Biogeochemical Systems -- OCN 401

Readings: Schlesinger Chapter 7; Erwin (2009)

I. Redox Biogeochemistry in Aquatic Systems

II. Wetlands & Layered Microbial Habitats

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Last Lecture Summary

- Redox reactions control organic-matter oxidation and element cycling in aquatic ecosystems
- Eh – pH diagrams can be used to describe the thermo-dynamic stability of chemical species under different biogeochemical conditions
- Biogeochemical reactions are mediated by the activity of microbes, and follow a sequence of high-to-low energy yield that is thermodynamically controlled
  - Example – organic matter oxidation:
    - O_2 reduction (closely followed by NO_3^- reduction) is the highest- yield redox reaction
    - CO_2 reduction to CH_4 is the lowest-yield redox reaction

https://www.youtube.com/watch?v=Gfch_b45zoQ#action=share


NOAA

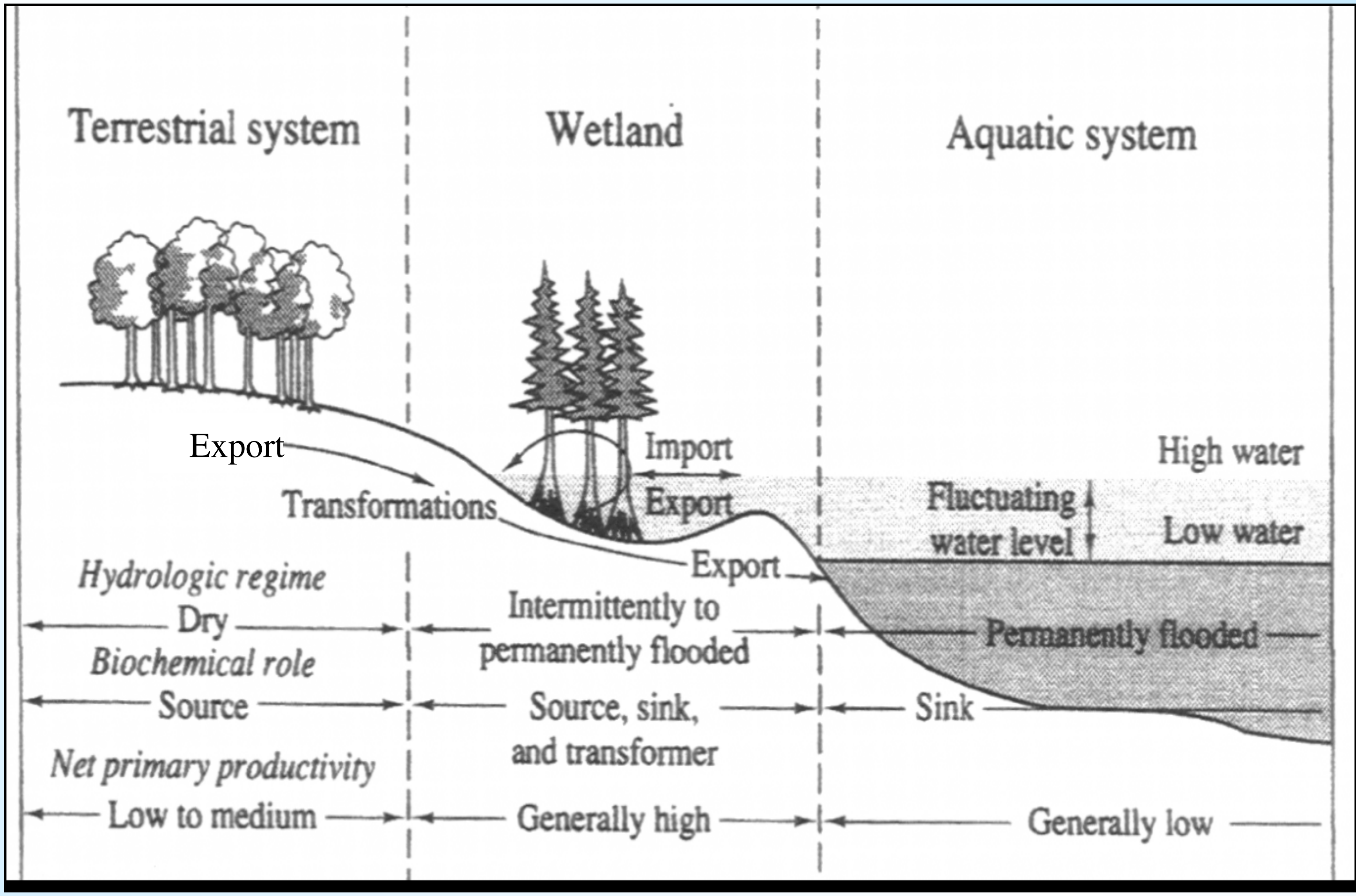
Wetlands

"hydric soils are those in their natural conditions are saturated, flooded, or ponded long enough during the cropping season to develop anaerobic conditions that favor the growth and regeneration of hydrophytic vegetation" -- USDA

Biologically active soil or sediment in which the content of water in or the overlying water column is great enough to inhibit oxygen diffusion into the soil/sediment and stimulate anaerobic chemical and biological processes that help biotic communities to adapt to anaerobic conditions

Wetlands Are the Interface Between Terrestrial and Aquatic Systems

- Terrestrial (dry) systems tend to have medium NPP, high + NEP
- Wetlands have high NPP, + or - NEP
- Aquatic systems have low NPP, - NEP



Drained wetlands or aquatic systems are major sites of "old C" oxidation

NPP = net primary production

NEP = net ecosystem production (P-R)

Wetland biogeochemical functions

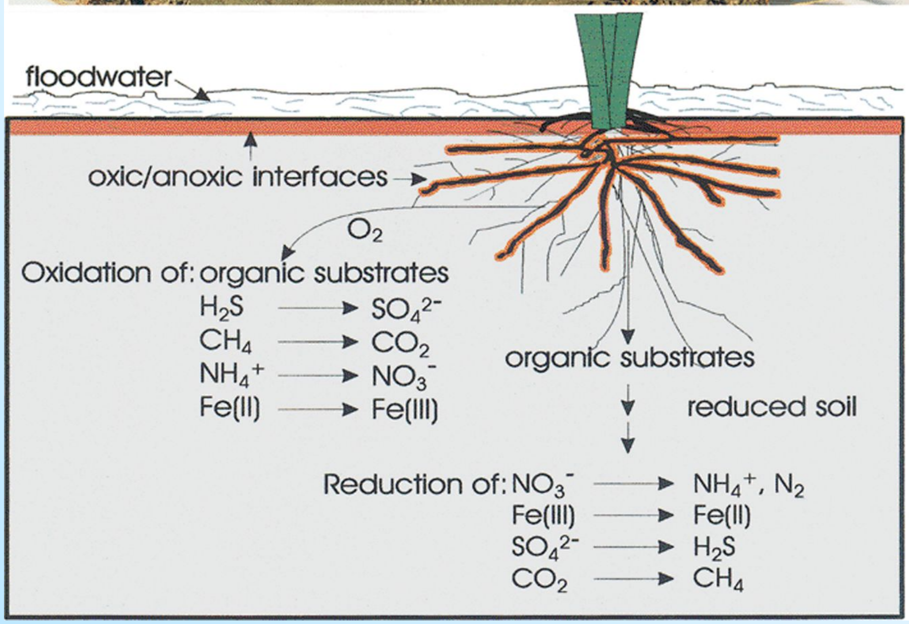
Depending upon wetland type, hydrologic regime, nutrient & contaminant inputs, wetlands can serve as:

SINK

SOURCE

TRANSFORMERS

Drained Soil vs. Flooded Soil



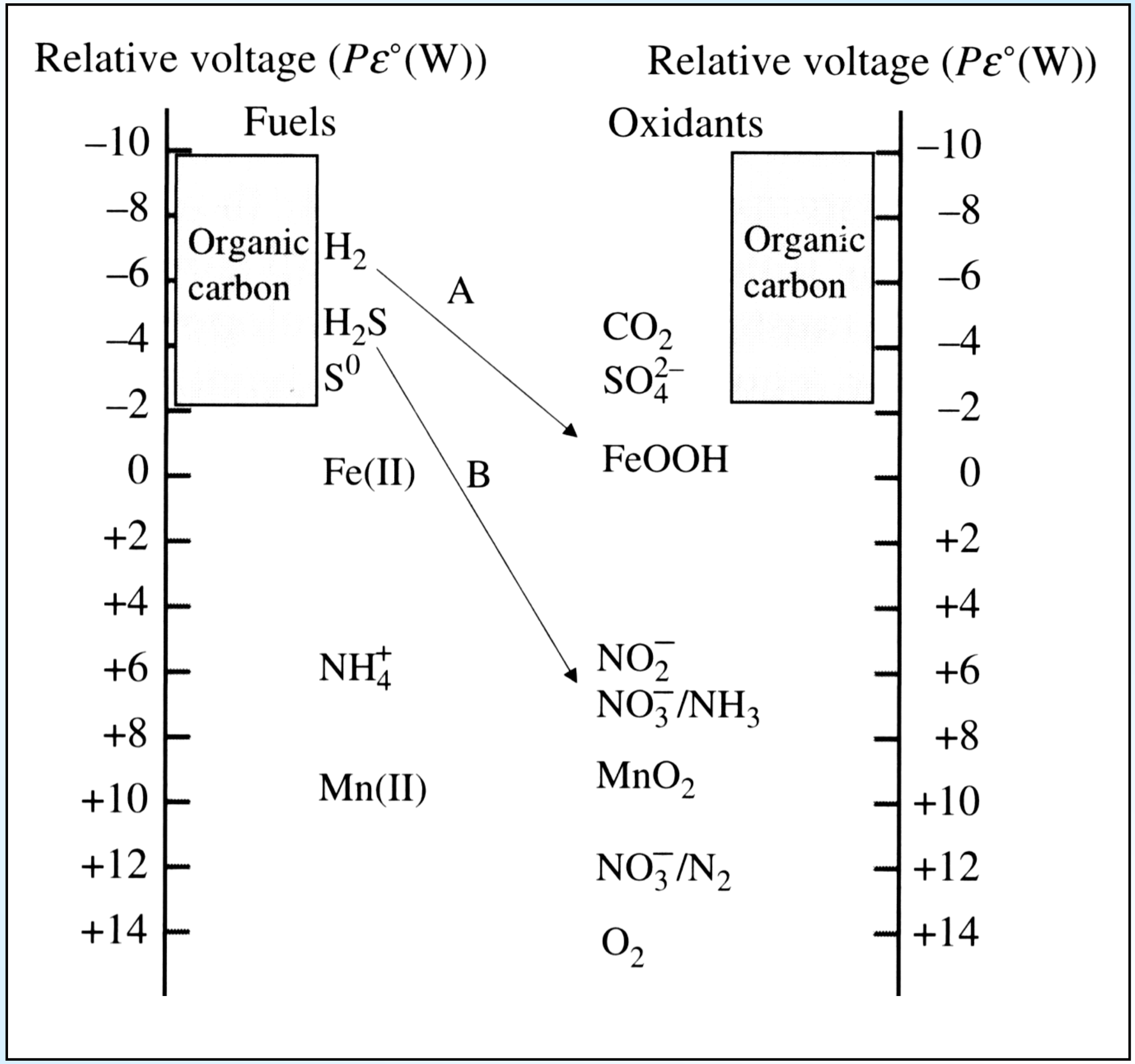
Environmentally Important Organic Matter Oxidation Reactions

