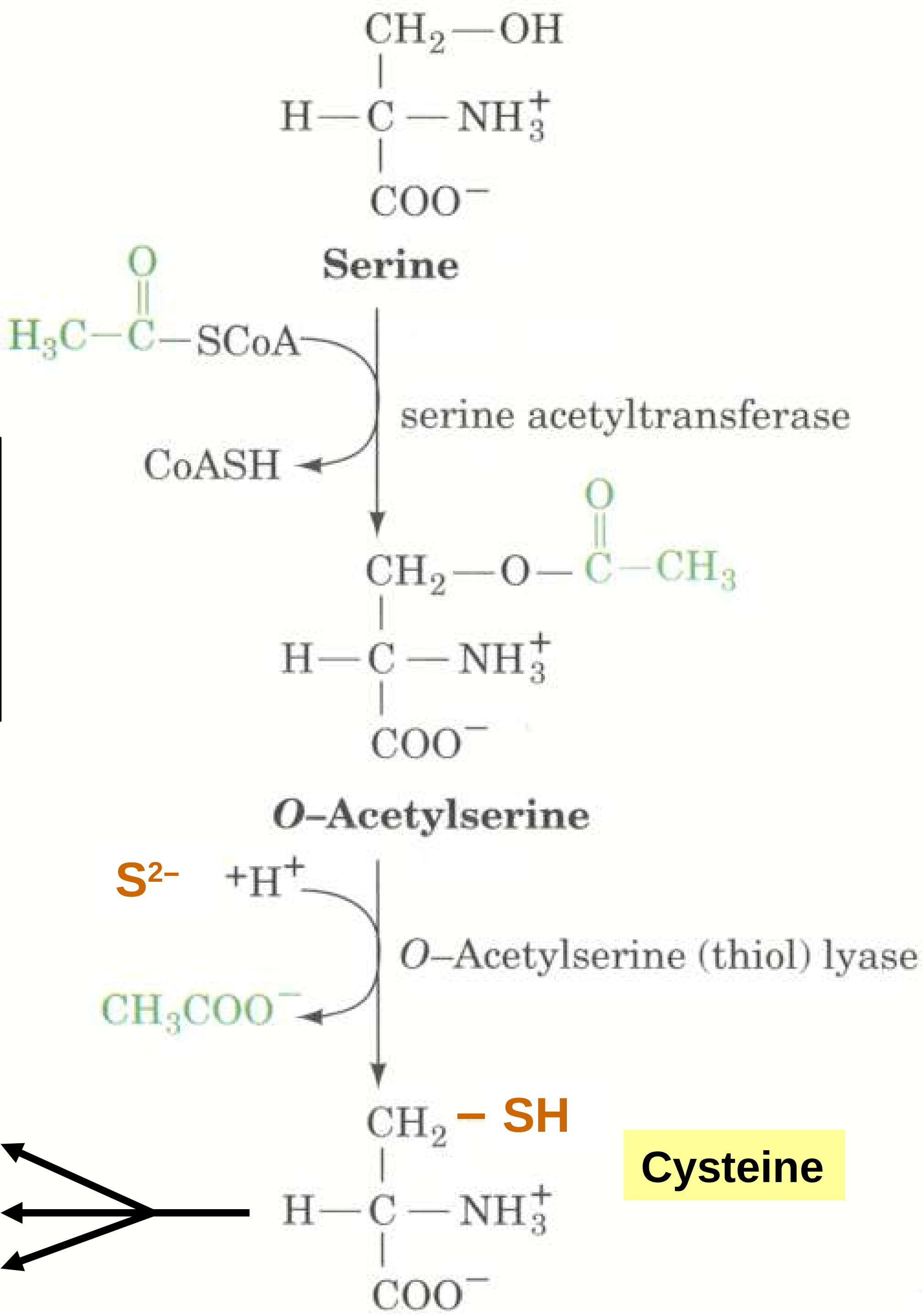
Step 1: Reduction of sulfate to sulfide





Bacterial sulfur assimilation

Step 2: Biosynthesis of cysteine



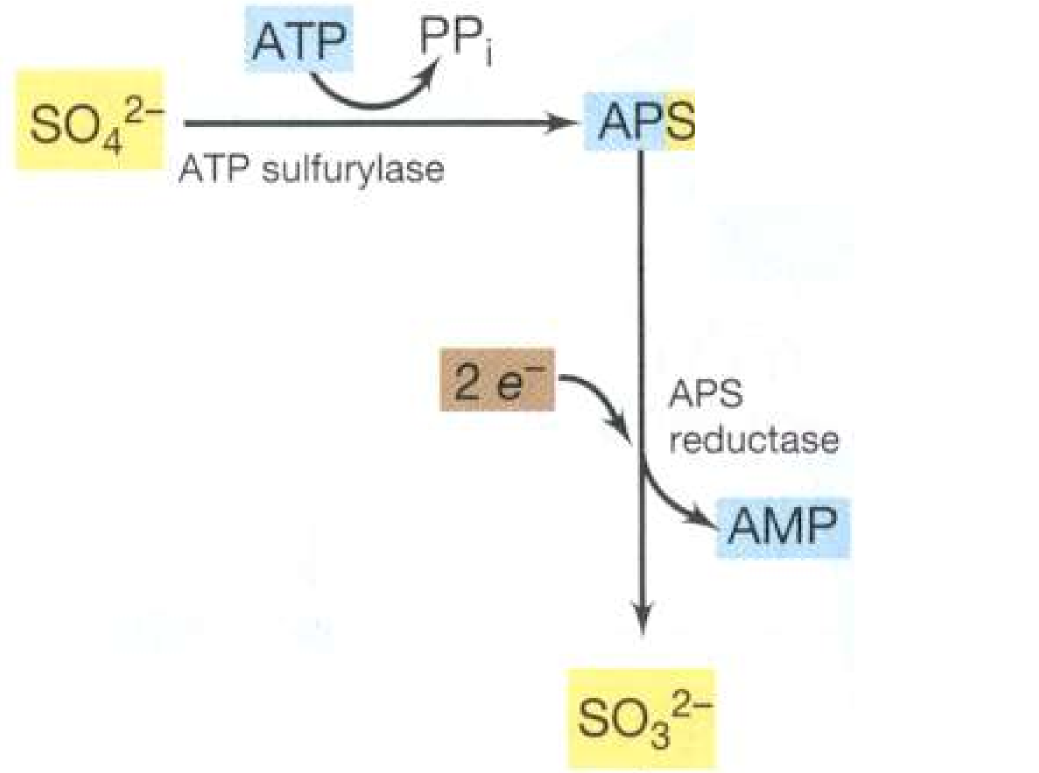
Cysteine

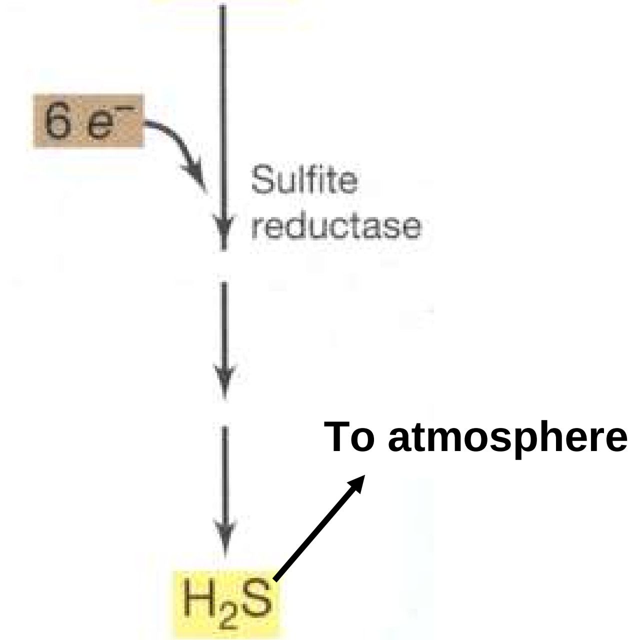
All other sulfur-containing compounds

Anaerobic respiration with sulfate as the terminal electron acceptor:

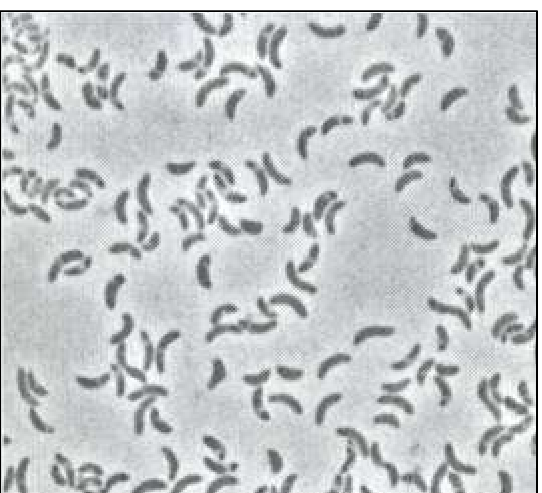
„Sulfate respiration“

„Dissimilatory sulfate reduction“

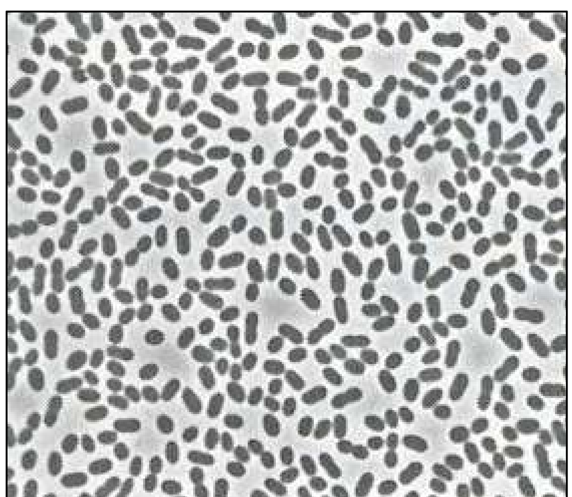


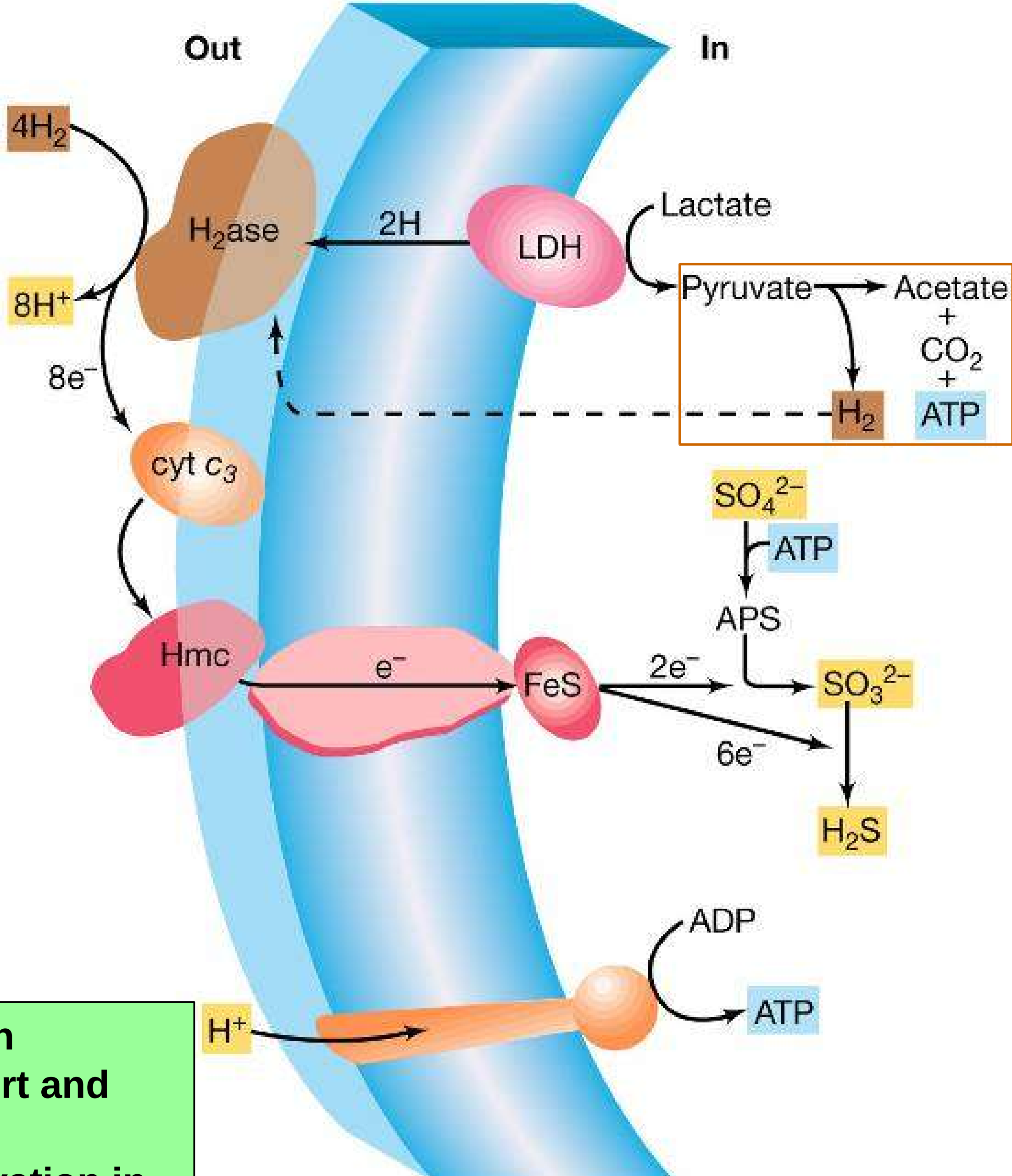


