GIOVANNELLI LAB

University of Naples "Federico II"

Marine Microbial Diversity

aa 2022-2023

Nutritional Groups 2

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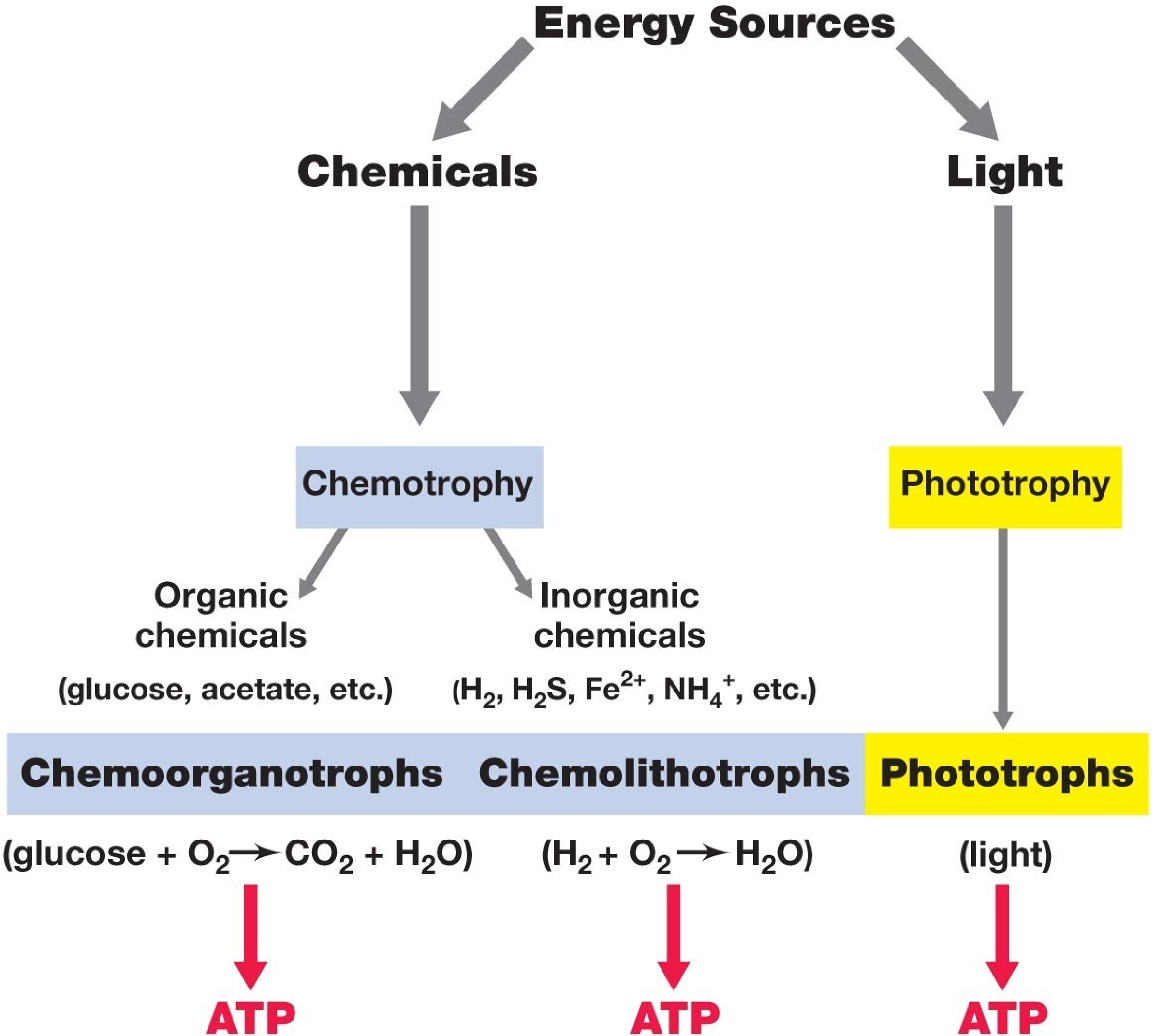
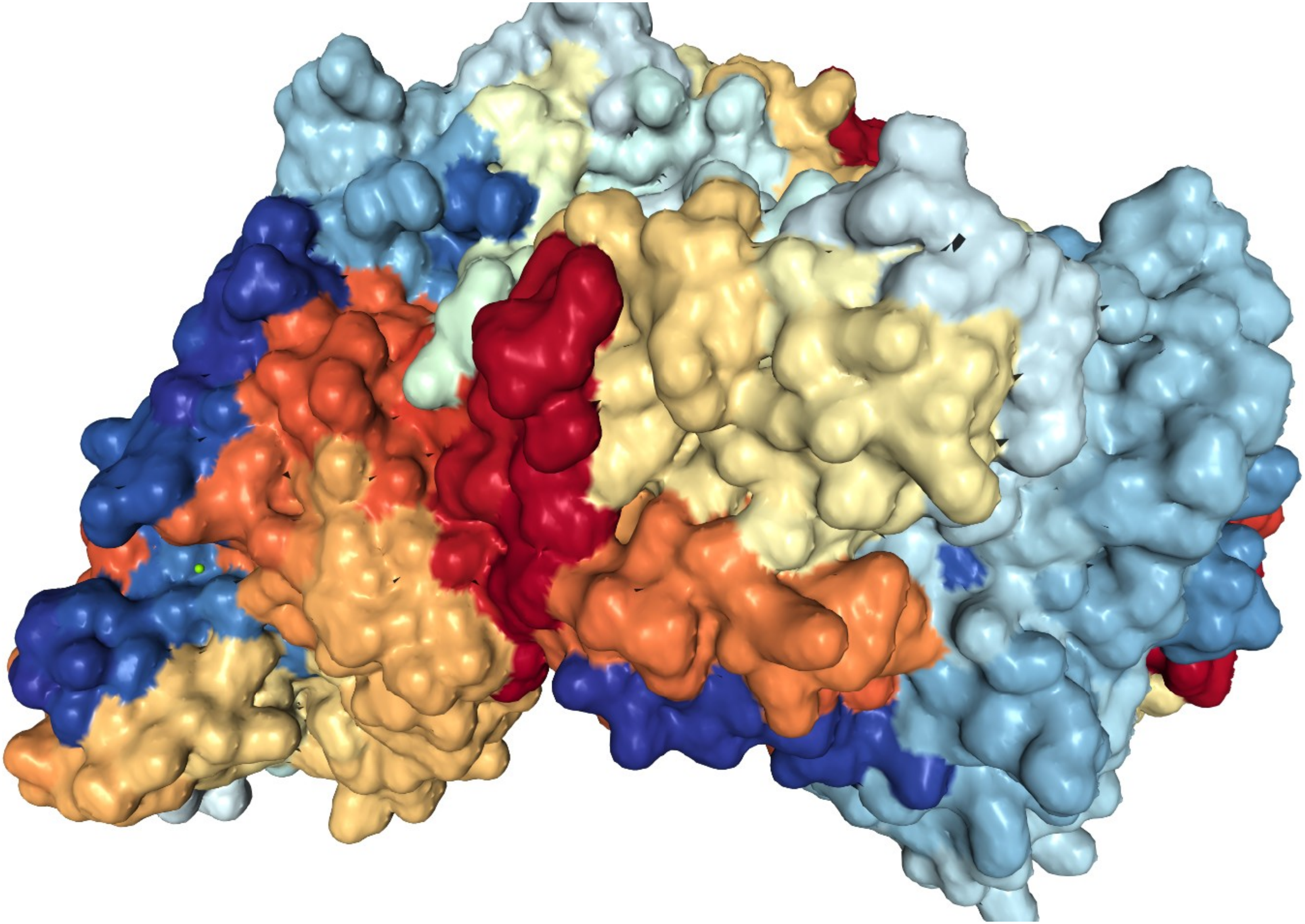
Life is based on RedOx reactions

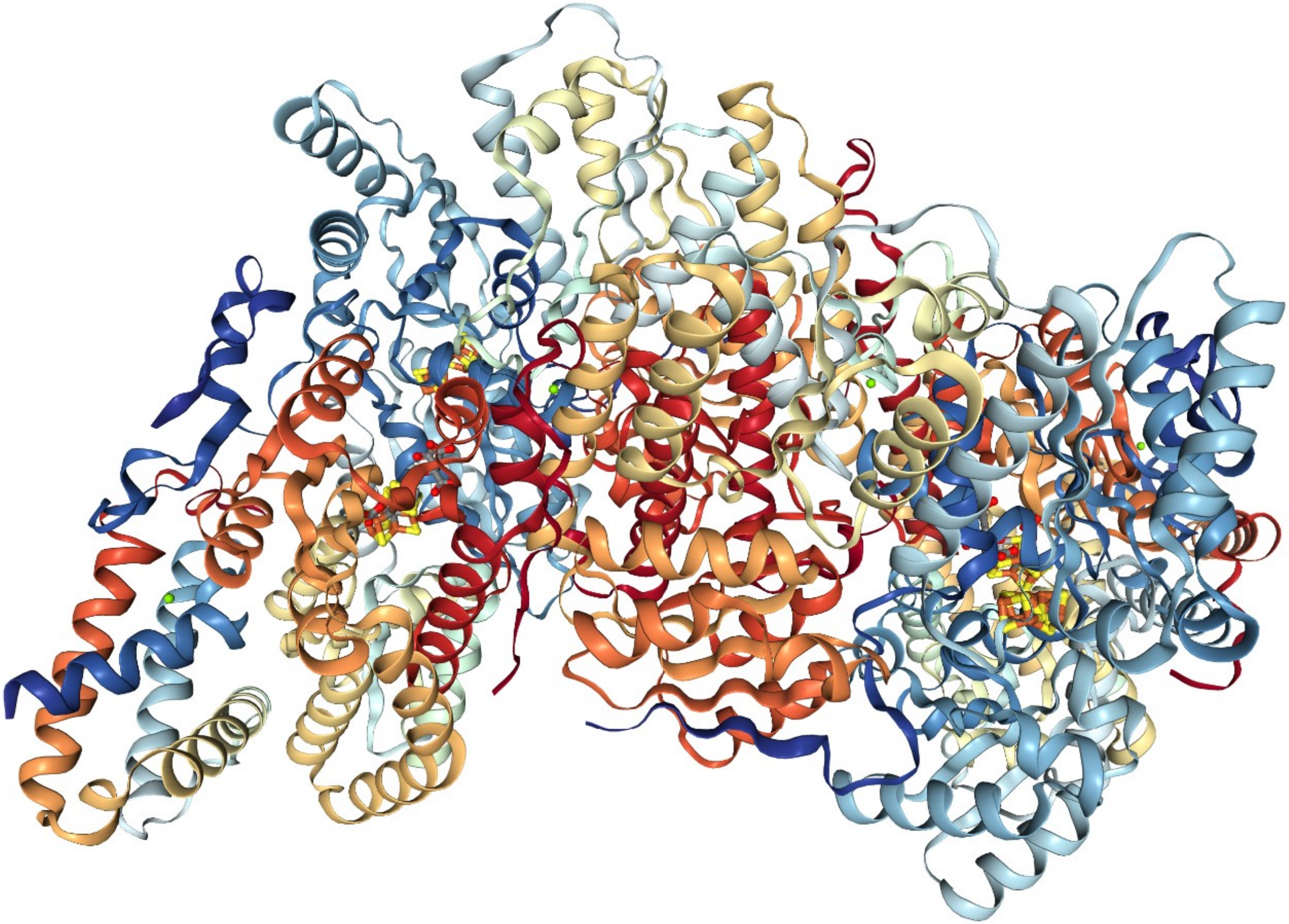
Refresher:
An ***oxidation-reduction*** *(redox)* ***reaction*** *is a type of chemical reaction that involves a* ***transfer of electrons*** *between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.*


Energy Sources
Chemicals
Light
Chemotrophy
Phototrophy
Organic chemicals
(glucose, acetate, etc.)
Inorganic chemicals
(H_2, H_2S, Fe^{2+}, NH_4^+, etc.)
Chemoorganotrophs
Chemolithotrophs
Phototrophs
(glucose + $O_2 \rightarrow CO_2 + H_2O$)
($H_2 + O_2 \rightarrow H_2O$)
(light)
ATP
ATP
ATP