Reducing Half-reaction	E_h (V)	ΔG
Reduction of O_2		
$O_2 + 4H^{+} + 4e^{-} \text{-->} 2H_2O$	+0.812	-29.9
Reduction of NO_3^{-}		
$2NO_3^{-} + 6H^{+} + 6e^{-} \text{-->} N_2 + 3H_2O$	+0.747	-28.4
Reduction of Mn (IV)		
$MnO_2 + 4H^{+} + 2e^{-} \text{-->} Mn^{2+} + 2H_2O$	+0.526	-23.3
Reduction of Fe (III)		
$Fe(OH)_3 + 3H^{+} + e^{-} \text{-->} Fe^{2+} + 3H_2O$	-0.047	-10.1
Reduction of SO_4^{2-}		
$SO_4^{2-} + 10H^{+} + 8e^{-} \text{-->} H_2S + 4H_2O$	-0.221	-5.9
Reduction of CO_2		
$CO_2 + 8H^{+} + 8e^{-} \text{-->} CH_4 + 2H_2O$	-0.244	-5.6

DECREASING ENERGY YIELD

Types of metabolism

- Light used directly by phototrophs
- Hydrothermal energy utilized via heat-catalyzed production of inorganics



Nealson and Rye 2004

Redox sequence of OM decomposition

	log K	log Kw
Aerobic Respiration		
$1/4CH_2O + 1/4O_2 = 1/4H_2O + 1/4CO_2(g)$	20.95	20.95
Denitrification		
$1/4CH_2O + 1/5NO_3 + 1/5H^+ = 1/4CO_2(g) + 1/10N_2(g) + 7/20H_2O$	21.25	19.85
Manganese Reduction		
$1/4CH_2O + 1/2MnO_2(s) + H^+ = 1/4CO_2(g) + 1/2Mn^{2+} + 3/4H_2O$	21.0	17.0
Iron Reduction		
$1/4CH_2O + Fe(OH)_3(s) + 2H^+ = 1/4CO_2(g) + Fe^{2+} + 11/4\ H_2O$	16.20	8.2
Sulfate Reduction		
$1/4CH_2O + 1/8SO_4^{2-} + 1/8H^+ = 1/4CO_2(g) + 1/8HS^- + 1/4H_2O$	5.33	3.7
Methane Fermentation		
$1/4CH_2O = 1/8CO_2(g) + 1/8CH_4$	3.06	3.06

Tracers are circled

Free energy available

$\Delta G_r° = -2.3\ RT\ \log K = -5.708\ \log K$

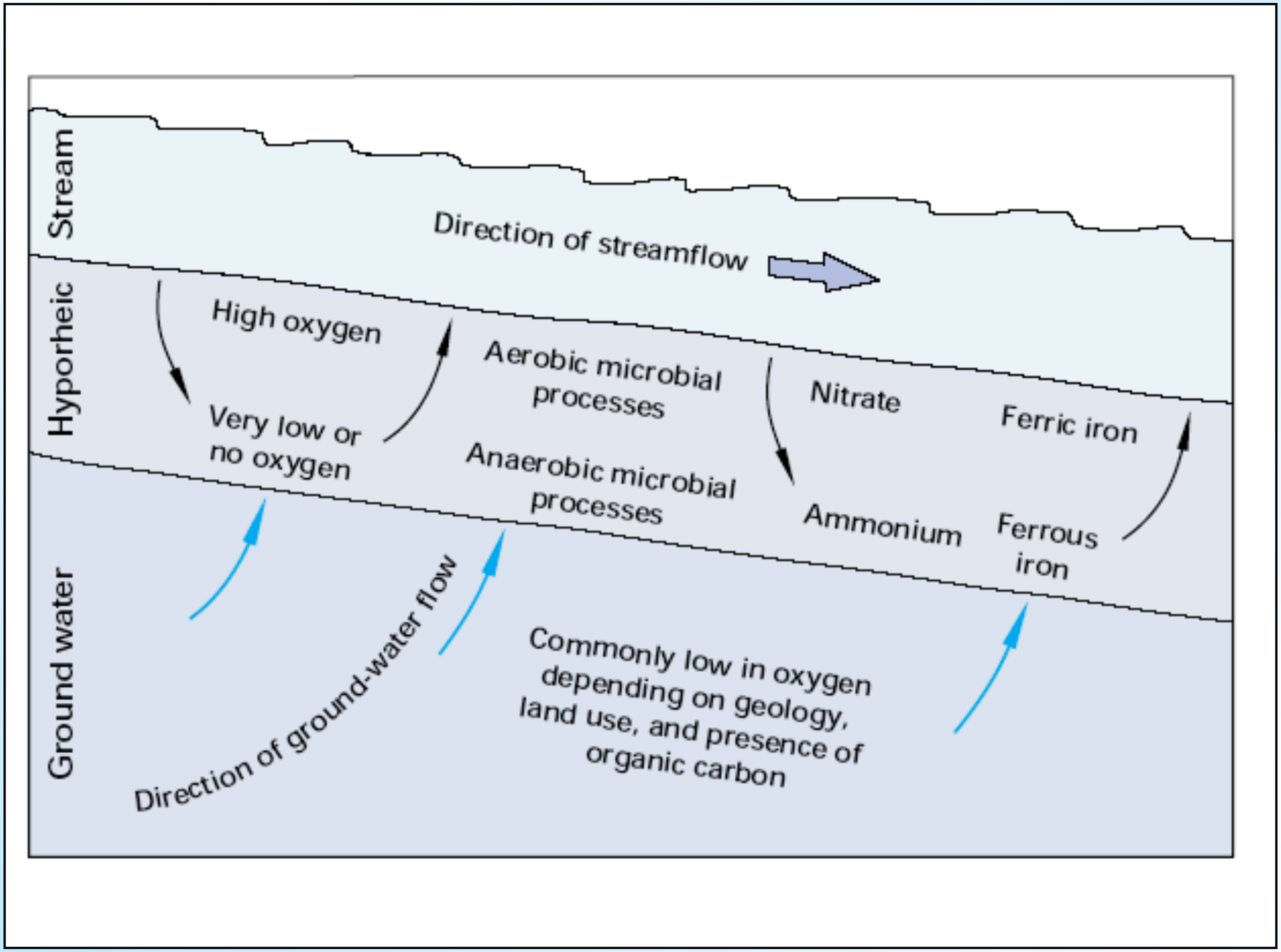
$R = 8.314\ J\ deg^{-1}\ mol^{-1}$

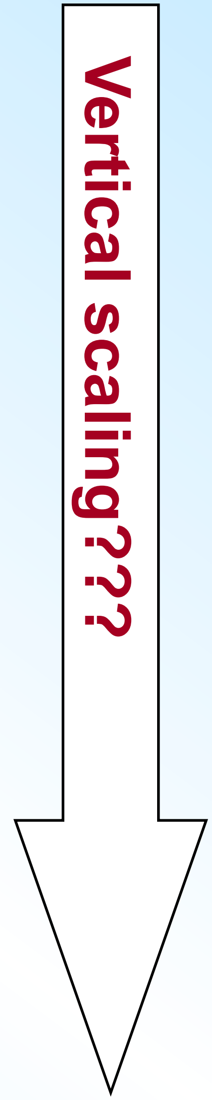
$T = °K = 273 + °C$

Limitations of Redox Potentials

- Most redox couples are not in equilibrium except in highly reduced soils.
- Biological systems continuously cycle electrons
- Redox potential is closely related to pH.
- Electrode surfaces can be contaminated by coatings of organics, oxides, sulfides, etc...

