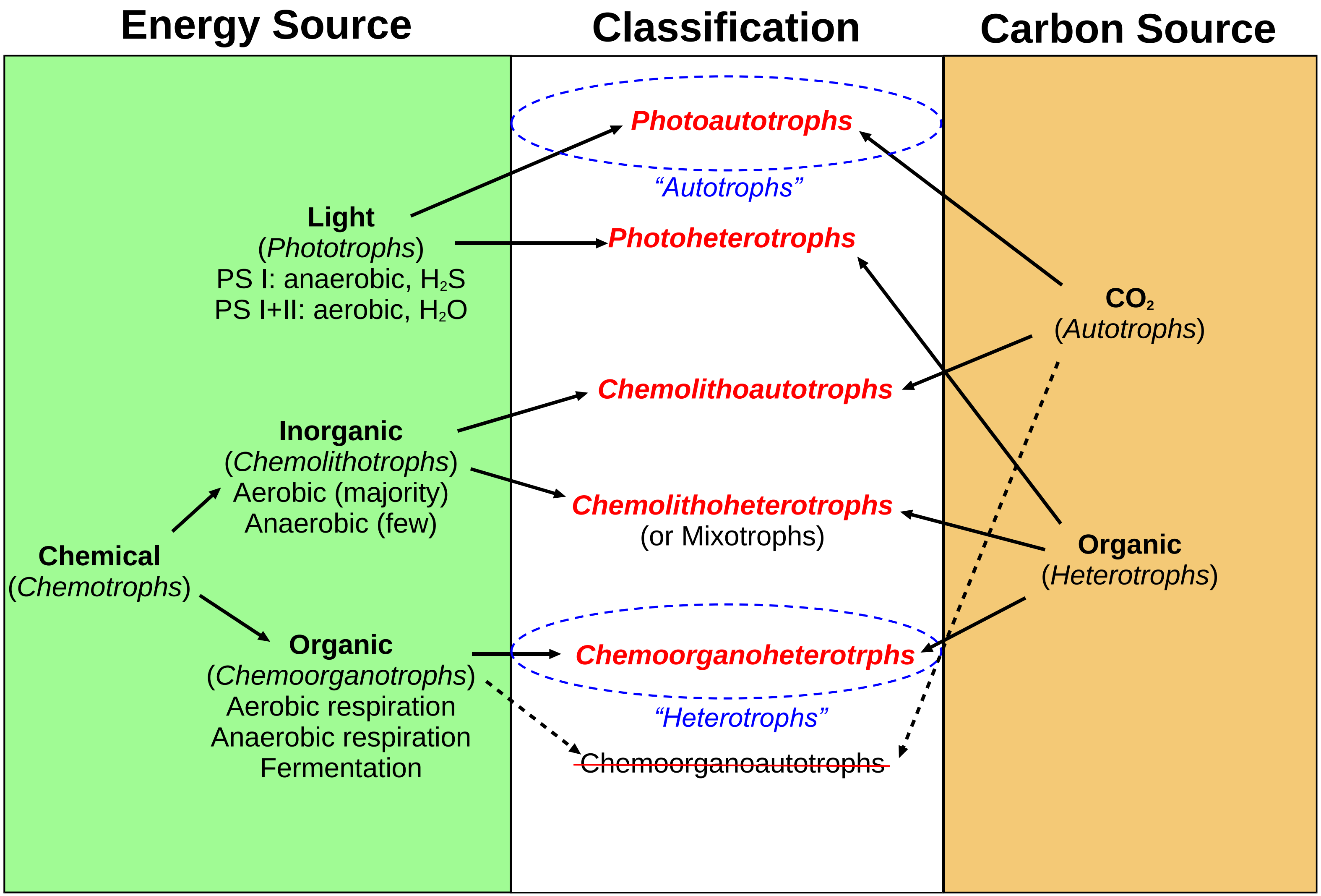
Microbial Biogeochemistry

Chemical reactions occurring in the environment mediated by microbial communities

Outline

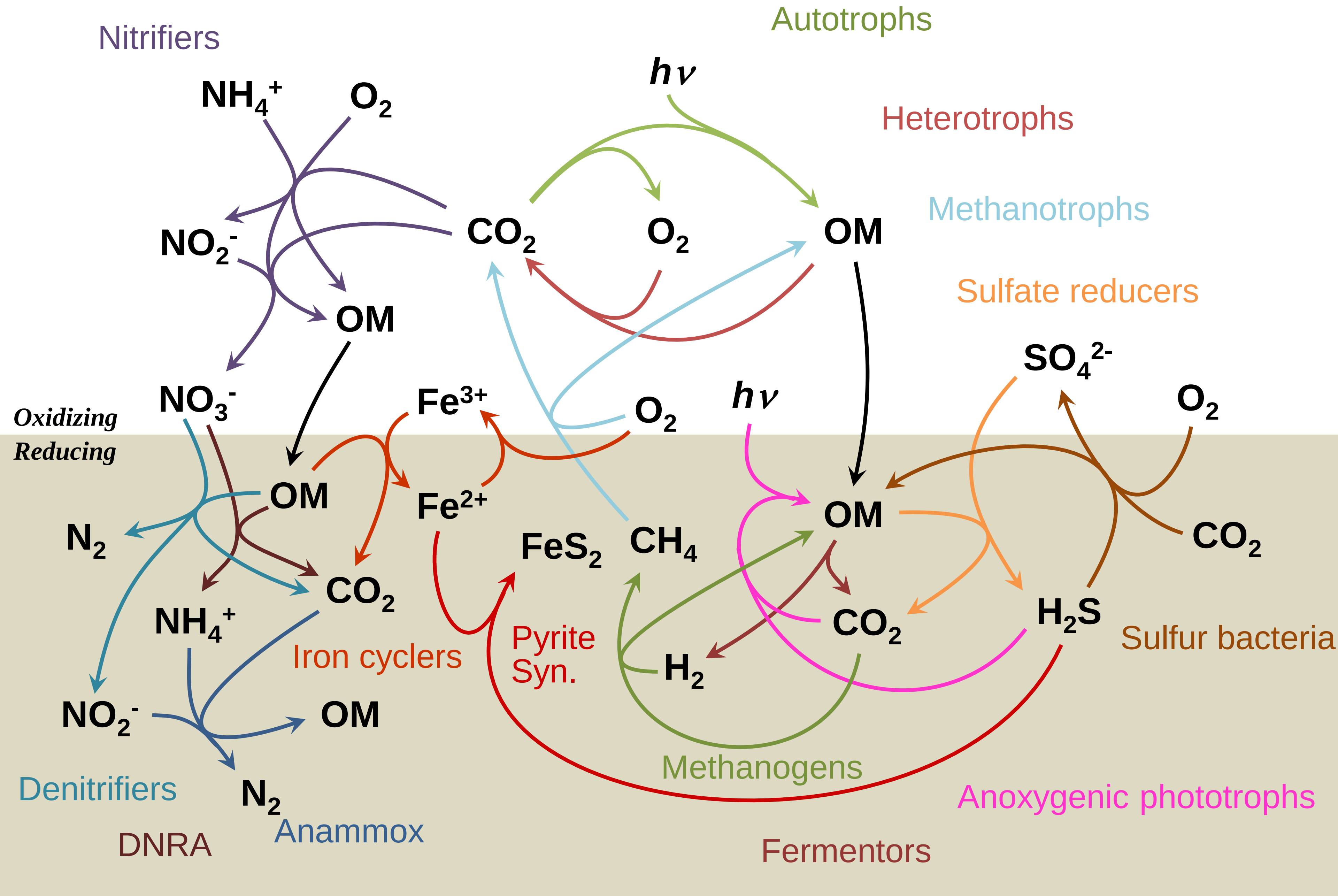
- Metabolic Classifications.
- Winogradsky columns, Microenvironments.
- Redox Reactions.
- Microbes and Processes in Winogradsky column.
- Competition and Redox cascade
- Winogradsky column biogeochemistry.
- Lab work