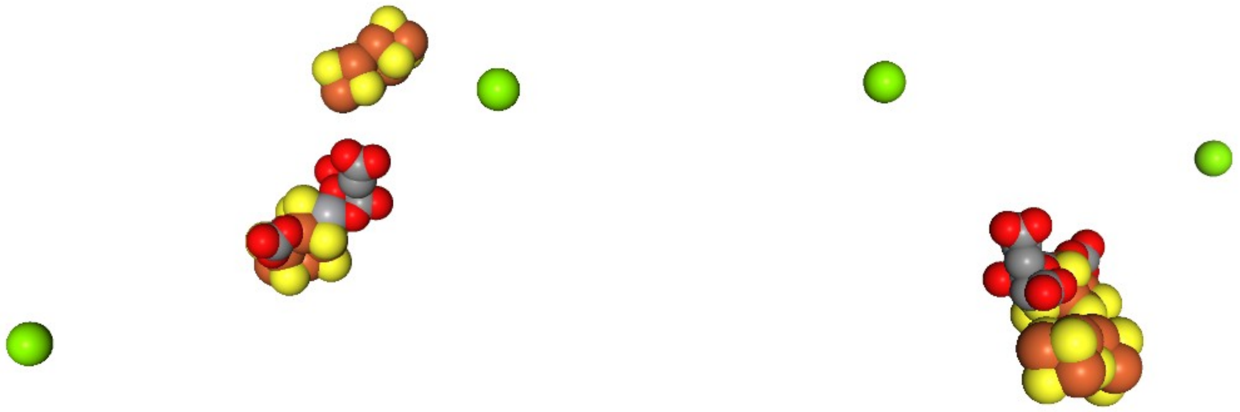
Life is *literally* electric



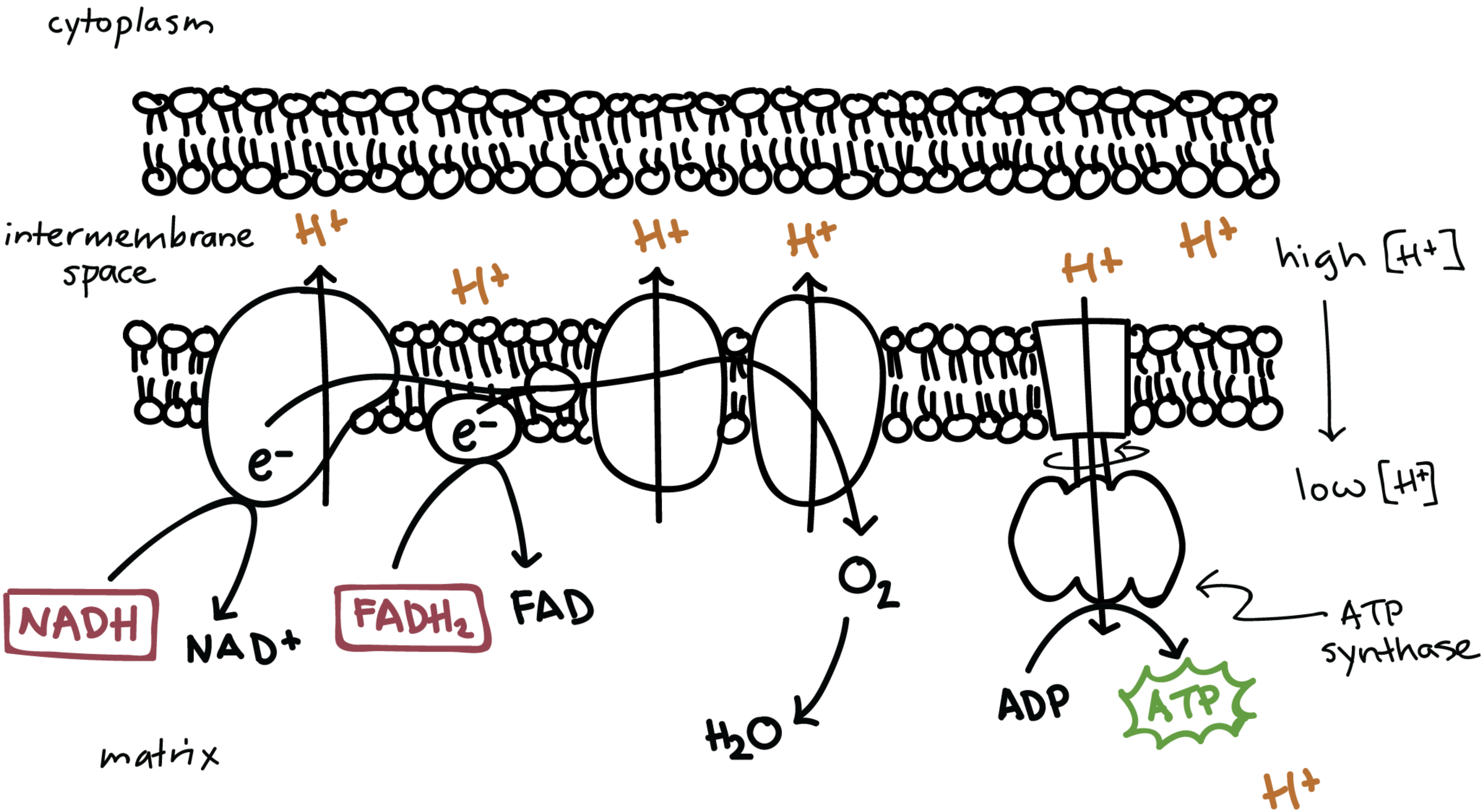
Life is *literally* electric



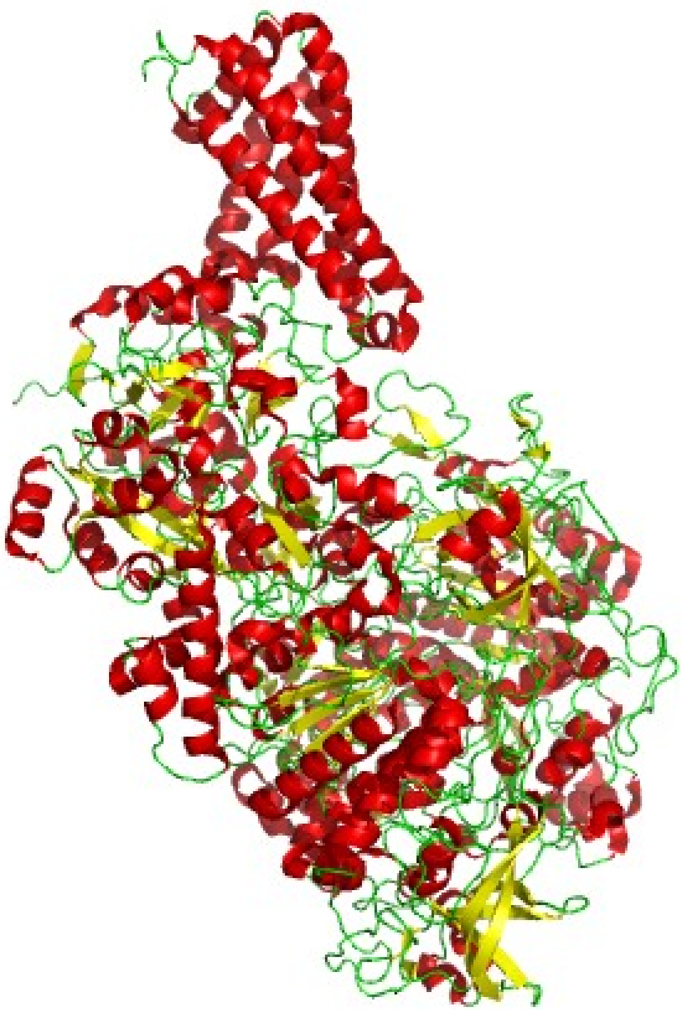
Life is *literally* electric



Life is *literally* electric

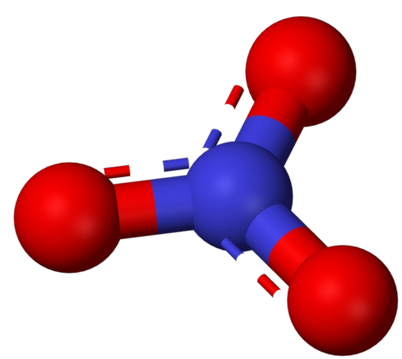


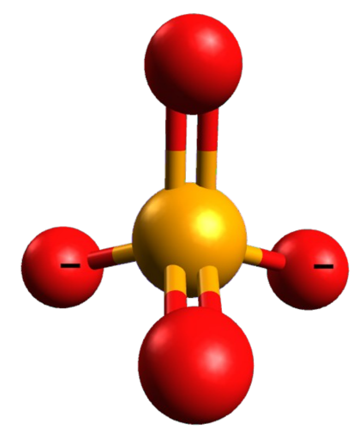
One more thing to keep in mind...



nitrite reductase enzyme ($NO_3^- \rightarrow NO_2^-$

While working primarily on **Nitrate***, this reductase enzyme can also act on* ***Selenate****, thus being* ***promiscuous*** *with regard to the substrate*





Heterotrophy

- *Heterotrophy is the use of organic carbon sources for anabolic purposes*
- *Major pathways are Glycolisys and Tri-Carboxylic Acid cycle (TCA cycle)*
- *Coupled to aerobic or anaerobic respiration. Aerobic chemorganoheterotrophy is a major sink of oxygen*
- *Many heterotrophic microorganisms have the "fermentation option"*

Fermentation

- *Fermentation is a major metabolism in absence of inorganic electron acceptors. Fermenting organisms can be obligate or facultative*
- *In fermentation redox balance is achieved by having the substrate serve as both electron donor and electron acceptor and that ATP is synthesized by substrate-level phosphorylation. PMF is not involved*
- *Redox balance is achieved in fermentations by the excretion from the cell of fermentation products, reduced substances such as acids or alcohols that are produced as end products of the catabolism of the original fermentable substance*
- *Fermentations are classified by either the substrate fermented or the products formed. A diverse array of products can be produced*

Aerobic and Anaerobic Respiration

- Respiration is the process of using an inorganic terminal electron acceptor in the electron transport chain
- Aerobic respiration is the dominant process in the extant biosphere
- Because the O_2/H_2O couple is most electropositive, more energy is available when O_2 is used as a terminal electron acceptor than when any other acceptor is used
- Other electron acceptors involved in anaerobic respiration are manganic ion (Mn_4^+), ferric iron (Fe_3^+), nitrate (NO_3^-), and nitrite (NO_2^-), sulfate (SO_4^{2-}), elemental sulfur (S^0), and carbon dioxide (CO_2) among others
- Prokaryotes performing aerobic and anaerobic respiration can be both heterotrophs and autotrophs

Assimilative and *Dissimilative* Reductions

- *Inorganic compounds (e.g. NO_3^-, SO_4^{2-}, CO_2) are reduced by many organisms as sources of cellular nitrogen, sulfur, and carbon (e.g. amino groups, sulfhydryl groups, organic carbon). This is assimilative reduction because the group is assimilated*

- *This is different from respiration, which is the reduction of inorganic compound for energy conserving reason. This is also known as dissimilative reduction, and often the product are excreted from the cell*

- *Most organisms carry out an assortment of assimilative metabolisms, whereas a more restricted group catalyze dissimilative metabolisms*

- *Several inorganic compounds can be both electron donor or electron acceptors (e.g. S^0) depending on the redox couple involved*

The Energetics of Chemolithotrophy

- Chemolithotrophs are organisms that obtain energy from the oxidation of inorganic compounds
- Chemolithotrophs can tap into many natural sources of inorganic electron donors, including geological, biological, and anthropogenic
- Mixotrophs are chemolithotrophs that require organic carbon as a carbon source
- Many sources of reduced molecules exist in the environment
- The oxidation of different reduced compounds yields varying amounts of energy

Types of Chemolithotrophy

e^- donors

H_2, NH_4^+, H_2S, $S^-_{(n)}$, S^0, $S_2O_3^{2-}$, S^{2-}, CH_4, CO, Fe^{2+}, As^{3+}, etc...

e^- acceptors

O_2, NO_3^-, NO_2^-, N_2O, NO, SO_4^{2-}, SO_3^{2-}, S^0, CO_2, Fe^{3+}, Mn^{2+}, SeO_4^{2-}, AsO_4^{3-}, UO_3^{2-}, TeO_4^{2-}, etc...

Hydrogen Oxidation

- *Hydrogen (H_2) is a common product of microbial metabolism, especially of some fermentations, serpentinization and volcanic activity*

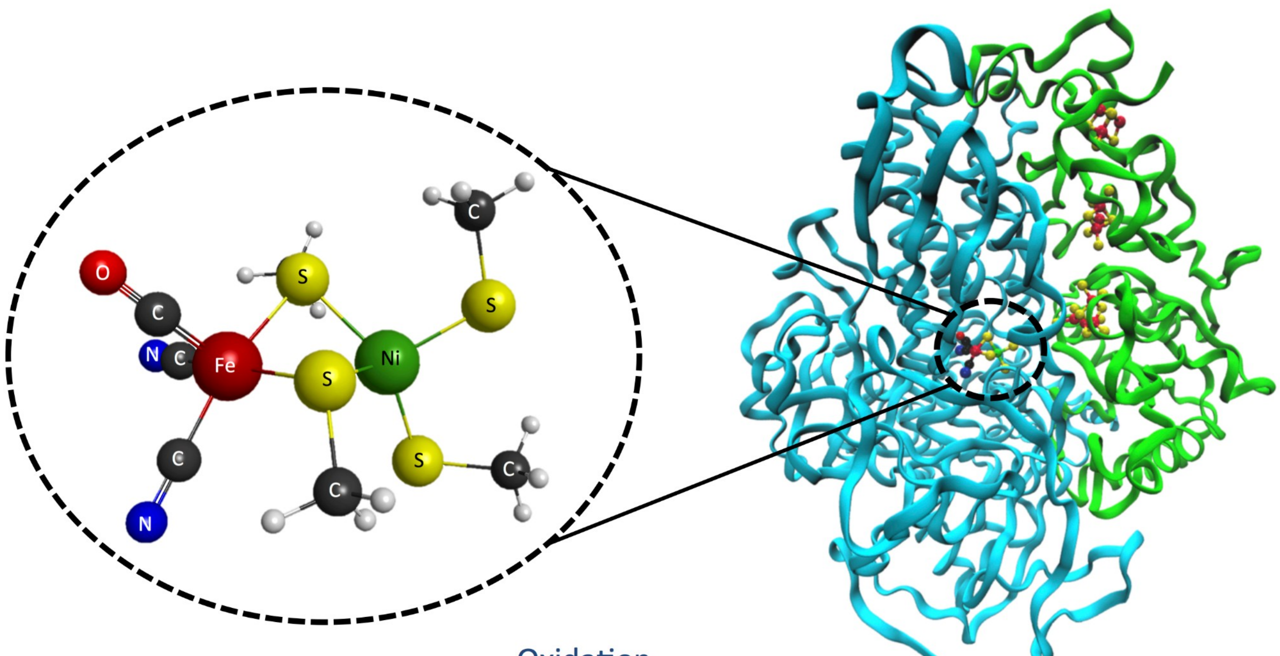
- *Hydrogen oxidizers obtain the most energy per two electrons oxidized*

- *A number of (phylogenetically different) aerobic chemolithotrophs can use hydrogen (known as knallgas bacteria), producing water as byproduct*

- *Anaerobic chemolithotrophs can also oxidize hydrogen at the expenses of other oxidized compounds (e.g. nitrate, sulfate, ferric iron, CO_2)*

Hydrogen Oxidation

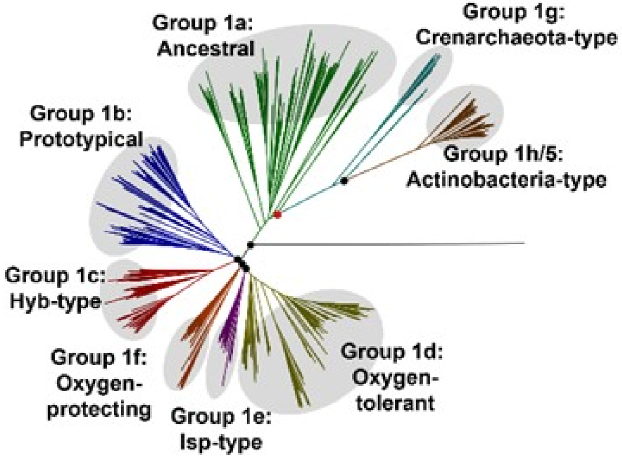
- *Hydrogenases are the key enzymes in hydrogen oxidation*
- *The active site can be either a [NiFe], [FeFe] or [Fe] center*
- *Hydrogenases are both membrane bound, periplasmic or cytosolic, and can be respiratory, assimilatory or hydrogen producing*



