

# Microbial Biogeochemistry

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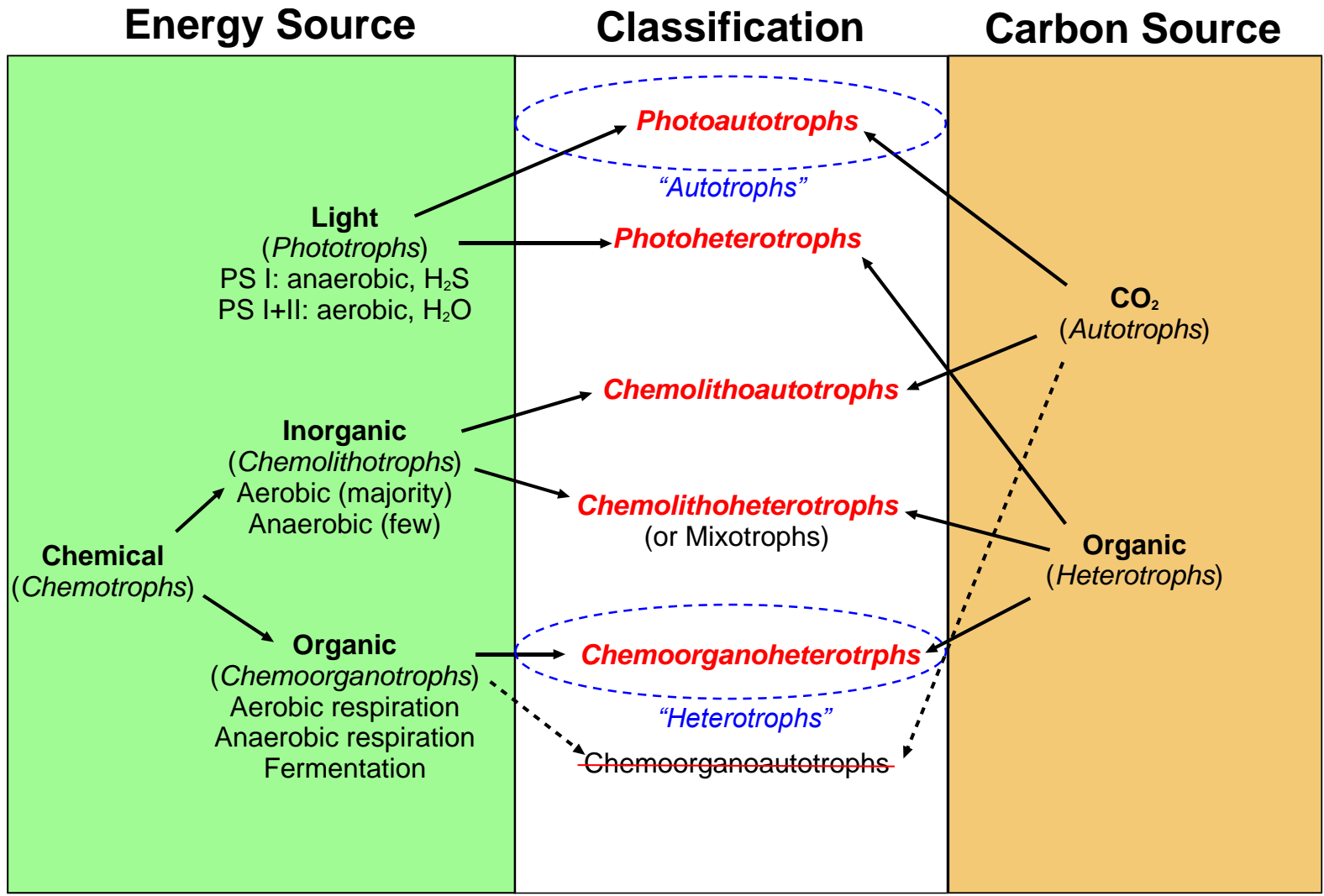
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Chemical reactions occurring in the environment mediated by microbial communities

## Outline

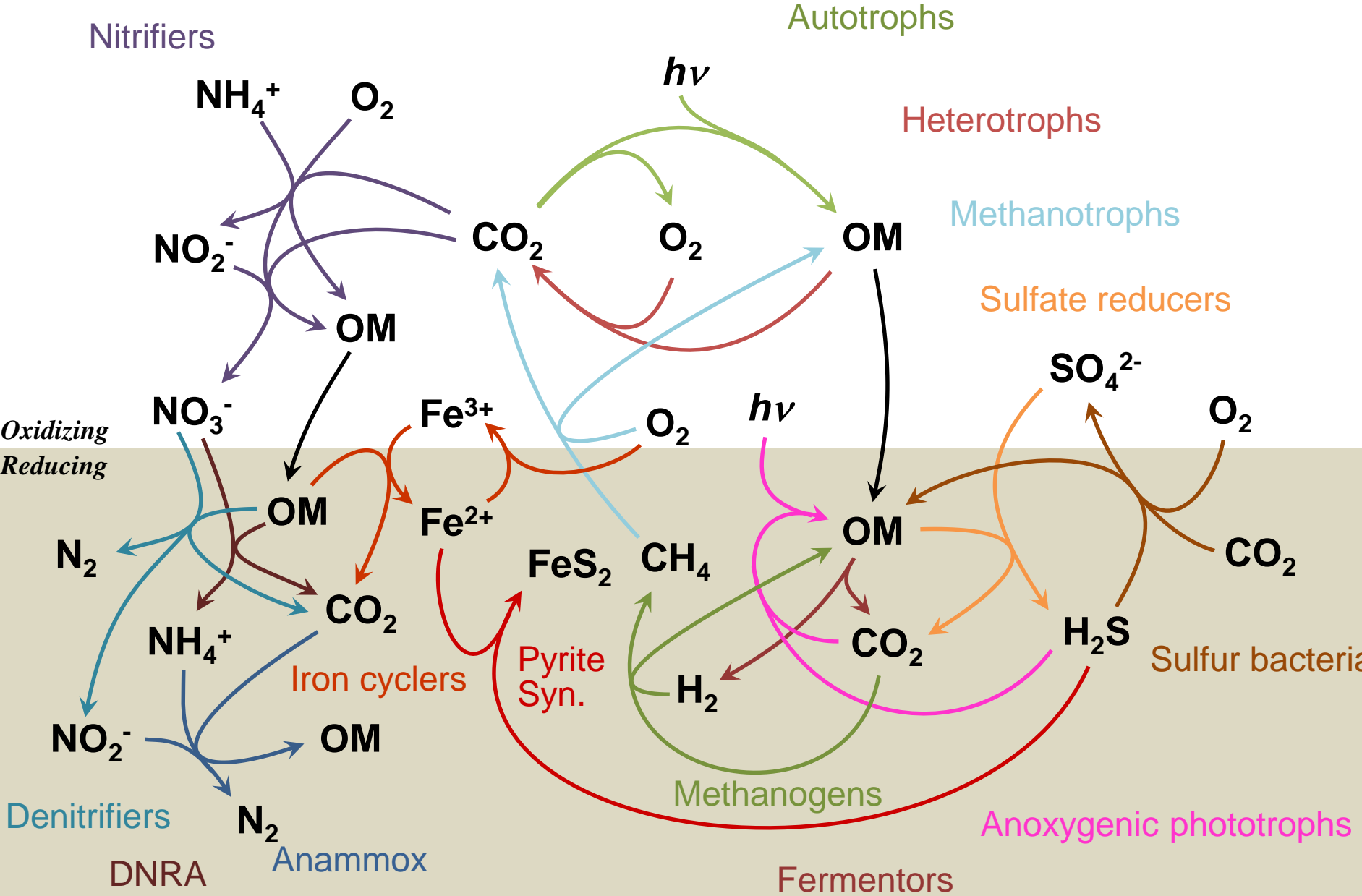
- Metabolic Classifications.
- Winogradsky columns, Microenvironments.
- Redox Reactions.
- Microbes and Processes in Winogradsky column.
- Competition and Redox cascade
- Winogradsky column biogeochemistry.
- Lab work

