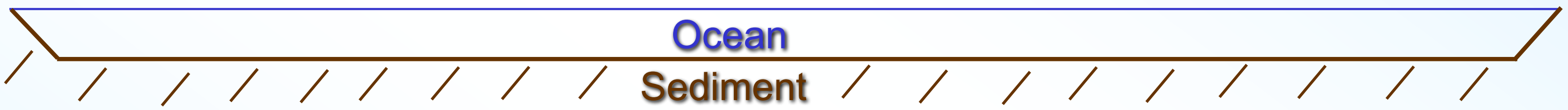
Chemistry in Sediments: Aerobic to Anaerobic Diagenesis

OCN 623 – Chemical Oceanography

Reading: Libes, Chapter 12

Why Study Sediments?

- Very large surface area of sediments with respect to the volume of seawater:



↕ Vertical distance = 4 - 6 km

↔ Horizontal distance = 1000's km

- Large area of contact between seawater and sediment
- Strong potential for the two reservoirs to interact

Types of sediments

- Hydrogenous: formed by reactions in the water
  - manganese nodules, iron hydroxides, sulfates, …
- Biogenous: produced by living organisms

  -calcite, silica, …
- Lithogenous: produced from the weathering
  - Al silicates, quartz, …
- Cosmogenous: produced from extraterrestrial sources
  - Ferric meteorites from space

What is Diagenesis?

- Greek etymology: *dia* -- "passing through"
  genesis -- "origin, birth"
- Diagenesis is the "sum of all processes that change a sediment or sedimentary rock subsequent to its deposition from water, but excluding metamorphism and weathering" (Berner, 1980)
- Simply: "Reactions in Modern sediments…"

Other geochemical transformations of sediments:

- Metamorphism: burial reactions that take place at high pressure and temperatures >150^{o}C
- Weathering: reactions resulting from the effect of atmospheric contact on sediments (after uplift)

Why is Diagenesis Important?

- Important part of global biogeochemical cycles because of size of sedimentary reservoir

- Geochemical balances of many elements depend on balance between burial and remobilization

- Surface sediments are habitat for a wide range of organisms

- Production of petroleum via diagenesis and further processing of organic rich sediments

Early Diagenesis

- Today' s topic
- Reactions that occur at sediment depths shallower than a few 100 m
- Reactions that occur at low temperature
- Uplift above sea-level does not occur, hence all interstitial space is filled will water
- Includes:
  - Chemical reactions
  - Dissolution of solids
  - Diffusion of dissolved species
  - Precipitation of dissolved species
  - Microbial activity
  - Compaction
  - Dewatering
  - Bioturbation of solids
  - Irrigation

Overall Result of Diagenesis

Terrestrial debris (inorganic, organic)

+

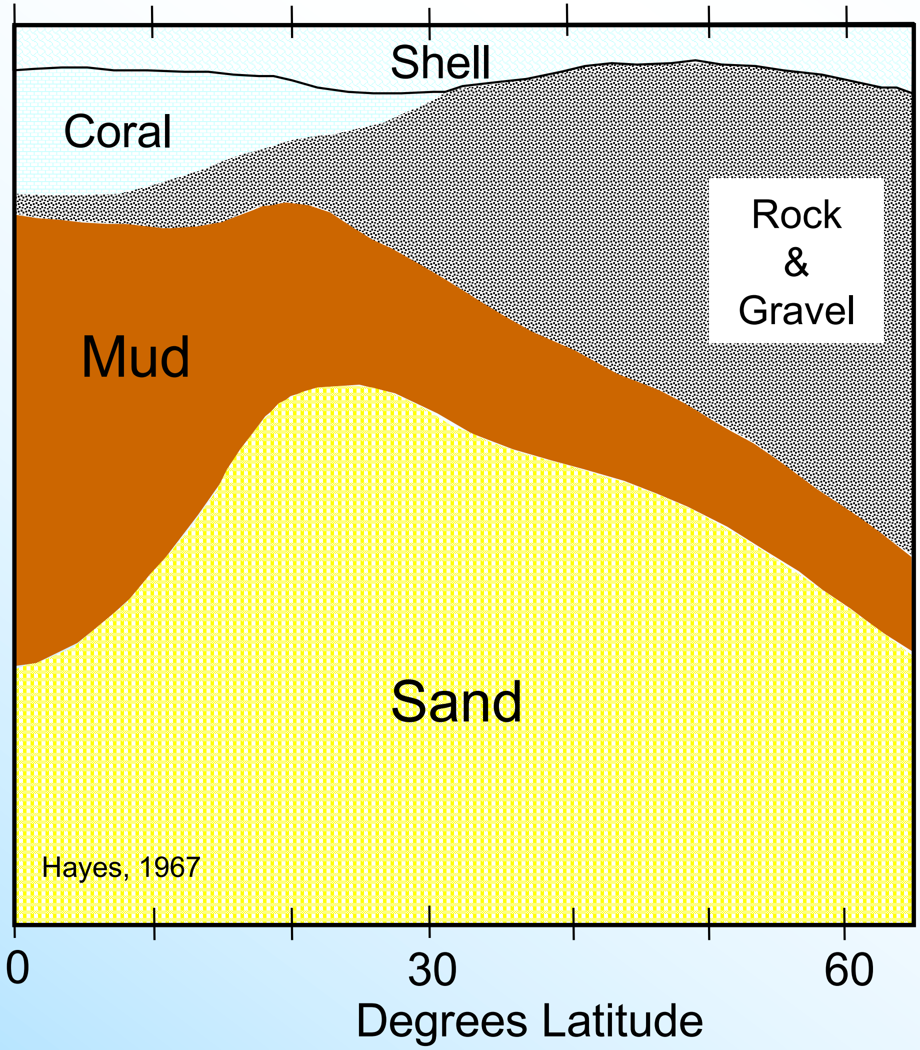
Reactive marine organic matter / biogenic debris