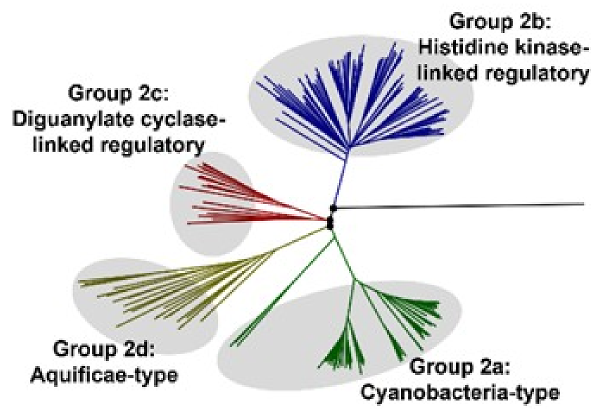
$$H_2 \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} 2H^+ + 2e^-$$

Hydrogen Oxidation

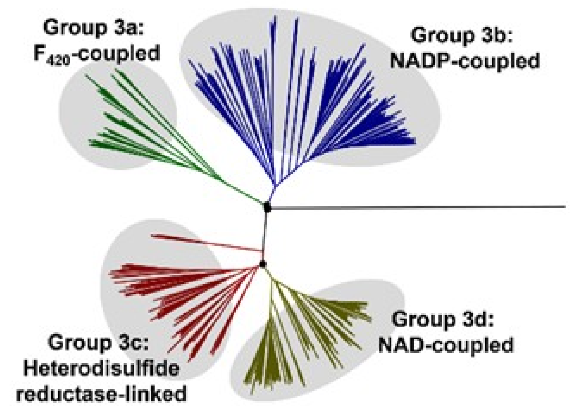
Group 1: Membrane-bound H_2-uptake [NiFe]-hydrogenases



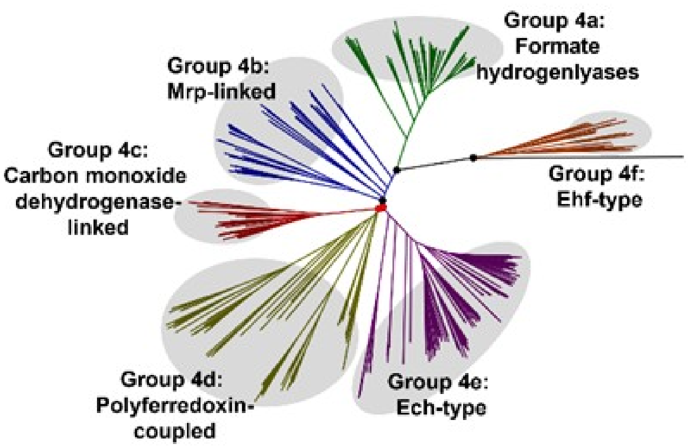
Groups 2: Cytosolic H_2-uptake [NiFe]-hydrogenases



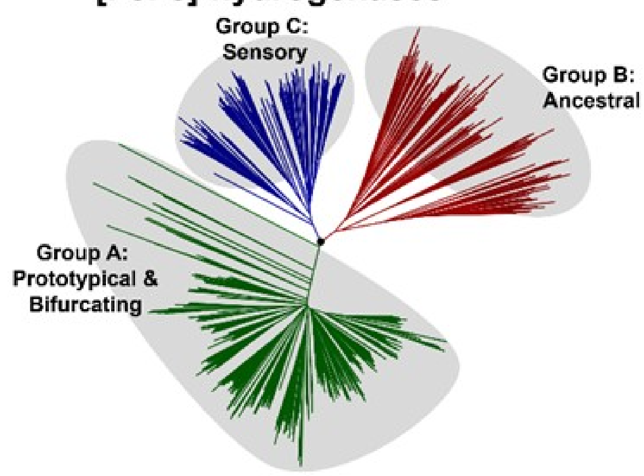
Group 3: Cytosolic bidirectional [NiFe]-hydrogenases



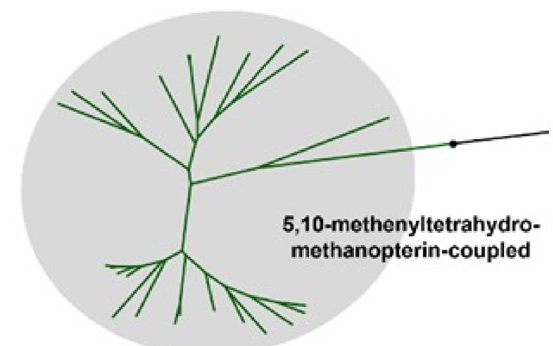
Group 4: Membrane-bound H_2-evolving [NiFe]-hydrogenases



[FeFe]-hydrogenases



[Fe]-hydrogenases



Hydrogen oxidation (aerobic)

Figure 12-14 Brock Biology of Microorganisms 11/e

Ralstonia eutropha

$$H_2 + 1/2O_2 \longrightarrow H_2O \qquad \Delta G^{0'} = -237kJ$$
$$6H_2 + 2O_2 + CO_2 \longrightarrow (CH_2O) + 5H_2O$$

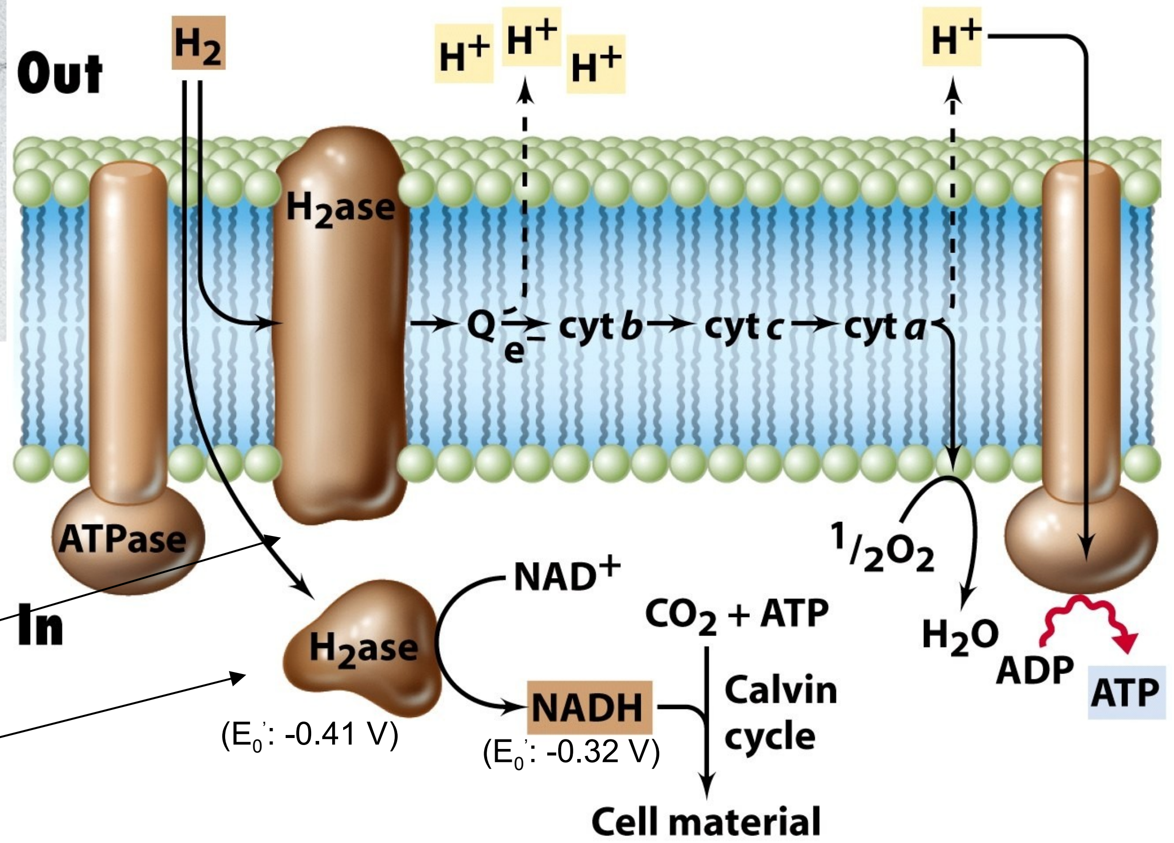
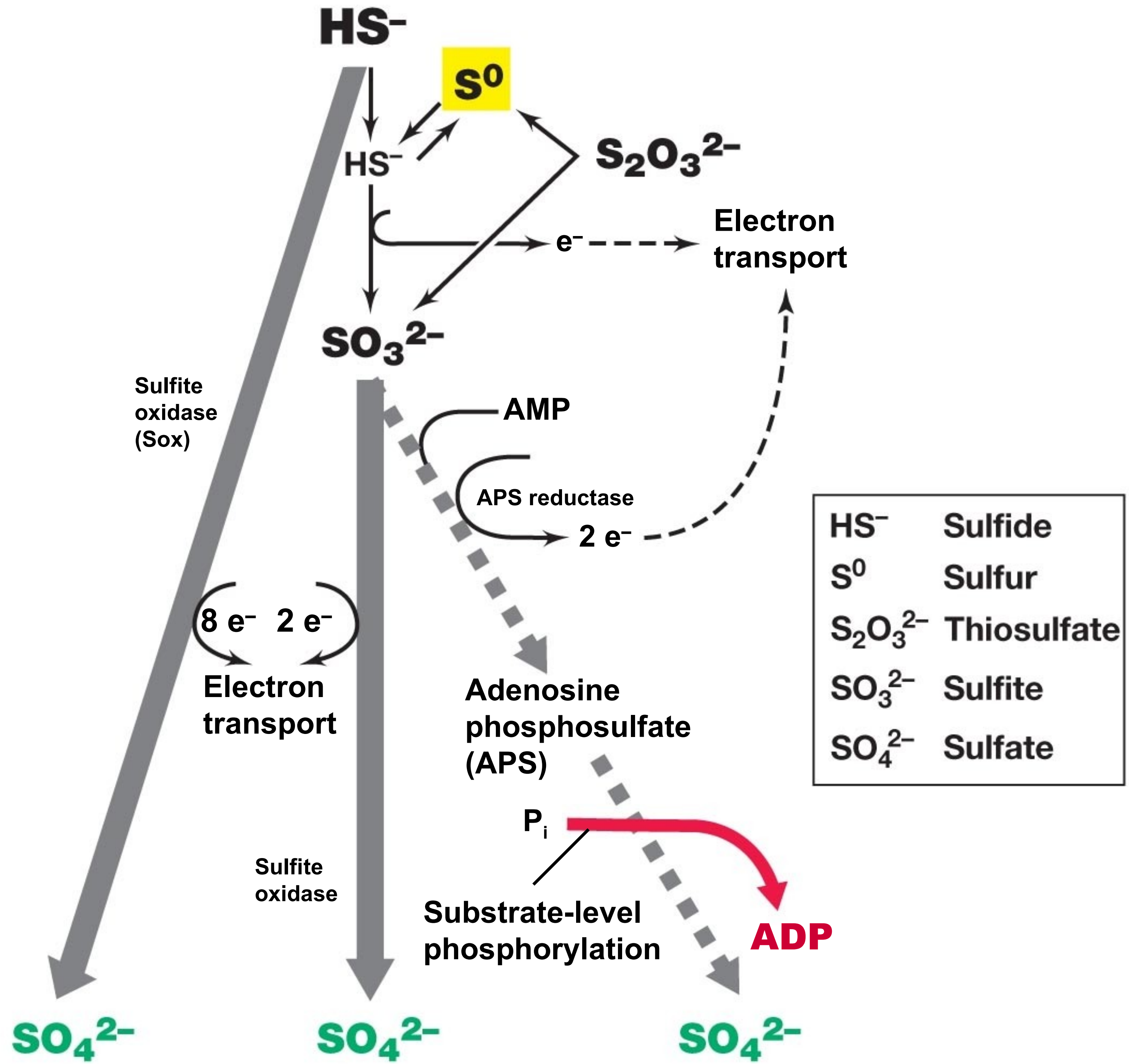


Figure 17-25 Brock Biology of Microorganisms 11/e

Two hydrogenases are present: the membrane-bound is involved in energetics (PMF), while the cytoplasmic (assimilatory) makes NADH for Carbon Fixation

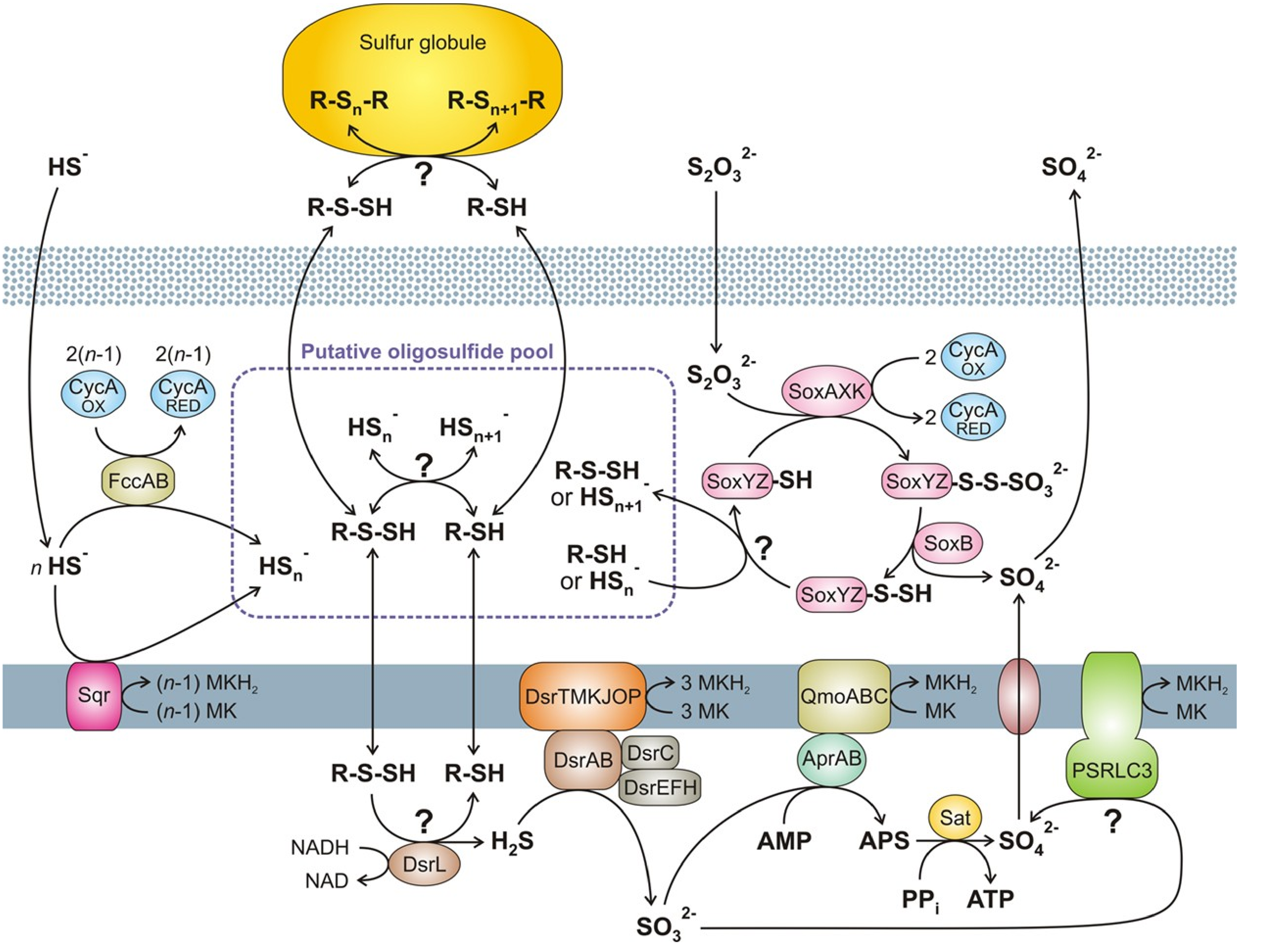
Oxidation of Reduced Sulfur Compounds

- *Many reduced sulfur compounds are used as electron donors*
- *H_2S, S^0, $S_2O_3^-$ are commonly used*
- *One product of sulfur oxidation is H^+, which results in a <u>lowering of the pH</u> of its surroundings*
- *Several enzymes are involved in sulfur compound oxidation (e.g. Sox, Aps, Sulfite Oxidase)*
- *Sulfur Oxidizers are major player in numerous extreme environments*
- *<u>Usually aerobic</u>, but some organisms can use <u>nitrate</u> as an electron acceptor*