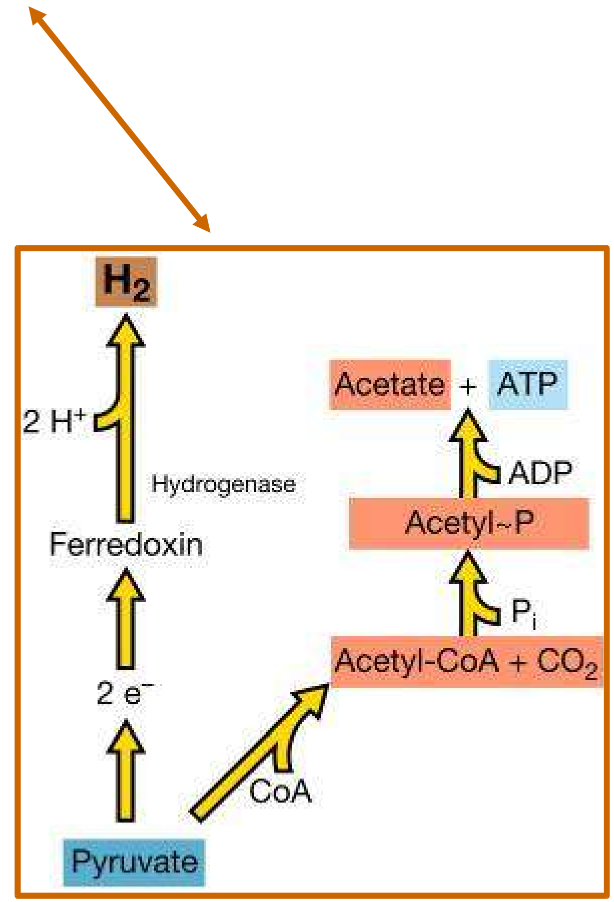
Desufovibrio



Desulfobacter

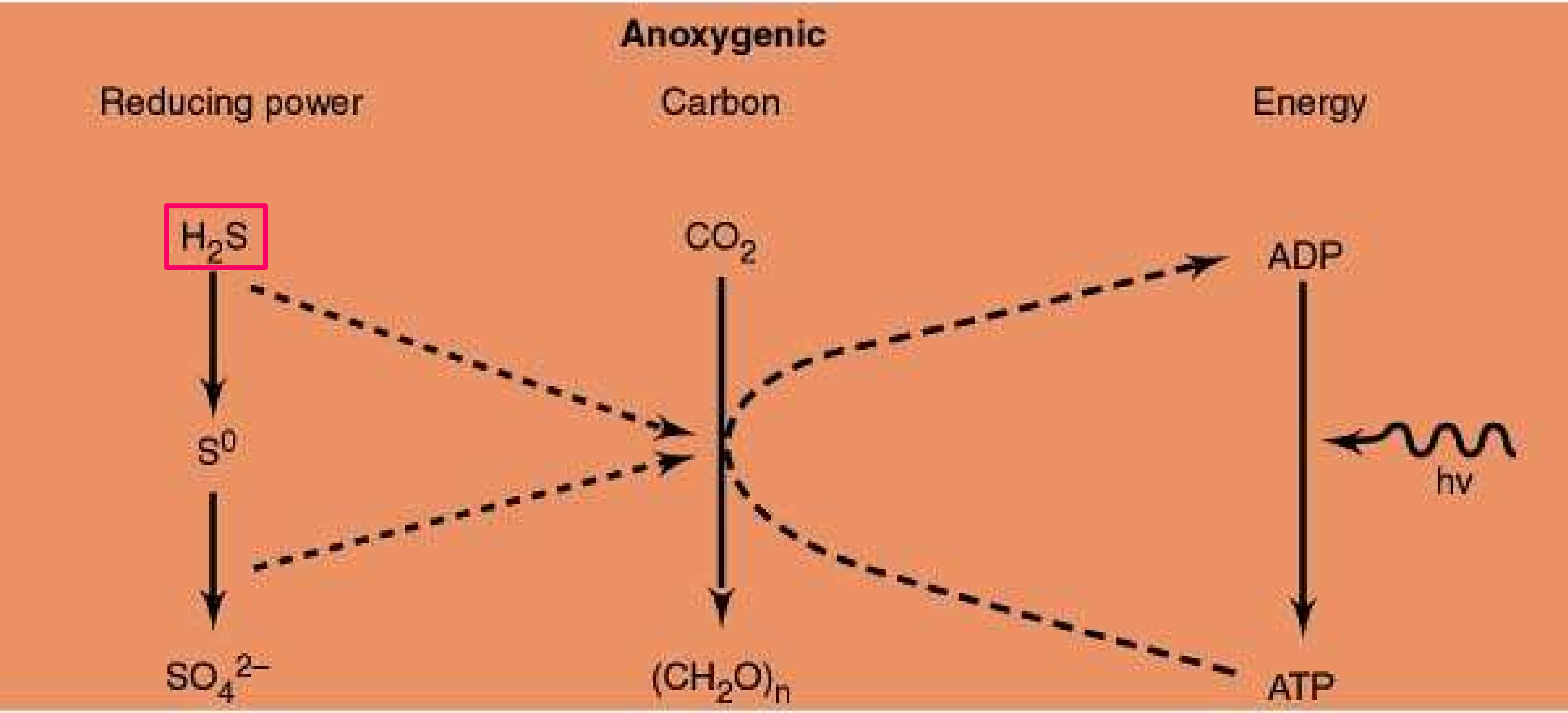


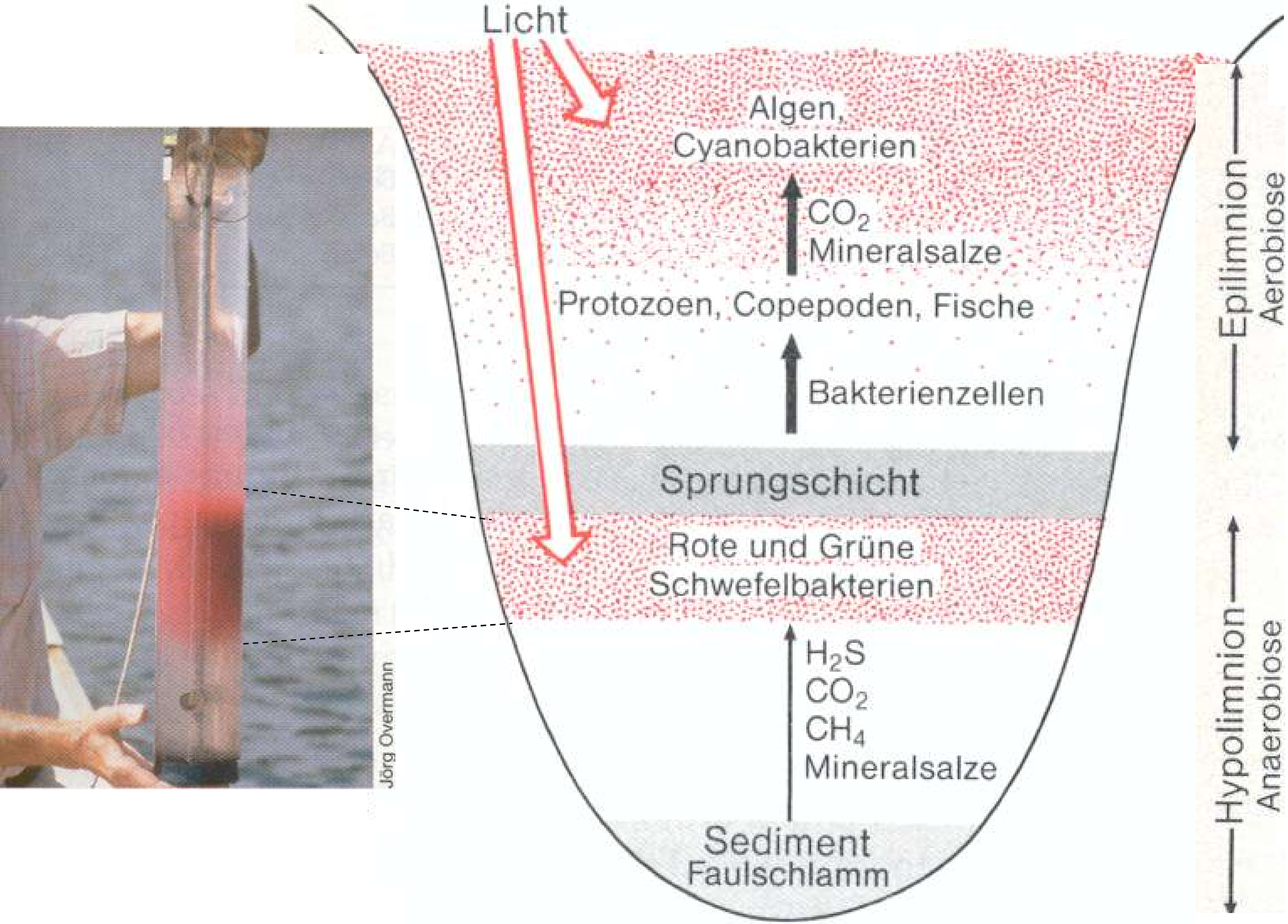