Diagenetic Reactions

Product	***Fate***
Remineralized (inorganic) C, N, P	Released, buried
Authigenic minerals (C, P, S, Si, Mn-Fe) (grow in place, not transported)	Buried
Residual OM	Buried

Composition of Marine Sediments

Relative Proportion of Inner (< 60 m) Continental Shelf Deposits:



What regions might have shelf dominated by muddy sediments?

How about gravel?

Physical Changes that Impact Sedimentary Diagenesis

- Alteration in particle size
- Changes in sediment porosity
- Compaction (which results in porewater advection)
- Burrowing/feeding of biota ("Bioturbation")
  - Depth of bioturbation: <10 cm to more than 1 m
  - Prevents formation of chemical gradients
  - Introduces O_2-rich bottom water into sediments

Compaction & Porosity

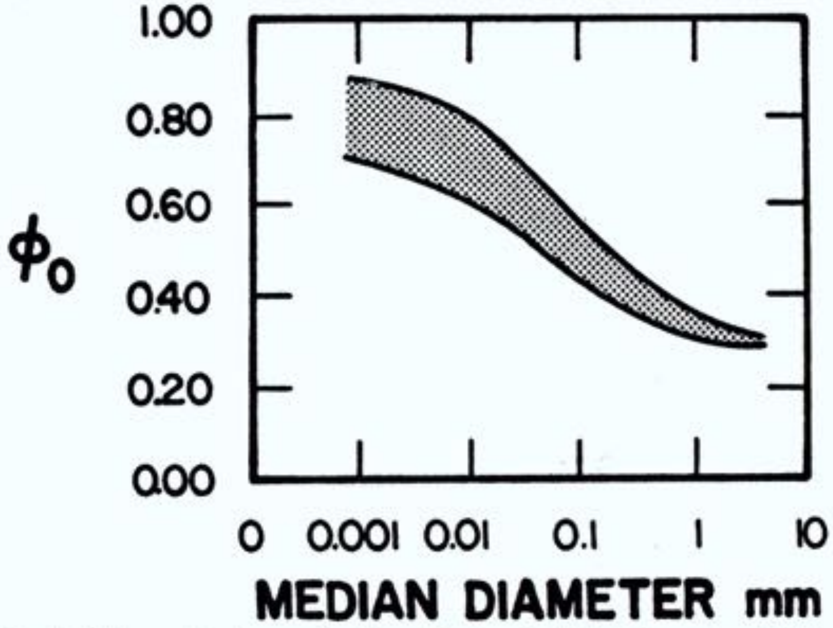


FIGURE 3-6. Initial porosity ϕ_0 as a function of grain size for terrigenous surfical sediments. The increase of porosity with decreasing median size reflects increasing proportions of clay minerals. (After Meade, 1966.)

ϕ = porosity of sediment
$(cm_{water}{}^{3}/cm_{sed}{}^{3})$

Mechanical compaction
-rearrangement
-bending & ductile deformation
-breakage of grains

Grain rotation

Bending and ductile ductile deformation

Grain crushing

Compaction & Porosity

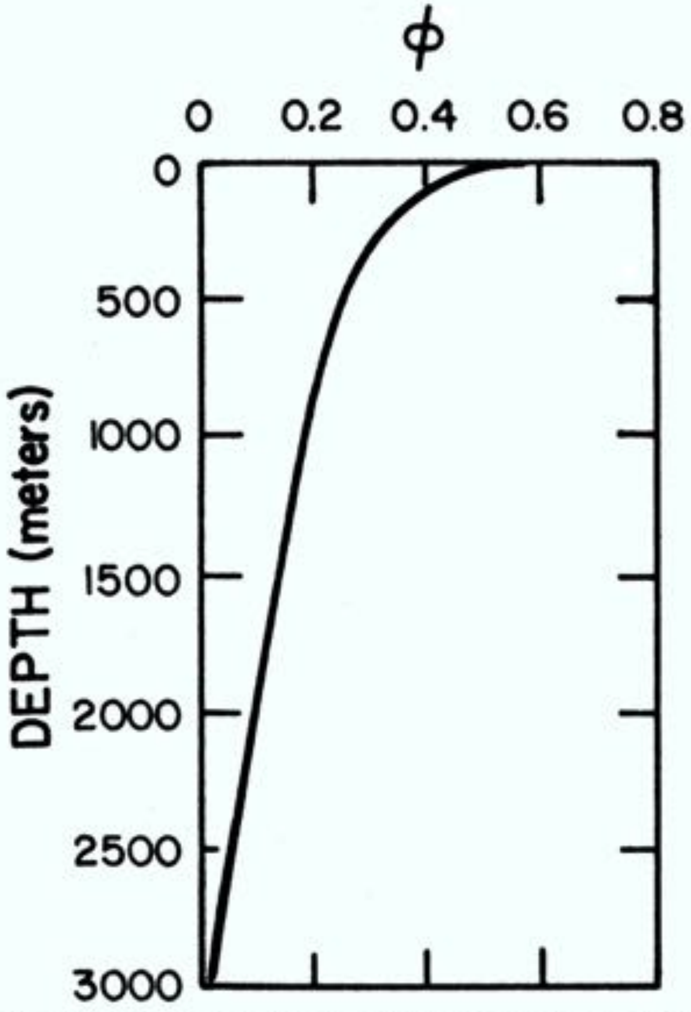


FIGURE 3-9. Porosity of clay sediments. Composite based on data for Recent, Tertiary, and Lias sediments. (After Engelhardt, 1977.)