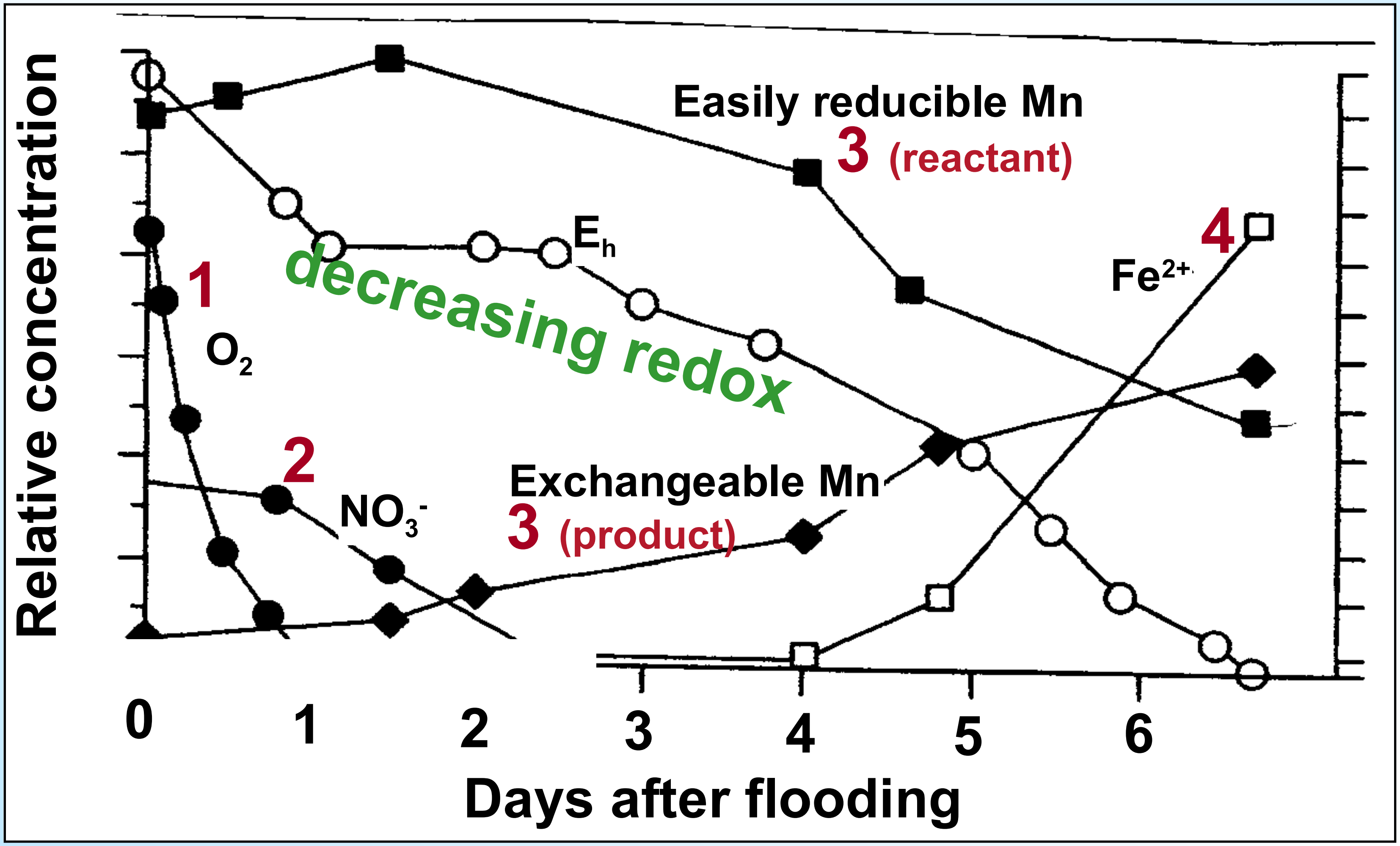
Example: shallow ground water



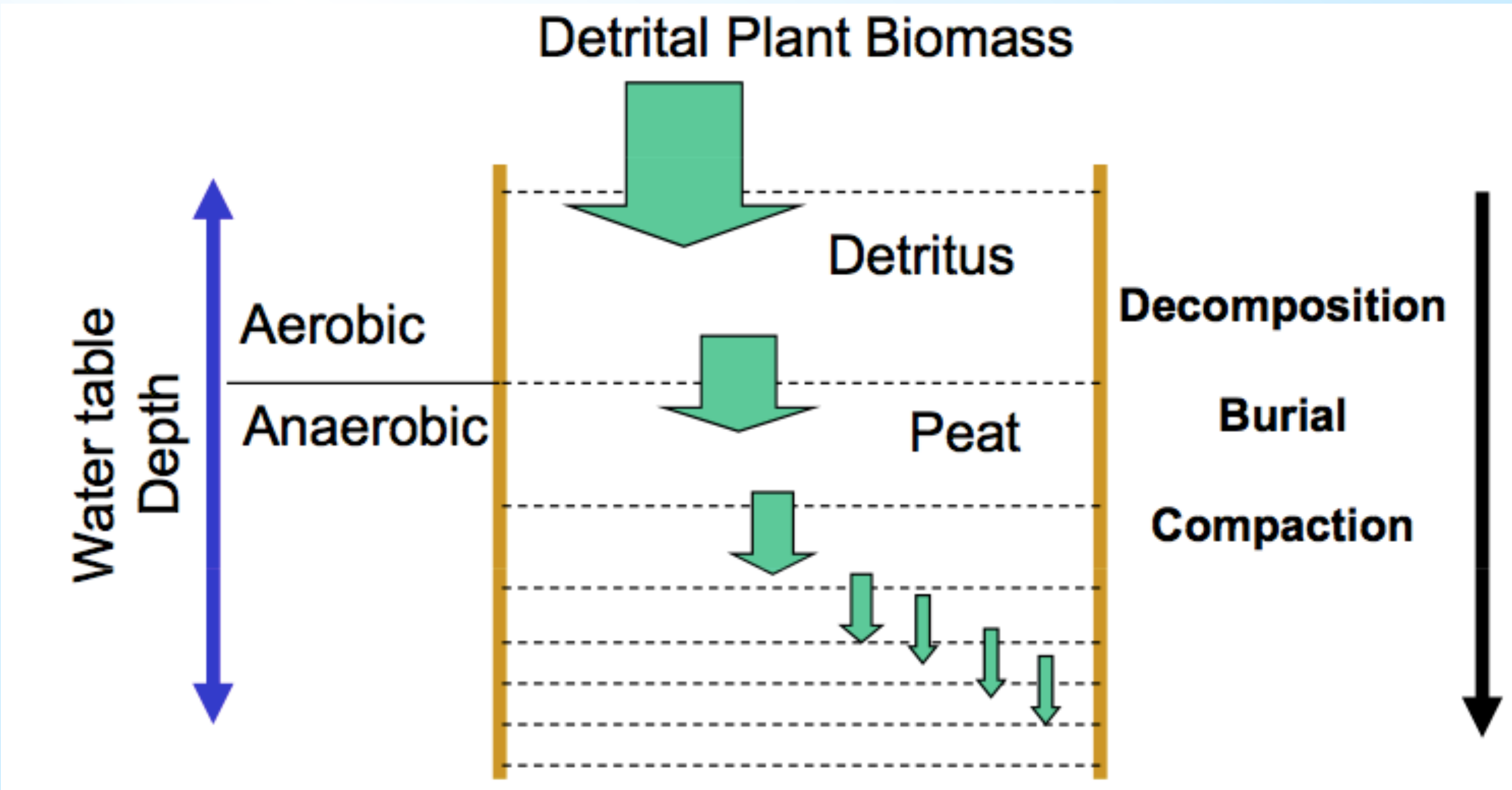


Example: Changing Composition in Flooded Soils

Temporal pattern reflects decreasing energy yield:



Organic matter accumulation

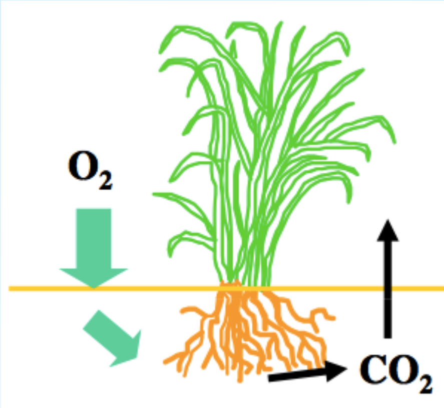


Graphic from K. Reddy, Univ. Florida Wetland Biogeochem Lab

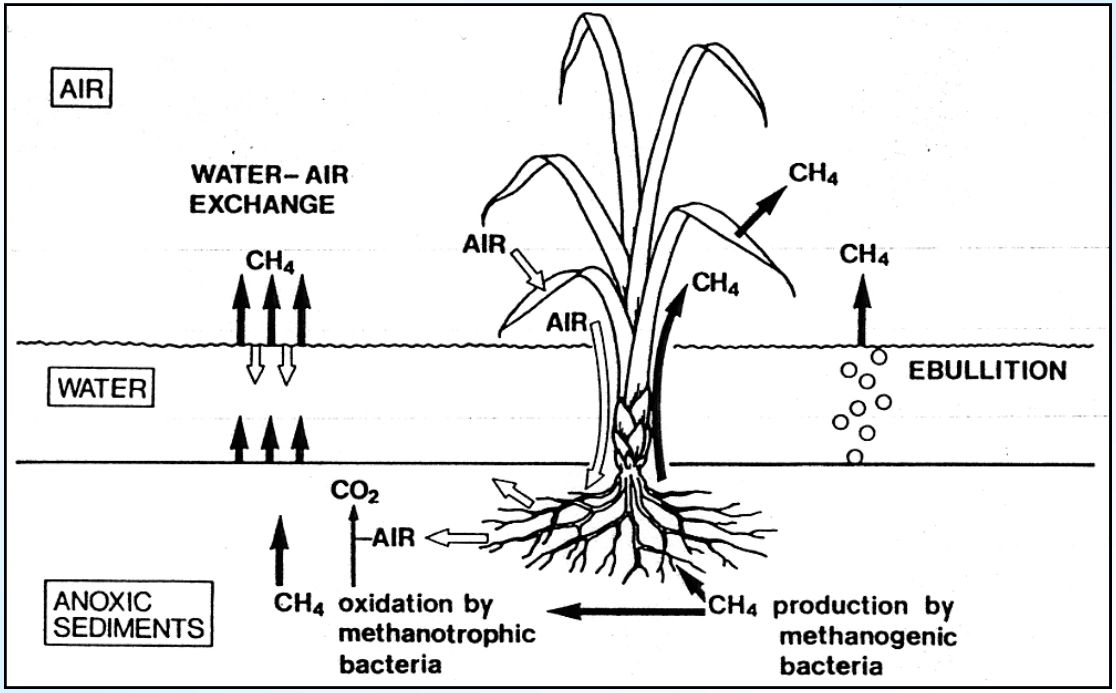
Methanogenesis in Wetlands

- High organic-carbon levels in sediment promote OM oxidation
- CO_2 is reduced to CH_4 during OM oxidation
- Release of CH_4 from plant leaves
- Plants pump air from leaves → roots → sediment
- CH_4 is oxidized by O_2 in root zone:
  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Drained soil



Flooded soil

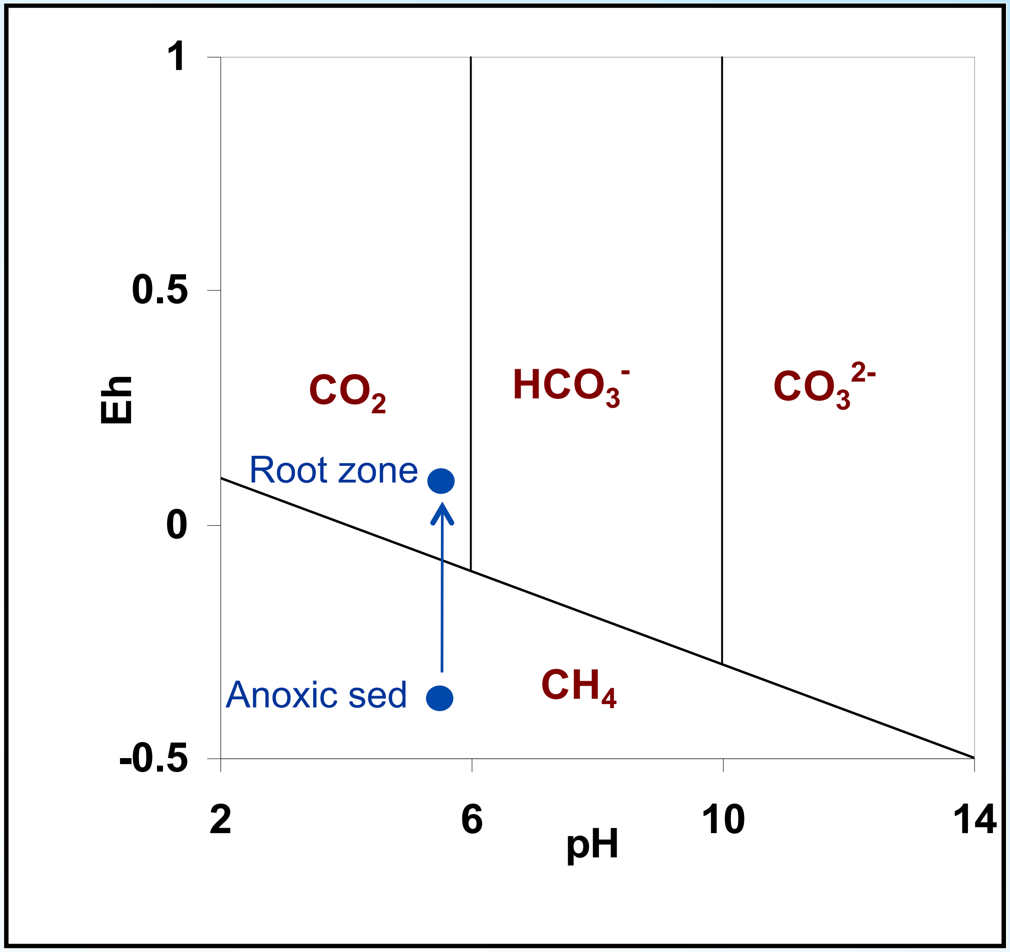


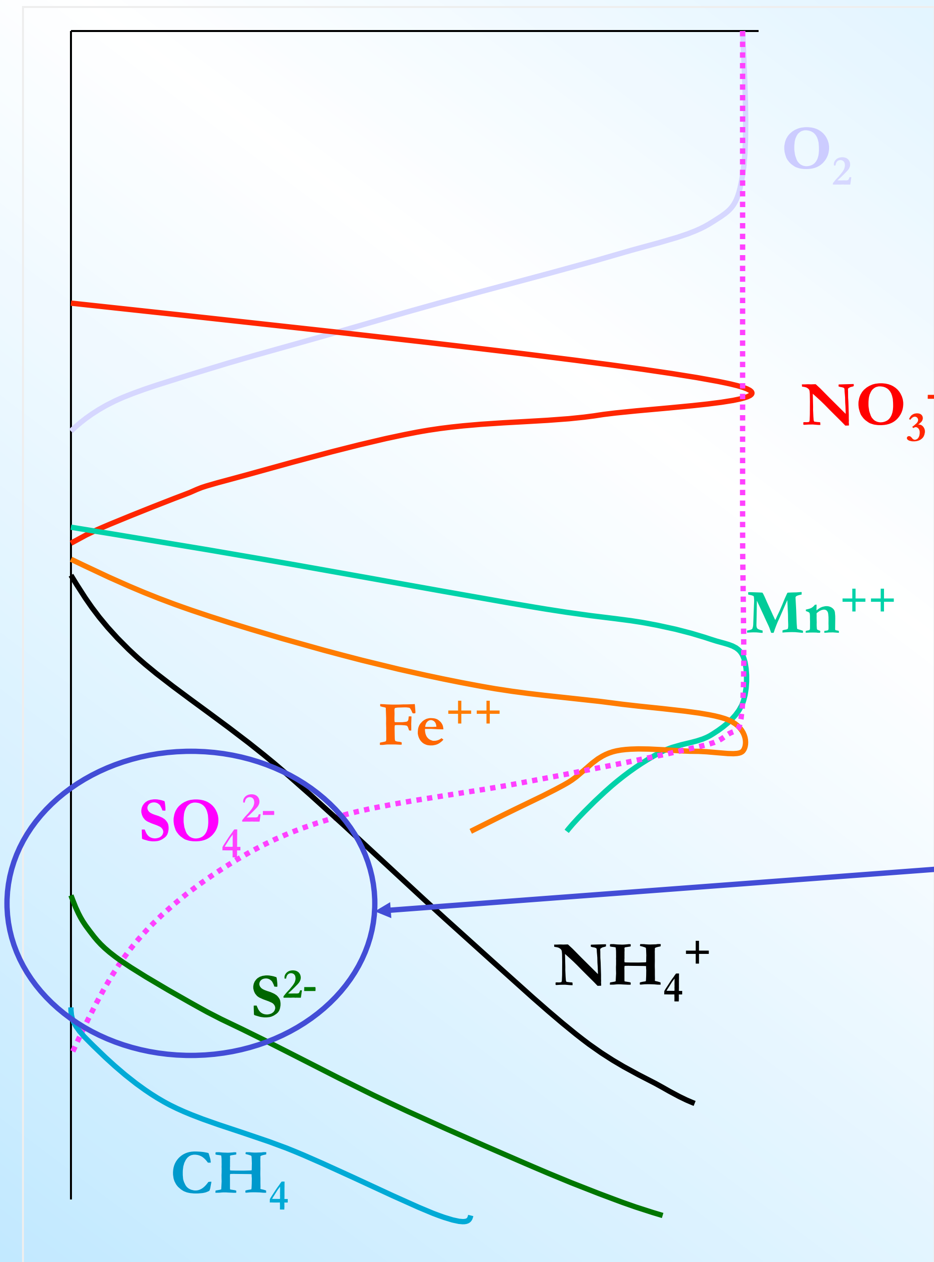
• Oxidation can be predicted from Eh-pH diagram of C in aqueous solution

• CO_2 and CH_4 are released both by direct "ebullution" and pumping from roots to leaves

• As much as 5-10% of net ecosystem production may be lost as CH_4

• Terrestrial and wetland methanogenesis is an important source of this "greenhouse gas"