HS⁻
S⁰
HS⁻
S₂O₃²⁻
e⁻
Electron transport
SO₃²⁻
Sulfite oxidase (Sox)
AMP
APS reductase
2 e⁻
8 e⁻ 2 e⁻
Electron transport
Adenosine phosphosulfate (APS)
Pi
Sulfite oxidase
Substrate-level phosphorylation
ADP
SO₄²⁻
SO₄²⁻
SO₄²⁻
HS⁻ Sulfide
S⁰ Sulfur
S₂O₃²⁻ Thiosulfate
SO₃²⁻ Sulfite
SO₄²⁻ Sulfate

(a)



Sulfur globule
R-S$_n$-R
R-S$_{n+1}$-R
?
HS$^-$
R-S-SH
R-SH
$S_2O_3^{2-}$
SO_4^{2-}
Putative oligosulfide pool
2(n-1)
2(n-1)
CycA OX
CycA RED
FccAB
HS$_n^-$
HS$_{n+1}^-$
?
R-S-SH
R-SH
n HS$^-$
HS$_n^-$
R-S-SH or HS$_{n+1}^-$
R-SH or HS$_n^-$
?
$S_2O_3^{2-}$
SoxAXK
2 CycA OX
2 CycA RED
SoxYZ-SH
SoxYZ-S-S-SO$_3^{2-}$
SoxB
SoxYZ-S-SH
SO_4^{2-}
Sqr
(n-1) MKH$_2$
(n-1) MK
DsrTMKJOP
3 MKH$_2$
3 MK
QmoABC
MKH$_2$
MK
MKH$_2$
MK
DsrAB
DsrC
DsrEFH
AprAB
PSRLC3
R-S-SH
R-SH
?
NADH
NAD
DsrL
H_2S
AMP
APS
Sat
SO_4^{2-}
?
PP$_i$
ATP
SO_3^{2-}

Sulfate Reduction

- Sulfate (SO_4^{2-}) is reduced by the sulfate-reducing bacteria (SBR), a highly diverse group of obligately anaerobic bacteria widely distributed in nature
- The end product of sulfate reduction is hydrogen sulfide (H_2S), an important natural product that participates in many biogeochemical processes
- Sulfate reduction is a widespread and important pathway of organic matter degradation in anaerobic sediments. Sulfate reducers can be autotrophic or heterotrophic
- A number of sulfate reducers are member of the class Deltaproteobacteria of the phylum Proteobacteria
- Hydrogen and a number of organic compounds and organic acids (e.g. Acetate, Lactate, Propionate, Butyrate, Ethanol and other alcohols Long-chain fatty acids) are used as electron donors in sulfate reduction

Sulfur Reduction

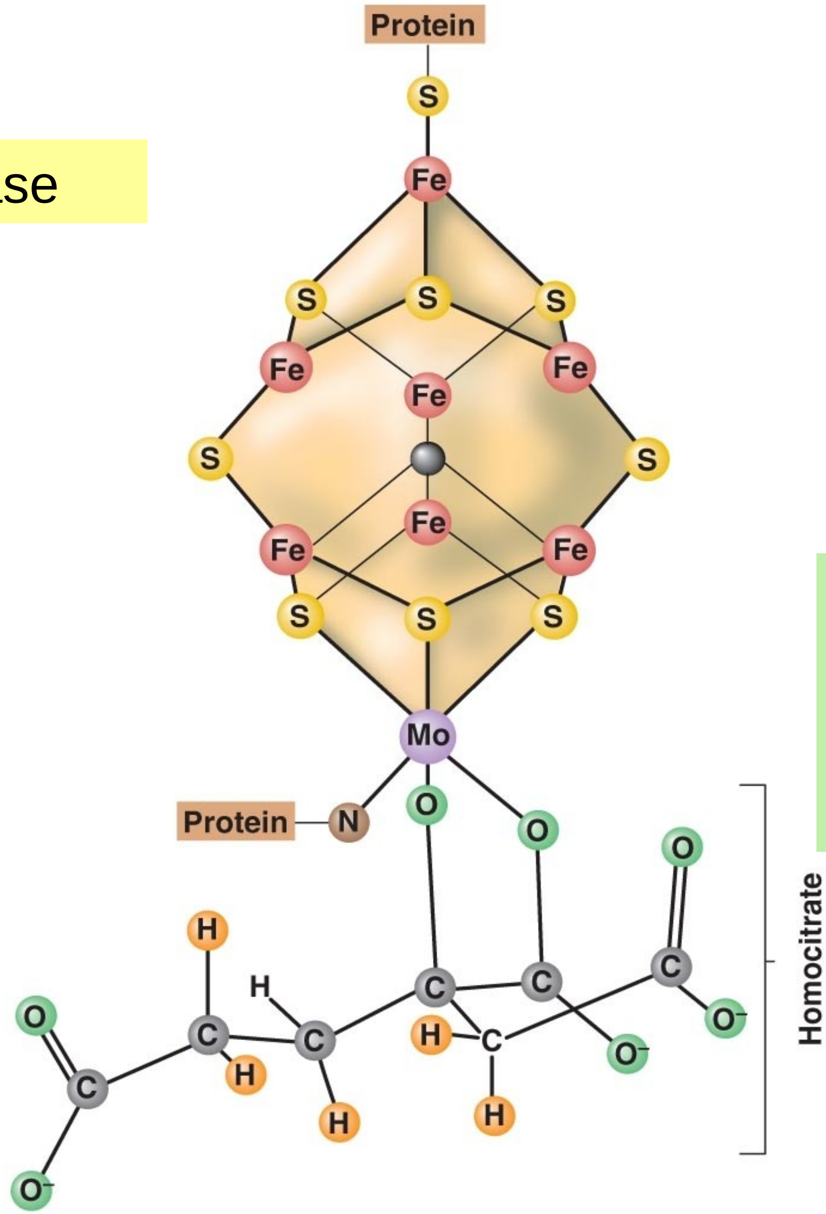
- *Besides sulfate, most sulfate-reducing bacteria can also conserve energy from the reduction of elemental sulfur to sulfide*
- *A variety of non-sulfate-reducing Bacteria and Archaea can also reduce sulfur in anaerobic respiration. These prokaryotes are phylogenetically diverse, and often can respire additional compounds (e.g. nitrate)*
- *Sulfur reduction has been proposed as a potentially ancestral metabolism*

Nitrogen Fixation

- Only certain prokaryotes can fix nitrogen
- Nitrogen fixation is a key process in the N cycle
- Some nitrogen fixers are free living and others are symbiotic
- Reaction is catalyzed by nitrogenase, sensitive to the presence of oxygen
- A wide variety of nitrogenases use different metal cofactors (MoFe, V, and FeS)
- Nitrogenases are promiscuos enzymes. They catalyze a high number of side reactions (e.g. cyanide, cyanate, acetylene, azide, hydrogen, thiocyanate, carbonyl sulfide)

FeMo-co, the Iron-Molybdenum Cofactor from Nitrogenase

Dinitrogenase

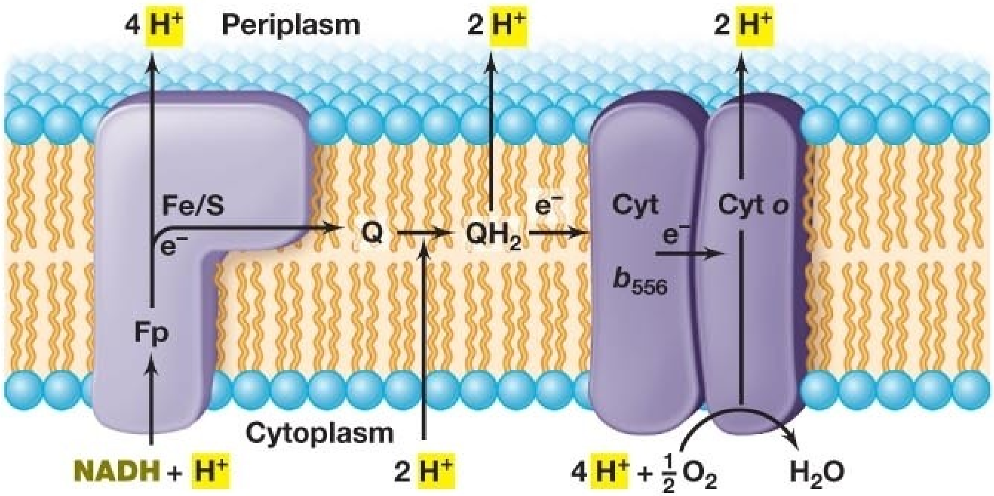


Alternative nitrogenase

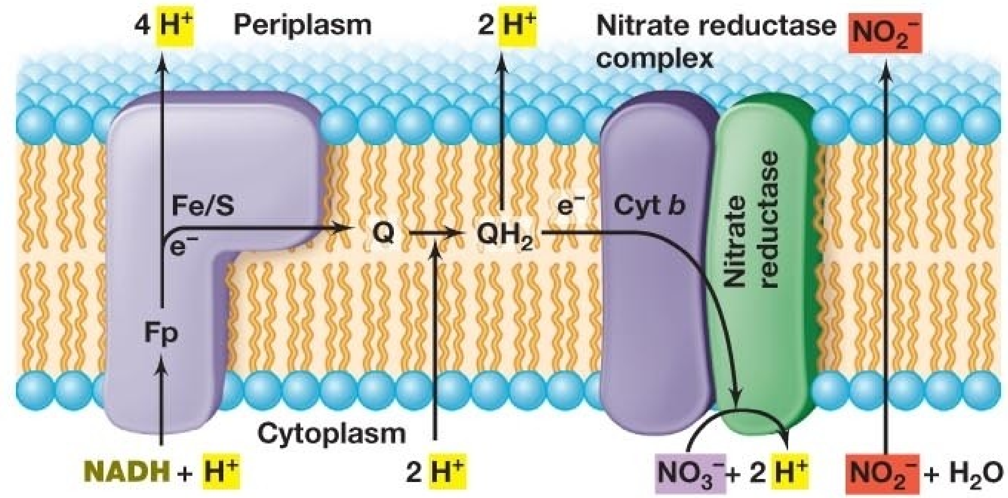
- V
- Mo
- Fe

Oxidizen Nitrogen Species Reduction

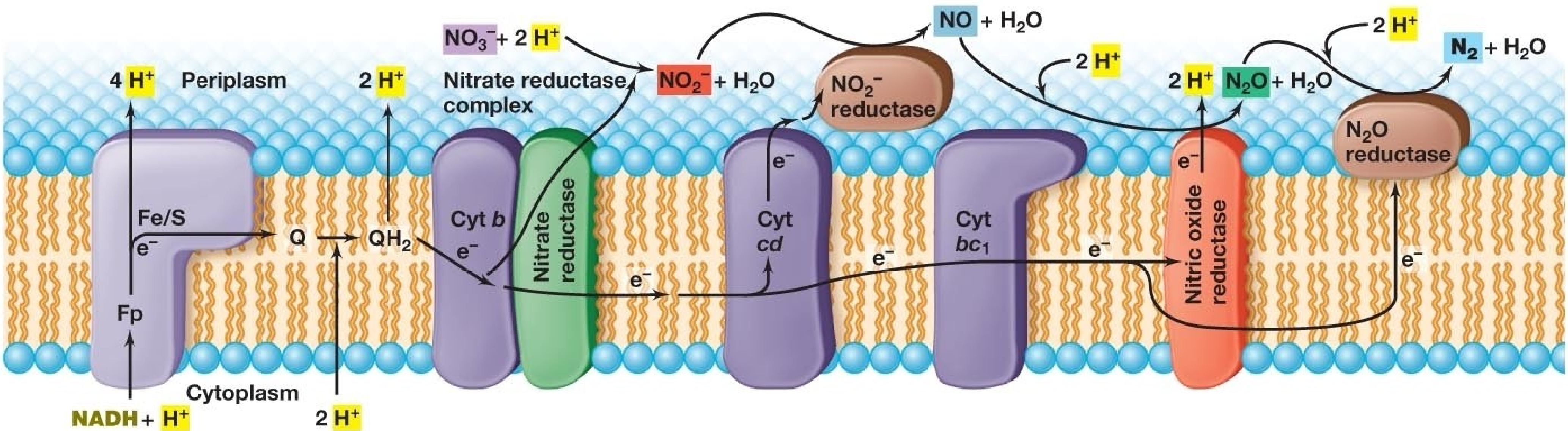
- *Inorganic nitrogen compounds are some of the most common electron acceptors in anaerobic respiration*
- *One of the most common alternative electron acceptors for dissimilative purposes is nitrate. It can be reduced with two electrons to nitrite, or reduced further to nitric oxide, nitrous oxide, and dinitrogen gas. This process is known as Denitrification*
- *Nitrate can also be reduced all the way to ammonia, in this case the process is known as Dissimilatory Nitrate Reduction to Ammonia (DNRA)*
- *Three different enzymes can catalyze the first step of nitrate reduction (nitrate to nitrite): assimilatory nitrate reductase (Nas), membrane bound nitrate reductase (Nar) and the periplasmic nitrate reductase (Nap)*