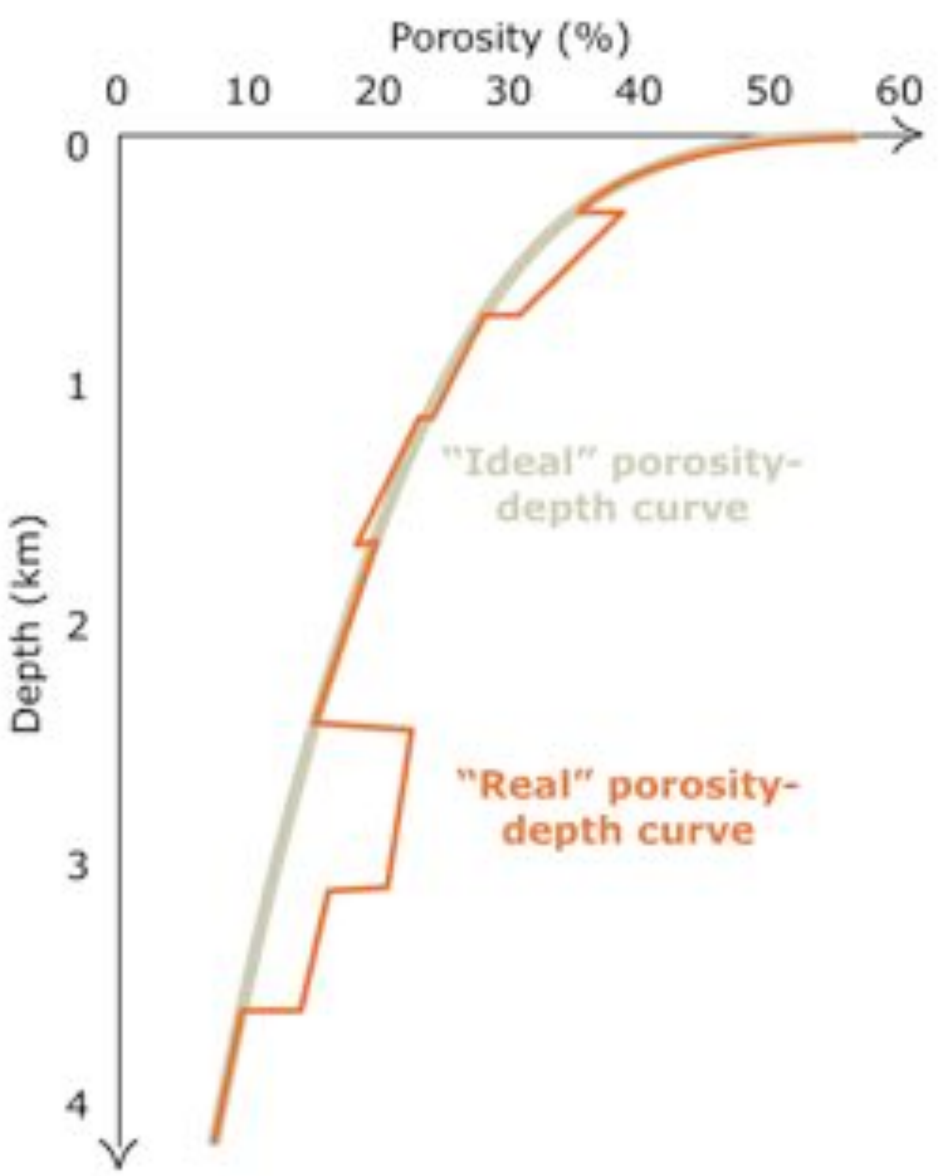
ϕ = porosity of sediment ($\mathrm{cm_{water}}^3 / \mathrm{cm_{sed}}^3$)

Idealized porosity estimation as an exponential function of an initial porosity at the surface

$$\phi = \phi_0 e^{-cz}$$

c is average compressibility
z is depth

Compaction & Porosity



Real porosity differs from the exponential function

Each sediment layer has its own composition & compressibility

Degree of compaction also depends on effective stress (geothermal gradients)