# Metabolic Classification of Life



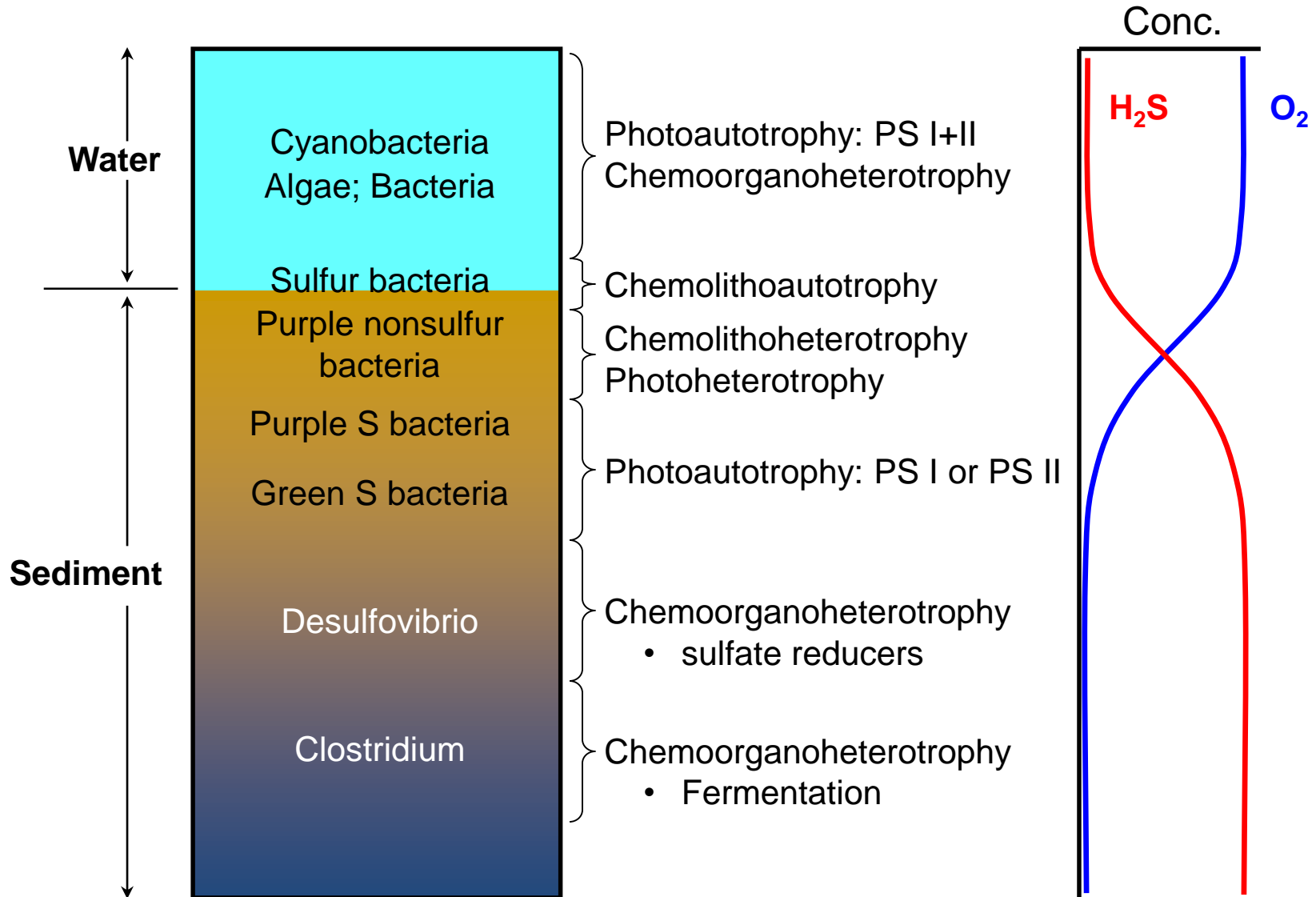
**Note, organisms that exhibit both autotrophy and heterotrophy are also called mixotrophs**

# Some Microbial Metabolic Redox Reactions



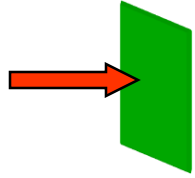
# Winogradsky Column

Microenvironments generated by chemical gradients.



# Transport Limitations; Advection

Advective transport:

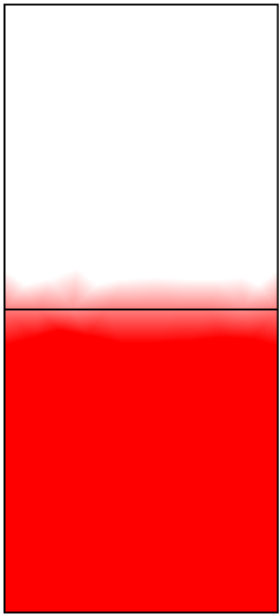


$$Flux = uC \equiv \left[ \frac{g}{m^2 s} \right]$$

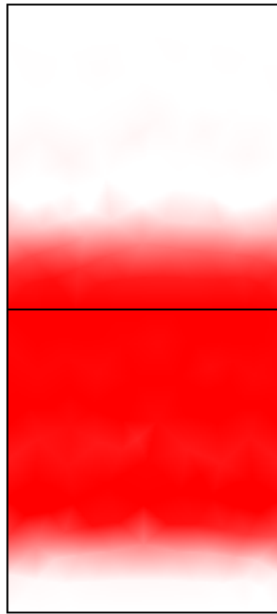
$u$ : Fluid velocity [ $m\ s^{-1}$ ]

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial z}(uC)$$

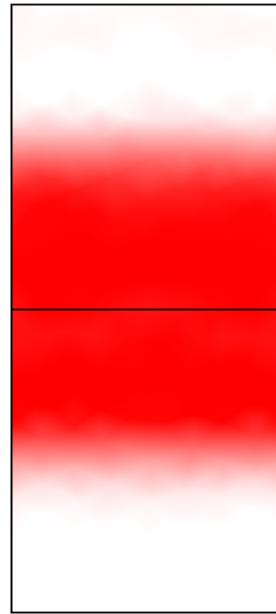
Time=0 Surface: C (C)



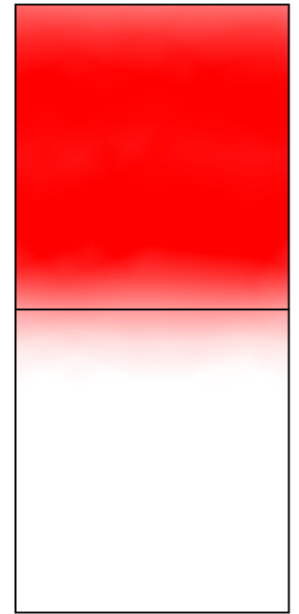
Time=0.4 Surface: C (C)



Time=1 Surface: C (C)



Time=2 Surface: C (C)

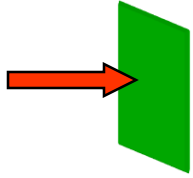


$u$



# Transport Limitations; Diffusion

Fickian Diffusion:

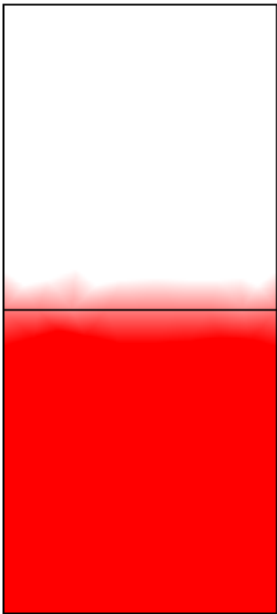


$$Flux = -D \frac{dC}{dz} \equiv \left[ \frac{g}{m^2 s} \right]$$

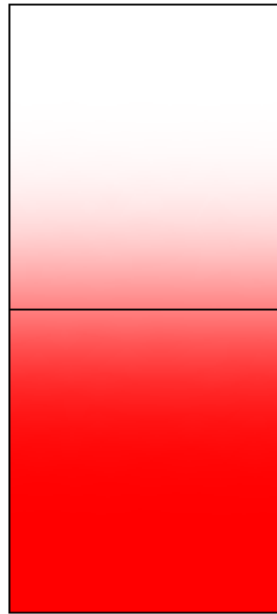
$D$ : Diffusion Coefficient [ $m^2 s^{-1}$ ]

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)$$

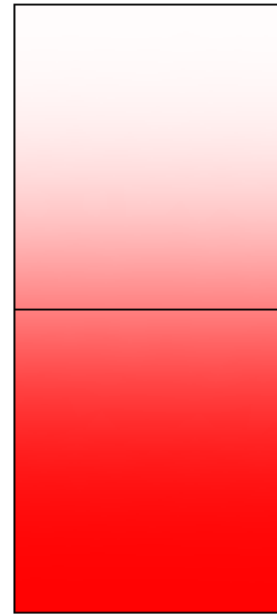
Time=0 Surface: C (C)



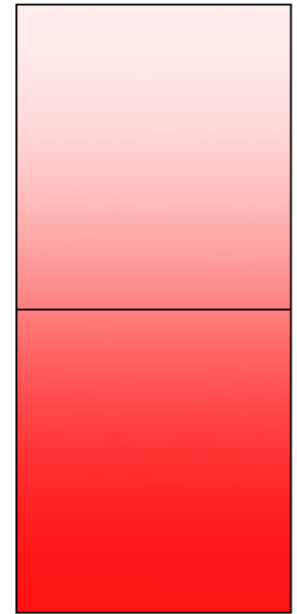
Time=0.4 Surface: C (C)



Time=1 Surface: C (C)

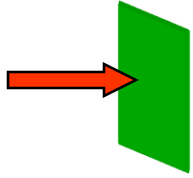


Time=2 Surface: C (C)



# Transport Limitations; Advection-Diffusion

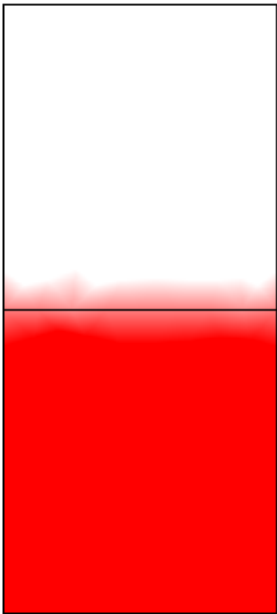
Transport by advection and diffusion:



$$\text{Flux} = -D \frac{dC}{dz} + uC \equiv \left[ \frac{g}{m^2 s} \right]$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} - uC \right)$$

Time=0 Surface: C (C)



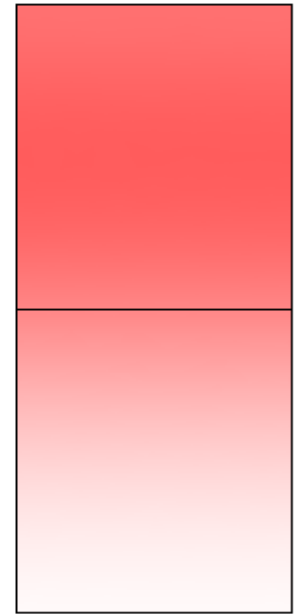
Time=0.4 Surface: C (C)



Time=1 Surface: C (C)



Time=2 Surface: C (C)