Metabolic Classification of Life



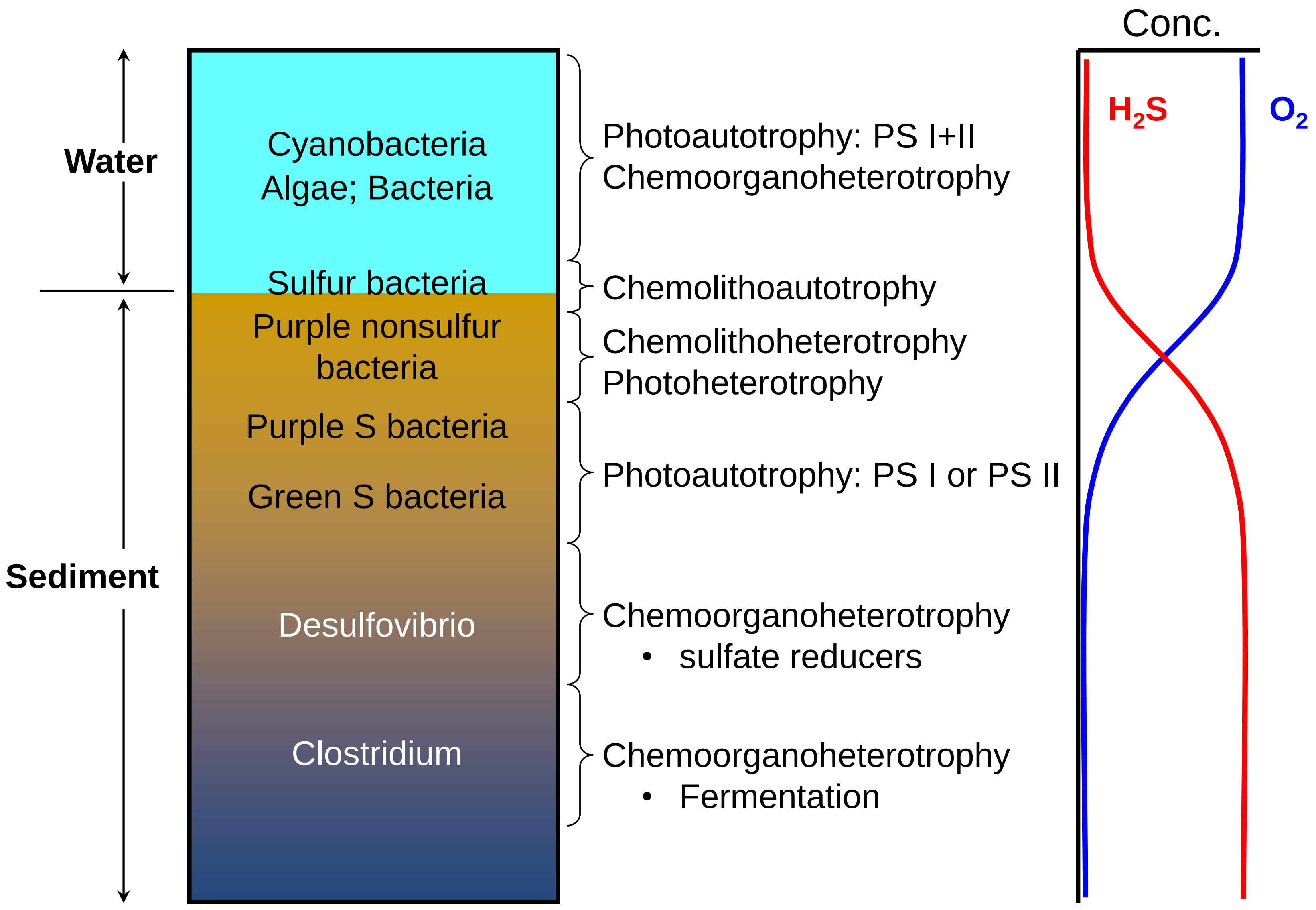
Note, organisms that exhibit both autotrophy and heterotrophy are also called mixotrophs

Some Microbial Metabolic Redox Reactions



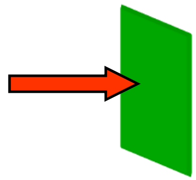
Winogradsky Column

Microenvironments generated by chemical gradients.



Transport Limitations; Advection

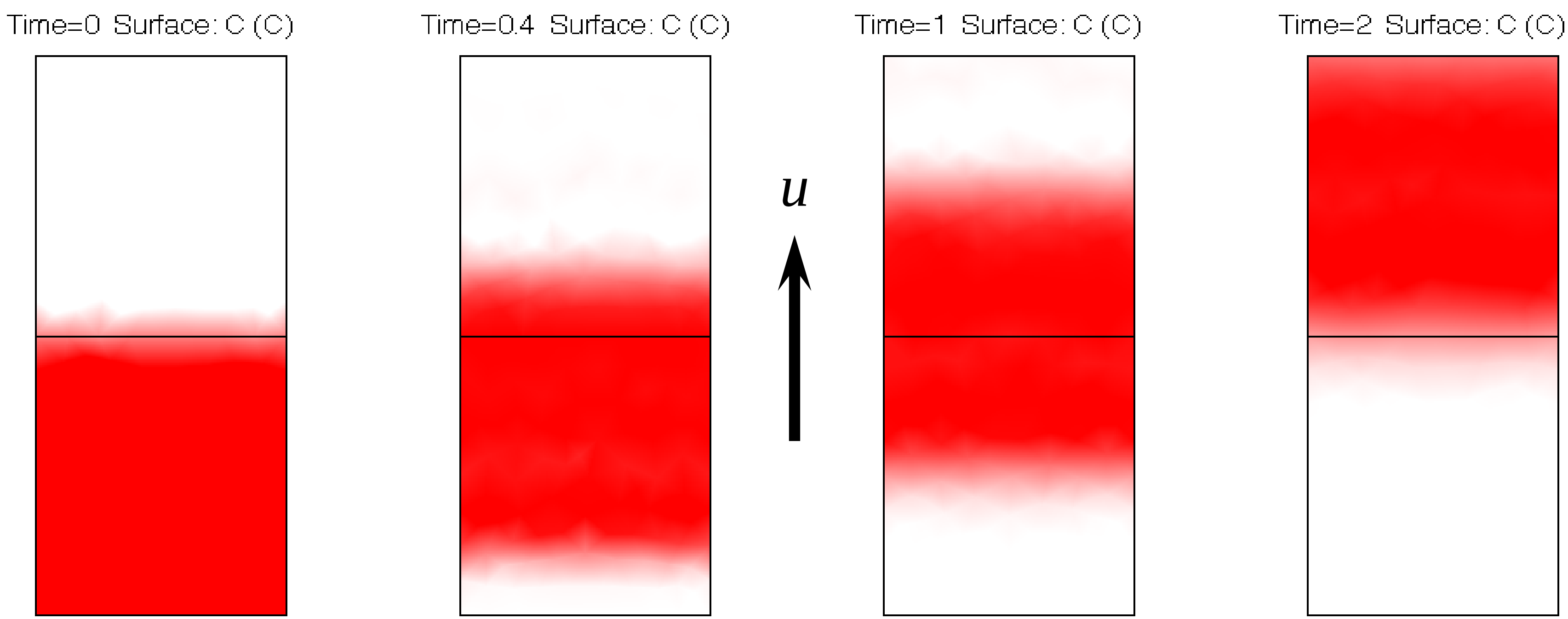
Advective transport:



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

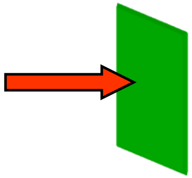
u: Fluid velocity [m s^{-1}]

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



Transport Limitations; Diffusion

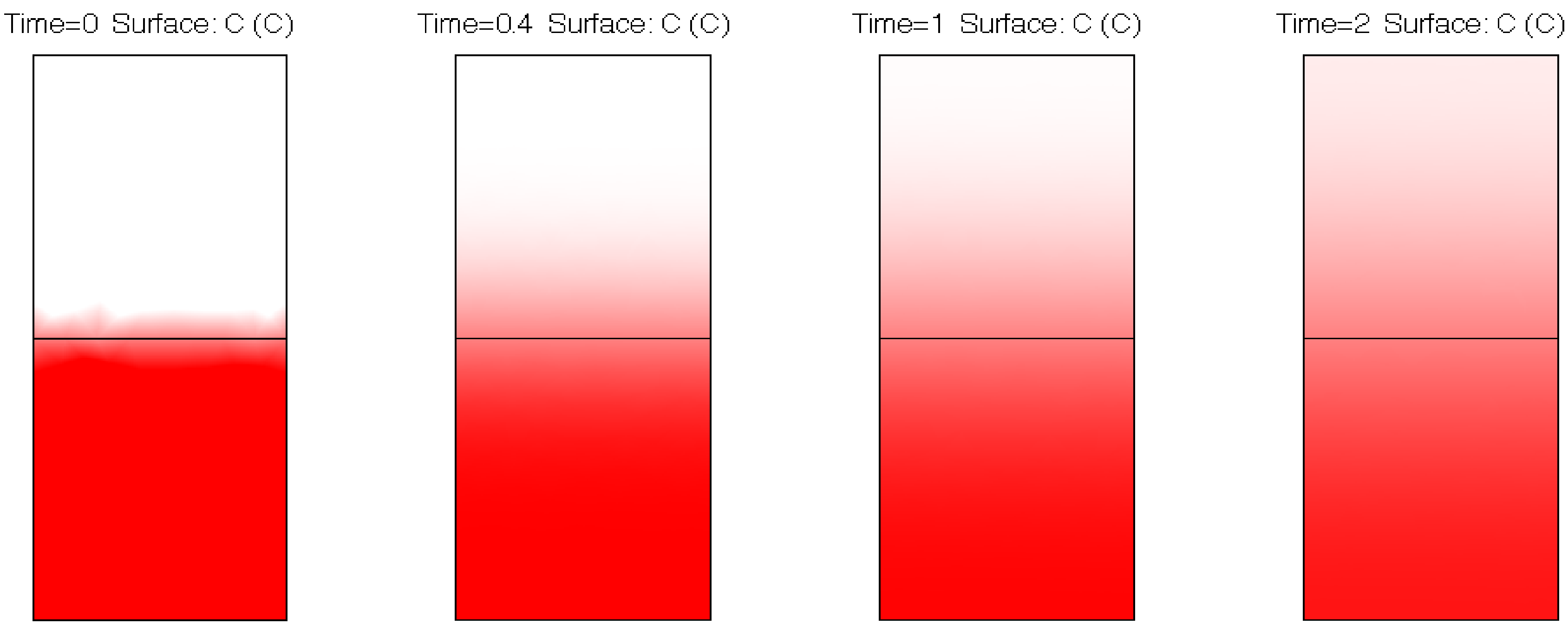
Fickian Diffusion:



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

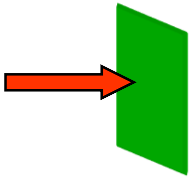
D: Diffusion Coefficient [$m^2\ s^{-1}$]