Bioturbation

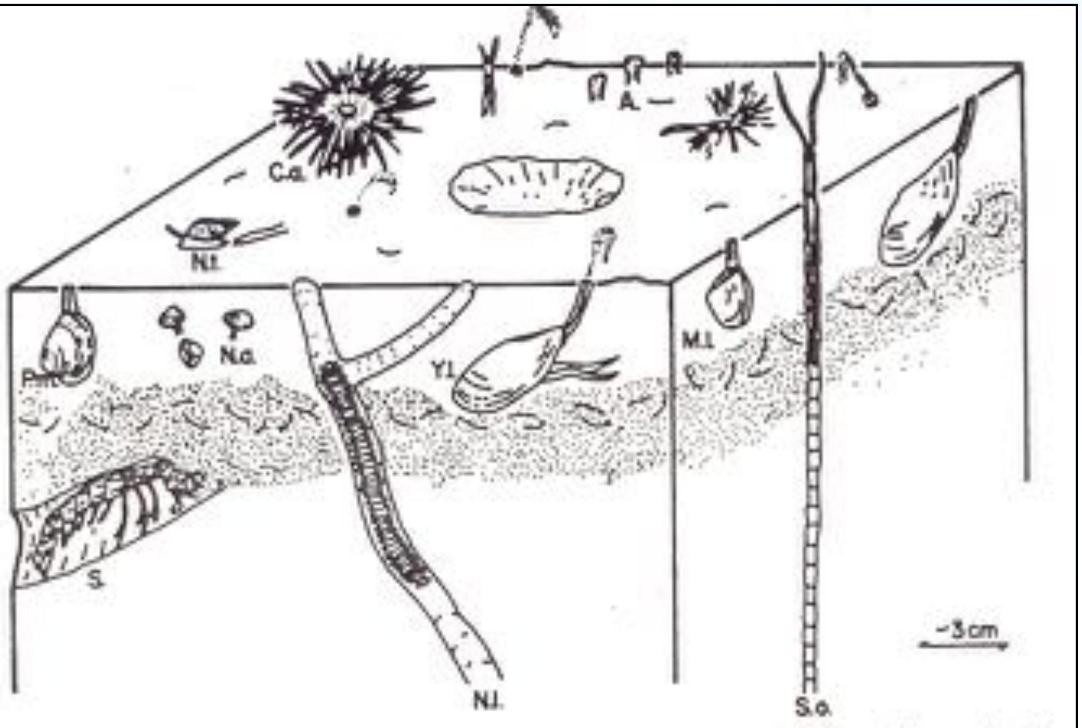