Electron transport and energy conservation in sulfate-reducing bacteria

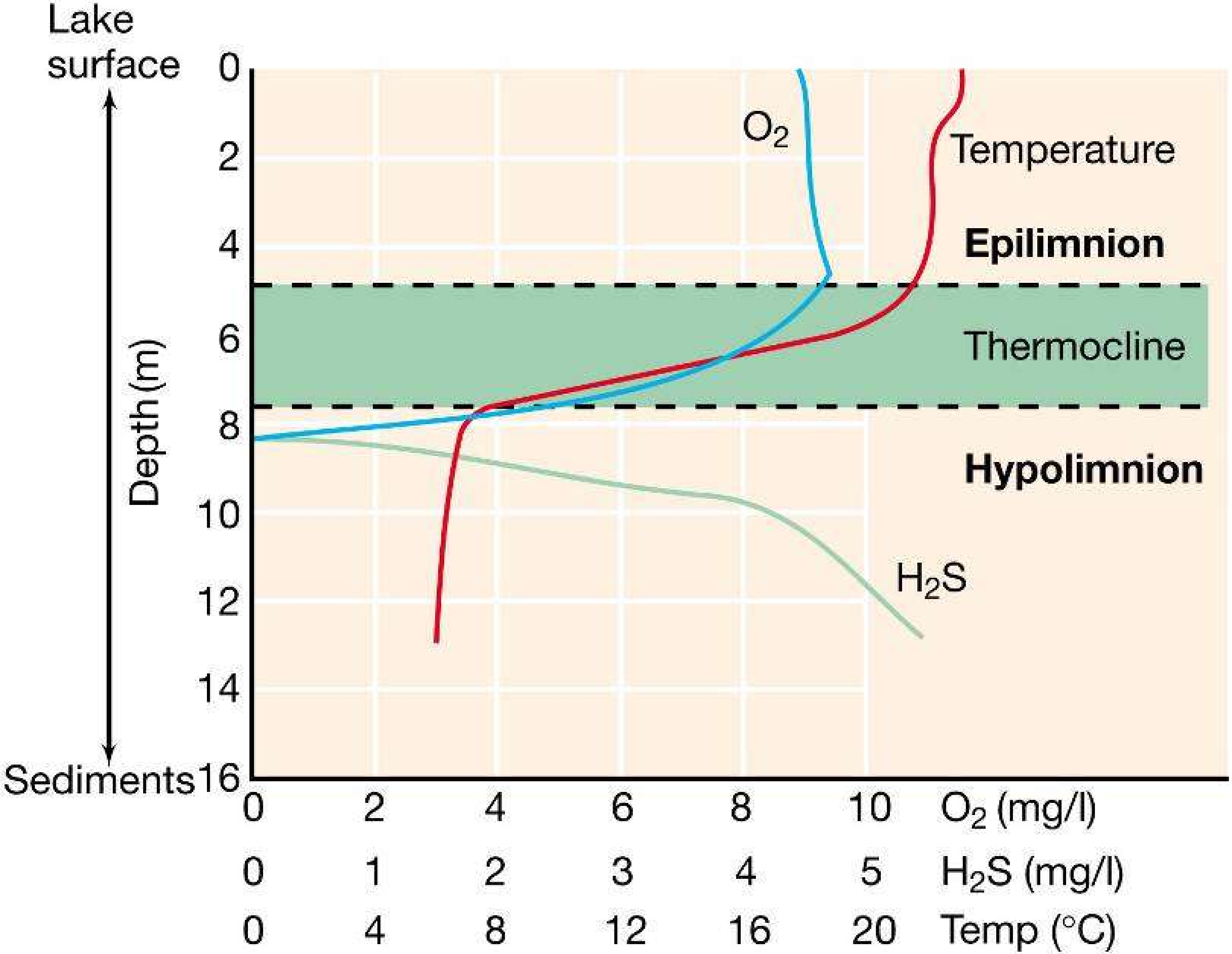
Anoxygenic photosynthesis is typical for anaerobic purple bacteria and green sulfur bacteria