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



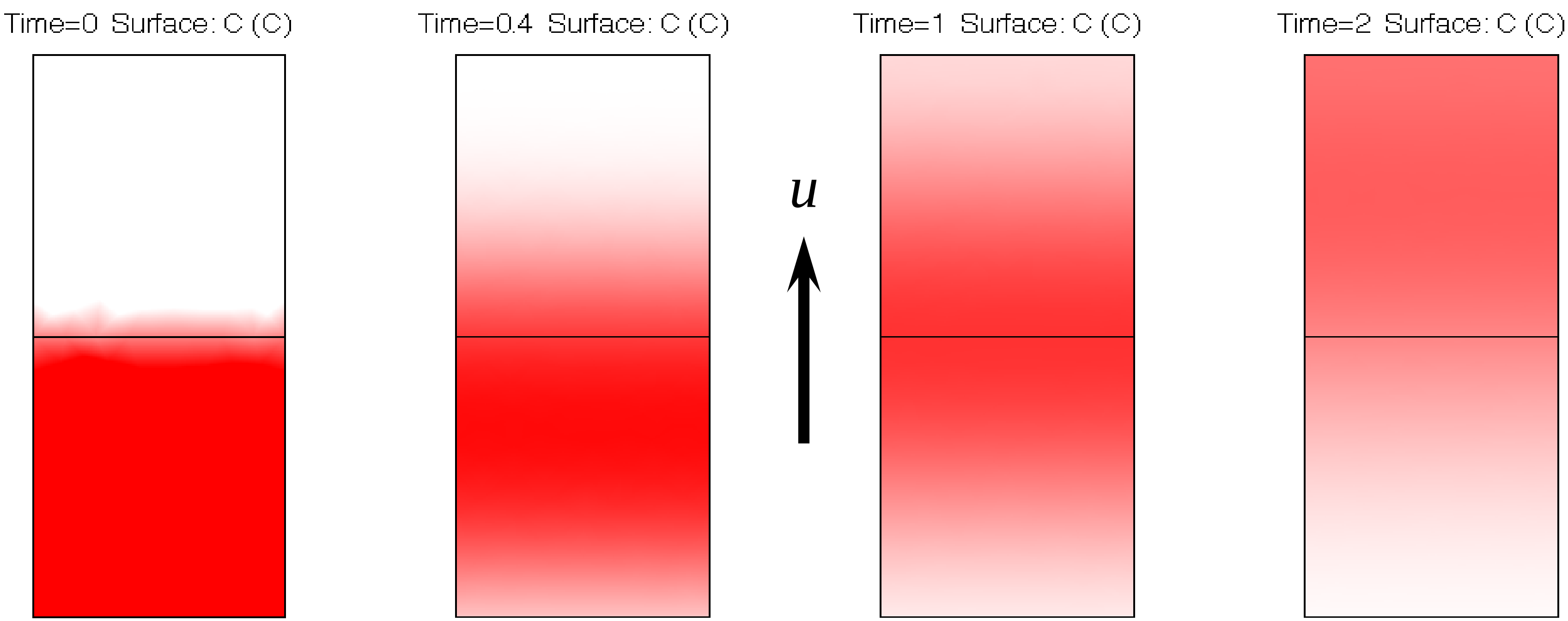
Transport Limitations; Advection-Diffusion

Transport by advection and diffusion:



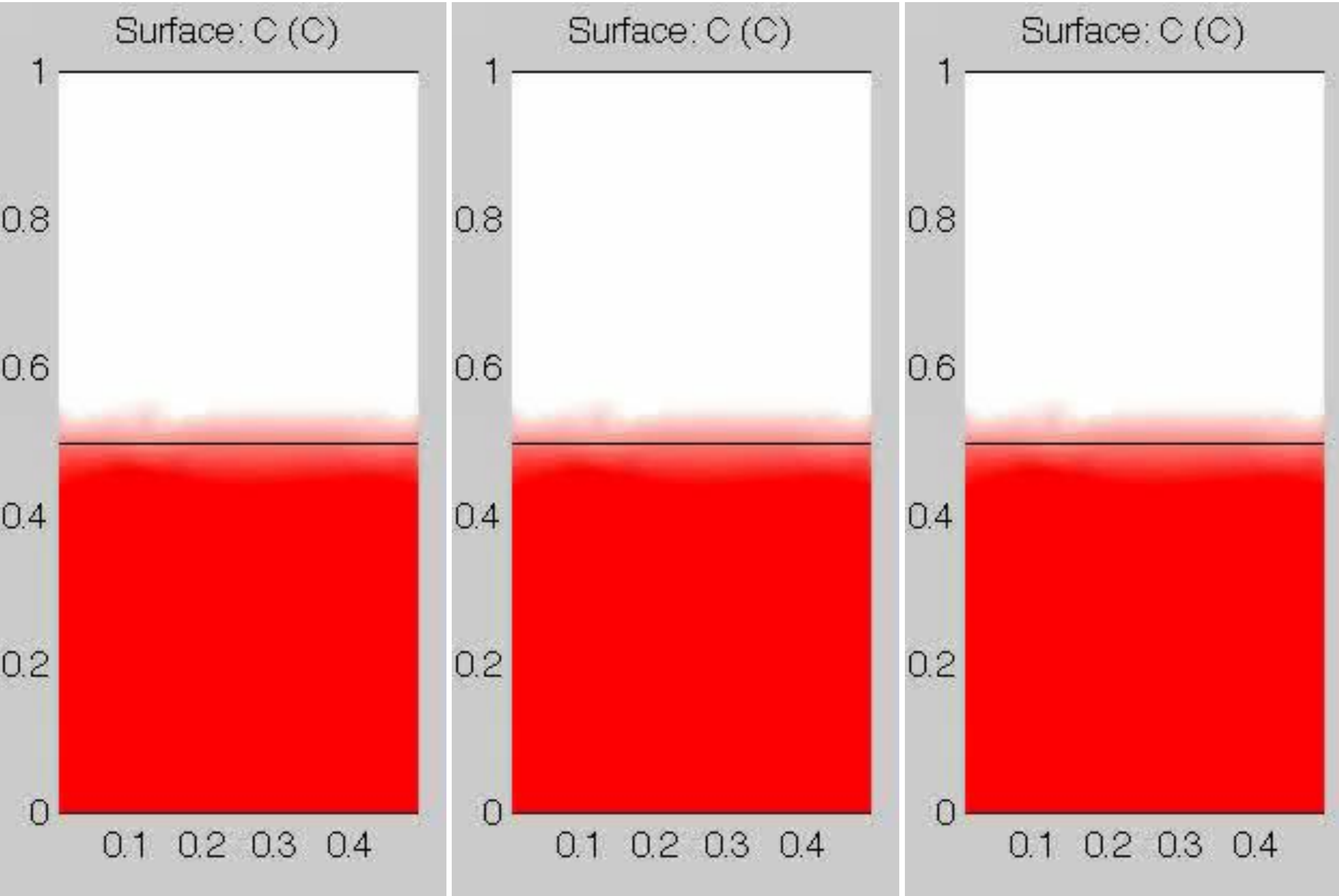
$$Flux = -D\frac{dC}{dz} + uC \equiv \left[\frac{g}{m^2 s}\right]$$

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



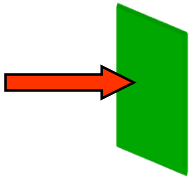
Simulations

Advection | Diffusion | Advection & Diffusion



Transport Limitations; Advection-Diffusion

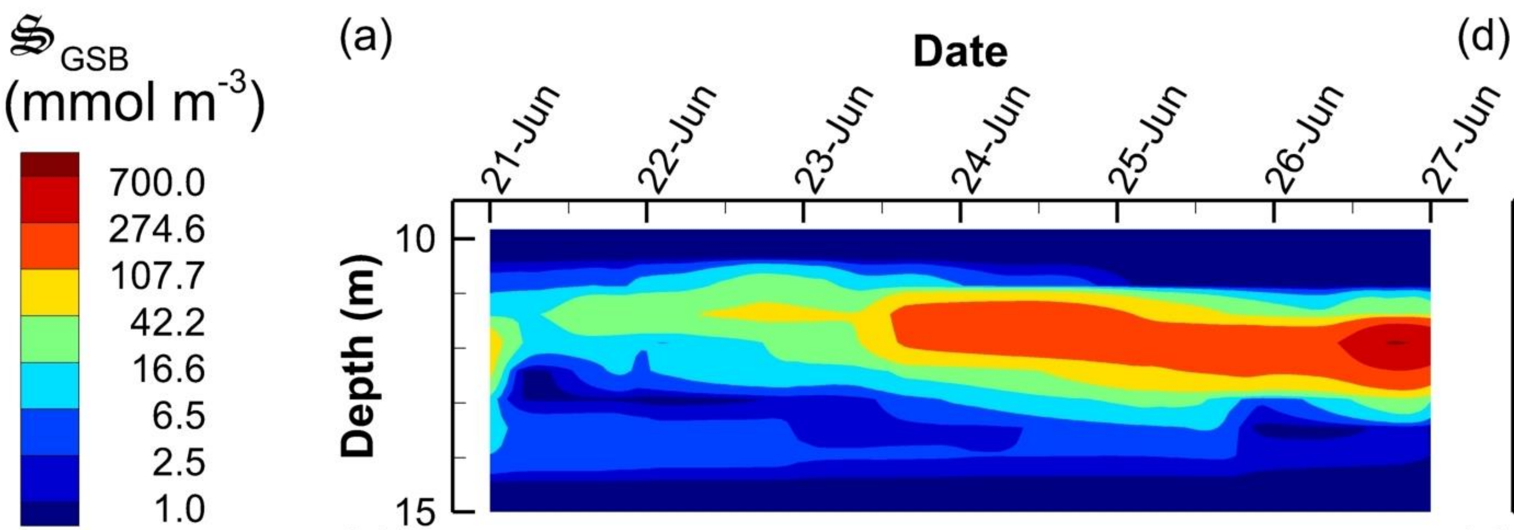
Transport by advection and diffusion:



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

Must also account for reactions!