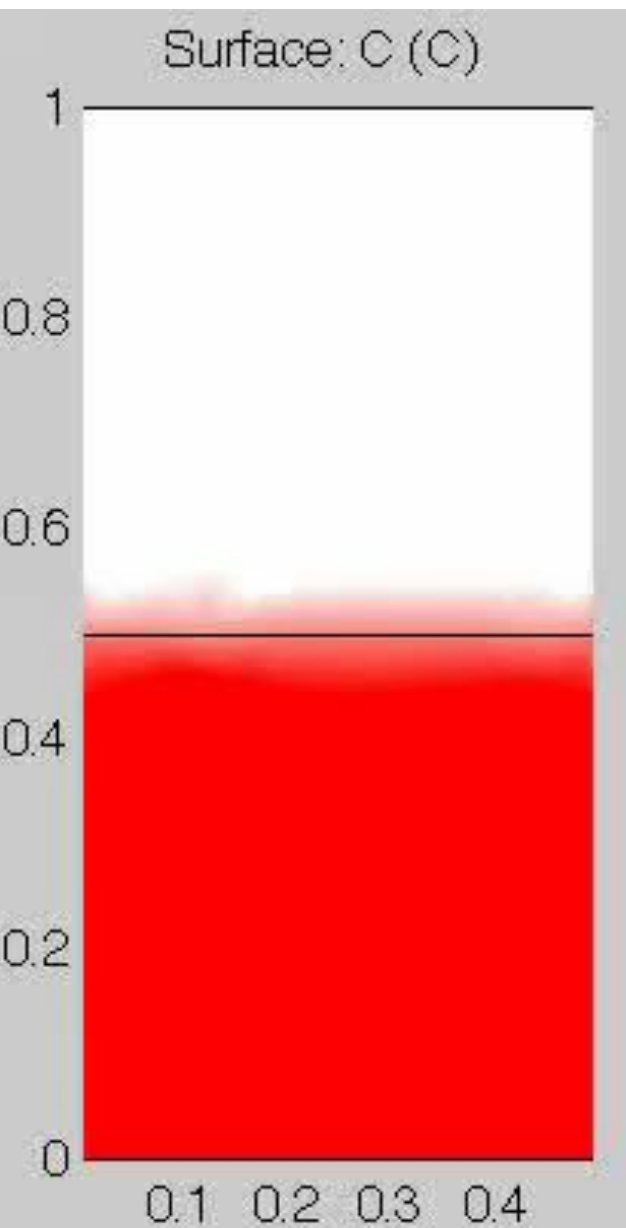


$u$

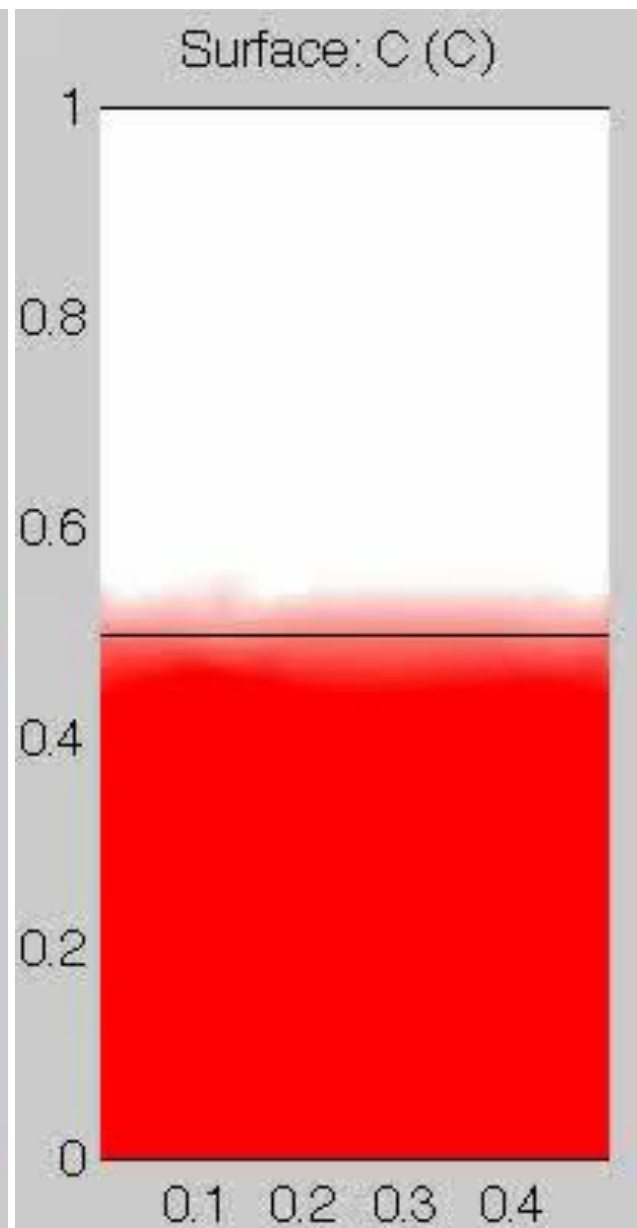


# Simulations

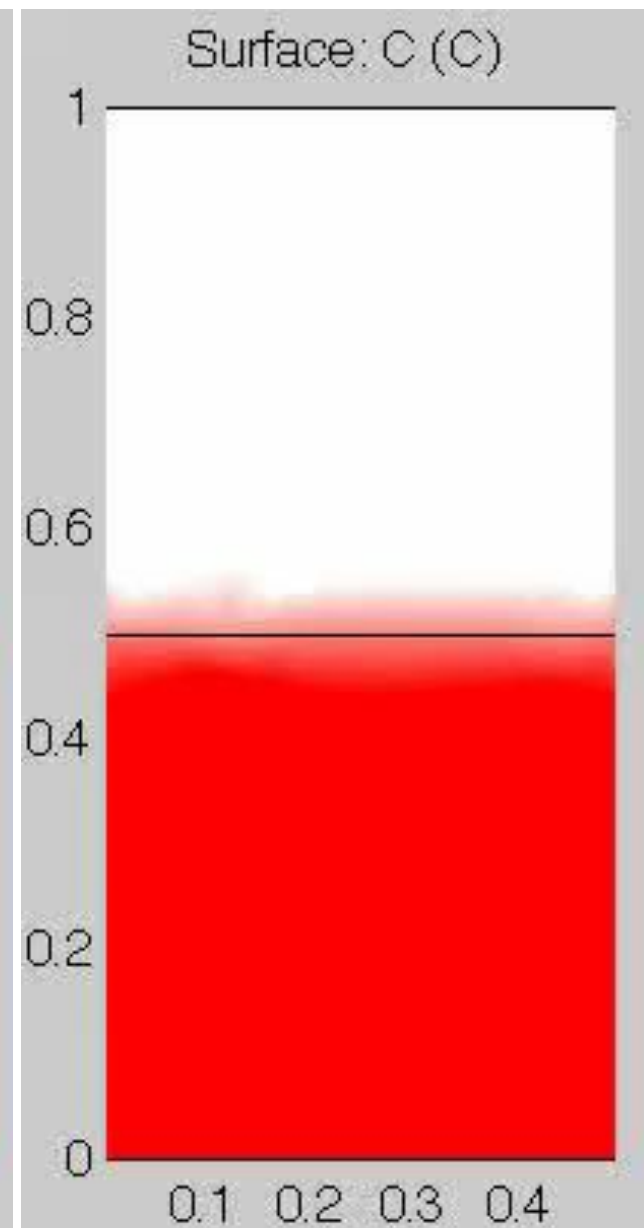
Advection



Diffusion



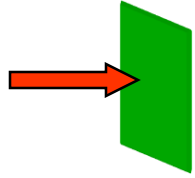
Advection & Diffusion





# Transport Limitations; Advection-Diffusion

Transport by advection and diffusion:

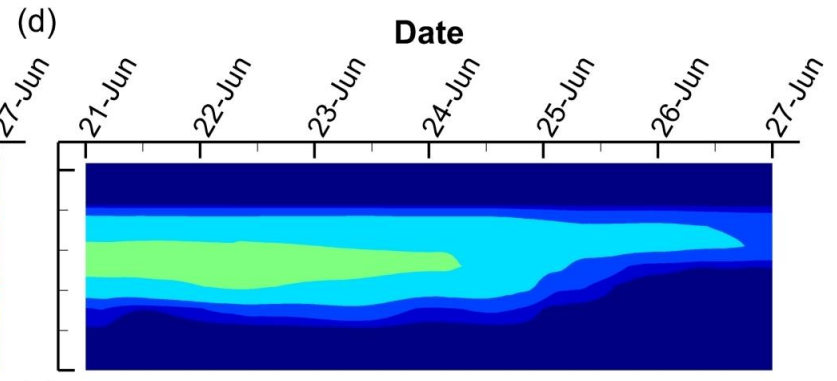
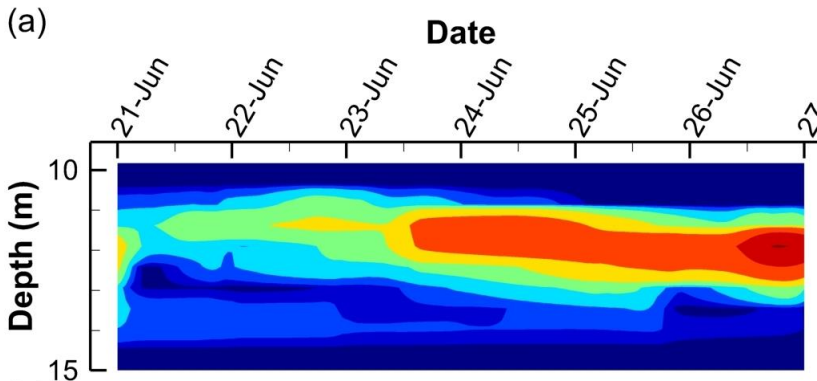
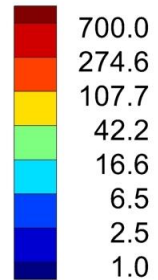


$$\text{Flux} = -D \frac{dC}{dz} + uC \equiv \left[ \frac{g}{m^2 s} \right]$$

Must also account for reactions!