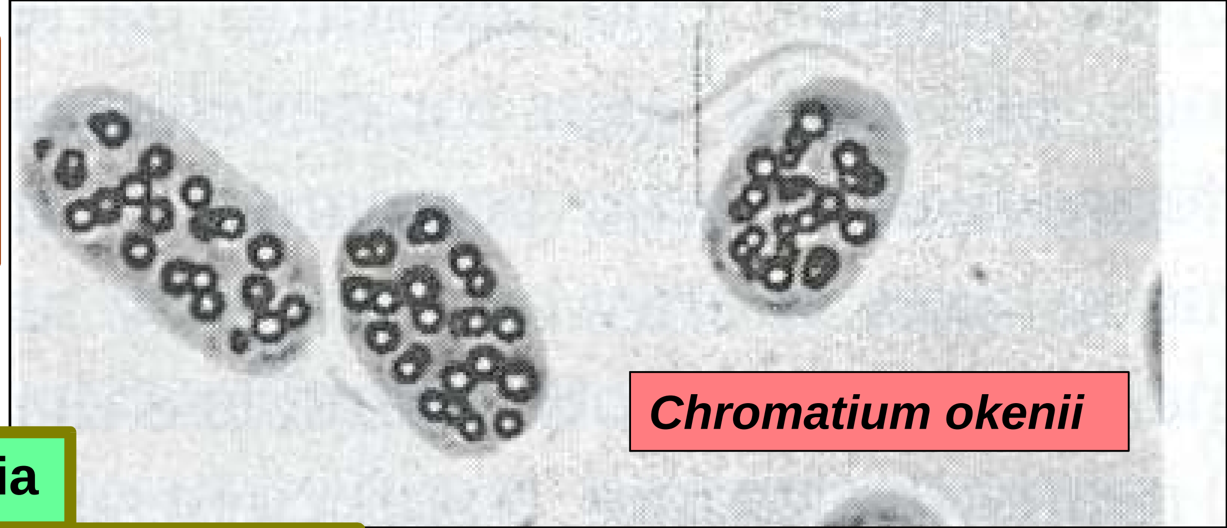


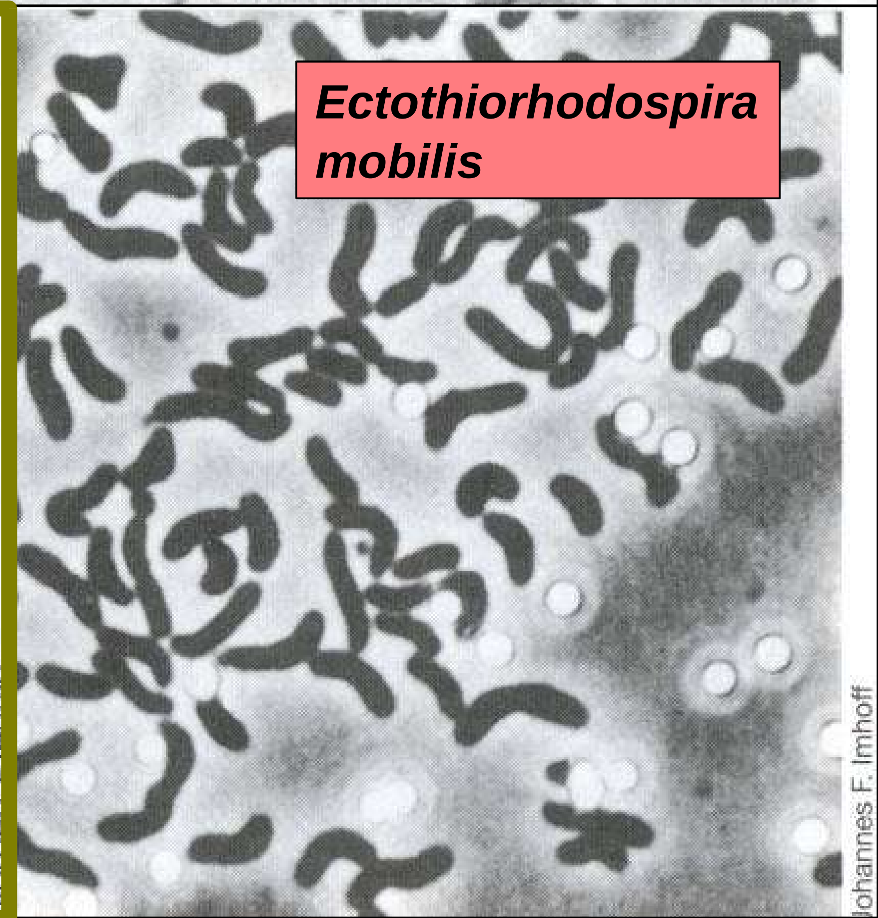
Licht
Algen, Cyanobakterien
CO_2
Mineralsalze
Protozoen, Copepoden, Fische
Bakterienzellen
Sprungschicht
Rote und Grüne Schwefelbakterien
H_2S
CO_2
CH_4
Mineralsalze
Sediment
Faulschlamm
Epilimnion
Aerobiose
Hypolimnion
Anaerobiose
Jörg Overmann