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



(see Vallino & Huber 2018)

Redox Reactions

Reduction and Oxidation:

Half Reactions

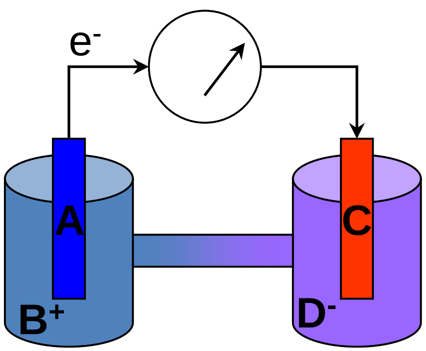
$A \rightarrow B^+ + e^-$ Oxidation

$C + e^- \rightarrow D^-$ Reduction

Complete Reaction

$A + C \rightarrow B^+ + D^-$

Redox Potential, E°



Reference Half Reaction:

$H_2(g) \rightarrow 2e^- + 2H^+$

Reference cell always at pH 0

Electron Tower (at pH 0) E° (mV)

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

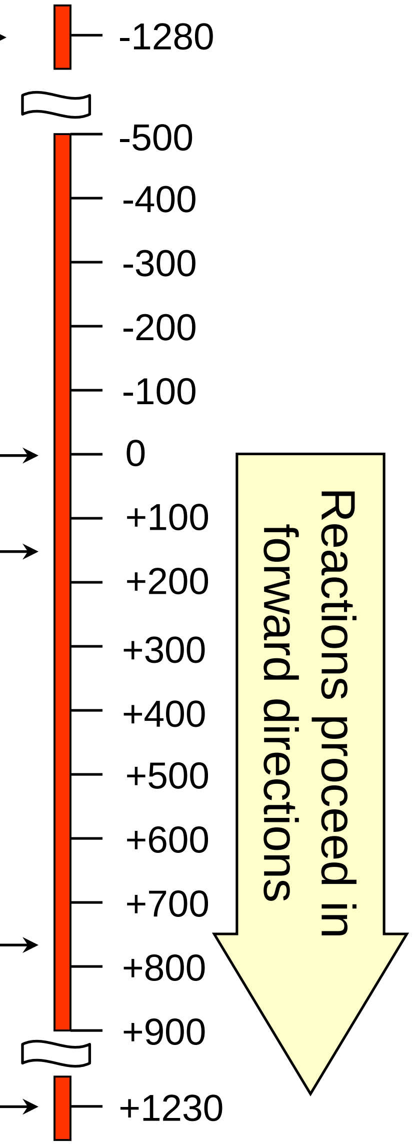
$ZnO(s) + H_2O + 2e^- \rightarrow Zn + 2OH^-$ → -1280

$2H^+ + 2e^- \rightarrow H_2$ → 0

$2MnO_2(s) + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$ → +118

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ → +770

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ → +1230



Alkaline Battery: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$: E° = 1.43 V

Redox Reactions-2

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

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

F = faraday (96493 Coulombs/mol)
R = gas const (8.314 J/K/mol)

m = no. of H^+ consumed in ½ rxn
n = no. of electrons in rxn.

Volt = J/(A·s)=J/C; C≡Coulomb

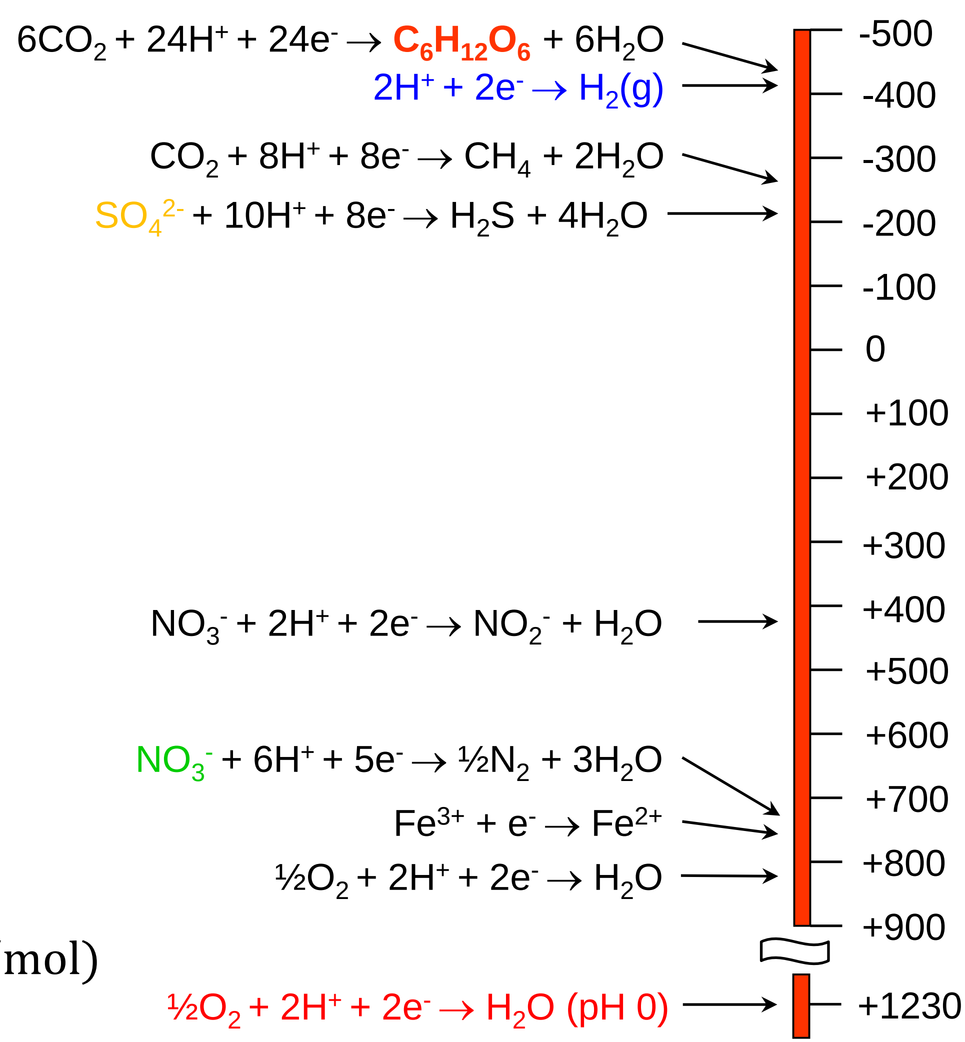
$$\Delta G^{\circ\prime} = -nE^{\circ\prime}F \text{ Gibbs Free Energy (kJ/mol)}$$

Reference Half Reaction:

$H_2(g) \rightarrow 2e^- + 2H^+$

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

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^{3+} or Fe^{2+}.

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

CH_4	-4	N_2	0	NH_3	-3	$S_2O_3^{2-}$	+2
CO_2	+4	NO_3^-	+5	H_2S	-2	SO_4^{2-}	+6

Fermentation and/or Disproportionation

- Organic carbon present, but no electron acceptors: O_2, NO_3^-, SO_2^{2-}, etc.
- Use organic carbon as both electron acceptor and donor:

$$C_6H_{12}O_6 \rightarrow 2\ CO_2 + 2\ C_2H_6O$$

$$4\ S + 4\ H_2O \rightarrow 3\ H_2S + SO_4^{2-} + 2\ H^+$$

$$2/3C_6H_{12}O_6 + 8H^+ + 8e^- \rightarrow 2\ C_2H_6O +$$

$$1/3C_6H_{12}O_6 + 2H_2O \rightarrow 2\ CO_2 + 8H^+ +$$

Autotrophy

$$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$$

$H_2S \rightarrow 2\ H^+ + S + 2\ e^-$	PS I or PS II	Anoxygenic Photosynthesis
$H_2O \rightarrow 2\ H^+ + ½\ O_2 + 2\ e^-$	PS I and PS II	Oxygenic Photosynthesis

Photosystem I Only

Energy production only
(cyclic photophosphorylation)