(a) **Aerobic respiration**



(b) **Nitrate reduction**



(c) **Denitrification**

Nitrification

- NH_3 and NO_2- are oxidized by nitrifying prokaryotes during the process of nitrification; major player in the N cycle

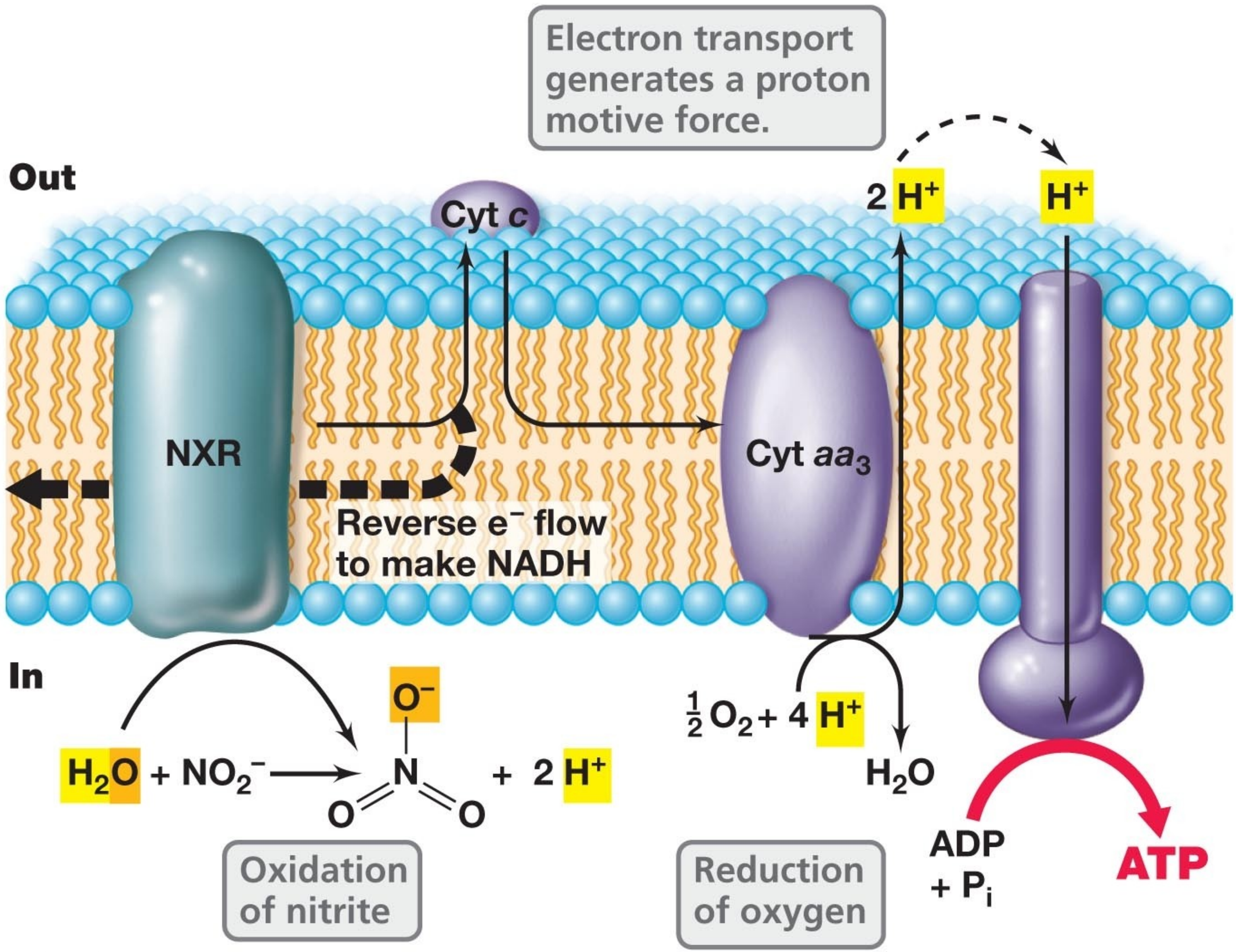
- Two groups of bacteria Carry out ammonia or nitrite oxidation: Nitrospirae and selected genera of the Proteobacteria (Nitrosomonas, Nitrosospira, Nitrosococcus, Nitrosolobus ,and Nitrobacter, Nitrospina, Nitrococcus)

- One group of archaea carries out ammonia oxidation (Thaumarchaeota)

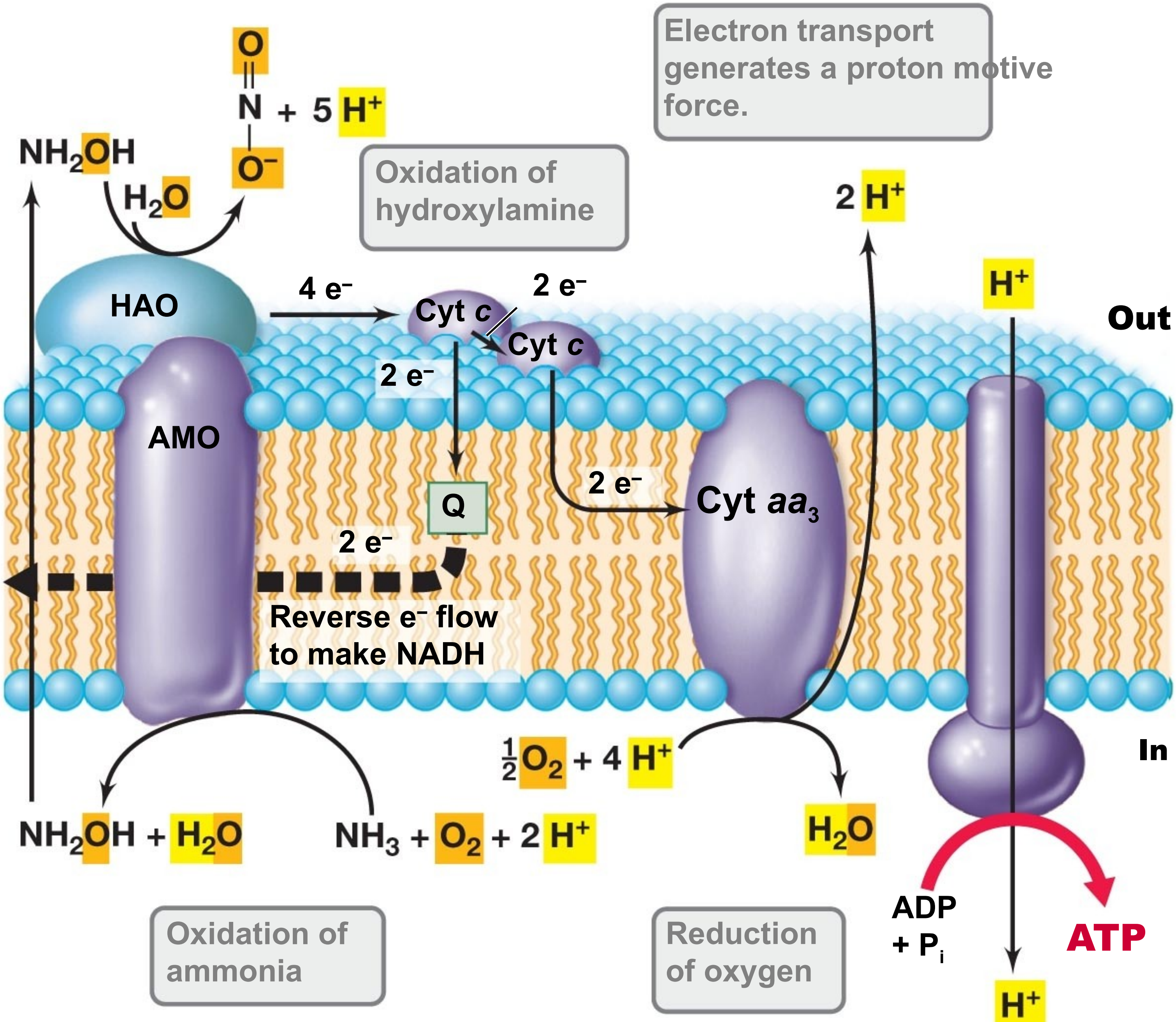
- Key enzymes are ammonia monooxygenase, hydroxylamine oxidoreductase, and nitrite oxidoreductase

- Only small energy yields from this reaction

Oxidation of Nitrite to Nitrate by Nitrifying Bacteria



Oxidation of Ammonia by Ammonia-Oxidizers



Oxidation of Ammonia (Nitrification): **Nitrosomonas** and **Nitrobacter**

Nitrification = 2 steps

Ammonia oxidation

$NH_3 + O_2 + 2H^+ + 2e^- \;->\; NH_2OH + H_2O$

ammonia monooxygenase

Bacteria need CO_2 and oxygen

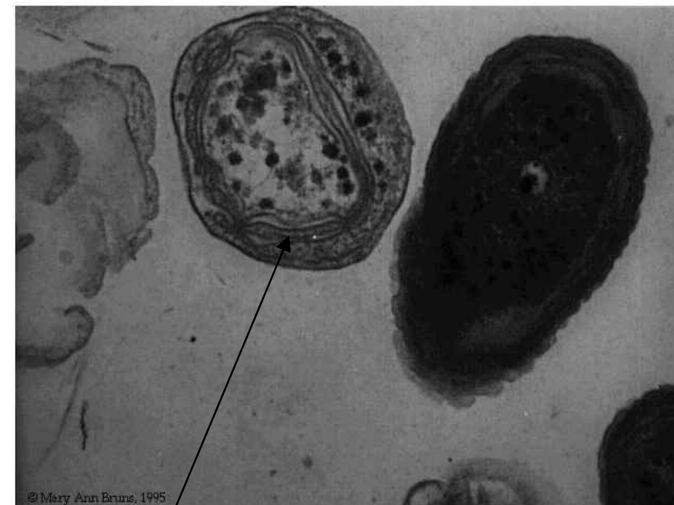
hydroxylamine oxidoreductase converts NH_2OH to NO_2^-

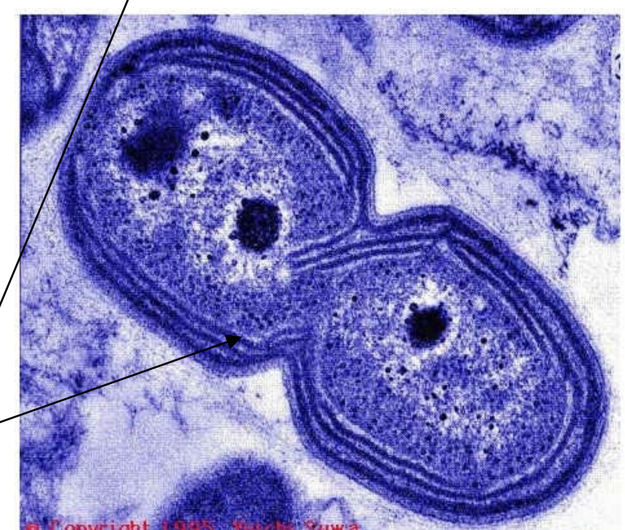
Nitrite oxidation

$NO_2^- + 1/2\, O_2 \;->\; NO_3^-$

nitrite oxidoreductase

Nitrosomonas sp.