Development of anoxic conditions in a temperate climate lake

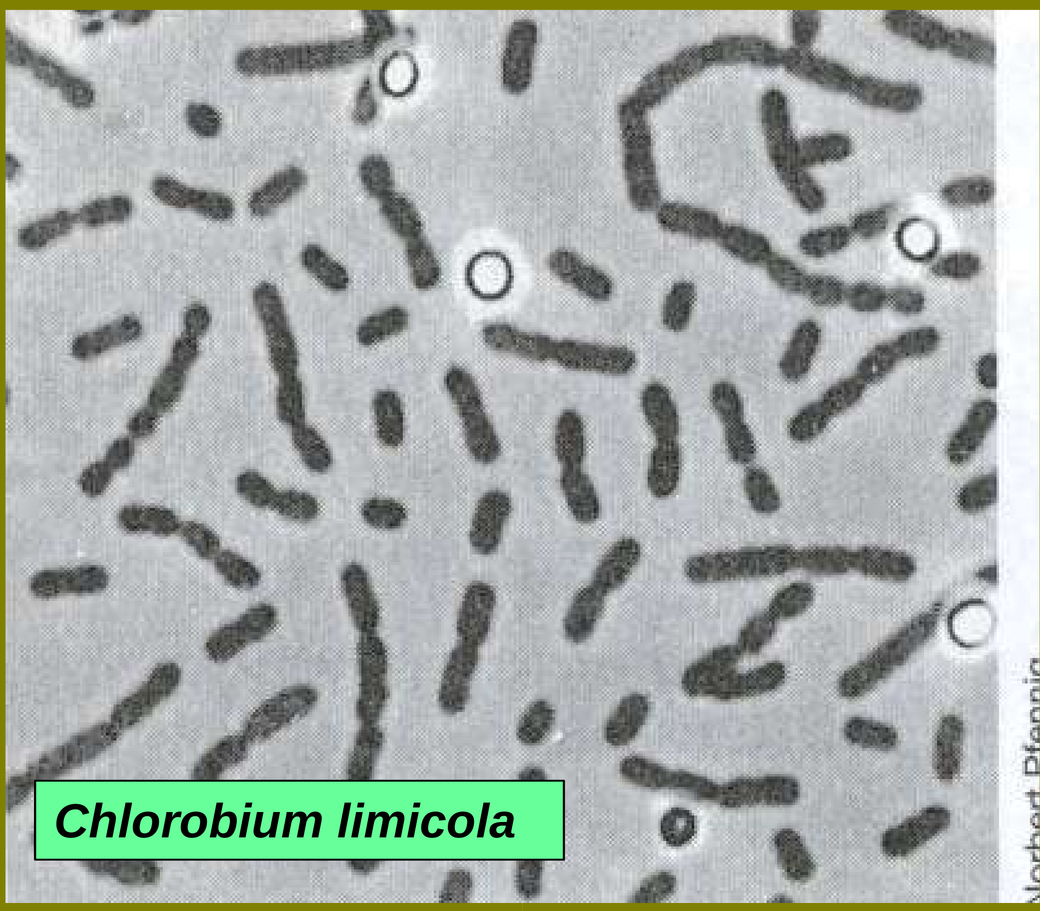


Phototrophic purple bacteria



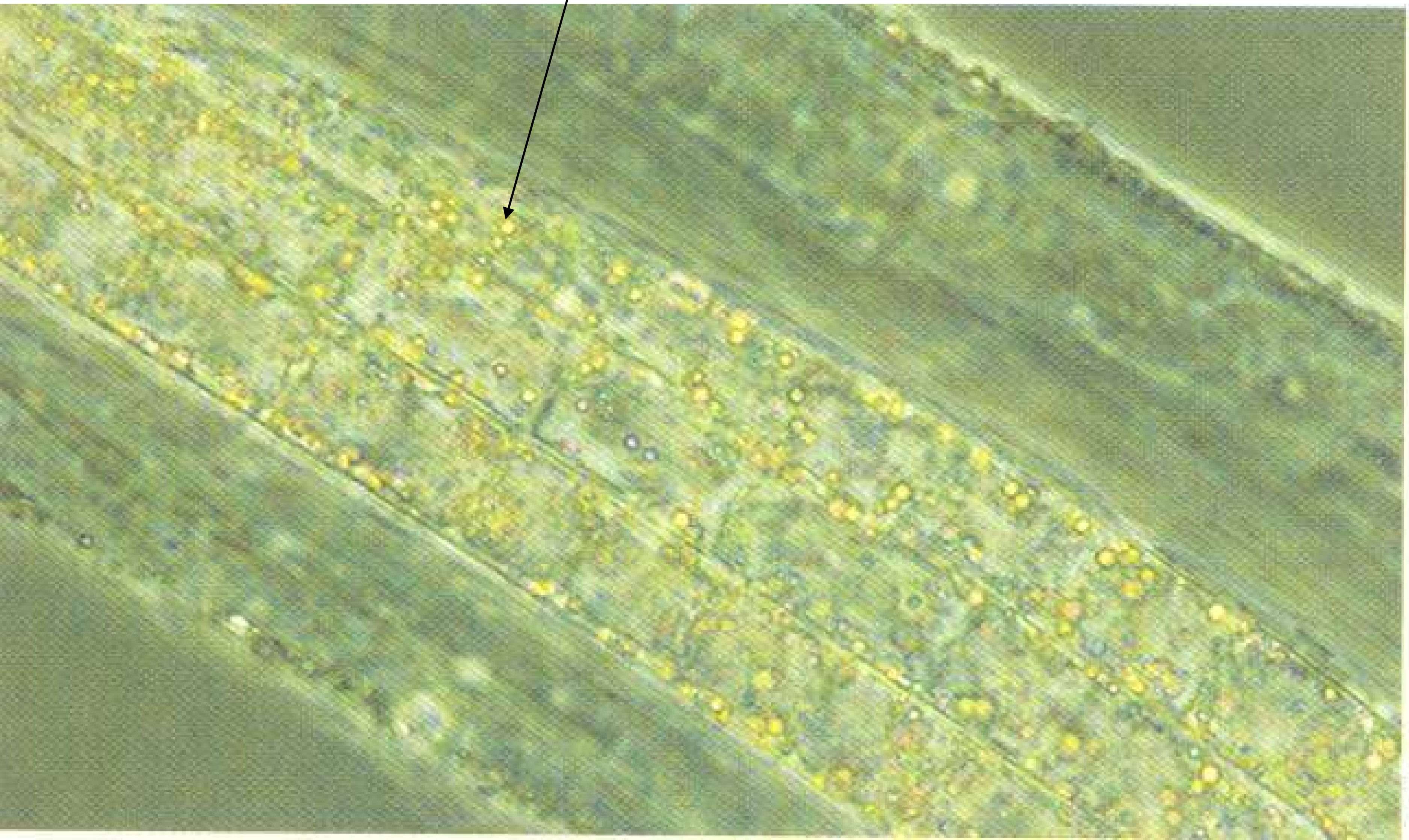


Phototrophic green bacteria



Oxidation of hydrogen sulfide to sulfur: $H_2S + \frac{1}{2} O_2 \longrightarrow S^0 + H_2O$

e.g. **in *Beggiatoa*, *Thiotrix*, *Thioplaca* (sulfur granules deposited intracellularly)**



M. Hüttel

Sulfur-rich hot spring, a habitat containing dense populations of *Sulfolobus*:

„Solfatare“ (Yellowstone National Park, USA)