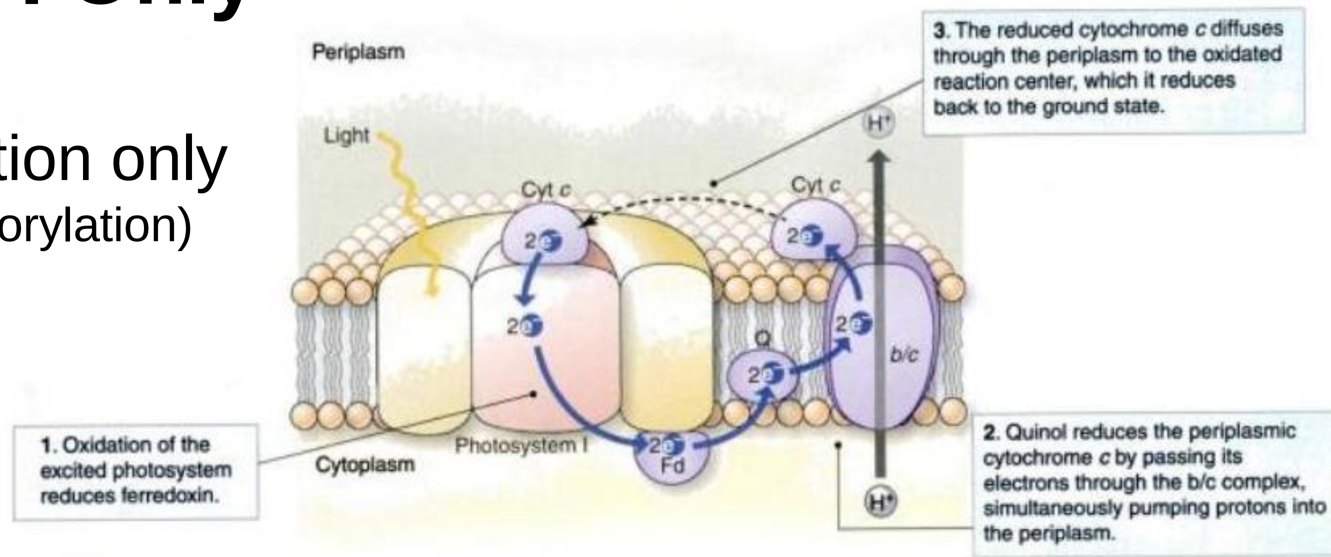
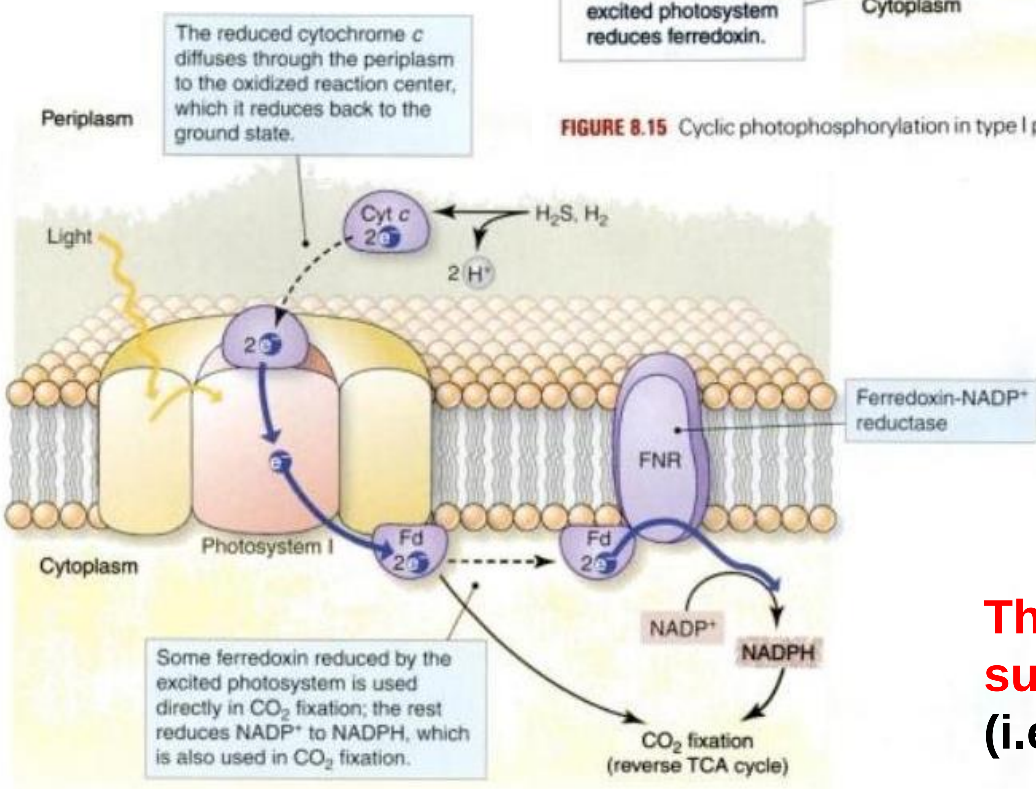


FIGURE 8.15 Cyclic photophosphorylation in type I photosynthesis.



NADPH production only needed to reduce CO_2

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

FIGURE 8.16 Noncyclic photophosphorylation in type I photosynthesis.

(Principles of Modern Microbiology, M. Wheelis)

Photosystem II Only

These occur in the green and purple **non**-sulfur bacteria

Energy production only

(cyclic photophosphorylation)

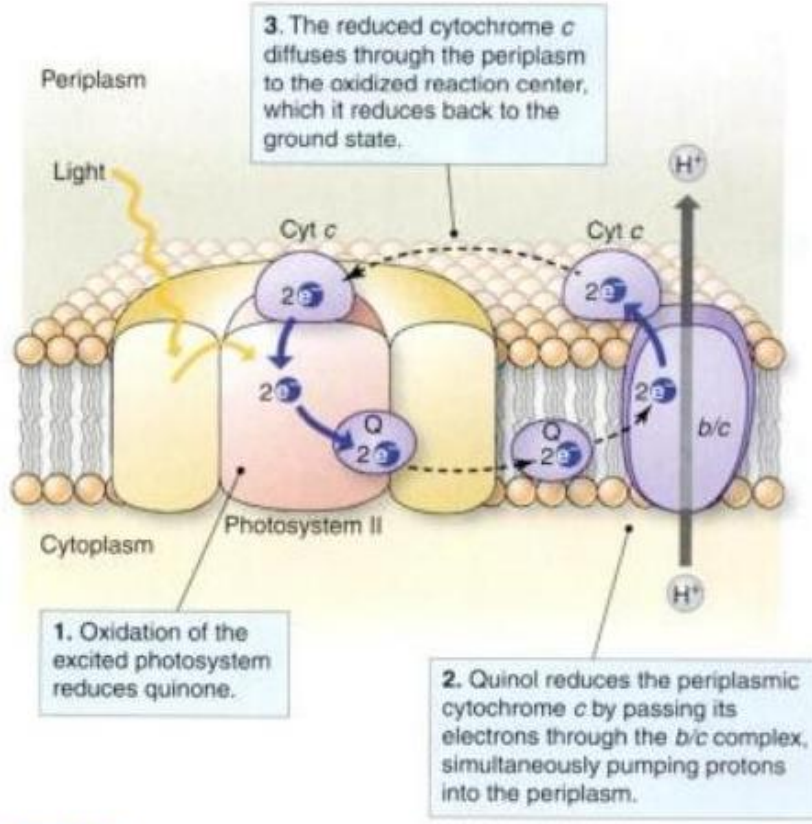


FIGURE 8.17 Cyclic photophosphorylation in type II photosynthesis.

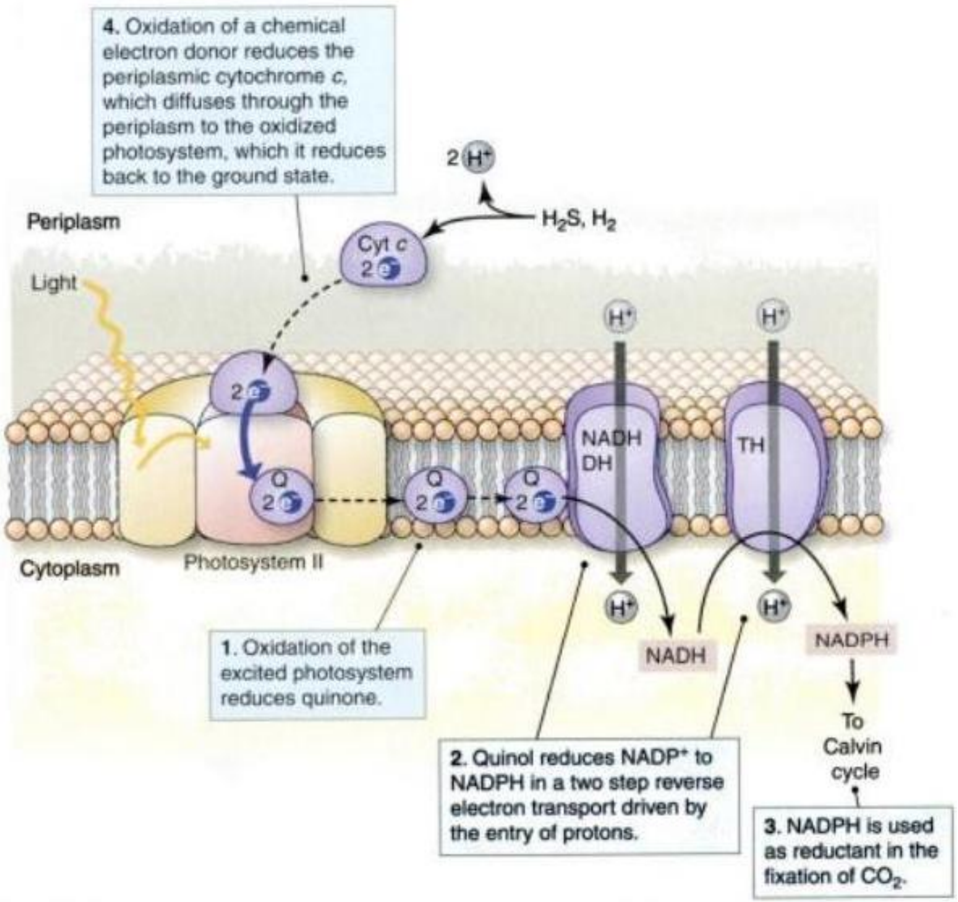


FIGURE 8.18 Noncyclic photophosphorylation in type II photosynthesis.

NADPH production only needed to reduce CO_2

(Principles of Modern Microbiology, M. Wheelis)

Photosystem I+II

These occur in the cyanobacteria, algae and plants.

Energy production only

(cyclic photophosphorylation)

NADPH production only needed to reduce CO_2

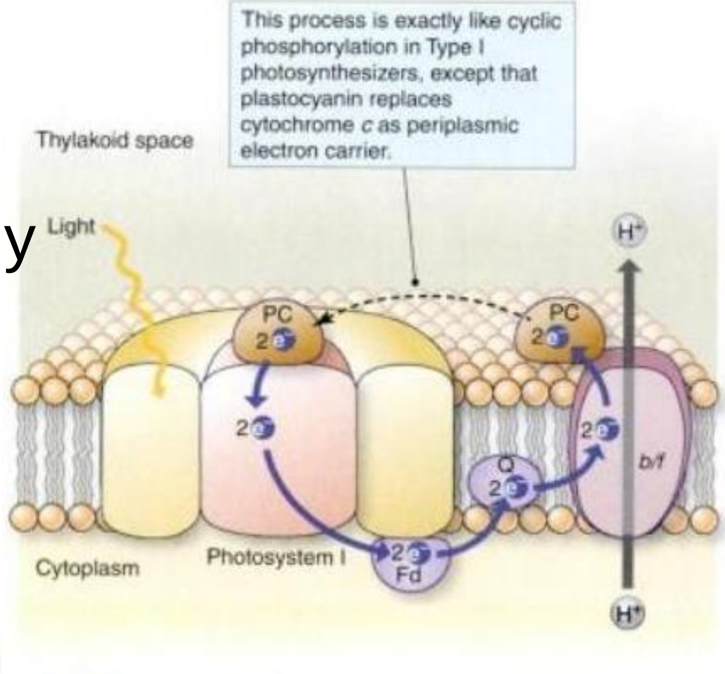


FIGURE 8.19 Cyclic photophosphorylation in cyanobacterial photosynthesis.