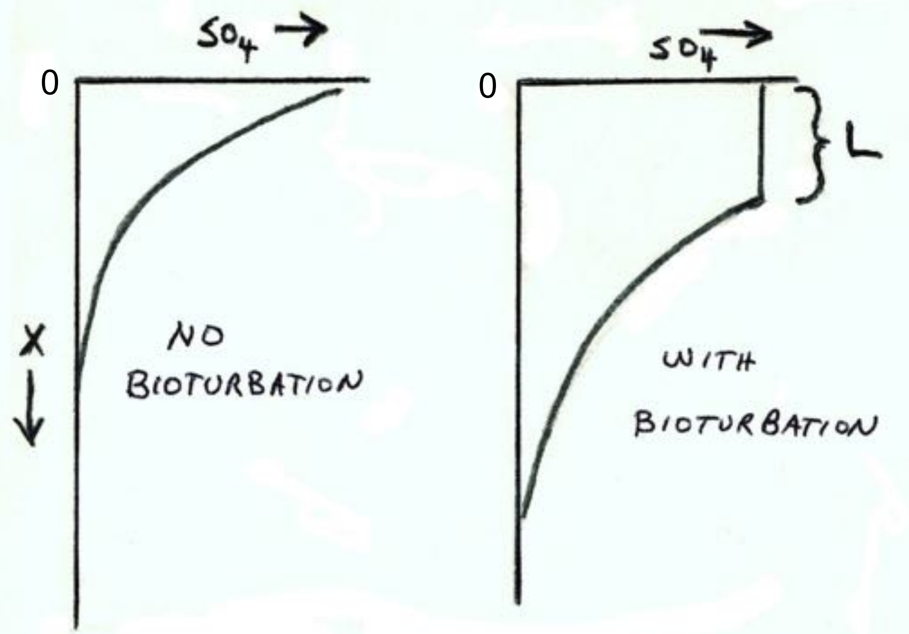
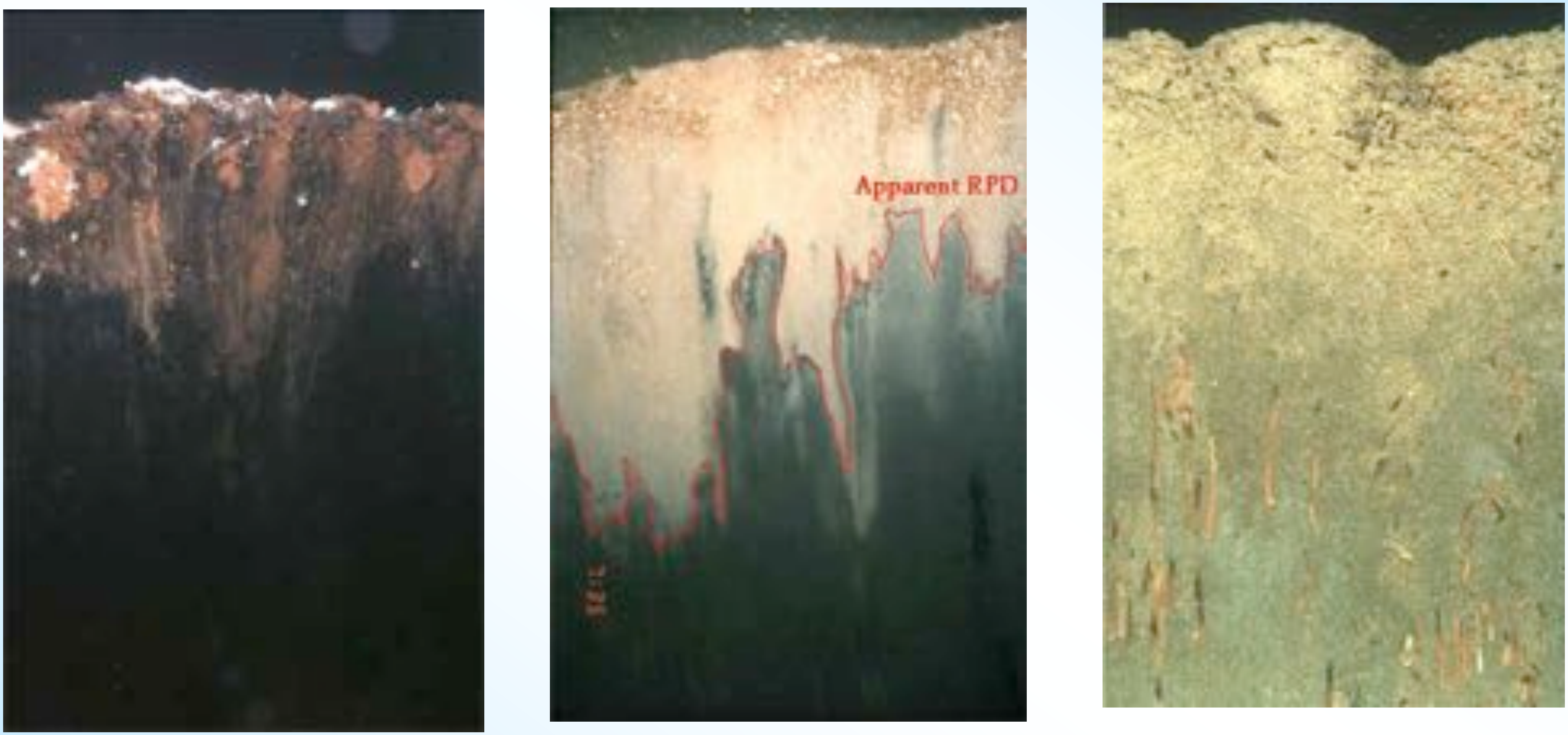