***Sulfolobus acidocaldarius*, a sulfur-oxidizing chemolithotroph**

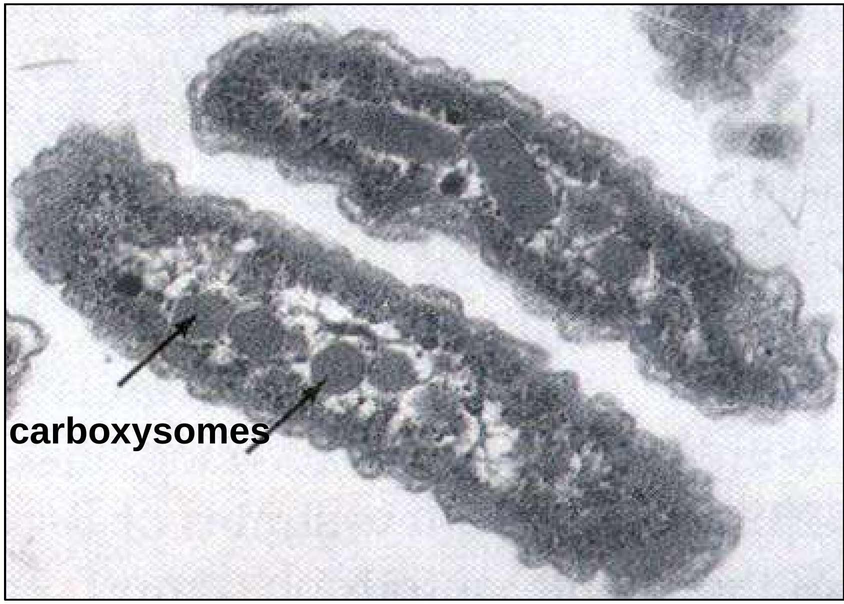
$$2\,S^0 + 3\,O_2 + 2\,H_2O \longrightarrow 2\,H_2SO_4$$

Further oxidations of sulfur compounds

typical for *Thiobacillus* spp.

•acidophilic, pH 2-3

•obligate lithoautotroph

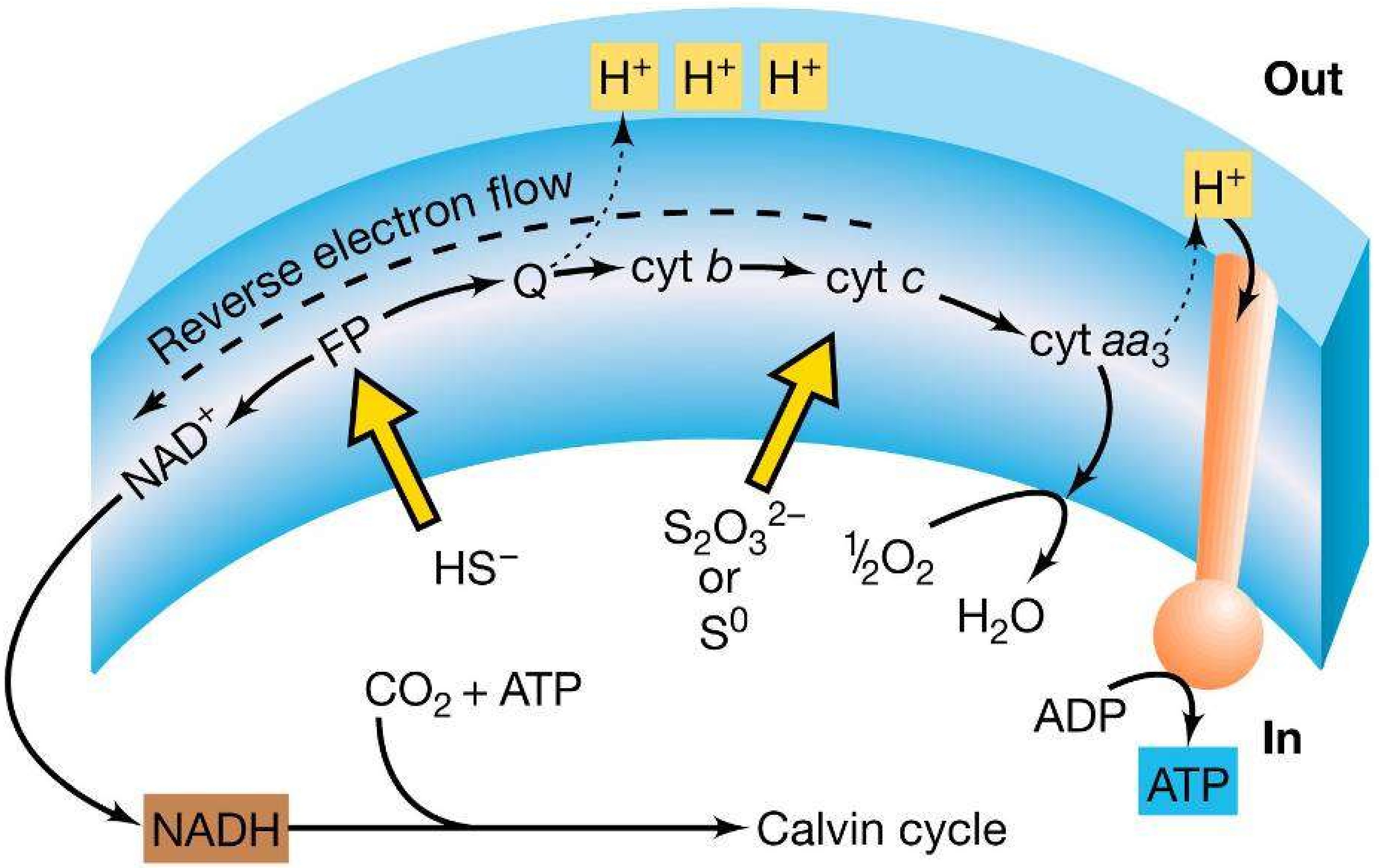


$$H_2S + 2O_2 \rightarrow \boxed{SO_4^{2-} + 2H^+}$$

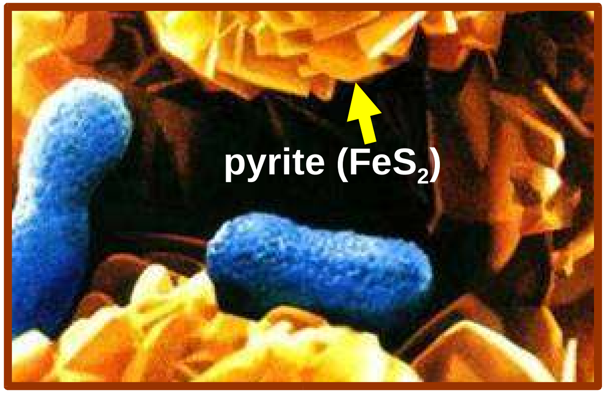
$$S^0 + H_2O + 1\tfrac{1}{2}O_2 \rightarrow \boxed{SO_4^{2-} + 2H^+}$$