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} - uC \right) + r$$

$S_{\text{GSB}}$   
( $\text{mmol m}^{-3}$ )



# Redox Reactions

Electron Tower (at pH 0) E° (mV)

**Reduction and Oxidation:**

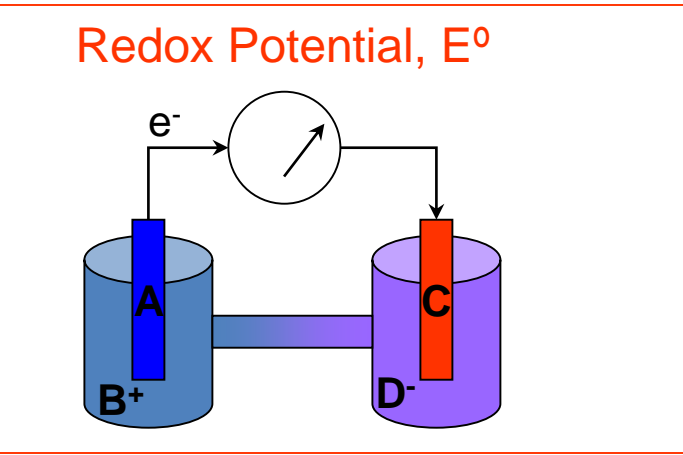
Half Reactions

A → B<sup>+</sup> + e<sup>-</sup>    Oxidation

C + e<sup>-</sup> → D<sup>-</sup>    Reduction

Complete Reaction

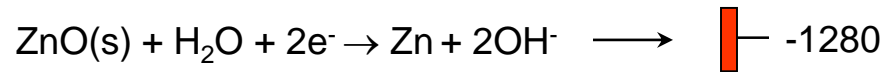
A + C → B<sup>+</sup> + D<sup>-</sup>



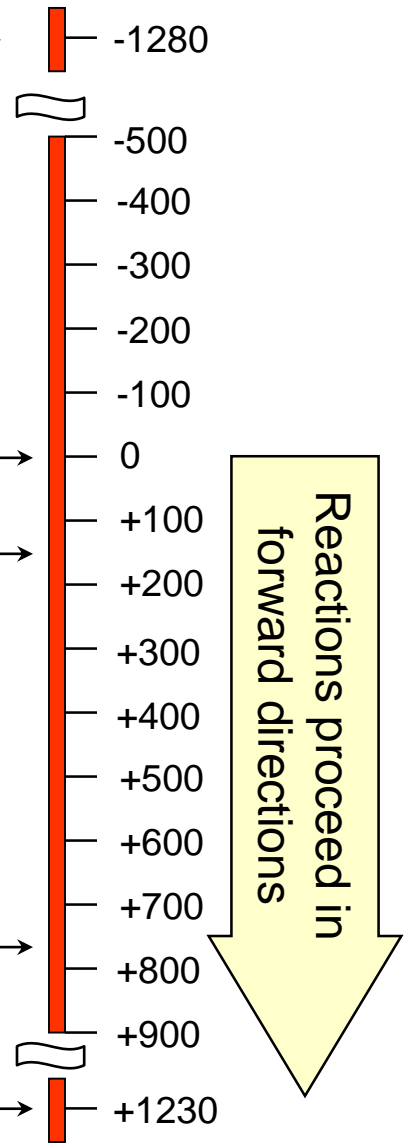
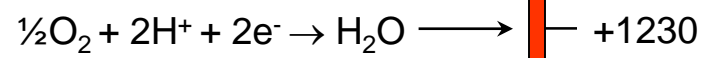
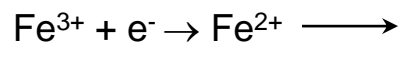
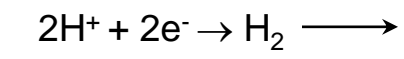
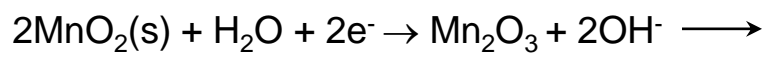
**Reference Half Reaction:**

H<sub>2</sub>(g) → 2e<sup>-</sup> + 2H<sup>+</sup>

*Reference cell always at pH 0*



Reactions always run at standard conditions, (1 M concentration and 1 atm, 25°C)



Alkaline Battery: Zn(s) + 2MnO<sub>2</sub>(s) → ZnO(s) + Mn<sub>2</sub>O<sub>3</sub>(s): E° = 1.43 V

# Redox Reactions-2

$$E_h = E^\circ - \frac{RT}{nF} \ln \frac{\prod_i [\text{Products}]_i^{\beta_i}}{\prod_j [\text{Reactants}]_j^{\alpha_j}}$$

$$E^{\circ'} = E^\circ - \frac{2.303RT}{nF} m \text{ pH}$$

$F$  = faraday (96493 Coulombs/mol)

$R$  = gas const (8.314 J/K/mol)

$m$  = no. of  $\text{H}^+$  consumed in  $\frac{1}{2}$  rxn

$n$  = no. of electrons in rxn.

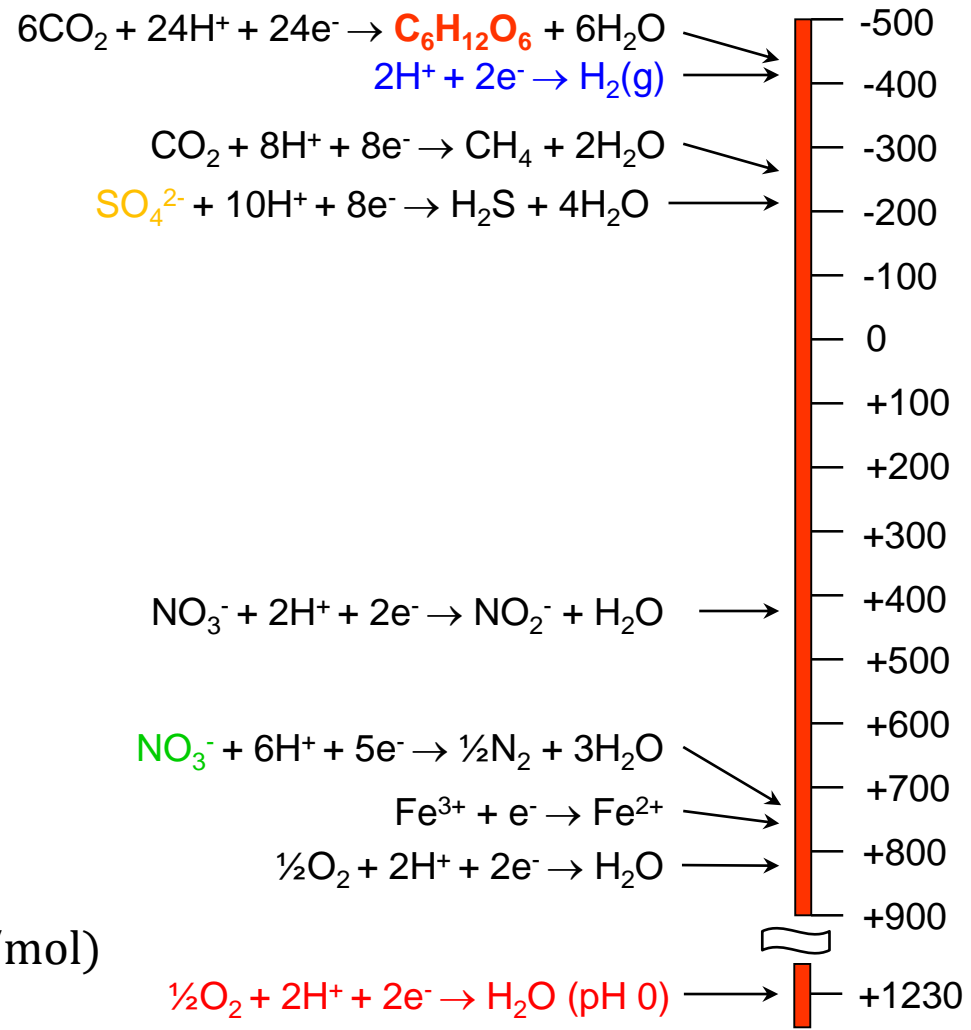
Volt =  $\text{J}/(\text{A}\cdot\text{s}) = \text{J}/\text{C}$ ;  $\text{C} \equiv \text{Coulomb}$

$$\Delta G^{\circ'} = -nE^{\circ'}F \text{ Gibbs Free Energy (kJ/mol)}$$

**Reference Half Reaction:**  
 $\text{H}_2(\text{g}) \rightarrow 2\text{e}^- + 2\text{H}^+$

*Reference cell at pH 0*

## Electron Tower (at pH 7)



Note, the number of electrons transferred does NOT change the potential or voltage

# Oxidation States and Fermentation

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## Oxidation states

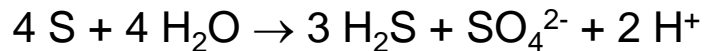
- Some (many) elements have more than one stable electron configuration.
- Consequently, an element can exist in reduced or oxidized states; e.g., Fe<sup>3+</sup> or Fe<sup>2+</sup>.