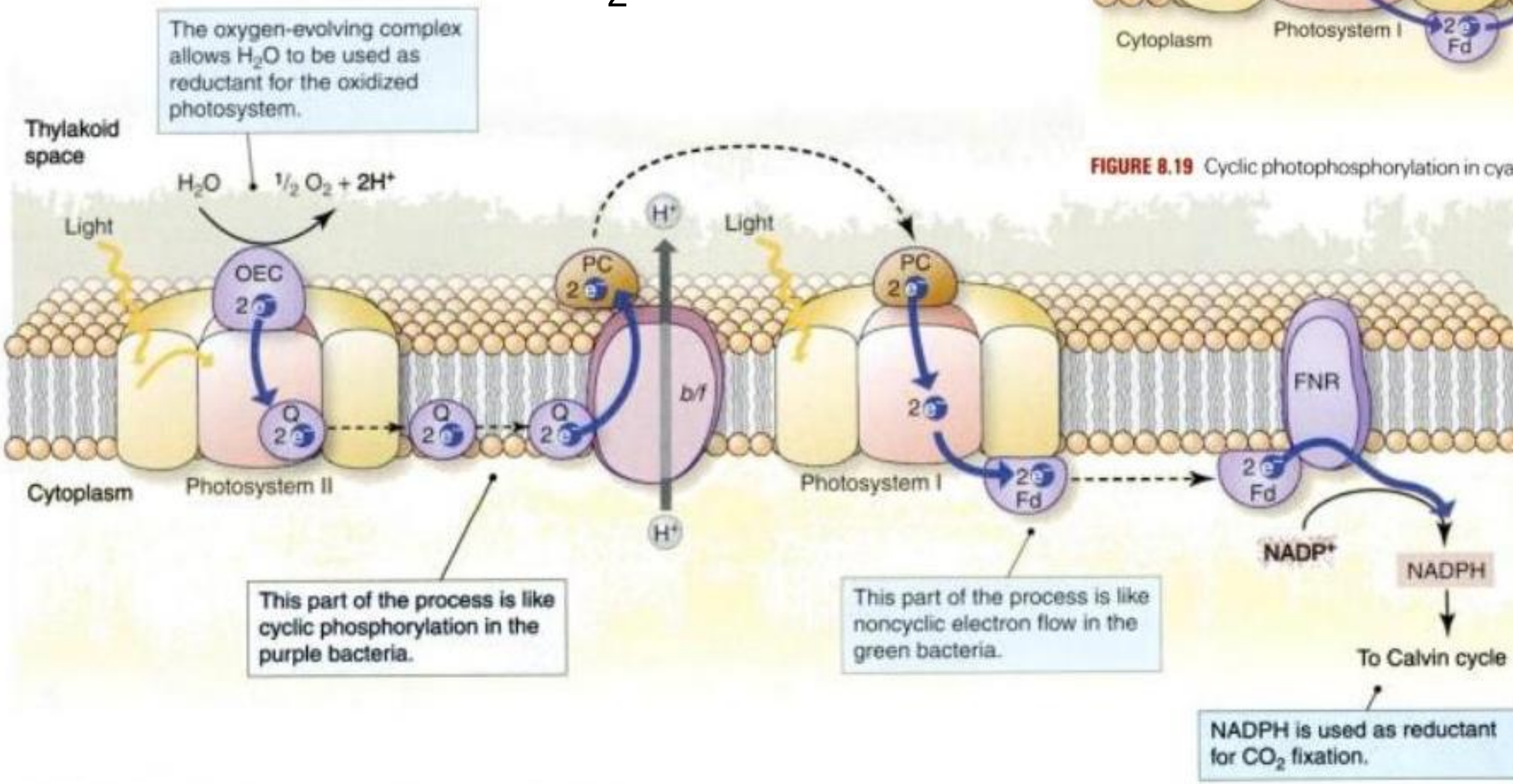
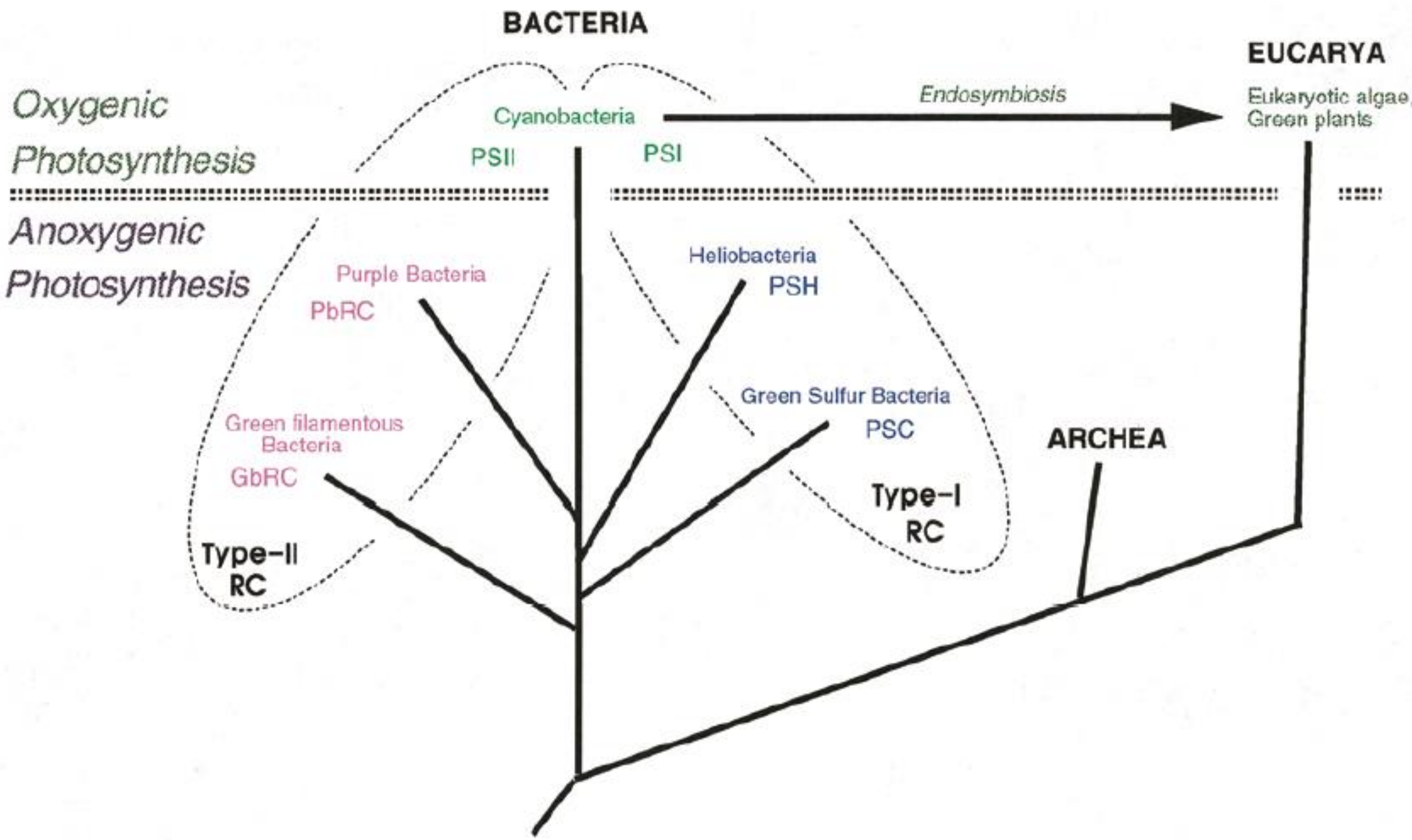


FIGURE 8.20 Noncyclic photophosphorylation in cyanobacteria.

(Principles of Modern Microbiology, M. Wheelis)

Phylogeny of PS I and II



Schubert et al. (1998) J. Mol. Biol. 280, 297-314

Microbes and Processes in Winogradsky column.

Aerobic Environment

- Algae and cyanobacteria (photoautotrophy using PS II)
- Bacteria and eukaryotes respiring (chemoorganoheterotrophy).
- Sulfide oxidizers (or sulfur bacteria): $H_2S + O_2 \rightarrow S$ or SO_4^{2-}
    - Some use CO_2 (chemolithoautotrophs), others use organic compounds (chemolithoheterotrophs)
    - Examples, *Thiobacillus* sp. And *Beggiatoa* sp.
- Methanotrophs: $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$ (chemoorganoheterotrophs)
    - Example, *Ralstonia* sp., *Pseudomonas* sp.

Anaerobic Environment

Fermentors (chemoorganoheterotrophs)

- Break down cellulose, etc. and ferment sugars into:
    - alcohols
    - acetate
    - organic acids
    - 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

Sulfur Compounds

- Sulfate reducers: use sulfate, $SO_4^{2-} + e^- \rightarrow S$ or H_2S, to oxidize organic compounds produced by fermentors. (chemoorganoheterotrophs).
  - Many genera of bacteria. Example, *Desulfovibrio* sp.

- Phototrophic bacteria: Use light and H_2S as electron donor (PS I) (photoautotrophs).
  - Examples, purple and green sulfur bacteria.