FIGURE 3-12. Schematic representation of major burrowing fauna from a sediment locality (NWC) in Long Island Sound. (From Aller, 1977; 1980.)



L = depth range of bioturbation

Bioturbation



aRPD = apparent redox potential discontinuity

NO Sedimentary Diagenesis

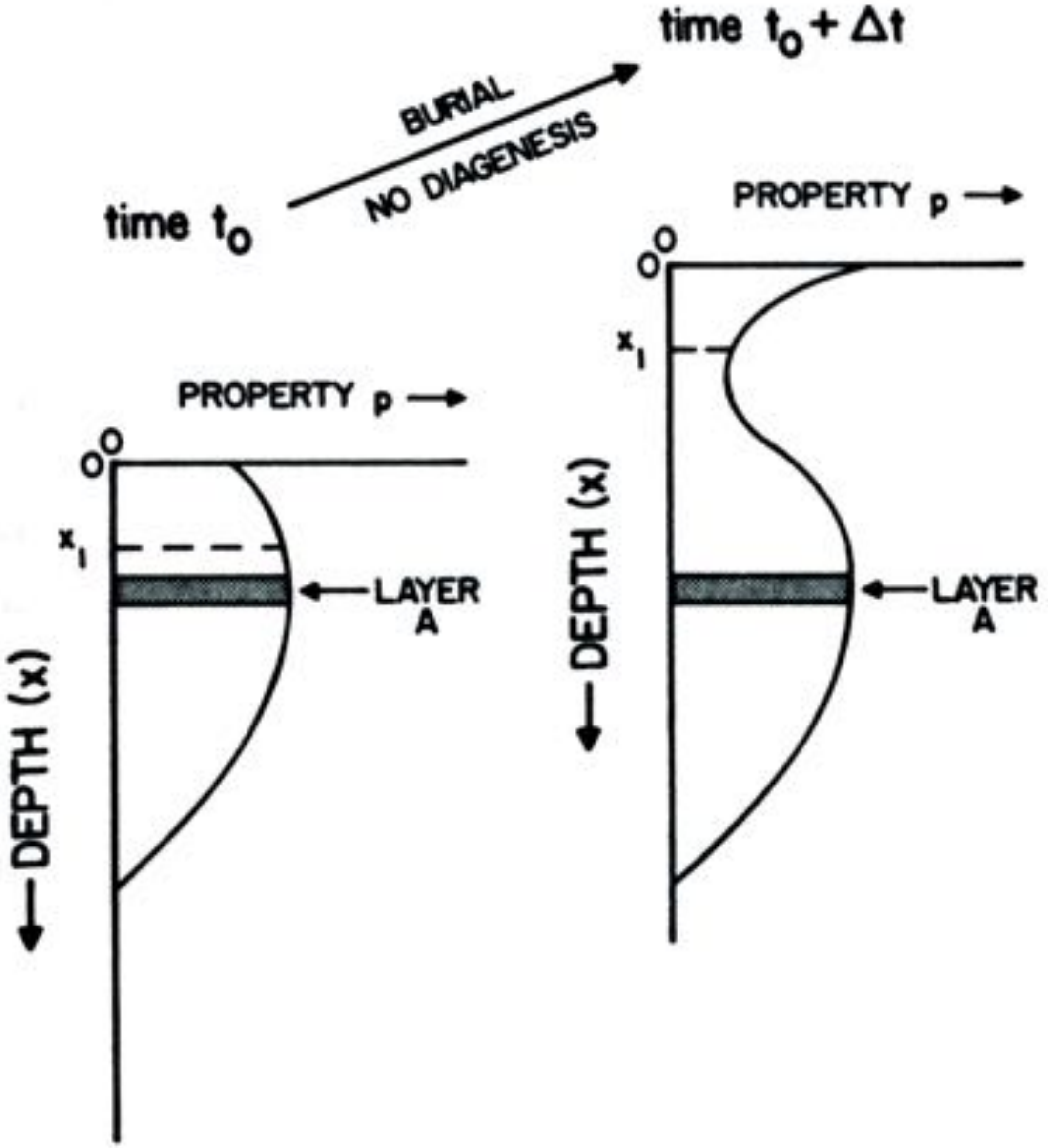