**Carbon, Nitrogen and Sulfur have several** (assume H: +1; O: -2)

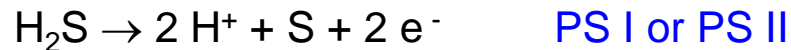
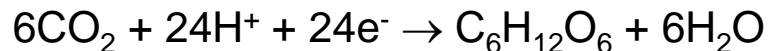
CH <sub>4</sub>	-4	N <sub>2</sub>	0	NH <sub>3</sub>	-3	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	+2
CO <sub>2</sub>	+4	NO <sub>3</sub> <sup>-</sup>	+5	H <sub>2</sub> S	-2	SO <sub>4</sub> <sup>2-</sup>	+6

## Fermentation and/or Disproportionation

- Organic carbon present, but no electron acceptors: O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, SO<sub>2</sub><sup>2-</sup>, etc.
- Use organic carbon as both electron acceptor and donor:

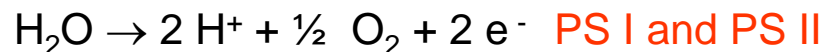


## Autotrophy



PS I or PS II

Anoxygenic Photosynthesis



PS I and PS II

Oxygenic Photosynthesis

# Photosystem I Only

Energy production only  
(cyclic photophosphorylation)

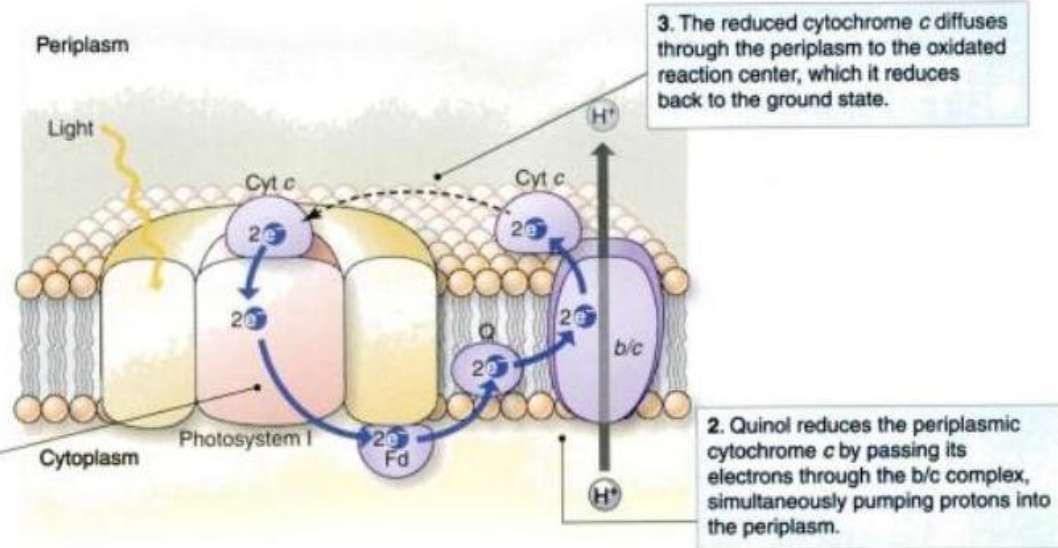


FIGURE 8.15 Cyclic photophosphorylation in type I photosynthesis.

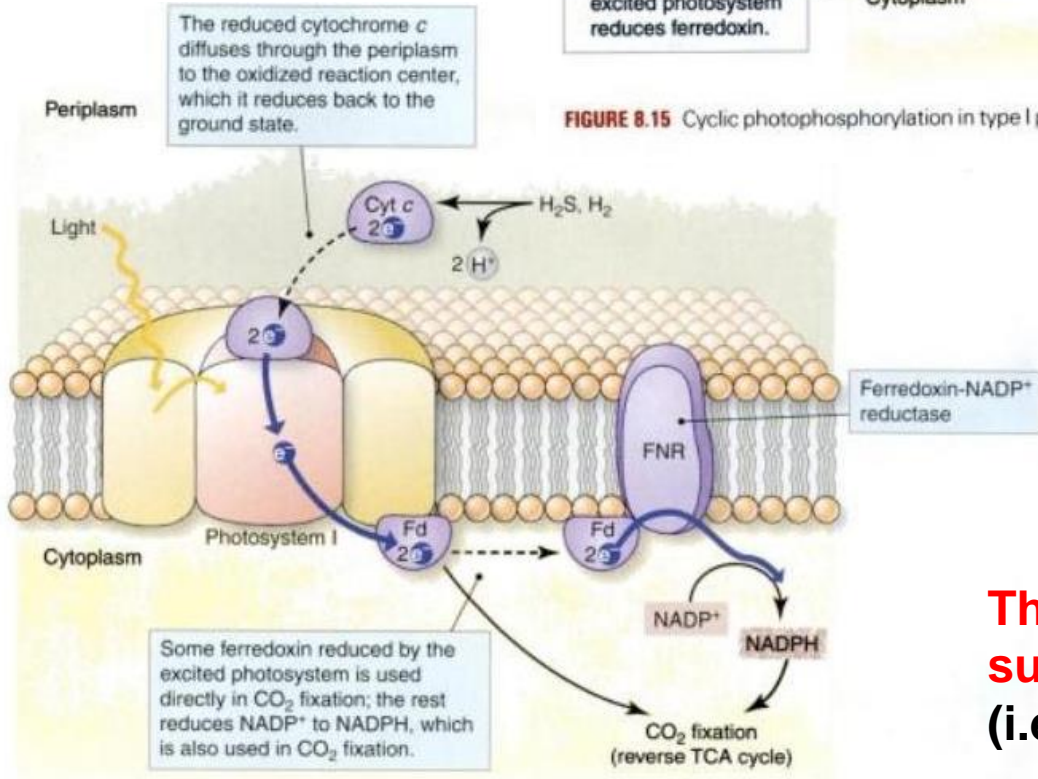


FIGURE 8.16 Noncyclic photophosphorylation in type I photosynthesis.

NADPH production only  
needed to reduce CO<sub>2</sub>

**These occur in the green and purple sulfur bacteria (i.e., your Winogradsky columns)**



# Photosystem II Only

These occur in the green and purple non-sulfur bacteria

Energy production only  
(cyclic photophosphorylation)

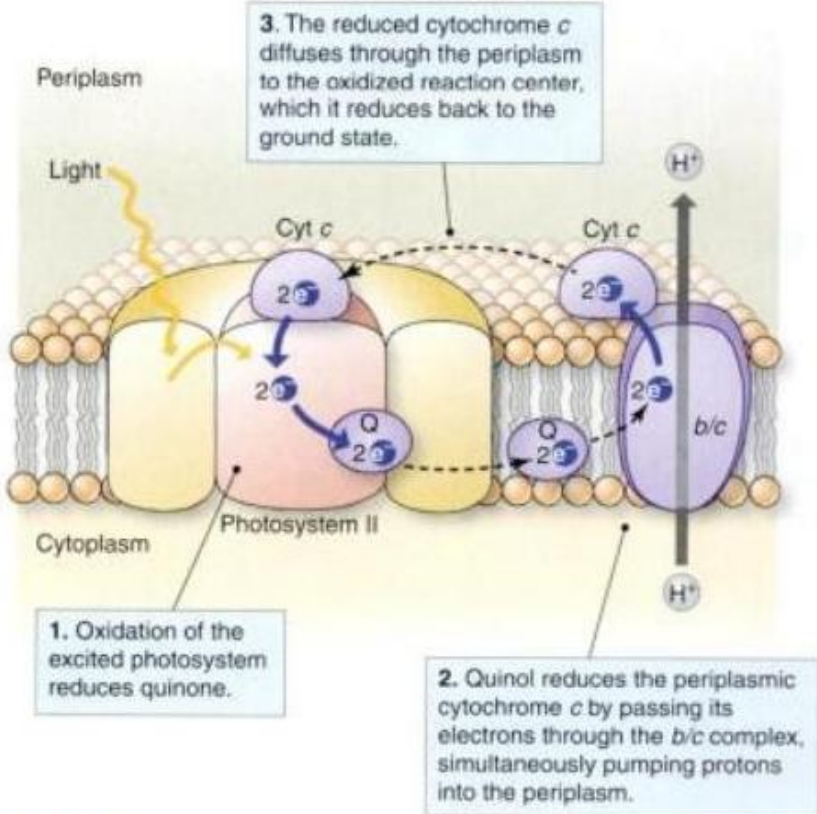


FIGURE 8.17 Cyclic photophosphorylation in type II photosynthesis.

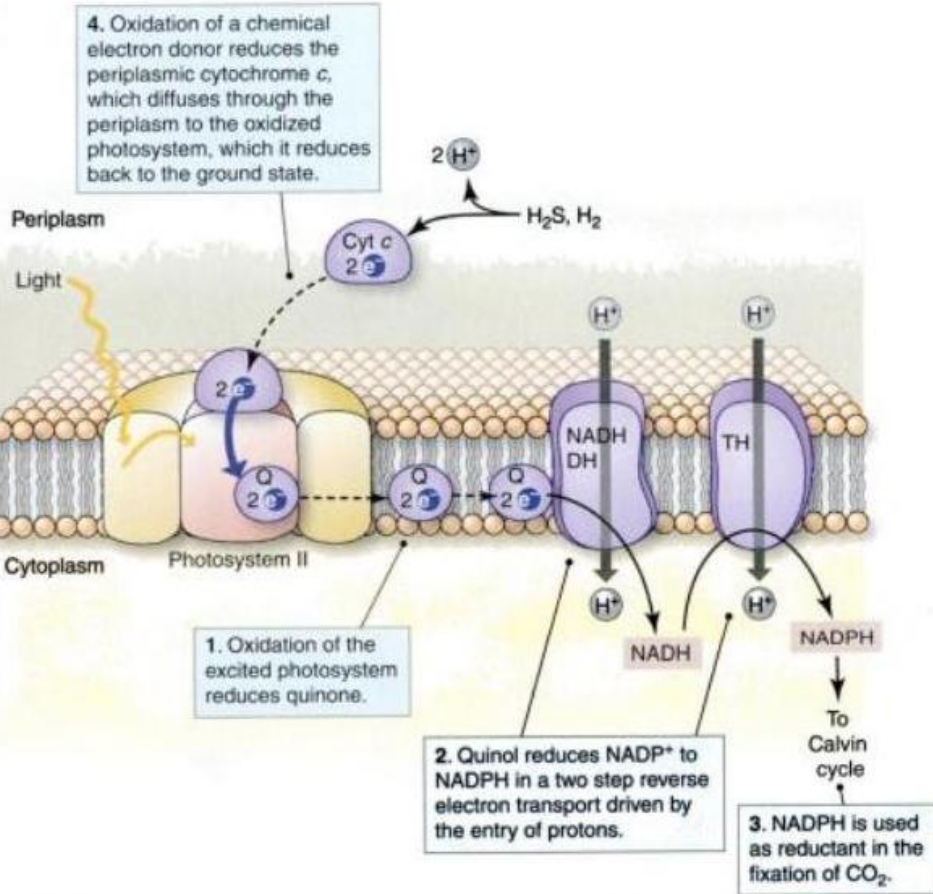


FIGURE 8.18 Noncyclic photophosphorylation in type II photosynthesis.