Methanogens and Acetogens

- Methanogens: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (chemolithoautotrophs)
  $Acetate^- + H_2O \rightarrow CH_4 + HCO_3^-$ (chemoorganoheterotrophs)
  - Example: *Methanobacterium* (Archaea)

- Acetogens: $2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$ (chemolithoautotrophs)
  - Example: *Homoacetogens*

Other possible microbes

Aerobic Environments

Hydrogen

- Hydrogen oxidizers: $H_2 + ½O_2 \rightarrow H_2O$ (both chemolithoheterotrophs and chemolithoautotrophs). However, it is unlikely that H_2 will make it to the aerobic interface (it will be used in the anaerobic environment first)
    - Example, *Ralstonia eutrophus*

Iron

- Iron oxidizers: $Fe^{2+} + H^+ + ¼O_2 \rightarrow Fe^{3+} + ½H_2O$ (chemolithoautotrophs)
  Occurs only at low pH (~2)
    - Example: *Thiobacillus ferrooxidans*

Ammonium

- Nitrifiers: $NH_3 + 1½\ O_2 \rightarrow NO_2^- + H^+ + H_2O$
  $NO_2^- + ½\ O_2 \rightarrow NO_3^-$
    - Example: *Nitrosomonas* and *Nitrobacter*, respectively. Both chemolithoautotrophs.

Anaerobic Environments

Nitrate

- Denitrifiers: $NO_3^- + 6H^+ + 5e^- \rightarrow ½N_2 + 3H_2O$
    - Reaction combined with oxidation of organic matter.

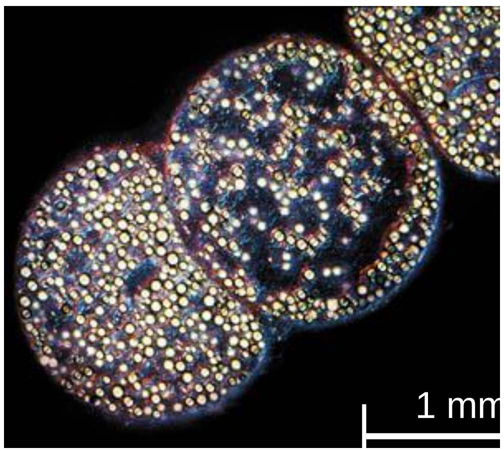
Iron

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

Chemical Potential Exploitation

H_2S oxidation by NO_3^-

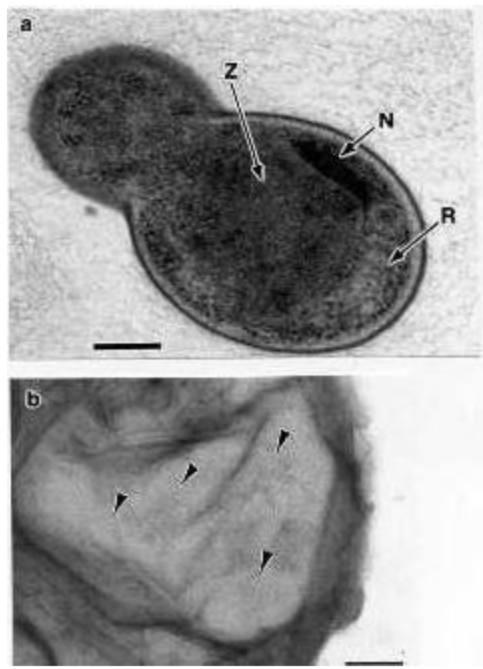
Schulz et al. 1999:
Thiomargarita namibiensis



Anammox

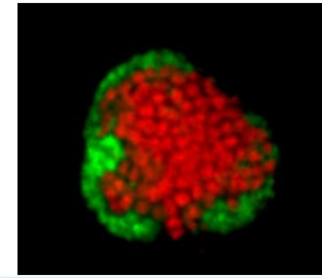
$NH_4^+ + NO_2^- = N_2 + 2H_2O$

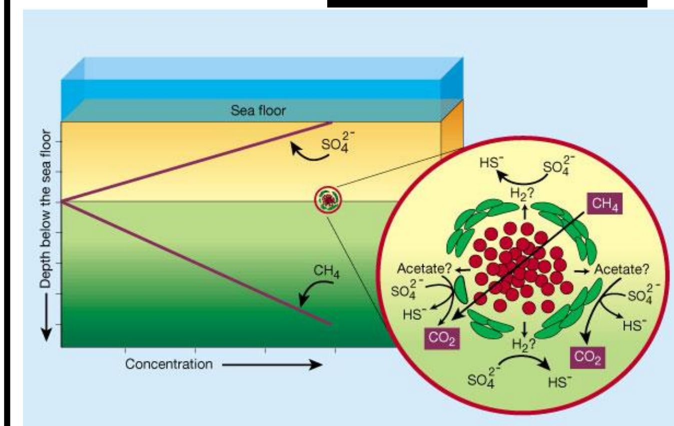
Strous et al. 1999:
Planctomycete



CH_4 oxidation by SO_4^{2-}

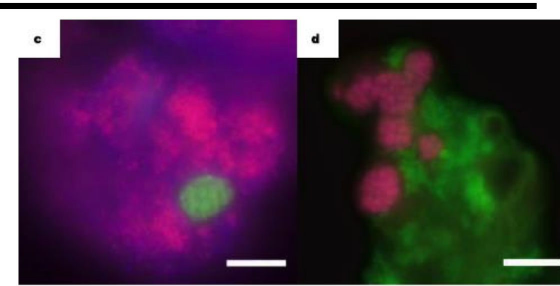
Boetius et al. 2000:





CH_4 oxidation by NO_3^- (Raghoebarsing et al. 2006)

$$5CH_4 + 8NO_3^- + 8H^+ \rightarrow 5CO_2 + 4N_2 + 14H_2O$$



Competition and Redox cascade

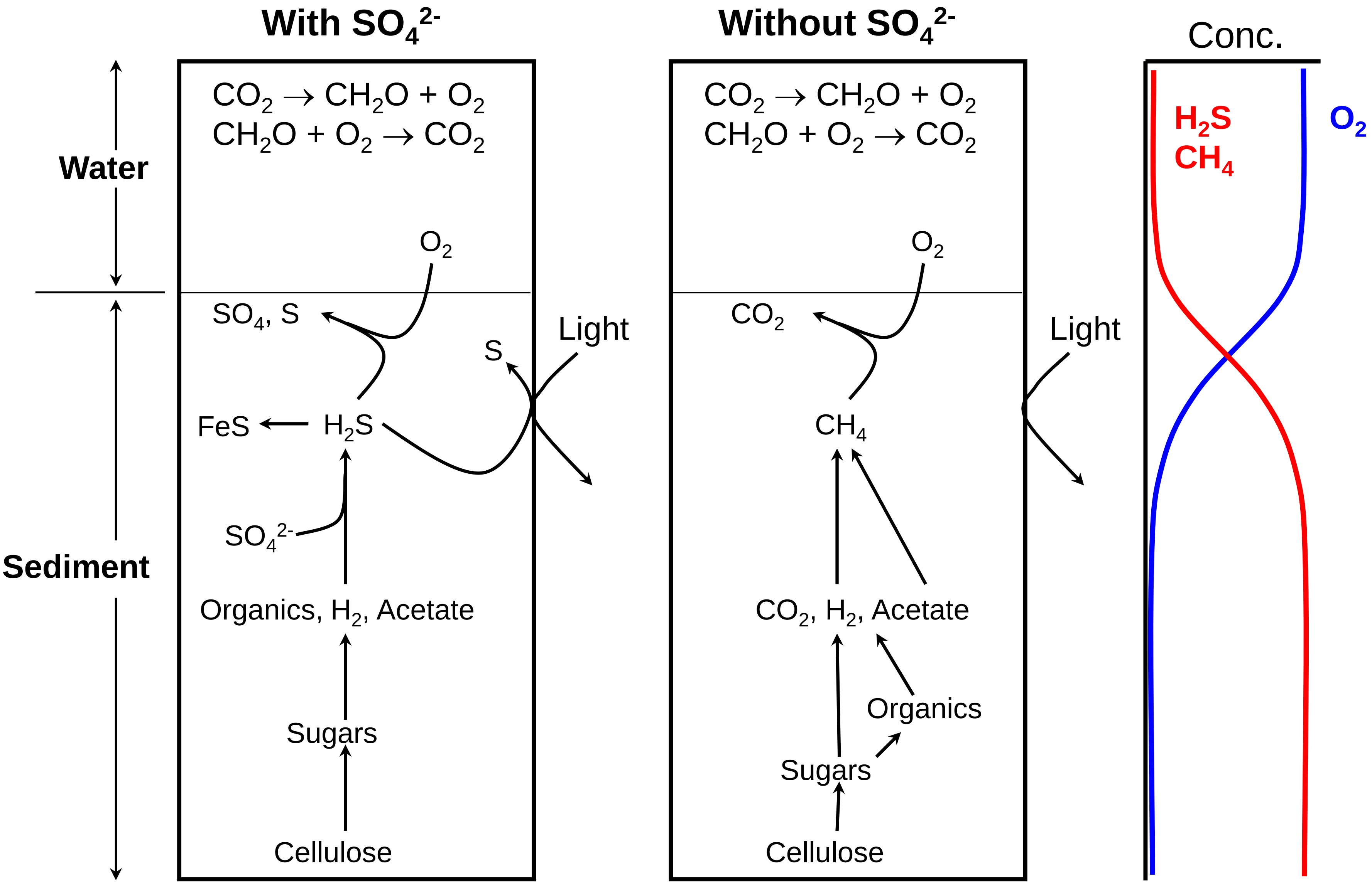
How do the chemical gradients arise in the Winogradsky column, or in natural environments?