Redox profiling

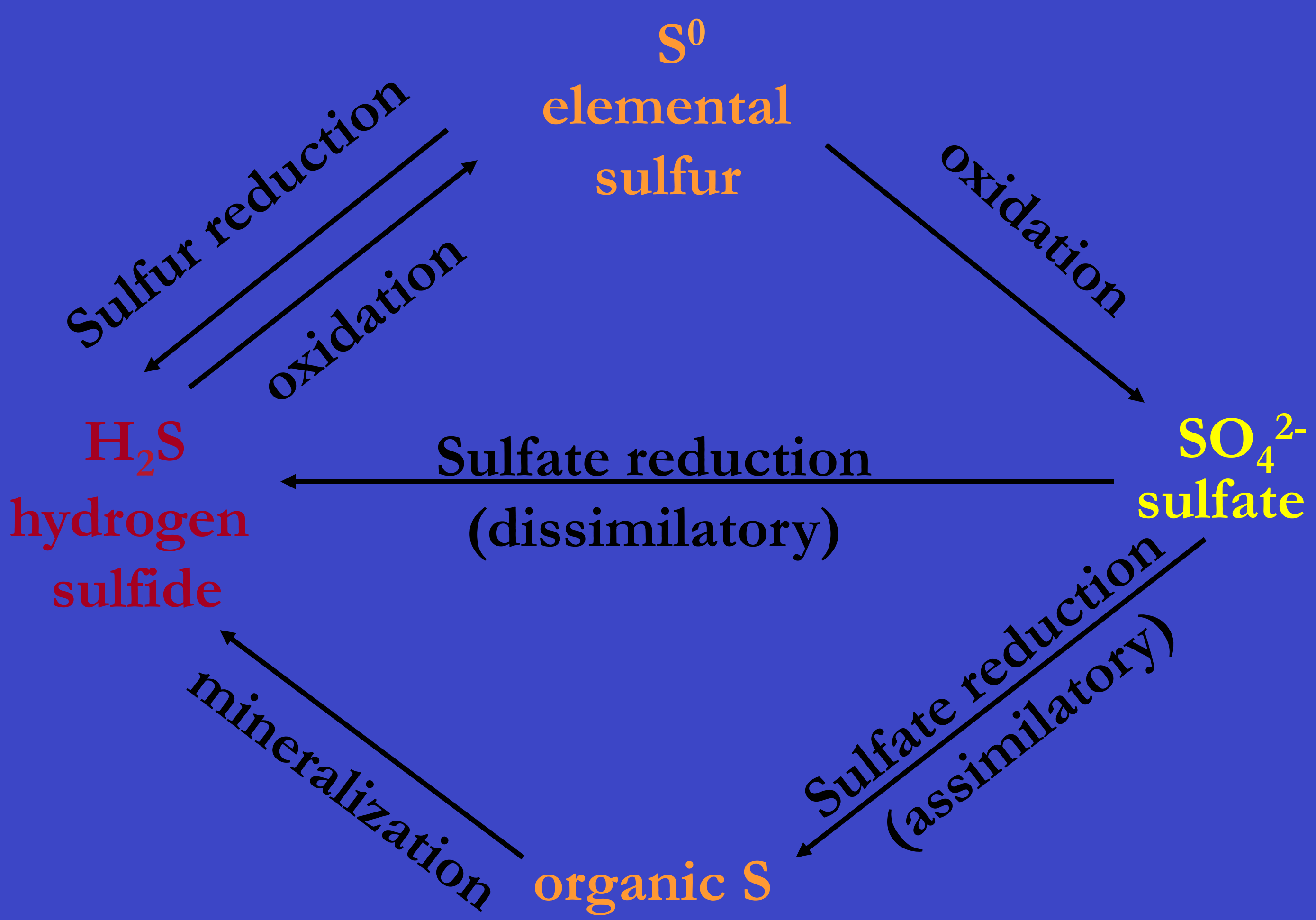
General guideline for OATZ progression

Vertical scale changes across environments

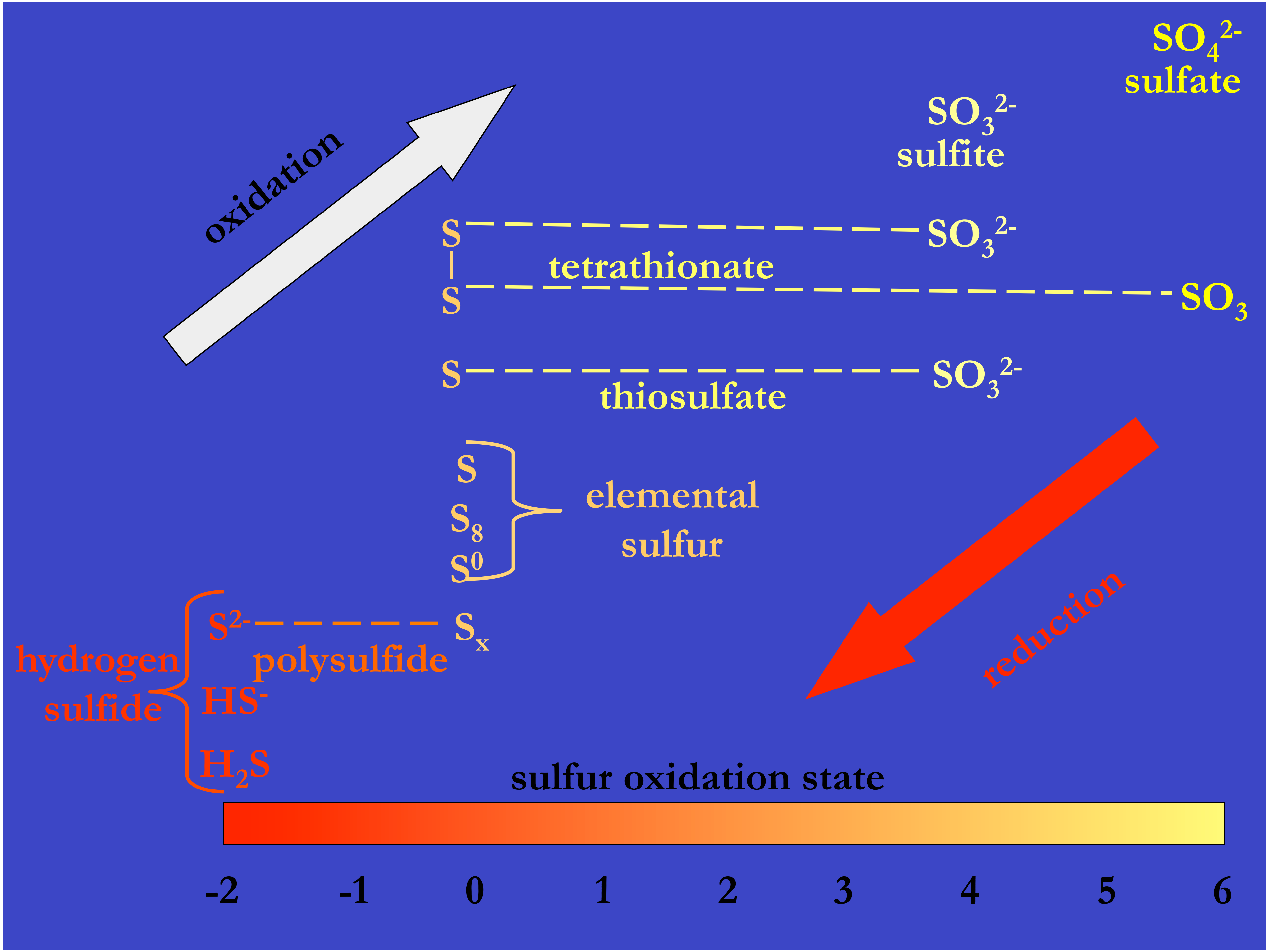
has been traditionally oversimplified to SO_4^{2-} and H_2S

Nealson and Stahl 1997

Sulfur redox cycling
general overview



Megonigal *et al.* 2004



SO_4^{2-}
sulfate
SO_3^{2-}
sulfite
oxidation
S
S
SO_3^{2-}
tetrathionate
SO_3
S
SO_3^{2-}
thiosulfate
S
S_8
S^0
elemental
sulfur
reduction
S^{2-}
S_x
polysulfide
hydrogen
sulfide
HS^-
H_2S
sulfur oxidation state
-2
-1
0
1
2
3
4
5
6

Sulfur redox cycling

significance

Dissimilatory sulfate reduction:

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + HS^- + H^+$$

Accounts for half or more of the total organic carbon mineralization in many environments

Highly reactive HS^- is geochemically relevant because of its involvement in precipitation of metal sulfides and potential for reoxidation

Sulfur redox cycling

important Fe/S chemistry

H_2S oxidation (ph >6):

$$O_2 + Fe^{2+} \rightarrow Fe^{3+}$$

$$Fe^{3+} + H_2S \rightarrow Fe^{2+} + S(0) \quad \text{as } S_8 \text{ and } S_x^{2-}$$

FeS formation and dissociation:

$$Fe^{2+} + H_2S \rightarrow FeS_{aq} + 2H^+$$

(FeS_{aq} formation is enhanced with increasing temperature)