FIGURE 2-1. Diagrammatic illustration of situation of no diagenesis. Upon burial, the value of property *p* changes for a fixed depth, x_1 (or $x = 0$), but does not change for a given layer *A*.

STEADY STATE
Sedimentary Diagenesis

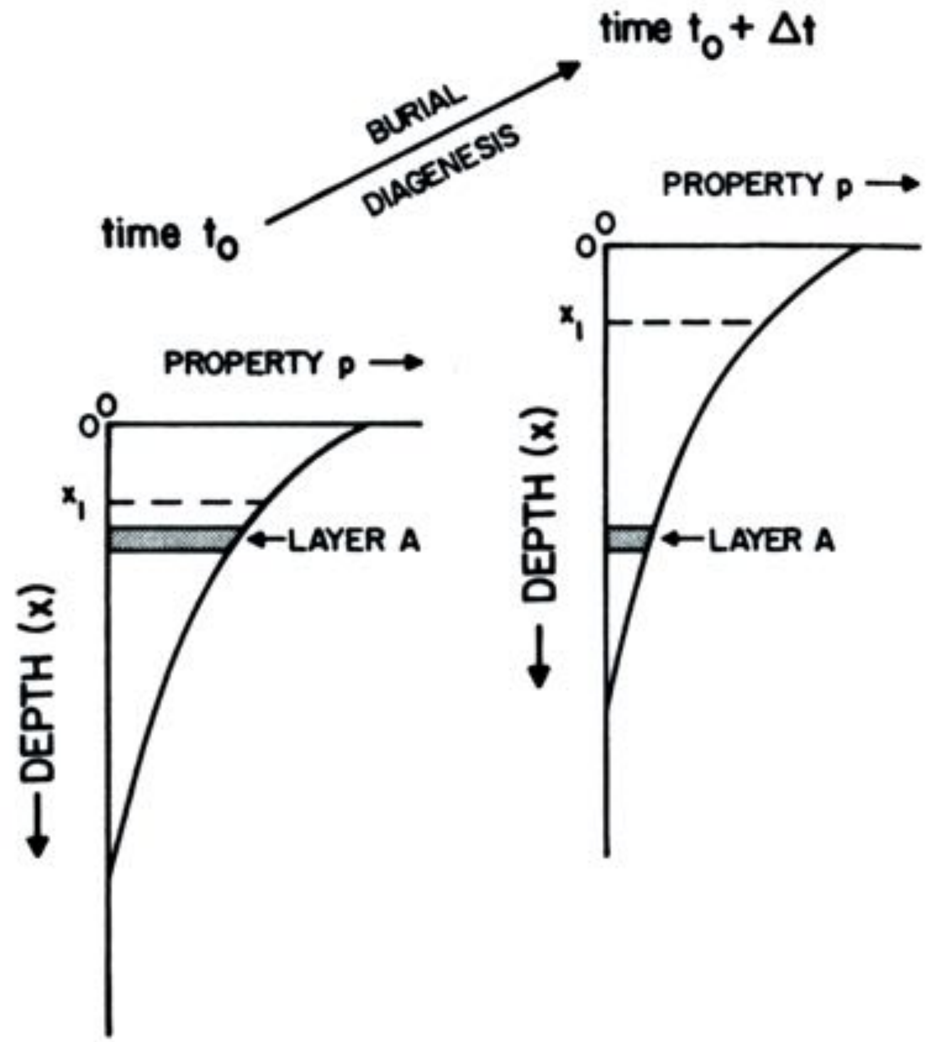
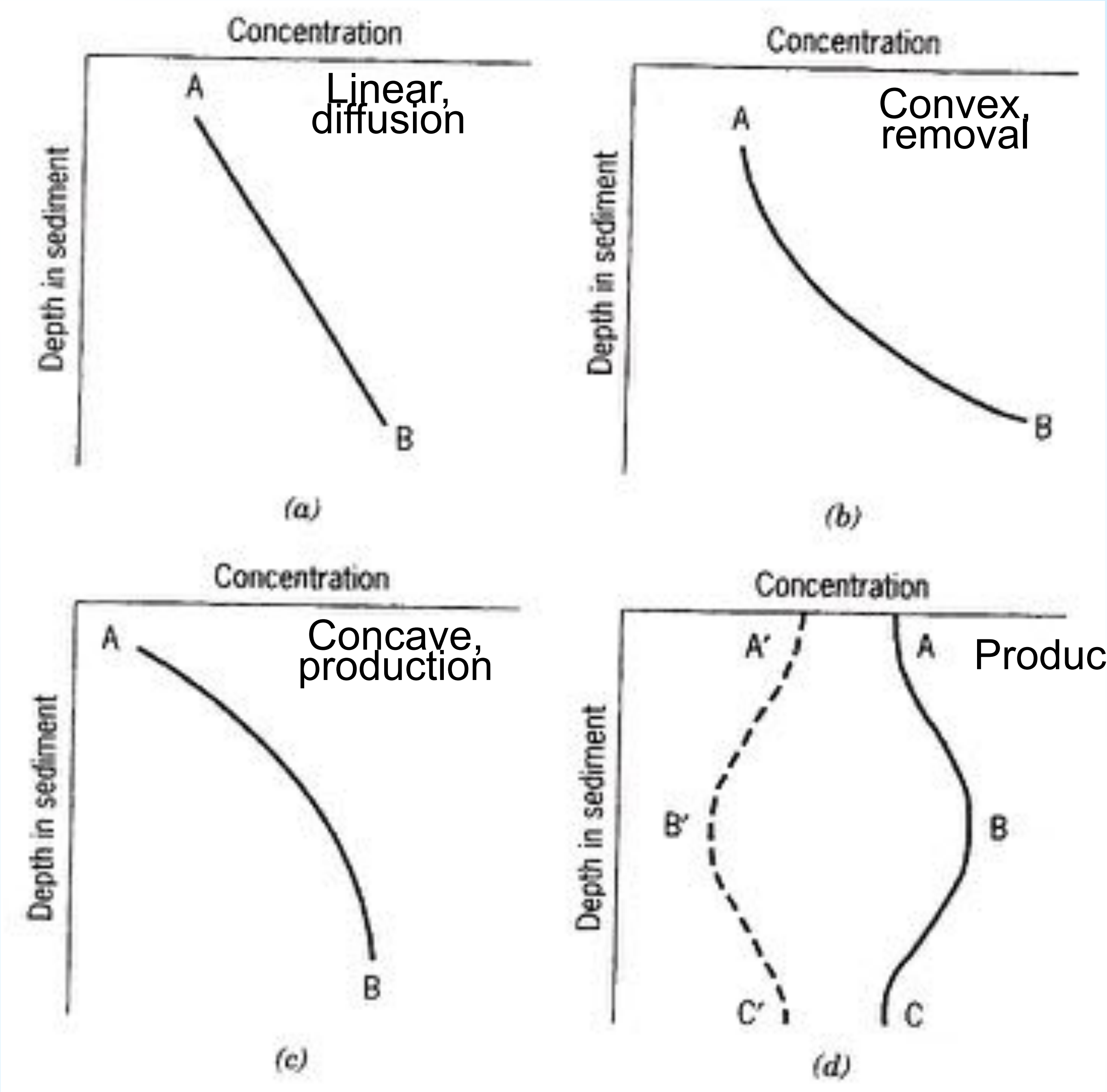