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 > Fermentation

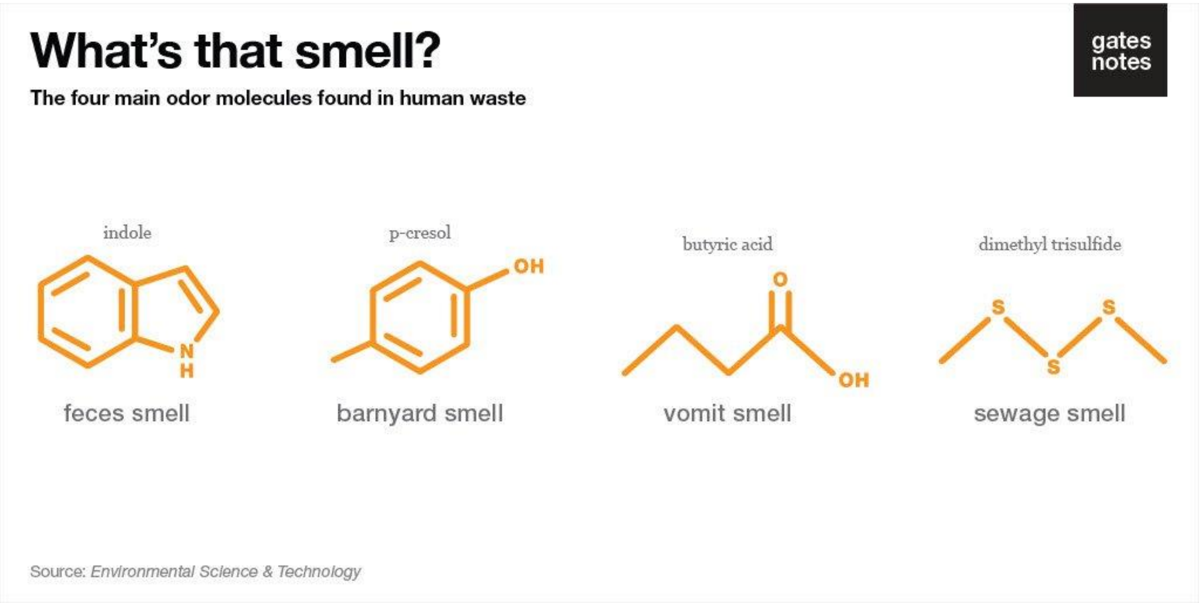
Winogradsky column biogeochemistry



Laboratory Work

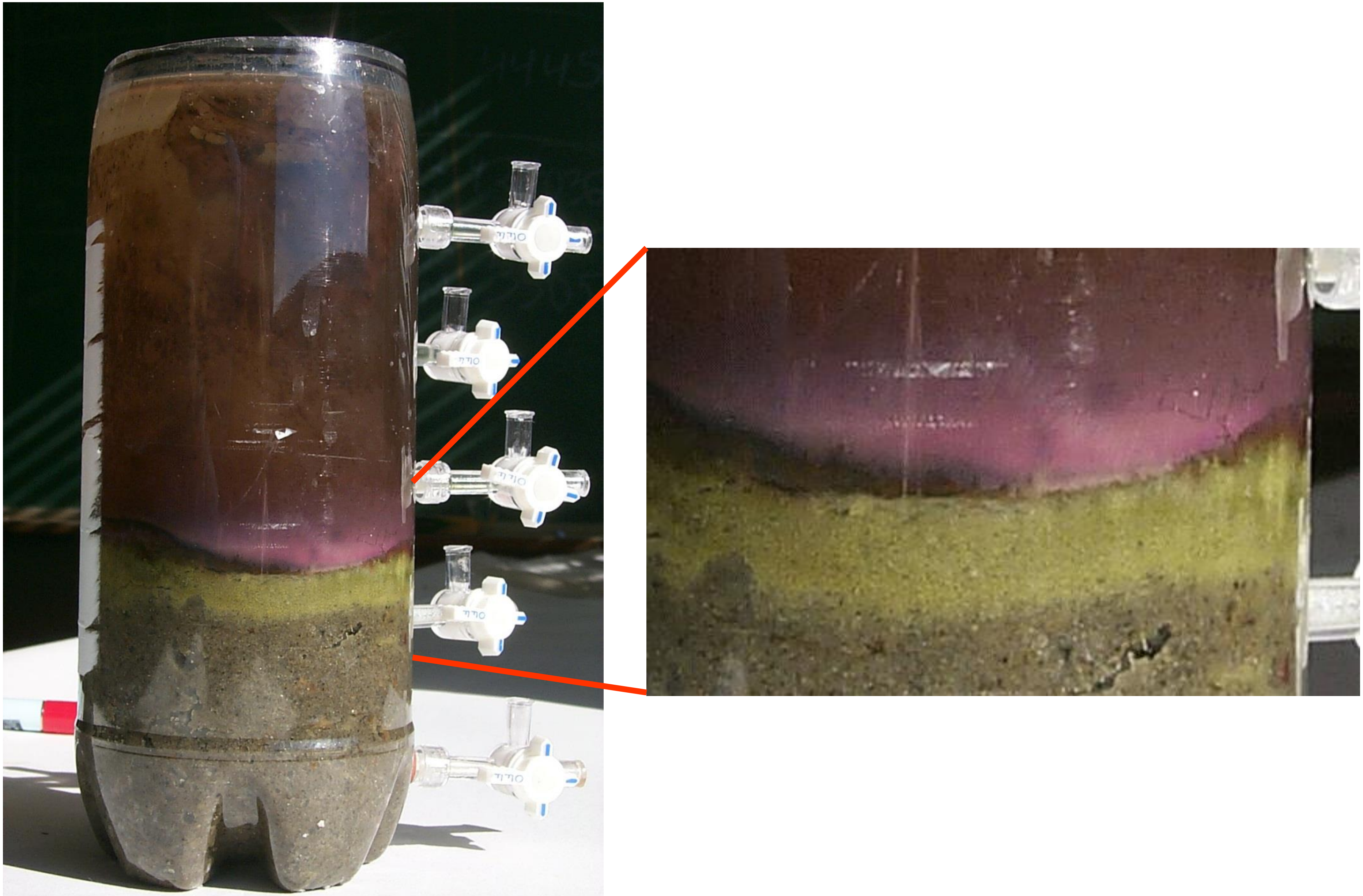
Tuesday: Measure methane profiles in columns using gas chromatogram.

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

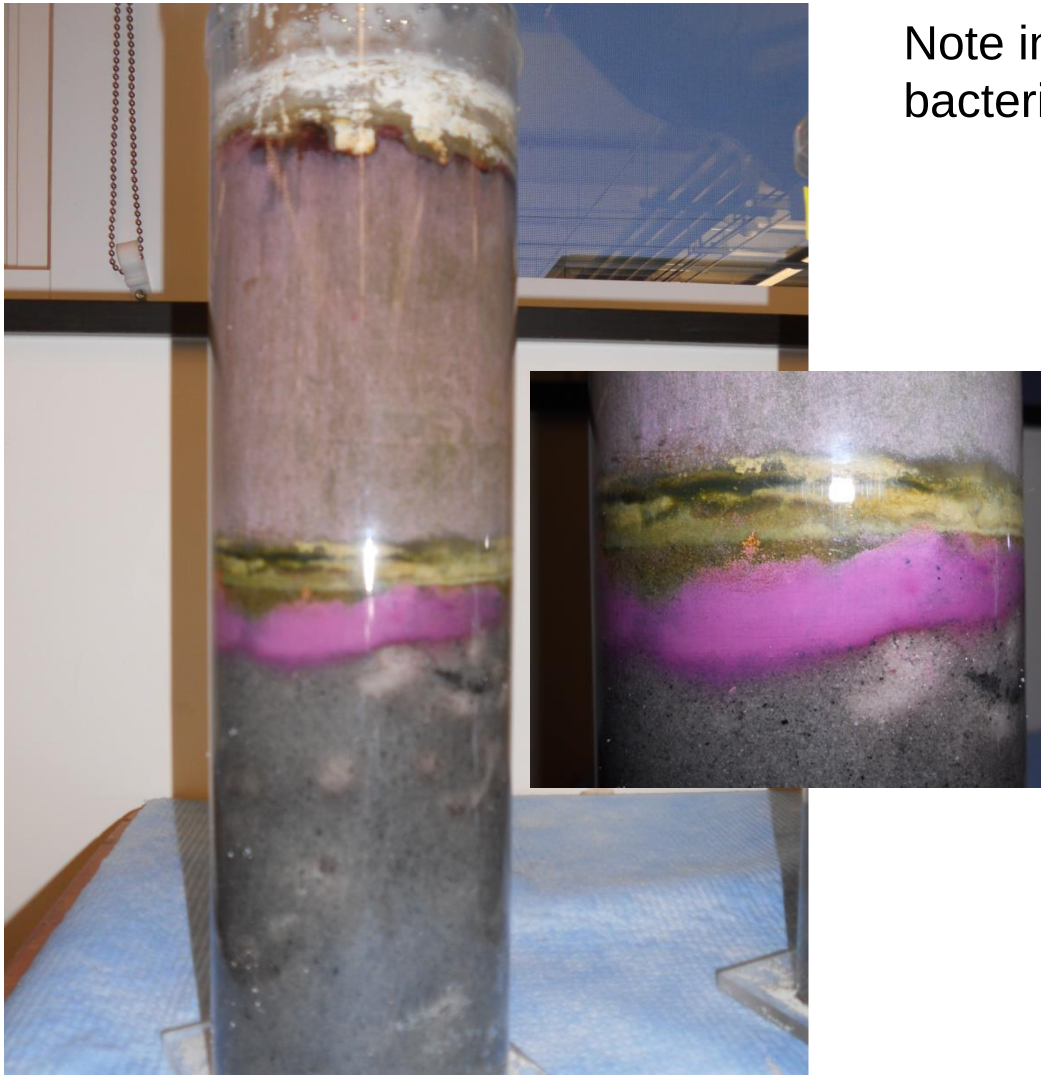


https://www.gatesnotes.com/Development/Smells-of-Success?WT.mc_id=20161202155430_Firmenich_BG-TW&WT.tsrc=BGTW&linkId=31842000

Winogradsky Column from 1999 Class



Winogradsky Column from 2011 Class



Saltwater with rice as carbon

Note inversion of green and purple sulfur bacteria