NADPH production only  
needed to reduce CO<sub>2</sub>

# Photosystem I+II

These occur in the cyanobacteria, algae and plants.

Energy production only  
(cyclic photophosphorylation)

NADPH production only  
needed to reduce CO<sub>2</sub>

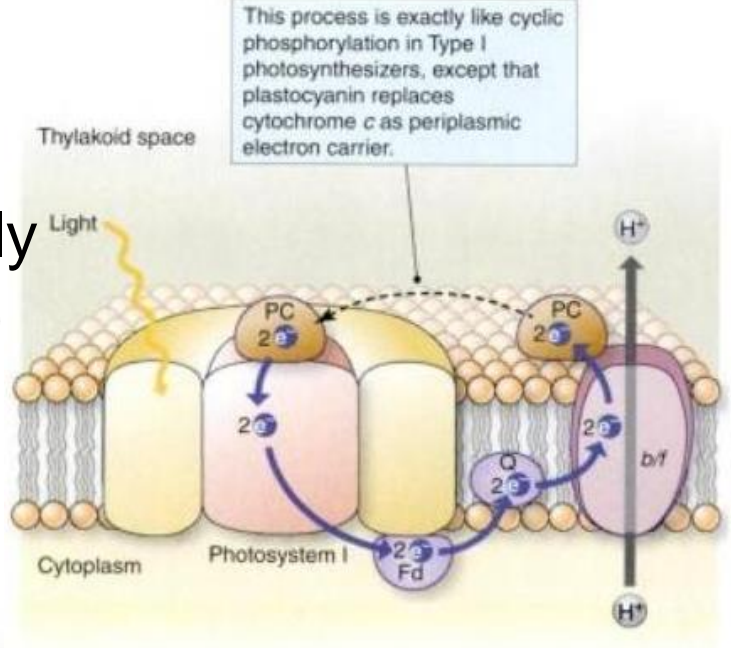


FIGURE 8.19 Cyclic photophosphorylation in cyanobacterial photosynthesis.

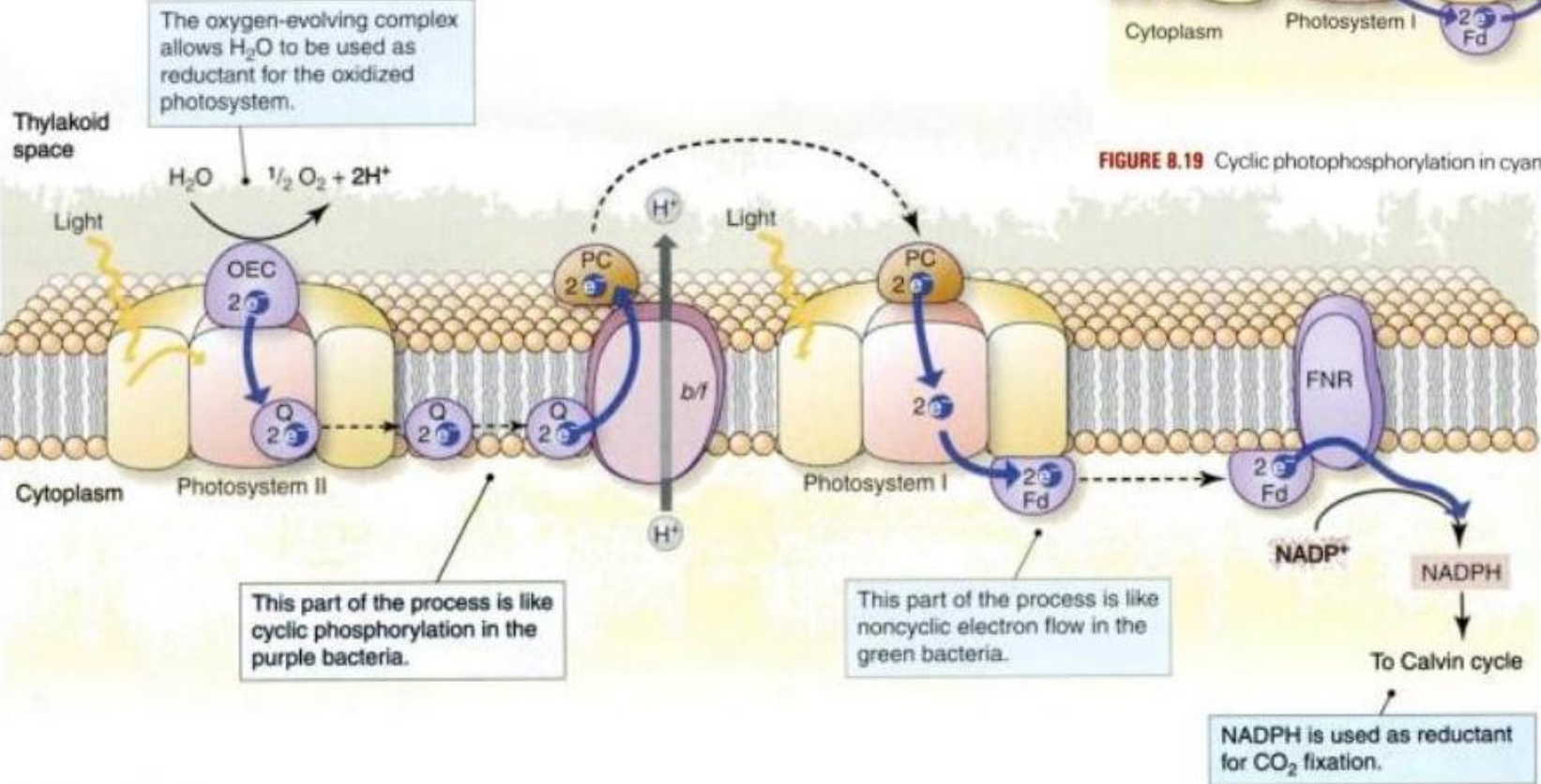
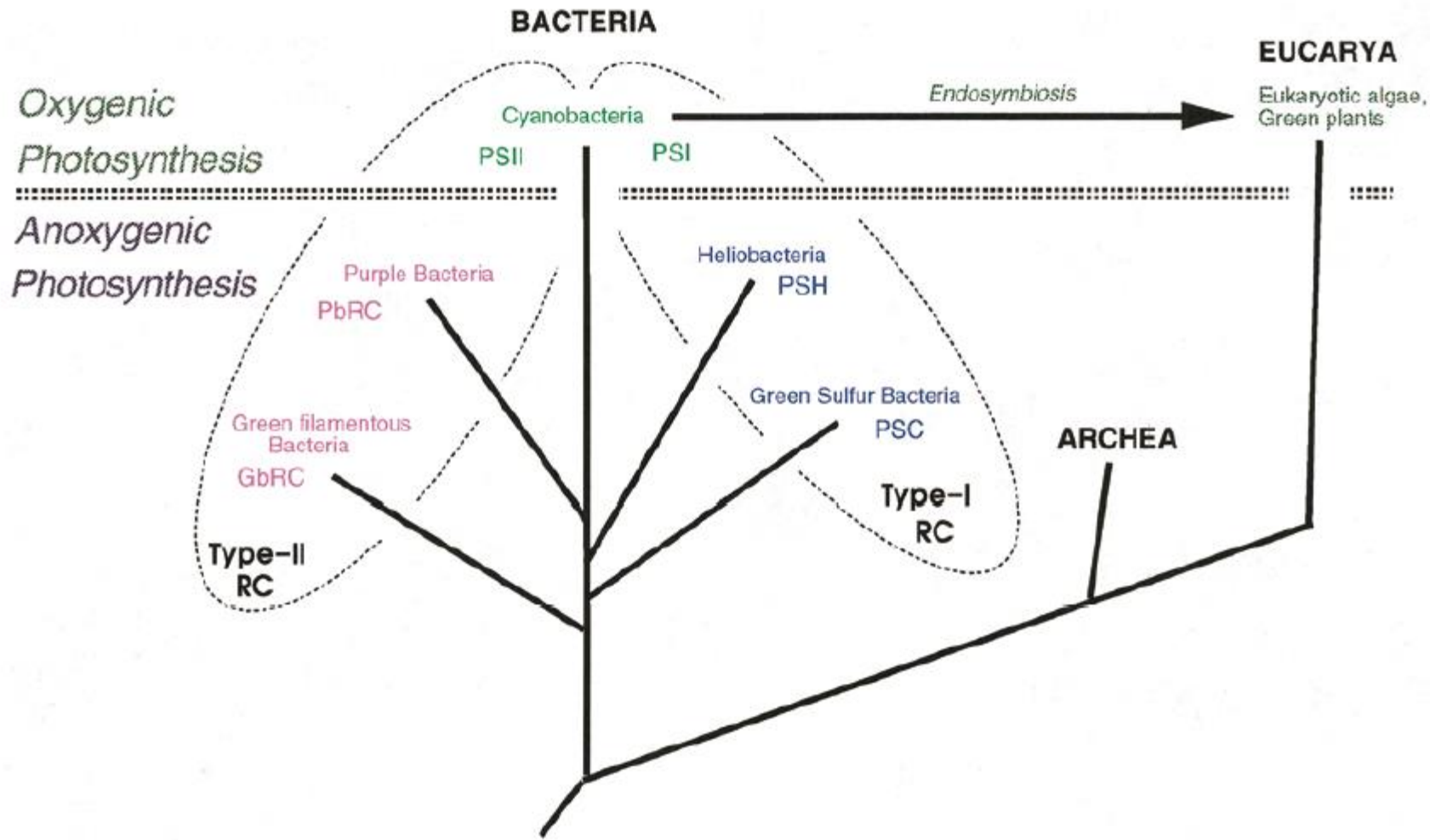


FIGURE 8.20 Noncyclic photophosphorylation in cyanobacteria.