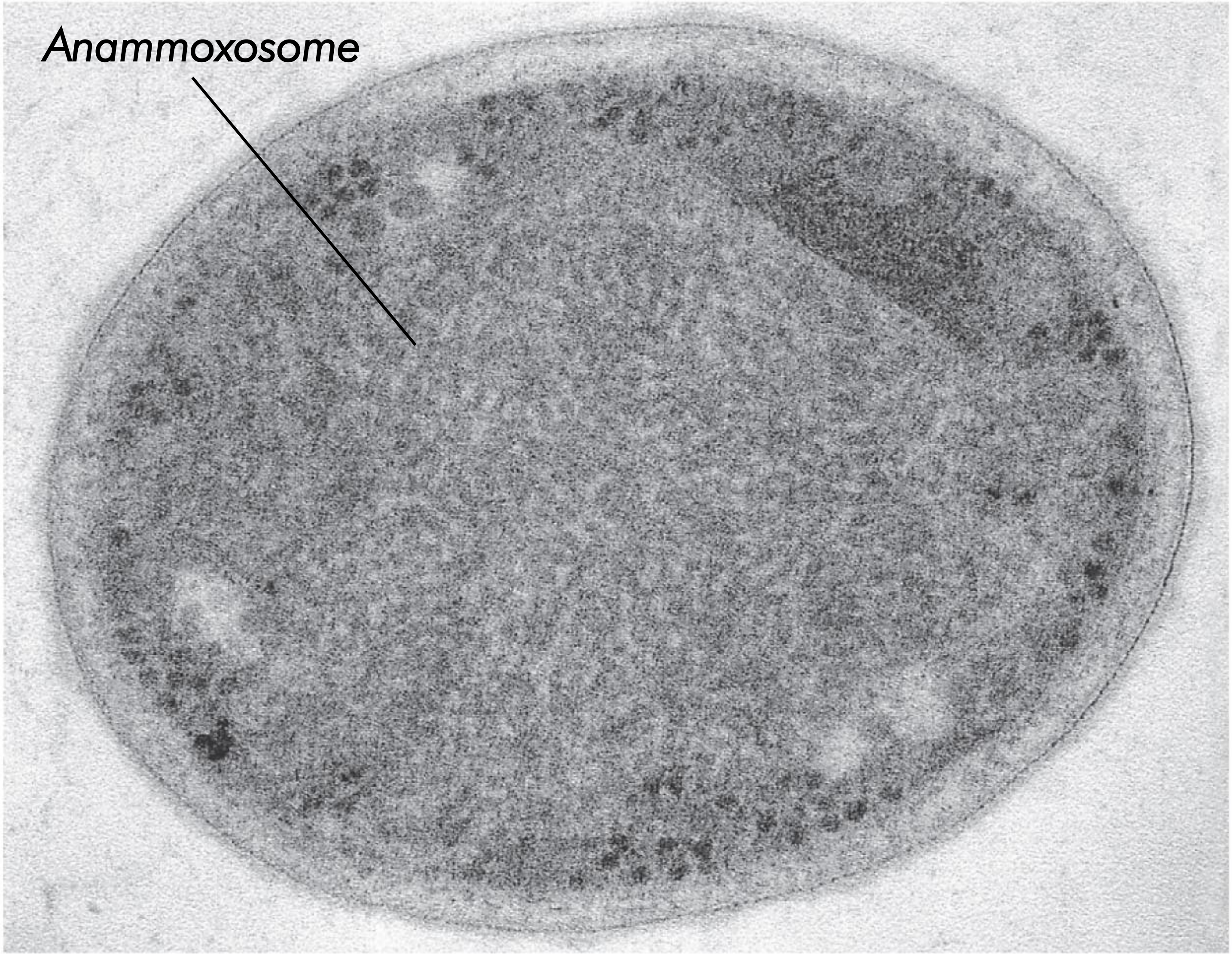




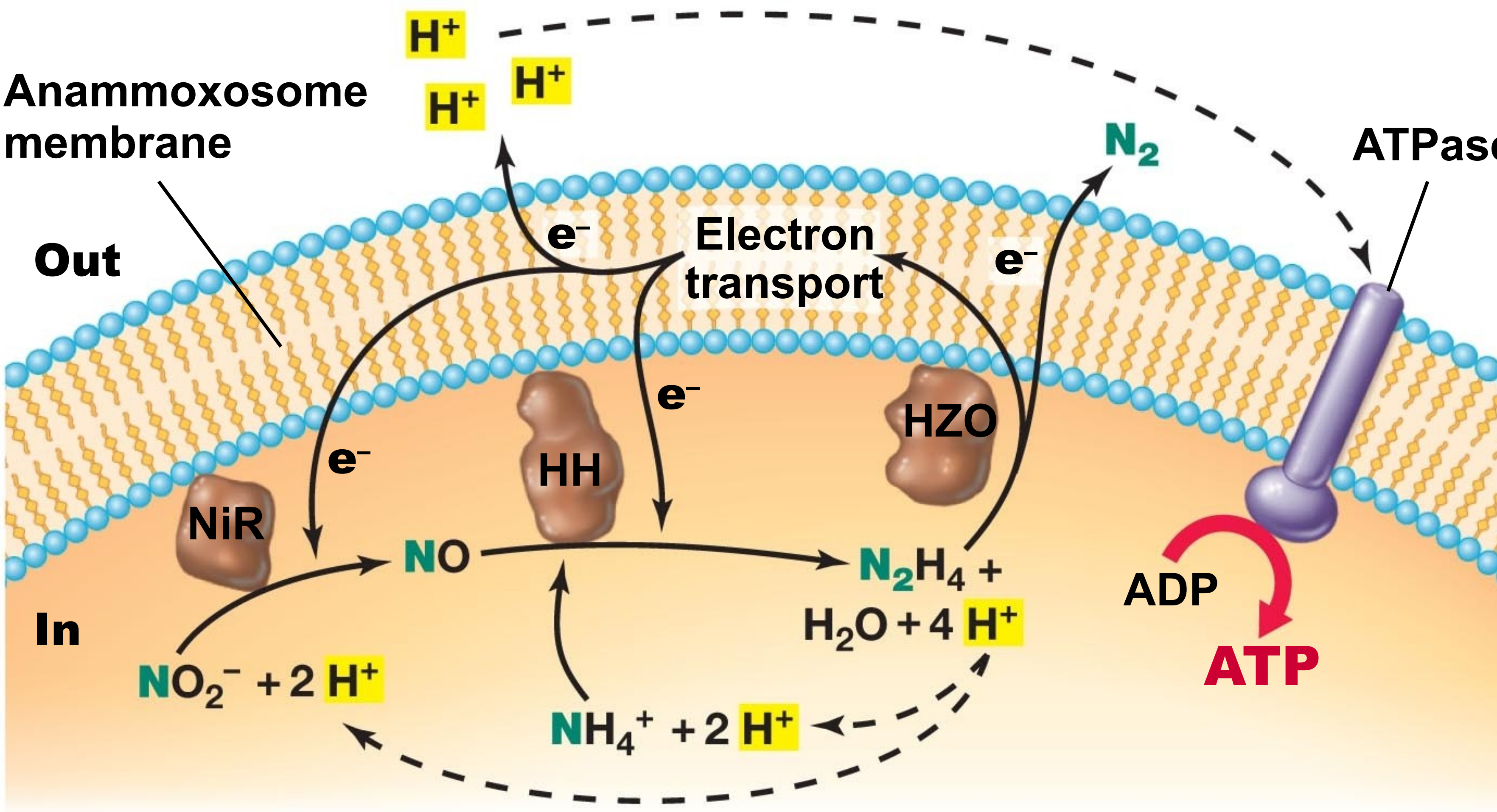
Note stacked membranes

Anaerobic Ammonia Oxidation Anammox

- Anammox: anerobic ammonia oxidation (discovered 1999!)
  - $NH_4^+ + NO_2^- \rightarrow N_2 + 2\ H_2O$
- Performed by unusual group of obligate anaerobes (Planctomycetes, order Brocadiales)
- Anammoxosome is a membrane-enclosed compartment where anammox reactions occur
  - Lipids that make up the anammoxsome are not the typical lipids of Bacteria
  - Protects cell from reactions occuring during anammox
  - Hydrazine ($H_2N{=}NH_2$), a very strong reductant, is an intermediate of anammox
- Major sink for fixed nitrogen. May be responsible for 30-50% of the N2 gas produced in the oceans. It limits oceanic primary productivity



(b)



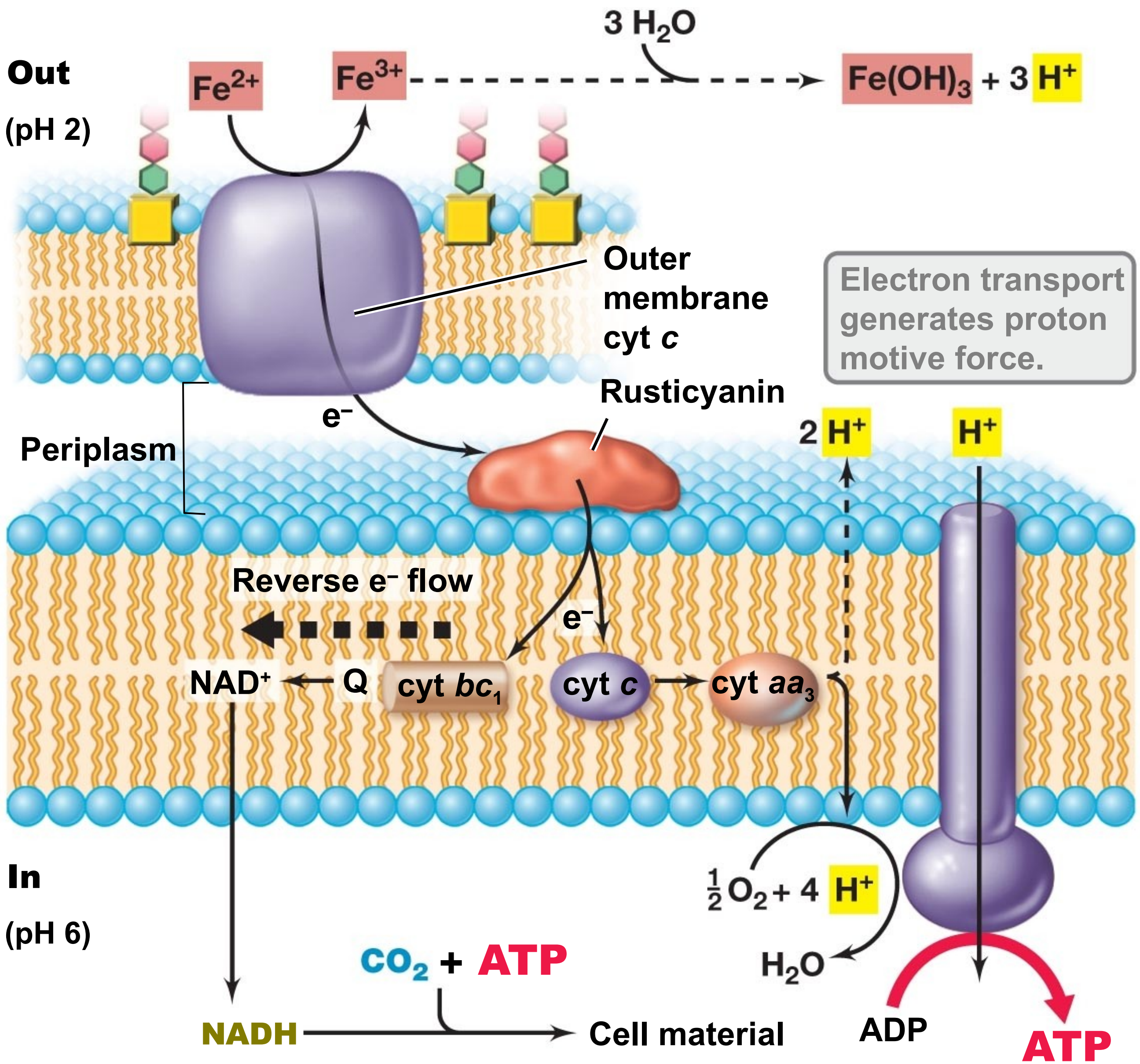
H^+
H^+
H^+
Anammoxosome membrane
N_2
ATPase
Out
e⁻
Electron transport
e⁻
e⁻
HZO
e⁻
HH
NiR
NO
N_2H_4 +
$H_2O + 4\ H^+$
ADP
ATP
In
$NO_2^- + 2\ H^+$
$NH_4^+ + 2\ H^+$

(c)

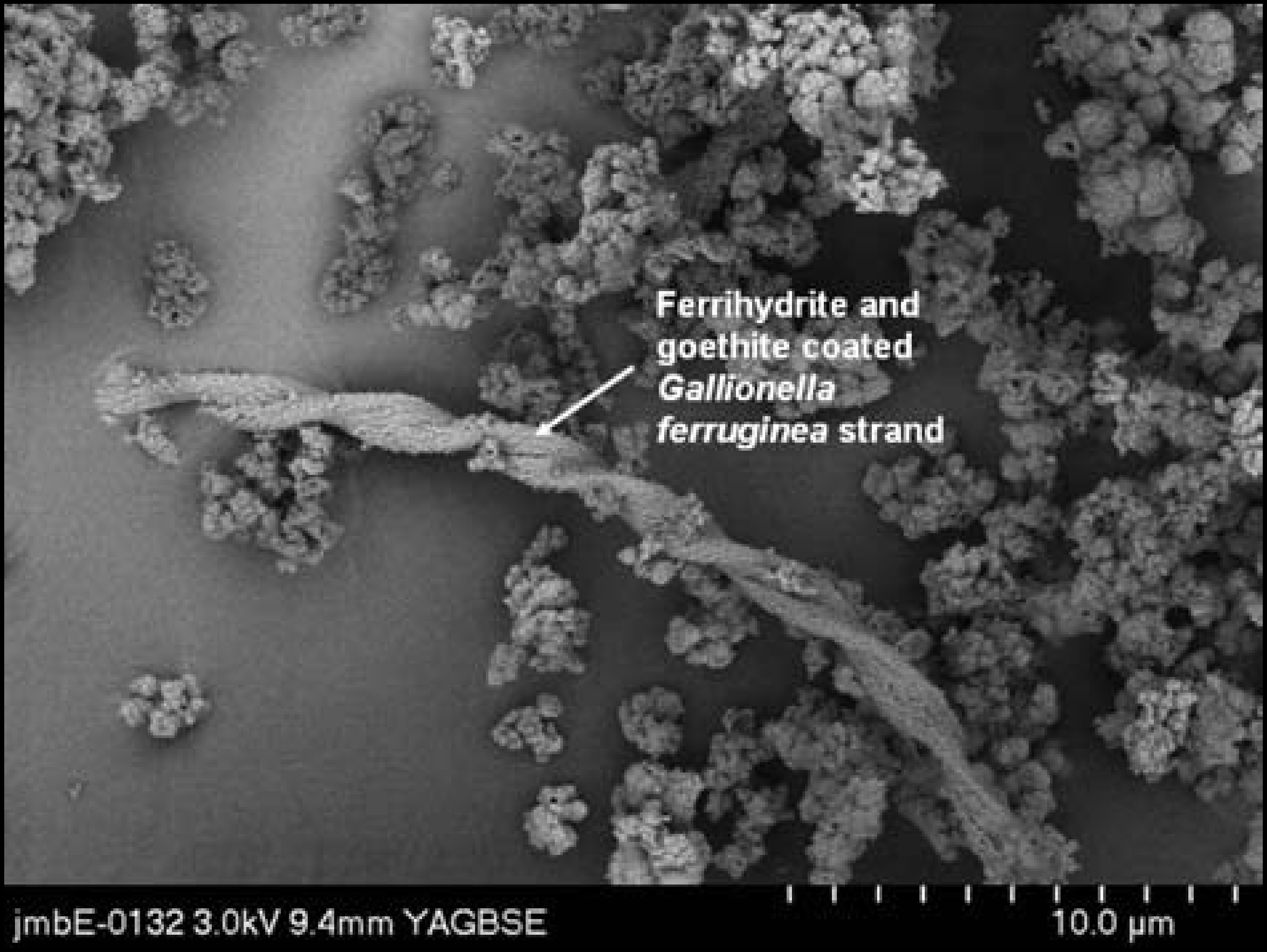
Iron Oxidation

- Ferrous iron (Fe^{2+}) oxidized to ferric iron (Fe^{3+})
- Ferric hydroxide precipitates in water
- Many Fe oxidizers are acidophiles (and can grow at pH < 1)
- Associated with mine drainage and geothermal emissions
- Both Bacteria and Archaea can oxidize iron
- Some anoxygenic phototrophs can oxidize Fe^{2+} anaerobically using Fe^{2+} as an electron donor for CO_2 reduction