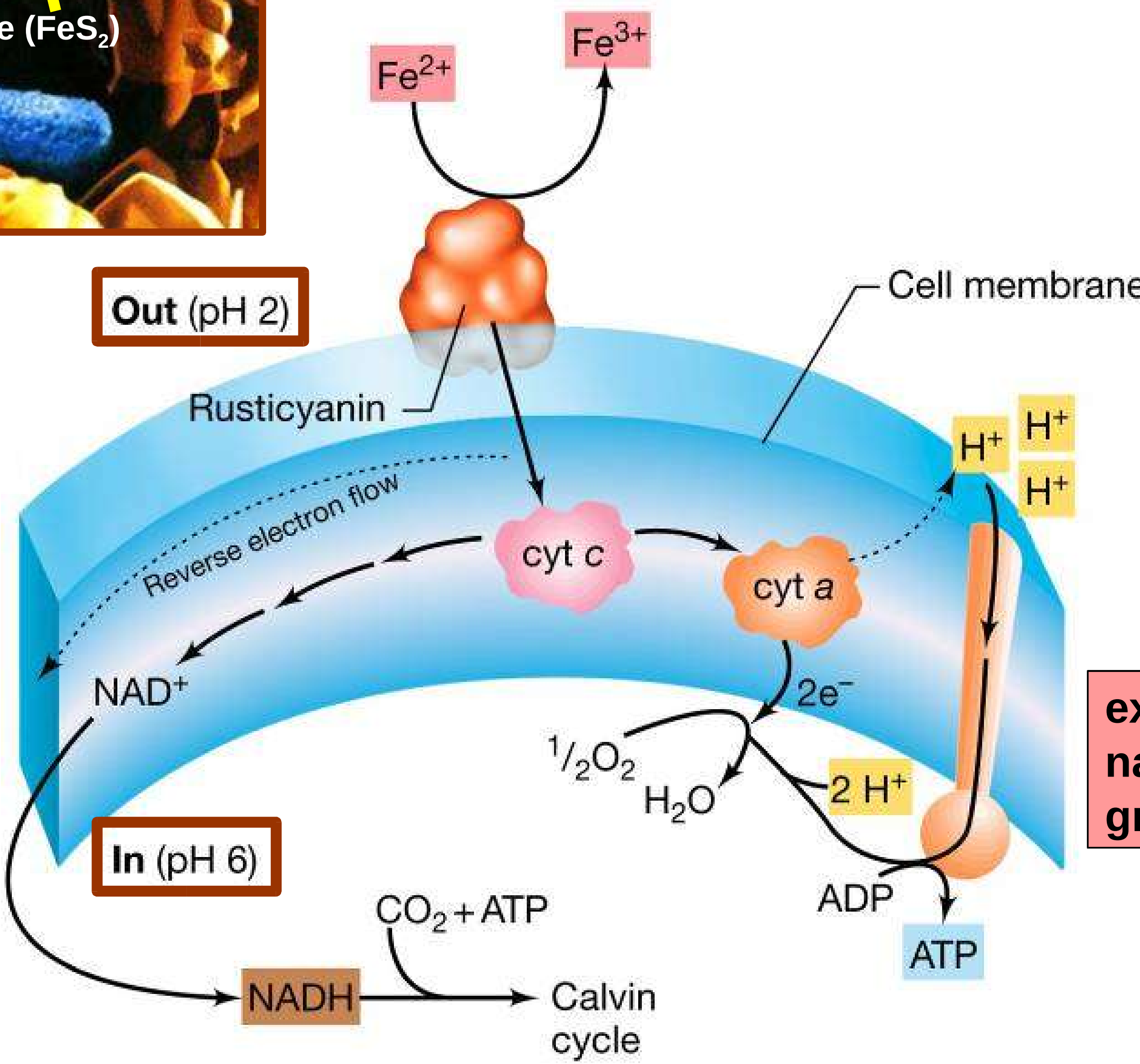
$$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow \boxed{2\,SO_4^{2-} + 2H^+}$$

Electron transport chain driven by oxidation of sulfur compounds



Energetics of iron oxidation by the acidophile *Thiobacillus ferrooxidans*





exploiting a natural pH gradient !

Bingham copper mine near Salt Lake City, Utah

Leaching: Mining of sulfidic ores (Cu, Zn, Ni, Mo, U)

Step 1: **Sulfide and sulfur oxidation (*Thiobacillus thiooxidans*)**

$$FeS_2 + 3\,½\,O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$$

$$S^0 + 1\,½\,O_2 + H_2O \longrightarrow H_2SO_4$$

Step 2: **Iron oxidation (*Thiobacillus ferrooxidans*)**

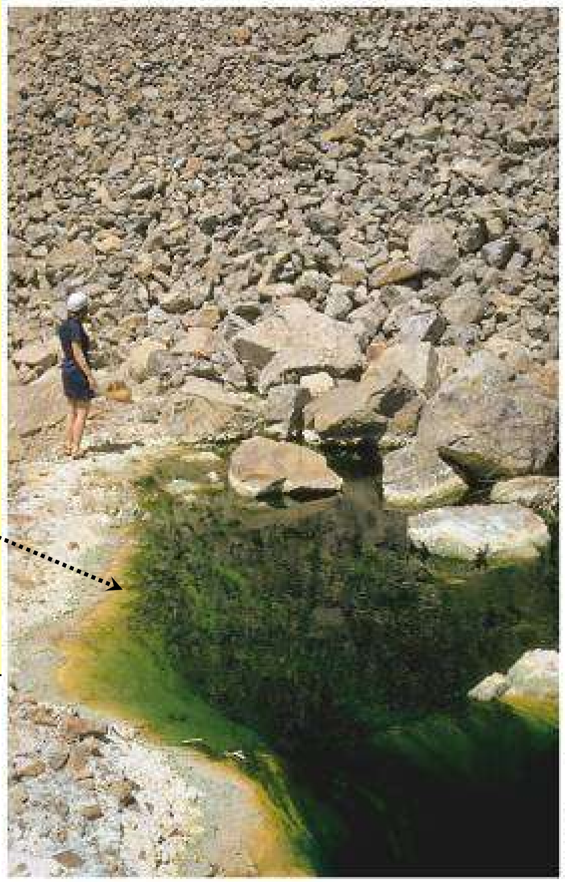
$$2\,Fe^{II}SO4 + ½\,O_2 + H_2SO_4 \longrightarrow Fe_2^{III}(SO_4)_3 + H_2O$$

Step 3: **Chemical oxidation („Leaching“)**

$$2Fe^{3+} + MeS \longrightarrow 2\,Fe^{2+} + S^0 + Me^{2+}\text{(soluble!)}$$

Step 4: **Chemical recovery of pure metal**

$$Fe^0 + Me^{2+} \longrightarrow Fe^{2+} + Me^0$$



T. D. Brock