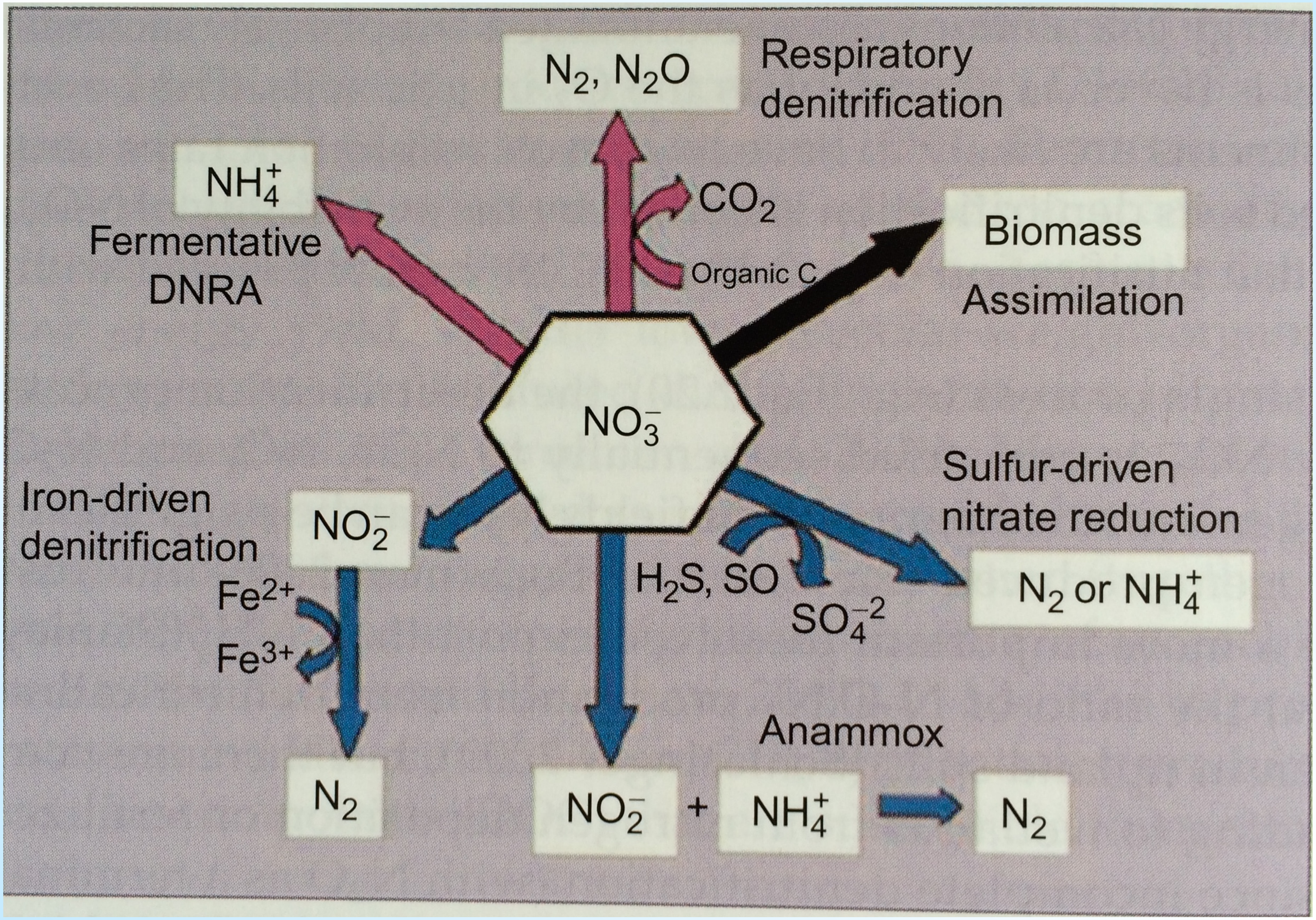
Pyrite formation:

$$FeS_{aq} + H_2S \rightarrow FeS_2 + H_2$$

or under milder reducing conditions:

$$FeS(s) + S_2O_3^{2-} \rightarrow FeS_2 + SO_3^{2-}$$

Nitrate cycling in absence of O_2



Schlesinger - Fig. 7.16

Marine Sediment Depth Profiles

Reaction	E_h (V)	ΔG
Reduction of O_2		
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+0.812	-29.9
Reduction of NO_3^-		
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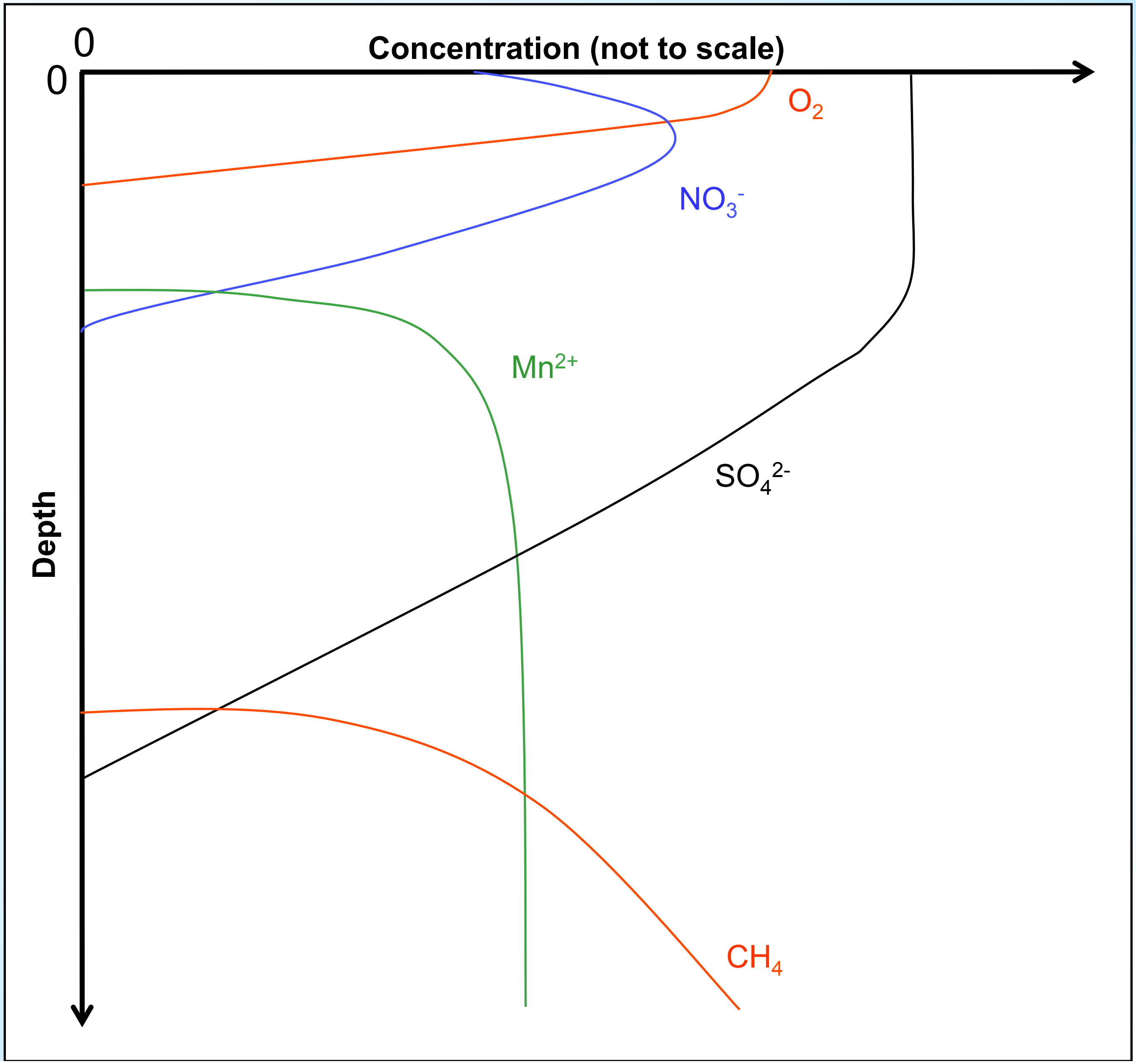
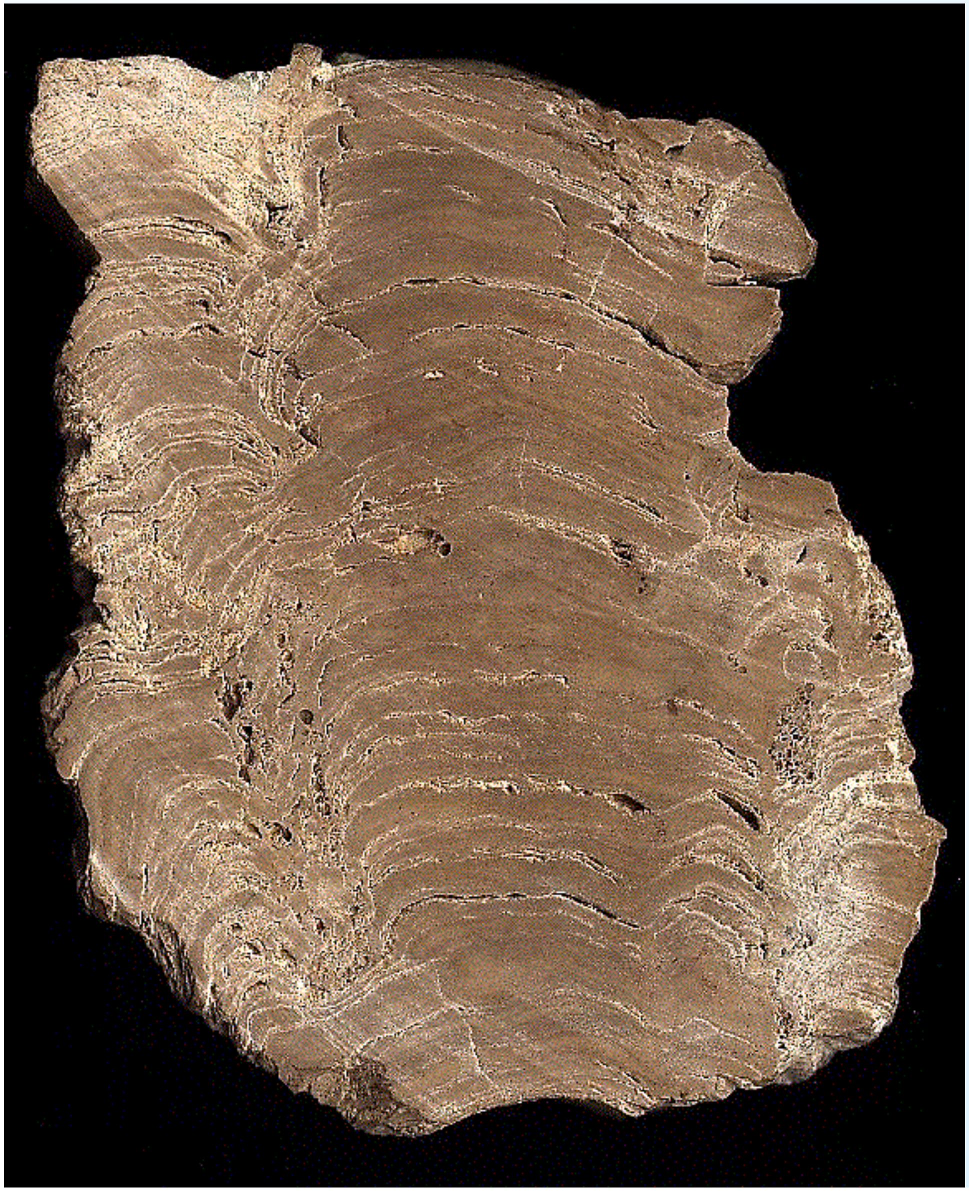
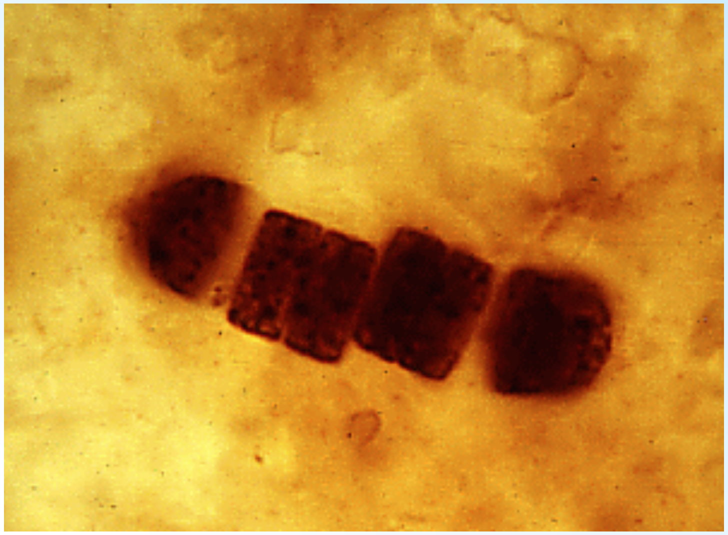