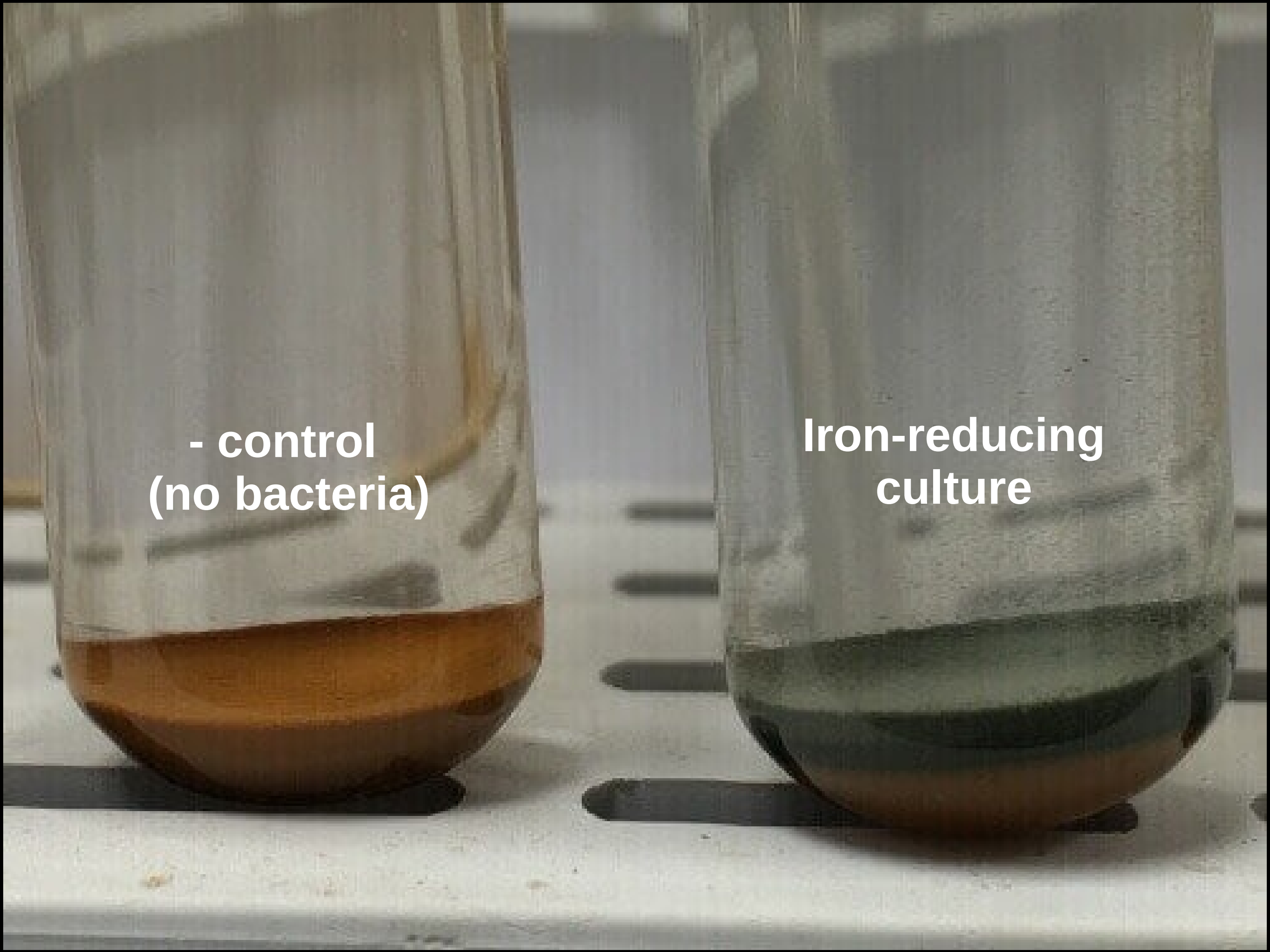
Iron-Oxidizing Bacteria



Iron Hydroxide Twisted Stalks



Iron-Reducing Bacteria



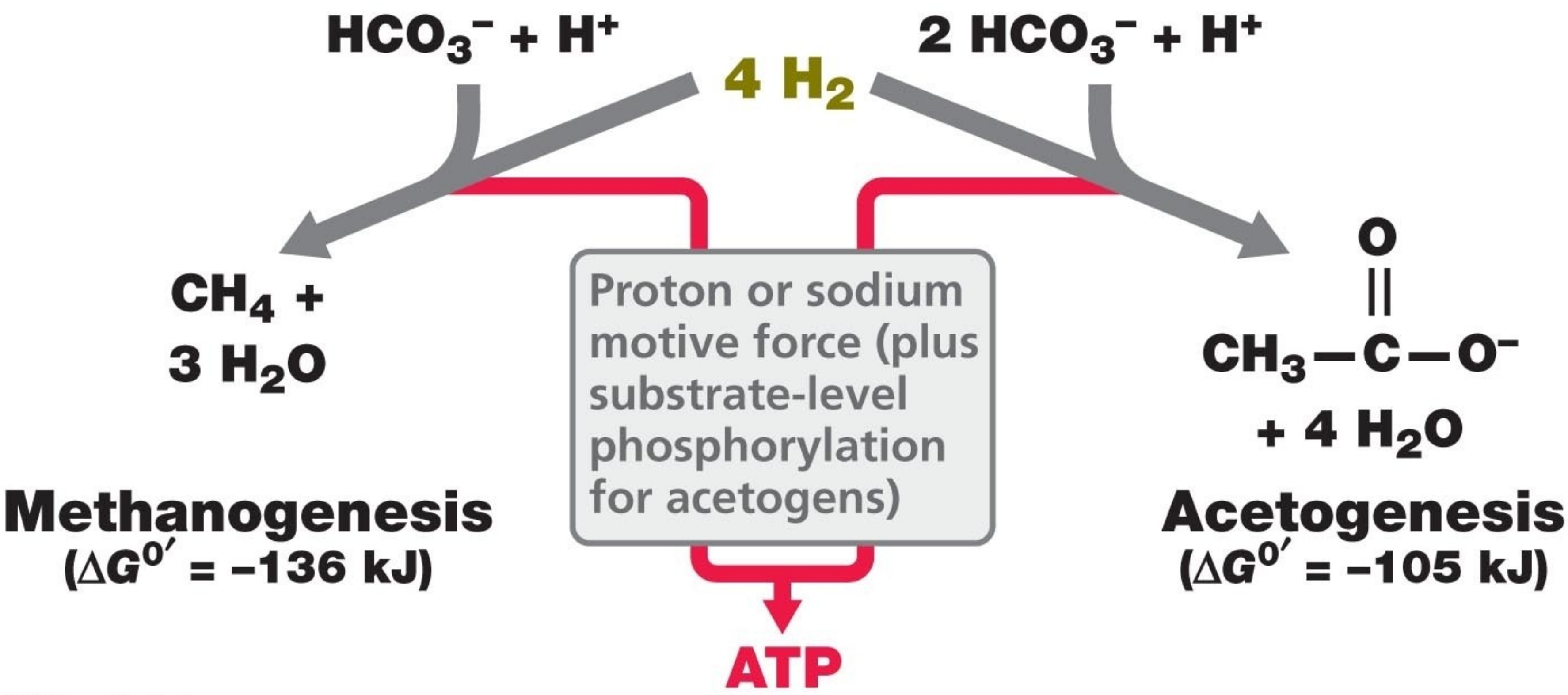
Methanogenesis and Acetogenesis

- *The production of methane (methanogenesis) is carried out by a strictly anaerobic group of Archaea. Acetogenesis is carried out prevalently by gram positive Bacteria (especially members of the genera Clostridium or Acetobacterium)*

- *The reduction of CO_2 by H_2 to form methane or acetic acid is a form of anaerobic respiration in which CO_2 is the electron acceptor AND carbon source. Other organic electron donors are used by some groups*

- *Energy conservation in acetogenesis results from both substrate-level phosphorylation and PMF. In methanogenesis substrate-level phosphorylation does not occur*

Methanogenesis and *Acetogenesis*



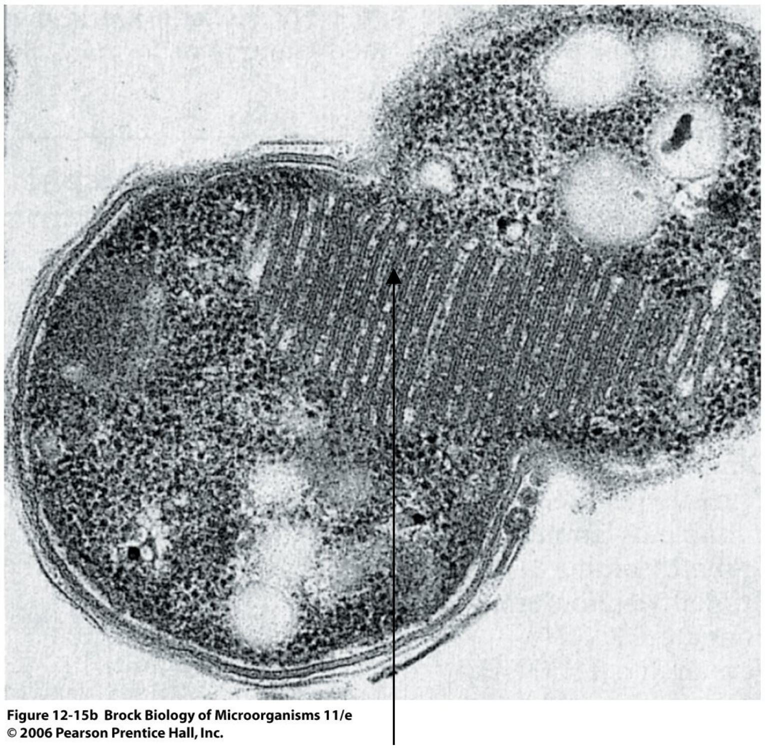
Methane Oxidation

- *Global sink of methane, a strong greenhouse gas*
- *Exists in two forms Aerobic Methane Oxidation, and Anaerobic Methane Oxidation*
- *Diverse members of the Bacteria carry out the former (Proteobacteria, Verrucomicrobia, while the latter is carried out by a polyphyletic of Archaea (ANME group) and Bacteria (NC10 candidate division)*
- *Aerobic Methane Oxidizers work alone in oxidizing methane, while ANME require a bacterial partner to carry out Anaerobic Methane Oxidation*

Aerobic *Methane* Oxidation

- *Limited to areas to where methane reaches oxic areas*
- *Methanotrophs (organisms performing aerobic methane oxidation) are a special class of Methylotrophs*
- *Aerobic-methane oxidizers are exclusively Bacteria of the phyla Proteobacteria (Alpha, Beta and Gamma classes) and Verrucomicrobia*
- *Aerobic Methane Oxidizers oxidize methane by first initiating reduction of an oxygen atom to H2O2 and transformation of methane to CH3OH using methane monooxygenases (MMOs)*