(Principles of Modern Microbiology, M. Wheelis)

# Phylogeny of PS I and II





# Microbes and Processes in Winogradsky column.

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## Aerobic Environment

- Algae and cyanobacteria (photoautotrophy using PS II)
- Bacteria and eukaryotes respiring (chemoorganoheterotrophy).
- Sulfide oxidizers (or sulfur bacteria):  $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S}$  or  $\text{SO}_4^{2-}$ 
  - Some use  $\text{CO}_2$  (chemolithoautotrophs), others use organic compounds (chemolithoheterotrophs)
  - Examples, *Thiobacillus* sp. And *Beggiatoa* sp.
- Methanotrophs:  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  (chemoorganoheterotrophs)
  - Example, *Ralstonia* sp., *Pseudomonas* sp.

## Anaerobic Environment

### Fermentors (chemoorganoheterotrophs)

- Break down cellulose, etc. and ferment sugars into:
  - alcohols
  - organic acids
  - acetate
  - hydrogen
- Many bacterial groups can conduct fermentation, but not all of these have the ability to decompose polymeric compounds such as cellulose.
- Example, *Clostridium* species

# Anaerobic Environments, Continued

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## Sulfur Compounds

- **Sulfate reducers:** use sulfate,  $\text{SO}_4^{2-} + \text{e}^- \rightarrow \text{S}$  or  $\text{H}_2\text{S}$ , to oxidize organic compounds produced by fermentors. (**chemoorganoheterotrophs**).
  - Many genera of bacteria. Example, *Desulfovibrio* sp.
- **Phototrophic bacteria:** Use light and  $\text{H}_2\text{S}$  as electron donor (PS I) (**photoautotrophs**).
  - Examples, purple and green sulfur bacteria.

## Methanogens and Acetogens

- **Methanogens:**  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$  (**chemolithoautotrophs**)  
 $\text{Acetate}^- + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^-$  (**chemoorganoheterotrophs**)
  - Example: *Methanobacterium* (Archaea)
- **Acetogens:**  $2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$  (**chemolithoautotrophs**)
  - Example: *Homoacetogens*

# Other possible microbes

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## Aerobic Environments

### Hydrogen

- **Hydrogen oxidizers:**  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  (both **chemolithoheterotrophs** and **chemolithoautotrophs**). However, it is unlikely that  $\text{H}_2$  will make it to the aerobic interface (it will be used in the anaerobic environment first)
  - Example, *Ralstonia eutrophus*

### Iron

- **Iron oxidizers:**  $\text{Fe}^{2+} + \text{H}^+ + \frac{1}{4}\text{O}_2 \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O}$  (**chemolithoautotrophs**)  
Occurs only at low pH (~2)
  - Example: *Thiobacillus ferrooxidans*

### Ammonium

- **Nitrifiers:**  
 $\text{NH}_3 + 1\frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}^+ + \text{H}_2\text{O}$   
 $\text{NO}_2^- + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_3^-$ 
  - Example: *Nitrosomonas* and *Nitrobacter*, respectively. Both **chemolithoautotrophs**.

## Anaerobic Environments

### Nitrate

- **Denitrifiers:**  $\text{NO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{N}_2 + 3\text{H}_2\text{O}$ 
  - Reaction combined with oxidation of organic matter.

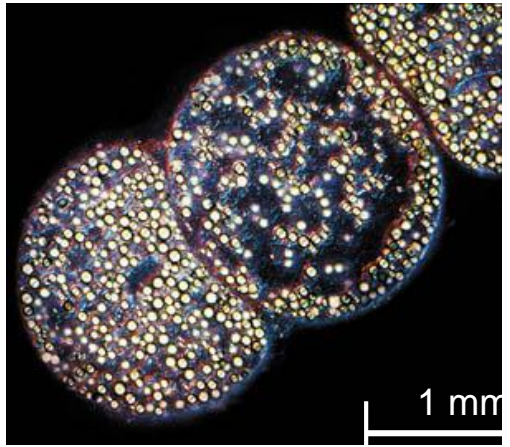
### Iron

- **Iron reducers:** Many organisms can utilize  $\text{Fe}^{3+}$  as electron acceptor.

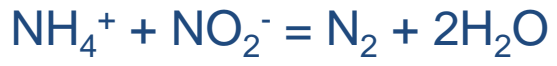
# Chemical Potential Exploitation

## H<sub>2</sub>S oxidation by NO<sub>3</sub><sup>-</sup>

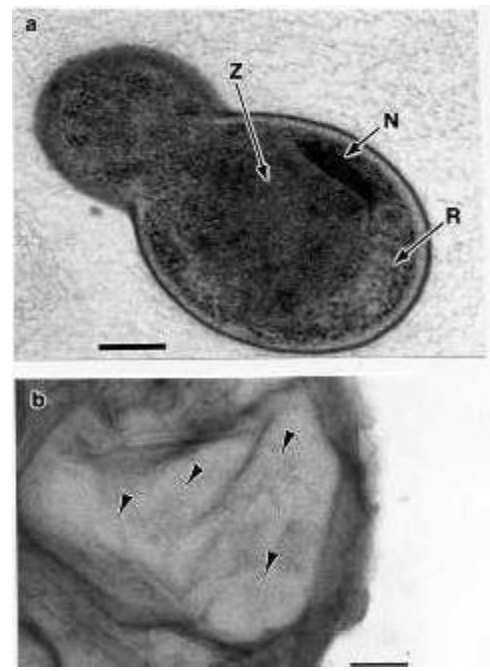
Schulz et al. 1999:  
*Thiomargarita namibiensis*



## Anammox

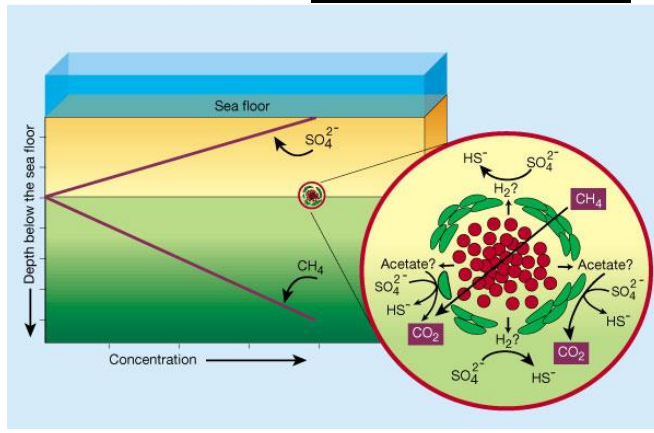
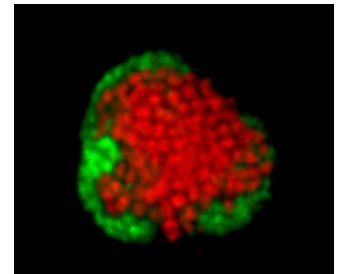


Strous et al. 1999:  
Planctomycete

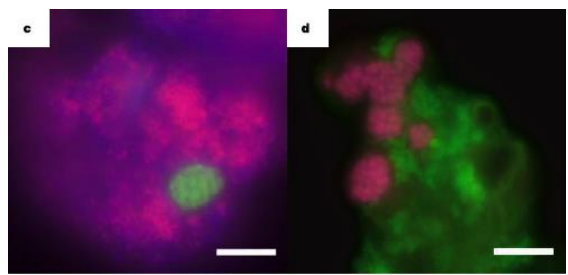
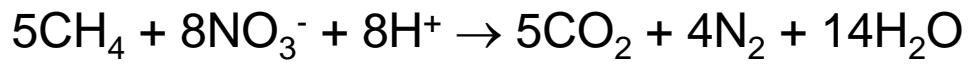


## CH<sub>4</sub> oxidation by SO<sub>4</sub><sup>2-</sup>

Boetius et al. 2000:



## CH<sub>4</sub> oxidation by NO<sub>3</sub><sup>-</sup> (Raghoebarsing et al. 2006)



# Competition and Redox cascade

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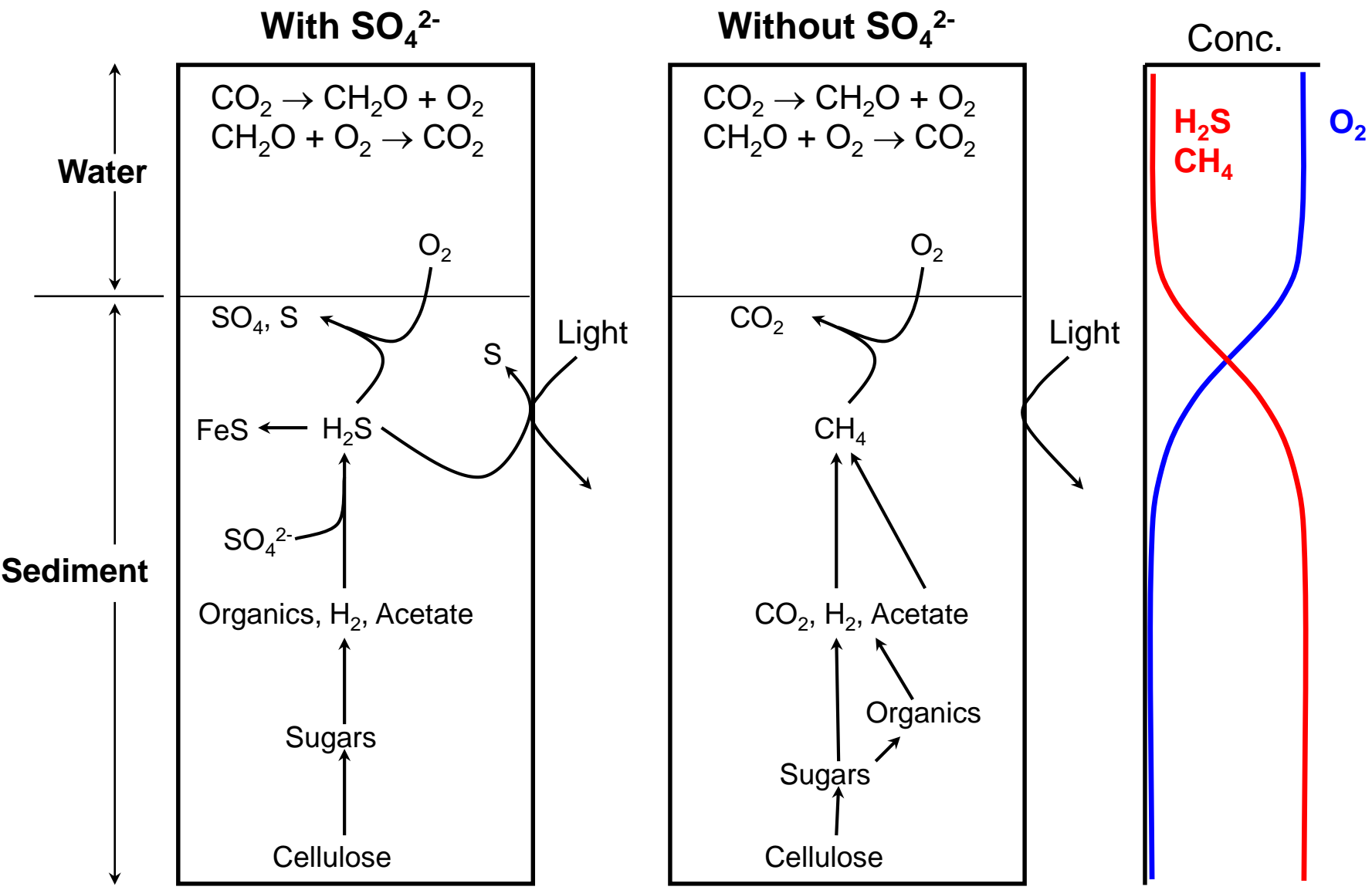
How do the chemical gradients arise in the Winogradsky column, or in natural environments?

Bacteria that are able to use the most energetic reactions in their surrounding environment will dominate that microenvironment. Transport combined with the microbial sources and sinks will determine the resulting chemical gradients. Chemical gradients can be transient as substrates are exhausted or products become toxic. This leads to succession.

Energetics are governed by the redox potentials of the possible reactions:

- Electron acceptors:  $O_2 > NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2-} > CO_2 > \text{Fermentation}$

# Winogradsky column biogeochemistry



# Laboratory Work

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**Tuesday:** Measure methane profiles in columns using gas chromatogram.

**Thursday:** Measure hydrogen sulfide profiles in columns using spectrometer assay.

**What's that smell?**  
The four main odor molecules found in human waste

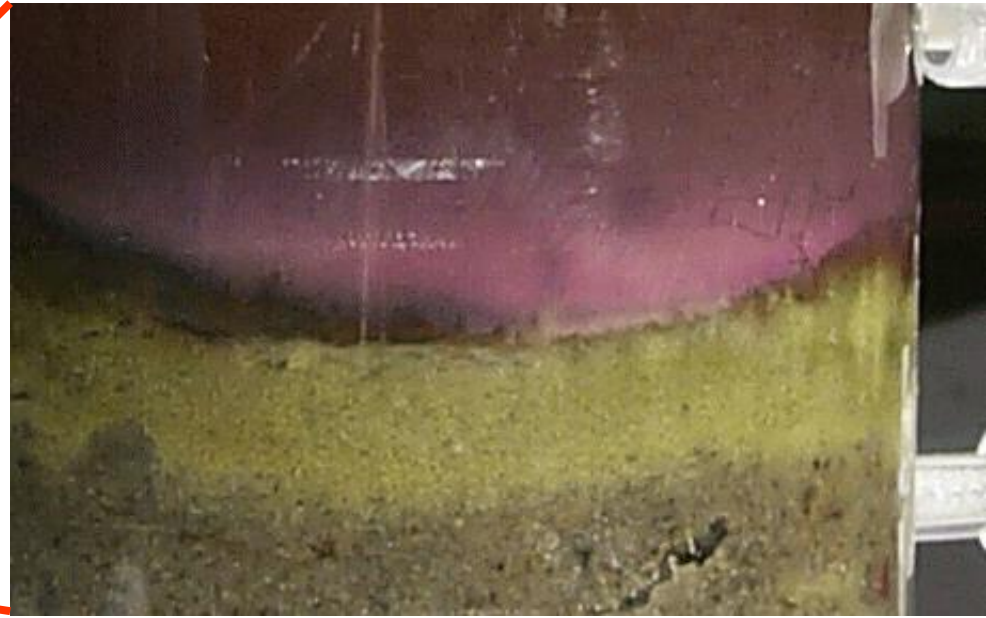
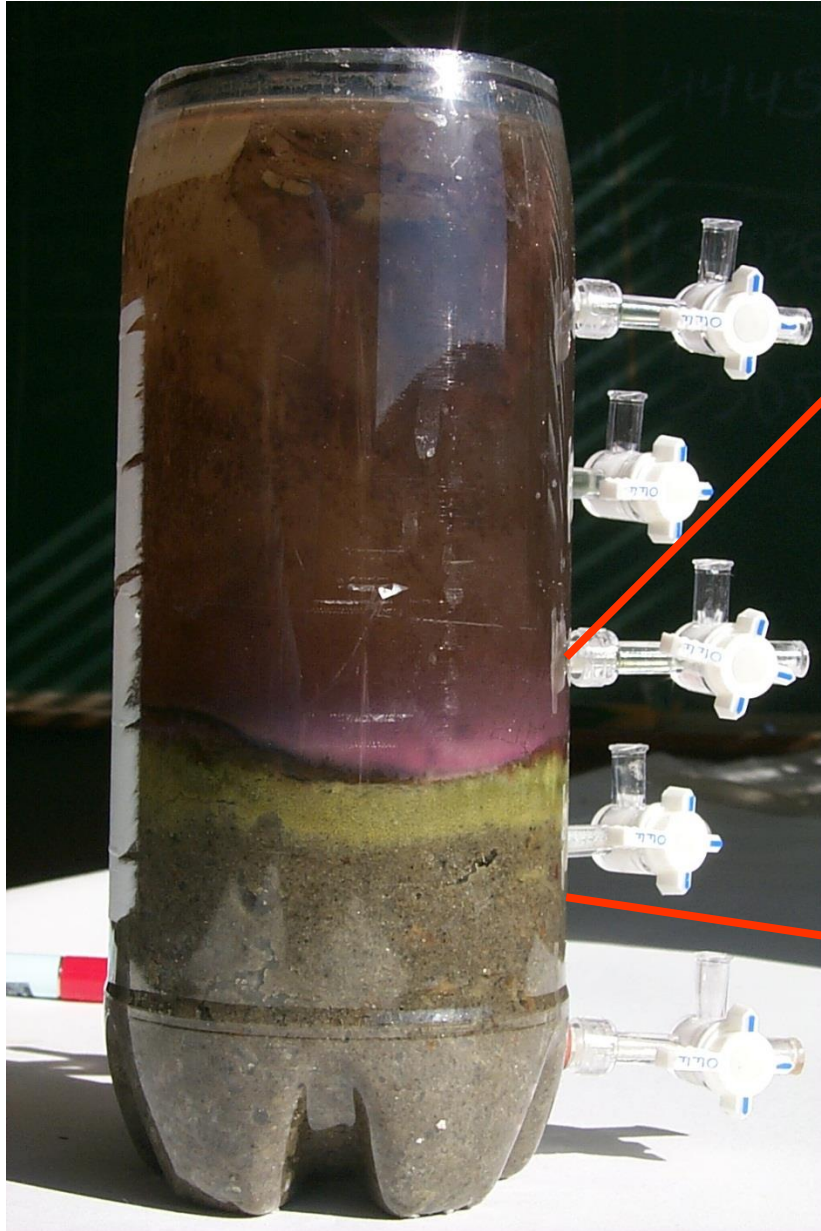
gates notes

<chem>c1ccc2c(c1)c[nH]2</chem> indole feces smell	<chem>Oc1ccc(C)cc1</chem> p-cresol barnyard smell	<chem>CCCC(=O)O</chem> butyric acid vomit smell	<chem>CSSC</chem> dimethyl trisulfide sewage smell
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Source: Environmental Science & Technology



# Winogradsky Column from 1999 Class





# Winogradsky Column from 2011 Class



Saltwater with rice as carbon

Note inversion of green and purple sulfur bacteria