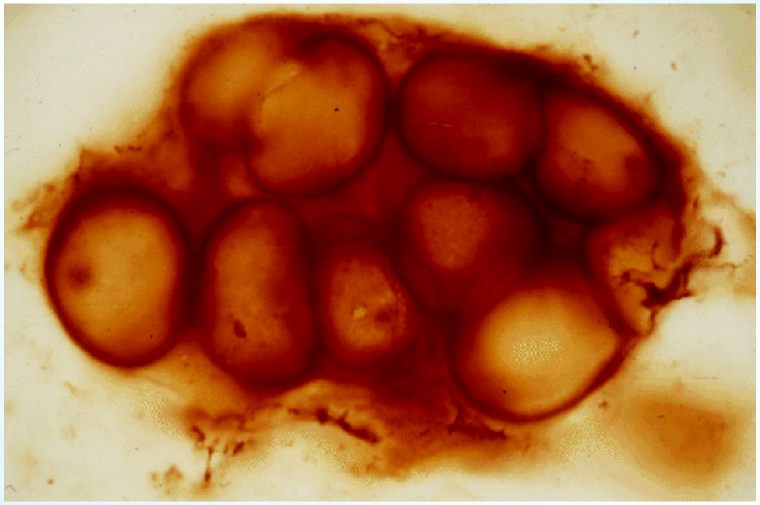
Microbial Mats

steep gradients

Wisconsin & Australia

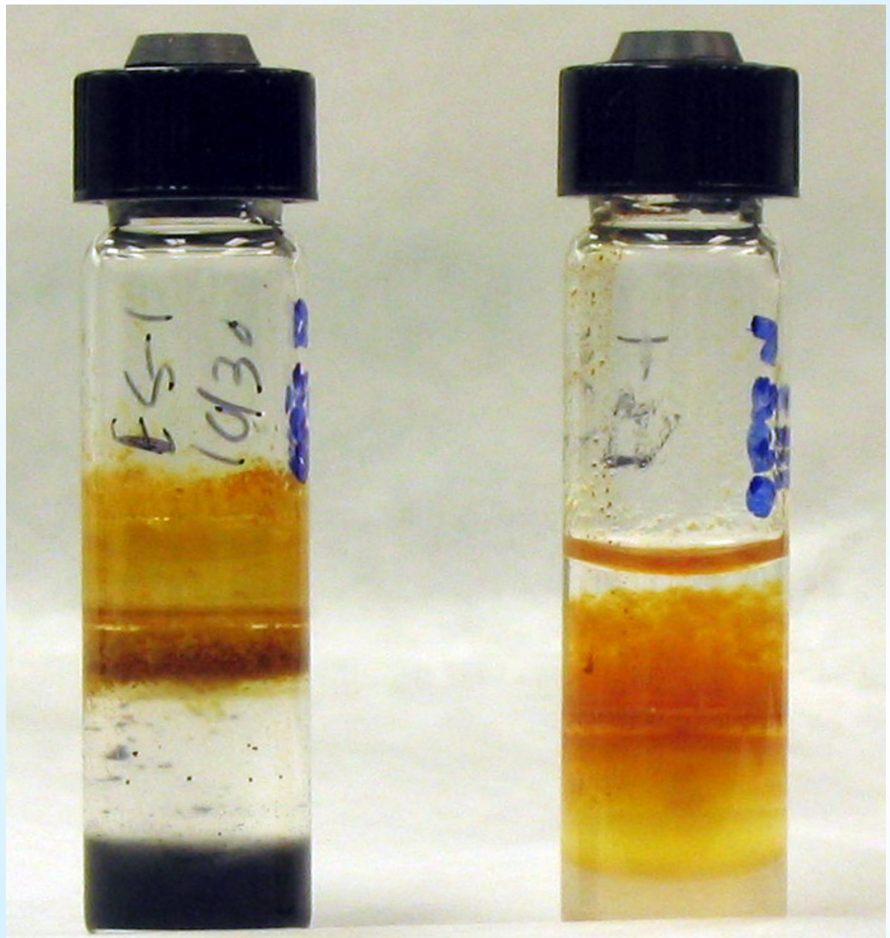






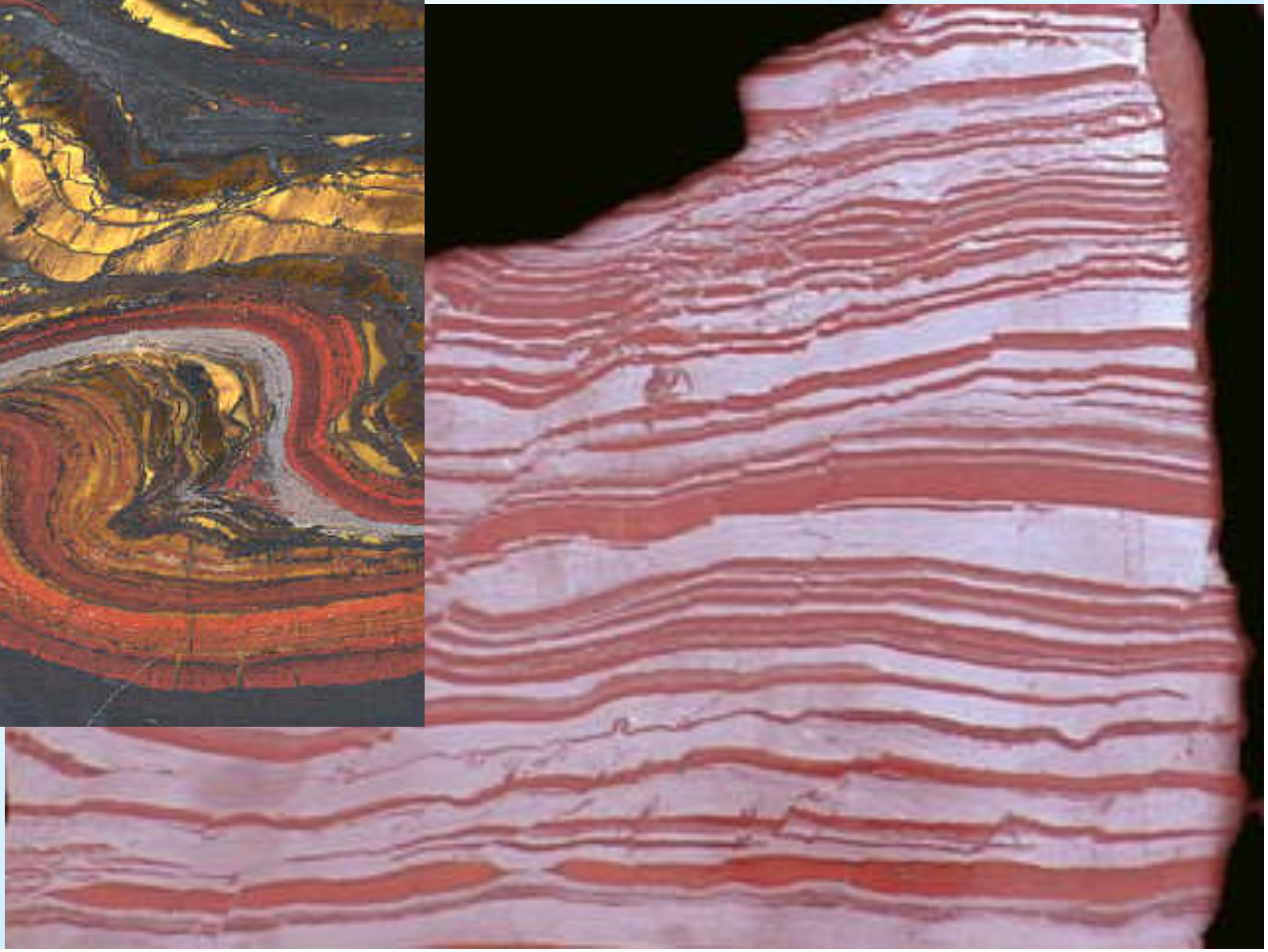
Hamelin Bay, Australia

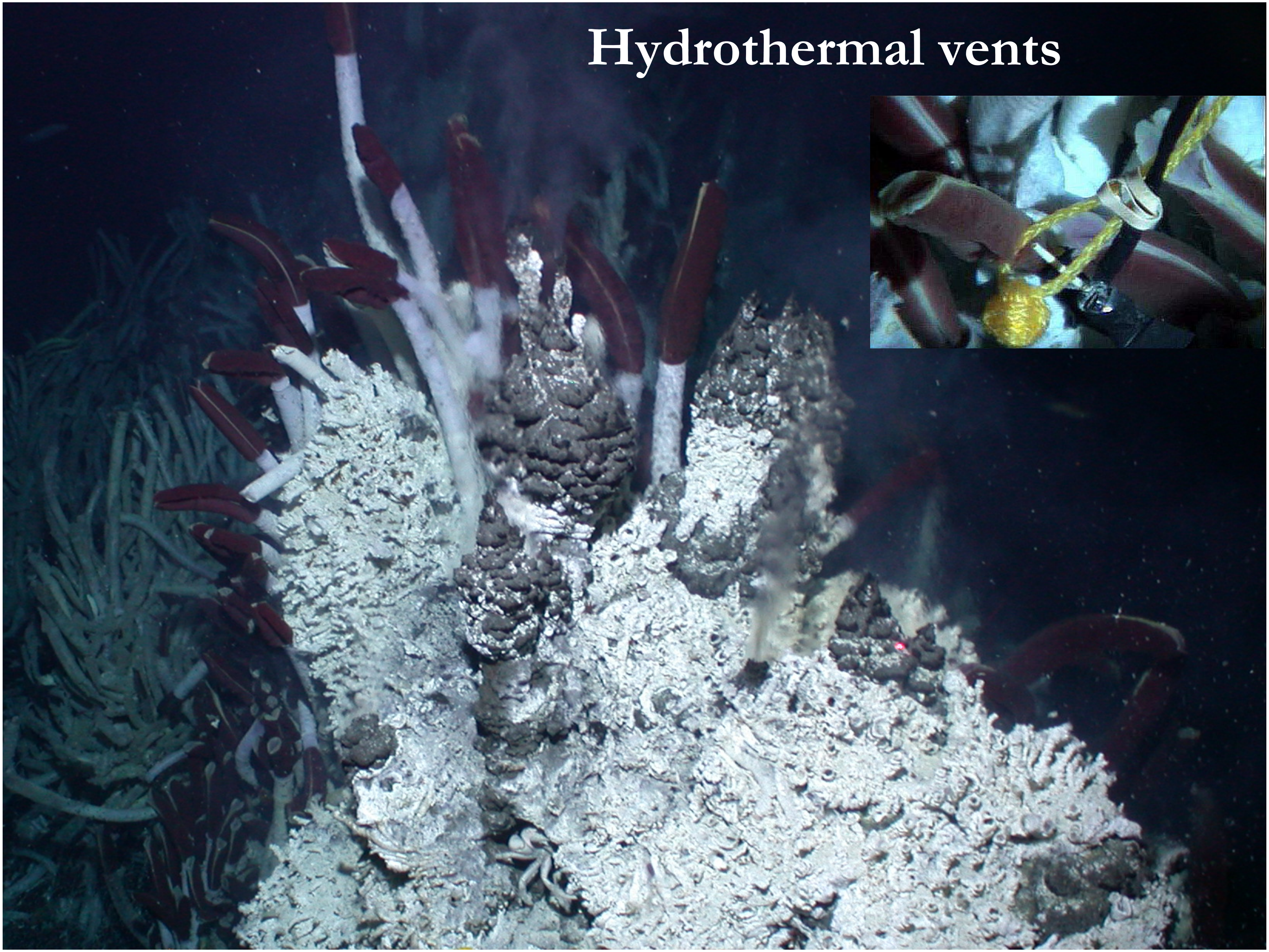
Laboratory Fe-oxidizing microbial cultures



Sobolev et al. 2001, Roden *et al.* 2004

Banded iron formation




Hydrothermal vents

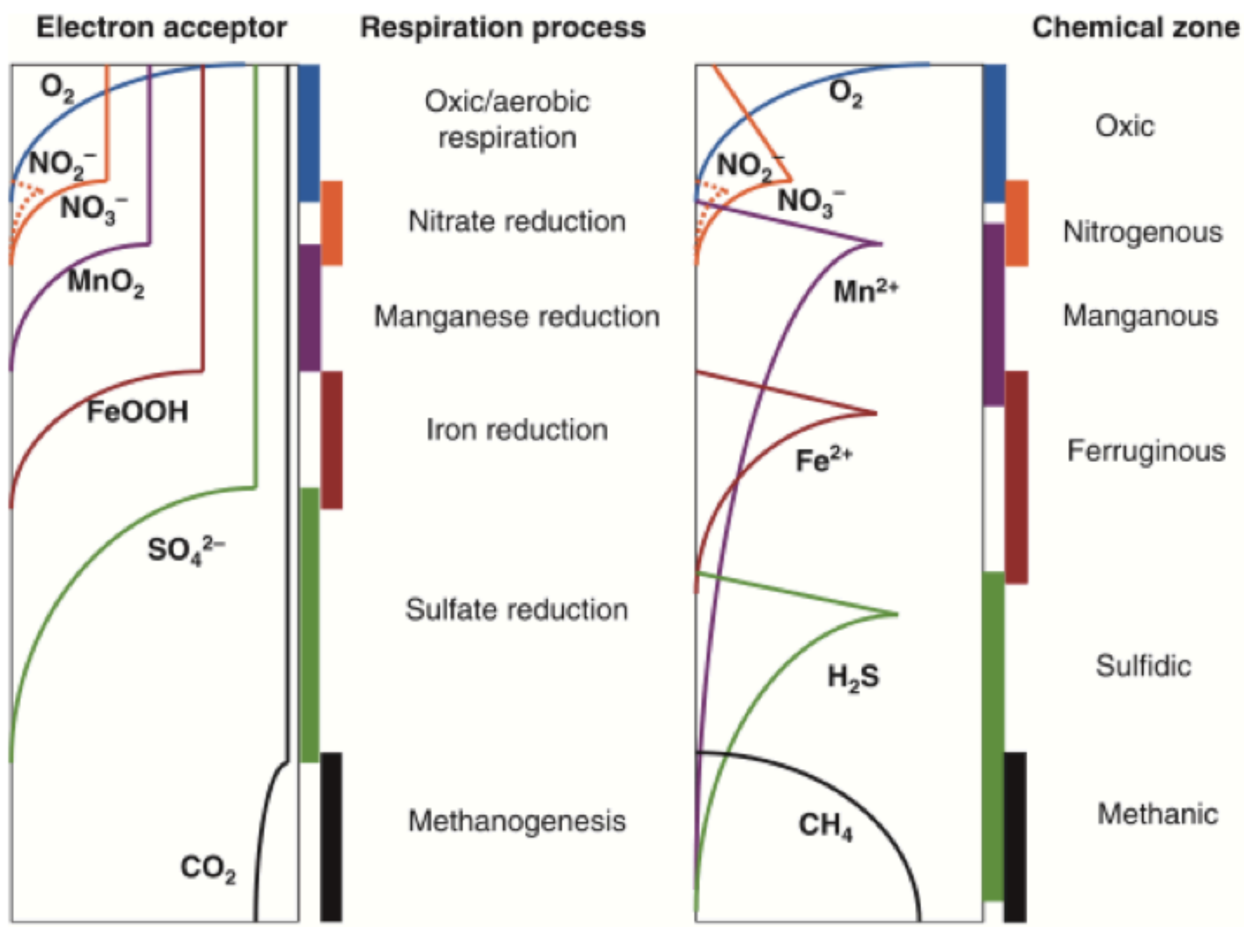
Geobiology

Geobiology (2009), 7, 385–392 DOI: 10.1111/j.1472-4669.2009.00214.x

Editorial

Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic' would go away

Canfield & Thamdrup



The bottom line

Oxic-anoxic transitions

There is a principle difference between gradients of compounds used for biomass synthesis and those needed for energy conservation, such as oxygen.

Nutrient limitation leads to a decrease of metabolic activity, but absence of an energy substrate causes a shift in the composition of a microbial community, or forces an organism to switch to a different type of metabolism.

Brune et al. 2000

In-class activity

Dominant processes in wetlands

(1) Self-assemble into groups of 5-6. Using only your noses, speculate on the dominant biogeochemical process taking place in each type of wetland sample.

(2) Switch to the next station until complete.

(3) Repeat stations & take off the Al foil & note if you'd make any changes in your original assessment.

(4) Not a homework assignment for points, but you should be able to complete Problem #1 on page 274 of your text.

Name:

	Smells like:	Infer salinity?	Rank order of org C supply 1= most 3= least	Where on Oahu could you find this?
A				
B				
C				

Which microbial metabolic pathway is dominating the oxidation of organic matter in each? Why?