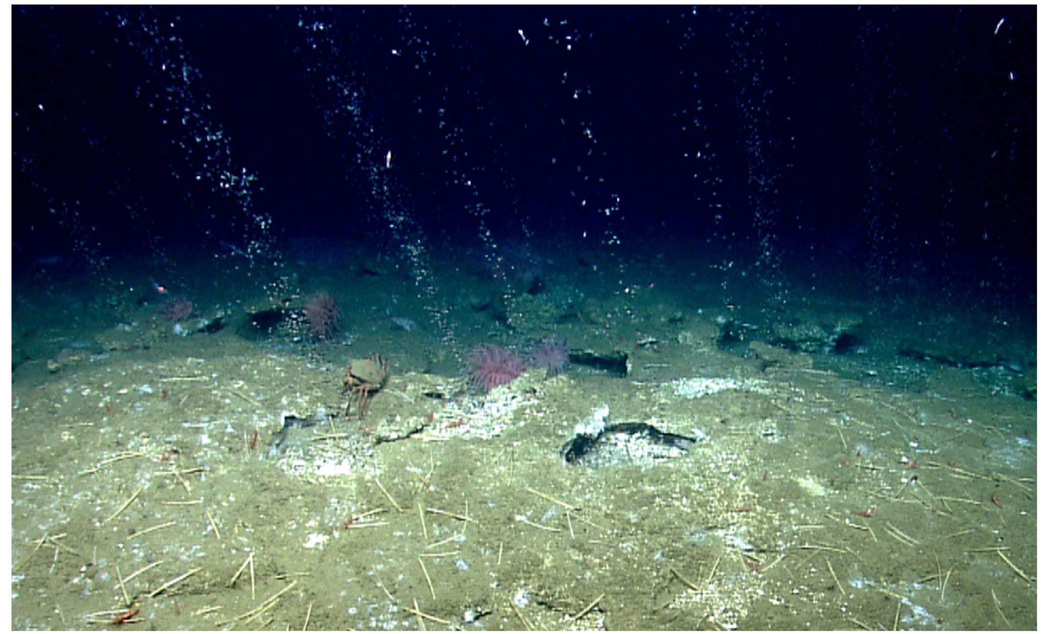
Aerobic Methane Oxidation



D. W. Ribbons

Figure 12-15b Brock Biology of Microorganisms 11/e

Note stacked membranes



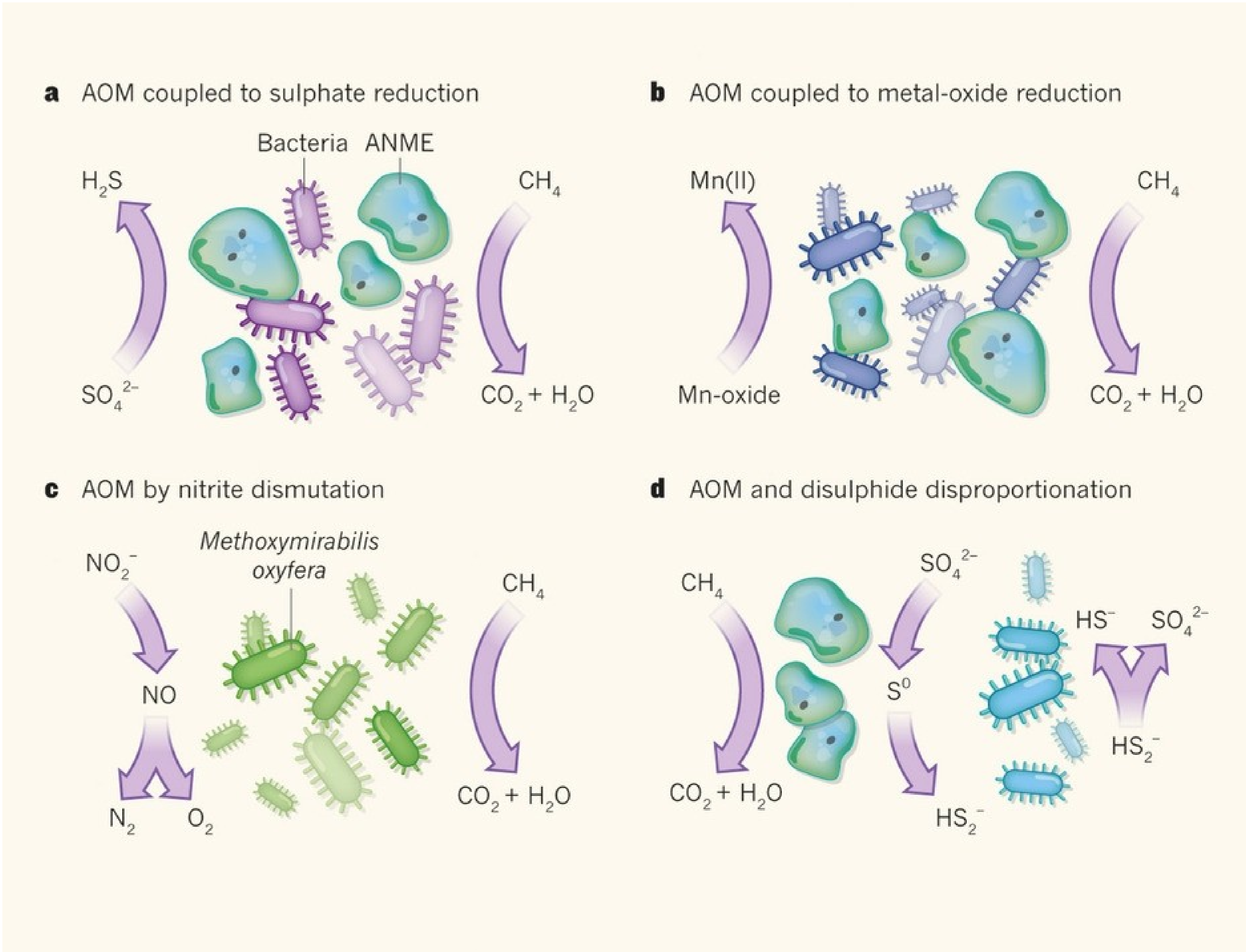
<u>Cold seeps: bubbling methane</u>

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Anaerobic Methane Oxidation

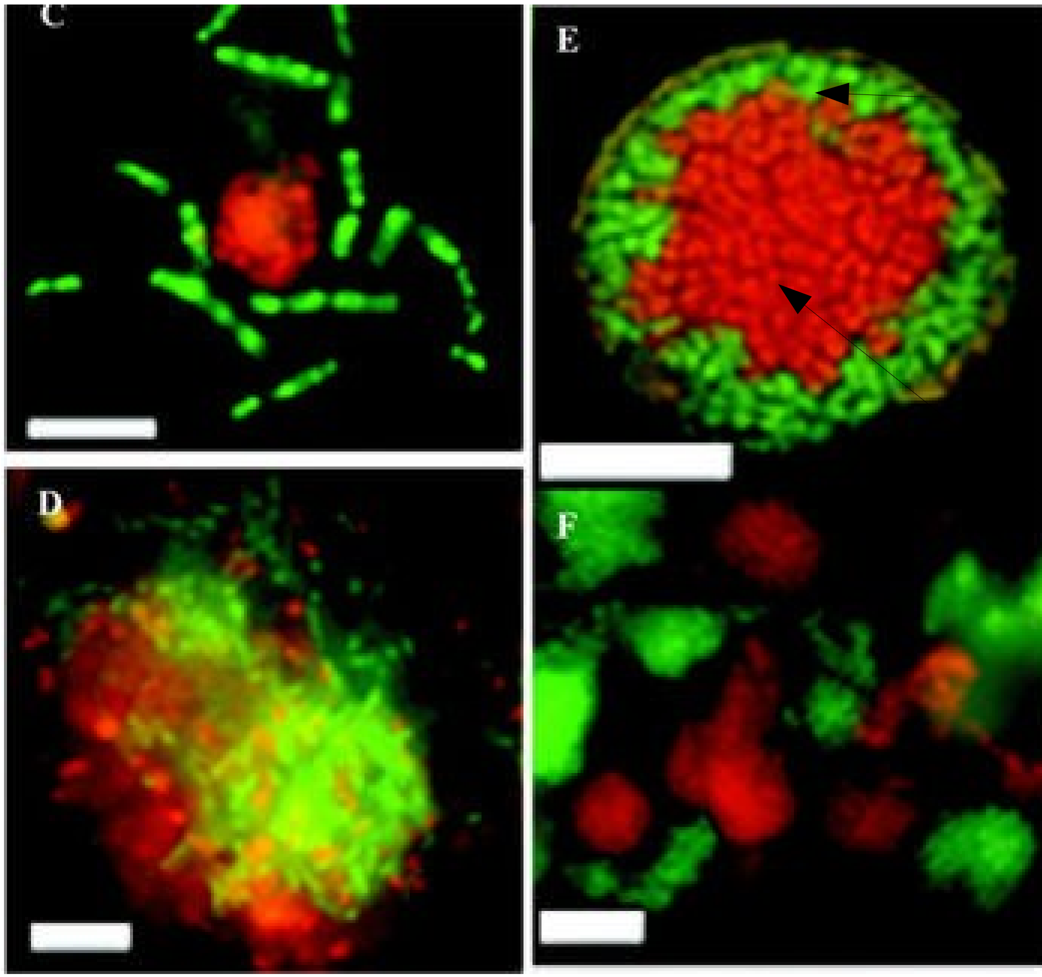
- *Anaerobic Oxidation of Methane – also known as AOM - is the major sink of methane worldwide*
- *It os responsible for the removal of up to 90% of the 85-300 Tg CH_4 yr^{-1} released from the seafloor*
- *AOM appens in anoxic sediments, and it has been reported in the methane-sulfate transition zone (from few mm to 200 mbsf) in worldwide sediments.*
- *AOM is driven by the yet uncultured anaerobic methanotrophic archaea group (ANME), usually syntrophically coupled to sulfate-reducing bacteria (SRB)*
- *Recently (**2010**!!!) a new intra-aerobic metabolism has been discovered, coupling anaerobic methane oxidation to nitrate reduction (n-damo)*

Types of AOM



Joye SB 2012. Nature 491, 538-539

ANME and SBR



ANME-1

Desulfosarcina spp.
SBR Bacteria

$$CH_4 + 2SO_2^{4-} \rightarrow 2HS^- + HCO_3^- + H_2O$$

Diversity of redox reactions

Reaction

$2NH_4^+ + 1.5O_2 \rightarrow N_2 + 2H^+ + 3H_2O$
$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$
$N_2 + 1.5O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$
$N_2 + 2.5O_2 + H_2O \rightarrow 2NO_3^- + 2H^+$
$NO_2^- + 0.5O_2 \rightarrow NO_3^-$
$NO_3^- + H_2 \rightarrow NO_2^- + H_2O$
$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$
$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$
$2NO_2^- + 3H_2 + 2H^+ \rightarrow N_2 + 4H_2O$
$NO_2^- + 3H_2 + 2H^+ \rightarrow NH_4^+ + 2H_2O$
$N_2 + 3H_2 + 2H^+ \rightarrow 2NH_4^+$
$4N_2 + 2H^+ + 9H_2O \rightarrow 3NO_3^- + 5NH_4^+$
$N_2 + 2H_2O \rightarrow NO_2^- + NH_4^+$
$4NO_2^- + 2H^+ + H_2O \rightarrow 3NO_3^- + NH_4^+$
$5NO_2^- + 2H^+ \rightarrow 3NO_3^- + N_2 + H_2O$

$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$CO + 0.5O_2 \rightarrow CO_2$
$CO_2 + H_2 \rightarrow CO + H_2O$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
$CO + 3H_2 \rightarrow CH_4 + H_2O$
$4CO + 2H_2O \rightarrow 3CO_2 + CH_4$

$H_2S + 0.5O_2 \rightarrow S° + H_2O$
$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$
$S° + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$
$SO_4^{2-} + 3H_2 + 2H^+ \rightarrow S° + 4H_2O$
$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$
$S° + H_2 \rightarrow H_2S$
$4S° + 4H_2O \rightarrow SO_4^{2-} + 3H_2S + 2H^+$

$3Fe^{2+} + 0.5O_2 + 3H_2O \rightarrow Fe_3O_4 + 6H^+$
$Fe_3O_4 + H_2 + 6H^+ \rightarrow 3Fe^{2+} + 4H_2O$

$2NH_4^+ + SO_4^{2-} \rightarrow N_2 + S° + 4H_2O$
$8NH_4^+ + 3SO_4^{2-} \rightarrow 4N_2 + 3H_2S + 2H^+ + 12H_2O$
$NH_4^+ + SO_4^{2-} \rightarrow NO_2^- + S° + 2H_2O$
$4NH_4^+ + 3SO_4^{2-} \rightarrow 4NO_2^- + 3H_2S + 2H^+ + 4H_2O$
$3NH_4^+ + 4SO_4^{2-} + 2H^+ \rightarrow 3NO_3^- + 4S° + 7H_2O$
$NH_4^+ + SO_4^{2-} \rightarrow NO_3^- + H_2S + H_2O$
$2NH_4^+ + 3S° \rightarrow N_2 + 3H_2S + 2H^+$
$NH_4^+ + 3S° + 2H_2O \rightarrow NO_2^- + 3H_2S + 2H^+$
$NH_4^+ + 4S° + 3H_2O \rightarrow NO_3^- + 4H_2S + 2H^+$
$N_2 + SO_4^{2-} \rightarrow 2NO_2^- + S°$
$4N_2 + 3SO_4^{2-} + 4H_2O \rightarrow 8NO_2^- + 3H_2S + 2H^+$
$3N_2 + 5SO_4^{2-} + 4H^+ \rightarrow 6NO_3^- + 5S° + 2H_2O$
$4N_2 + 5SO_4^{2-} + 2H^+ + 4H_2O \rightarrow 8NO_3^- + 5H_2S$
$N_2 + 3S° + 4H_2O \rightarrow 2NO_2^- + 3H_2S + 2H^+$
$N_2 + 5S° + 6H_2O \rightarrow 2NO_3^- + 5H_2S + 2H^+$
$3NO_2^- + SO_4^{2-} + 2H^+ \rightarrow 3NO_3^- + S° + H_2O$
$4NO_2^- + SO_4^{2-} + 2H^+ \rightarrow 4NO_3^- + H_2S$
$NO_2^- + S° + H_2O \rightarrow NO_3^- + H_2S$

$2NH_4^+ + 3CO_2 \rightarrow N_2 + 3CO + 2H^+ + 3H_2O$
$8NH_4^+ + 3CO_2 \rightarrow 4N_2 + 3CH_4 + 8H^+ + 6H_2O$
$NH_4^+ + 3CO_2 \rightarrow NO_2^- + 3CO + 2H^+ + H_2O$
$4NH_4^+ + 3CO_2 + 2H_2O \rightarrow 4NO_2^- + 3CH_4 + 8H^+$
$NH_4^+ + 4CO_2 \rightarrow NO_3^- + 4CO + 2H^+ + H_2O$
$NH_4^+ + CO_2 + H_2O \rightarrow NO_3^- + CH_4 + 2H^+$
$2NH_4^+ + CO \rightarrow N_2 + CH_4 + 2H^+ + H_2O$
$NH_4^+ + CO + H_2O \rightarrow NO_2^- + CH_4 + 2H^+$
$3NH_4^+ + 4CO + 5H_2O \rightarrow 3NO_3^- + 4CH_4 + 6H^+$
$N_2 + 3CO_2 + H_2O \rightarrow 2NO_2^- + 3CO + 2H^+$
$4N_2 + 3CO_2 + 10H_2O \rightarrow 8NO_2^- + 3CH_4 + 8H^+$
$N_2 + 5CO_2 + H_2O \rightarrow 2NO_3^- + 5CO + 2H^+$
$4N_2 + 5CO_2 + 14H_2O \rightarrow 8NO_3^- + 5CH_4 + 8H^+$
$N_2 + CO + 3H_2O \rightarrow 2NO_2^- + CH_4 + 2H^+$
$3N_2 + 5CO + 13H_2O \rightarrow 6NO_3^- + 5CH_4 + 6H^+$
$NO_2^- + CO_2 \rightarrow NO_3^- + CO$
$4NO_2^- + CO_2 + 2H_2O \rightarrow 4NO_3^- + CH_4$
$3NO_2^- + CO + 2H_2O \rightarrow 3NO_3^- + CH_4$

$2NH_4^+ + 3Fe_3O_4 + 16H^+ \rightarrow N_2 + 9Fe^{2+} + 12H_2O$
$NH_4^+ + 3Fe_3O_4 + 16H^+ \rightarrow NO_2^- + 9Fe^{2+} + 10H_2O$
$NH_4^+ + 4Fe_3O_4 + 22H^+ \rightarrow NO_3^- + 12Fe^{2+} + 13H_2O$
$N_2 + 3Fe_3O_4 + 16H^+ \rightarrow 2NO_2^- + 9Fe^{2+} + 8H_2O$
$N_2 + 5Fe_3O_4 + 28H^+ \rightarrow 2NO_3^- + 15Fe^{2+} + 14H_2O$
$NO_2^- + Fe_3O_4 + 6H^+ \rightarrow NO_3^- + 3Fe^{2+} + 3H_2O$

$H_2S + CO_2 \rightarrow S° + CO + H_2O$
$4H_2S + CO_2 \rightarrow 4S° + CH_4 + 2H_2O$
$H_2S + 4CO_2 \rightarrow SO_4^{2-} + 4CO + 2H^+$
$H_2S + CO_2 + 2H_2O \rightarrow SO_4^{2-} + CH_4 + 2H^+$
$3H_2S + CO \rightarrow 3S° + CH_4 + H_2O$
$3H_2S + 4CO + 8H_2O \rightarrow 3SO_4^{2-} + 4CH_4 + 6H^+$
$S° + 3CO_2 + H_2O \rightarrow SO_4^{2-} + 3CO + 2H^+$
$4S° + 3CO_2 + 10H_2O \rightarrow 4SO_4^{2-} + 3CH_4 + 8H^+$
$S° + CO + 3H_2O \rightarrow SO_4^{2-} + CH_4 + 2H^+$

Amend et al. 2003 Geobiology

$$2NH_4^+ + 1.5O_2 \rightarrow N_2 + 2H^+ + 3H_2O$$
$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$
$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

$$H_2S + 0.5O_2 \rightarrow S° + H_2O$$
$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

$$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$$
$$S° + H_2 \rightarrow H_2S$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$$
$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$$
$$2NO_2^- + 3H_2 + 2H^+ \rightarrow N_2 + 4H_2O$$

$$3Fe^{2+} + 0.5O_2 + 3H_2O \rightarrow Fe_3O_4 + 6H^+$$
$$Fe_3O_4 + H_2 + 6H^+ \rightarrow 3Fe^{2+} + 4H_2O$$

Amend et al. 2003 Geobiology

This week read

Jelen B, Giovannelli D, Falkowski PG . 2016. The Role of Microbial Electron Transfer in the Coevolution of the Geosphere and Biosphere. Annual Review of Microbiology, 70:45–62.

DOI: 10.1146/annurev-micro-102215-095521