FIGURE 2-2. Diagrammatic illustration of situation of steady state diagenesis. Upon burial, the value of property *p* does not change for a fixed depth, x_1 (or $x = 0$), but does change for a given layer *A*. (Modified after Berner, 1971.)

Sedimentary Diagenesis



Linear, diffusion

Convex, removal

Concave, production

Production/consumption

Redox Control of Diagenesis

- Diagenesis driven by decomposition of organic matter (OM)
  - OM in sediments is thermodynamically unstable
- Decomposition occurs by various processes, each of which leads to formation of specific species in solution and precipitation of authigenic minerals
  - Involves series of reactions using electron acceptors that are consumed sequentially
  - Each successive reaction is energetically less favorable, and does not occur until the electron acceptor from the (previous) more favorable reaction has been mostly consumed

Why is organic matter an electron donor?

- Example: net reaction for aerobic oxidation of organic matter:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

- In this case, oxygen is the ***electron acceptor*** – the half-reaction is:

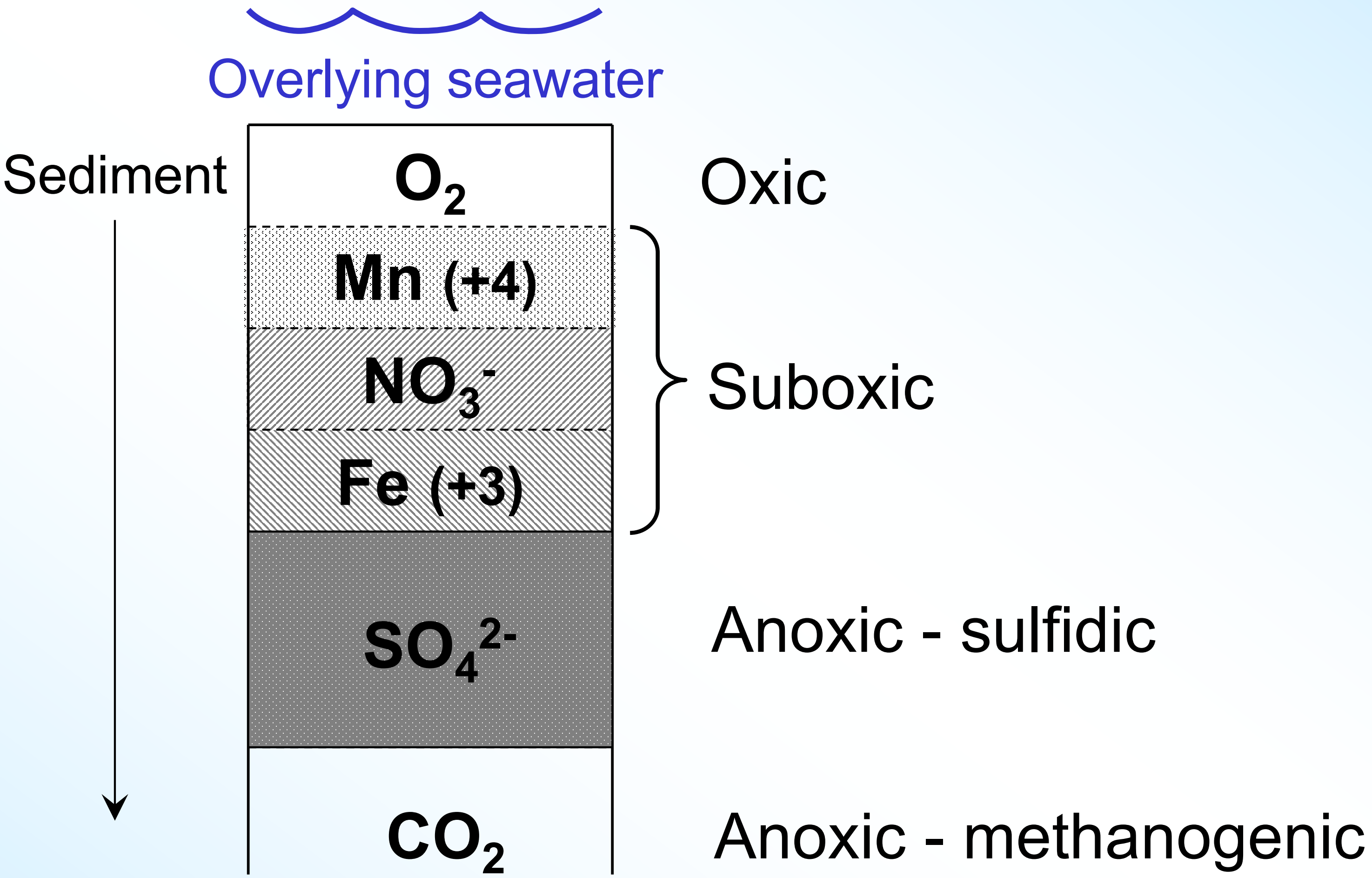
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

- Different organisms use different electron acceptors, depending on availability due to local redox potential

- The more oxidizing the environment, the higher the energy yield of the OM oxidation (the more negative is ΔG, the Gibbs free energy)

Redox Reaction Succession

Sequence of dominant OM oxidizers



Overlying seawater

Sediment

O_2 Oxic

Mn (+4)

NO_3^- Suboxic

Fe (+3)

SO_4^{2-} Anoxic - sulfidic

CO_2 Anoxic - methanogenic

Diagenetic reactions occur (with increasing depth in the sedimentary column) according to the free energy released

Oxic respiration

ΔG^o_R = -3190 kJ/mol CH_2O

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

(see Table 12.1 in Libes for full reactions)

- Common in oxygenated waters
- Common in surface sediments
- Typically there is much more OM in sediments than O_2 available, so O_2 is generally depleted rapidly in interstitial waters of sediments

Manganese Reduction

ΔG^o_R = -3090 kJ/mol CH_2O

$$CH_2O + MnO_2 + 2\ H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

- Solid-phase MnO_2 is reduced and released to solution
- Dissolved Mn^{2+} then diffuses upwards to the oxygenated zone of the sediments, is reoxidized and precipitated as manganese oxides
- Leads to build-up of Mn in shallow sediments (see text)

Nitrate Reduction

$\Delta G^o_R = -3030 \text{ kJ/mol } CH_2O$

$$CH_2O + HNO_3 \rightarrow N_2 + CO_2 + H_2O$$

- Nitrate that is released during oxic respiration is consumed in this process

- Several different species of reduced N can be produced

Iron Reduction

ΔG^o_R = -1410 kJ/mol CH_2O

$$CH_2O + Fe_2O_3 + 2H^+ \rightarrow Fe^{2+} + CO_2 + H_2O$$

- Reduces solid-phase iron oxy-hydroxides to soluble Fe^{2+}
- Reduced Fe^{2+} typically combines at depth in the sediments with S^{2-} to form *iron-monosulfide (FeS)*, then *pyrite (FeS_2)*
- Slightly different ΔG^o_R depending on whether using Fe_20_3 or FeOOH (-1410 vs –1330)

Sulfate Reduction

$\Delta G^o_R = -380$ kJ/mol CH_2O

$$CH_2O + SO_4^{2-} \rightarrow S^{2-} + CO_2 + H_2O$$

- Sulfate reduction is very important in marine sediments because sulfate is a major constituent of seawater (28 mM)

Methanogenesis

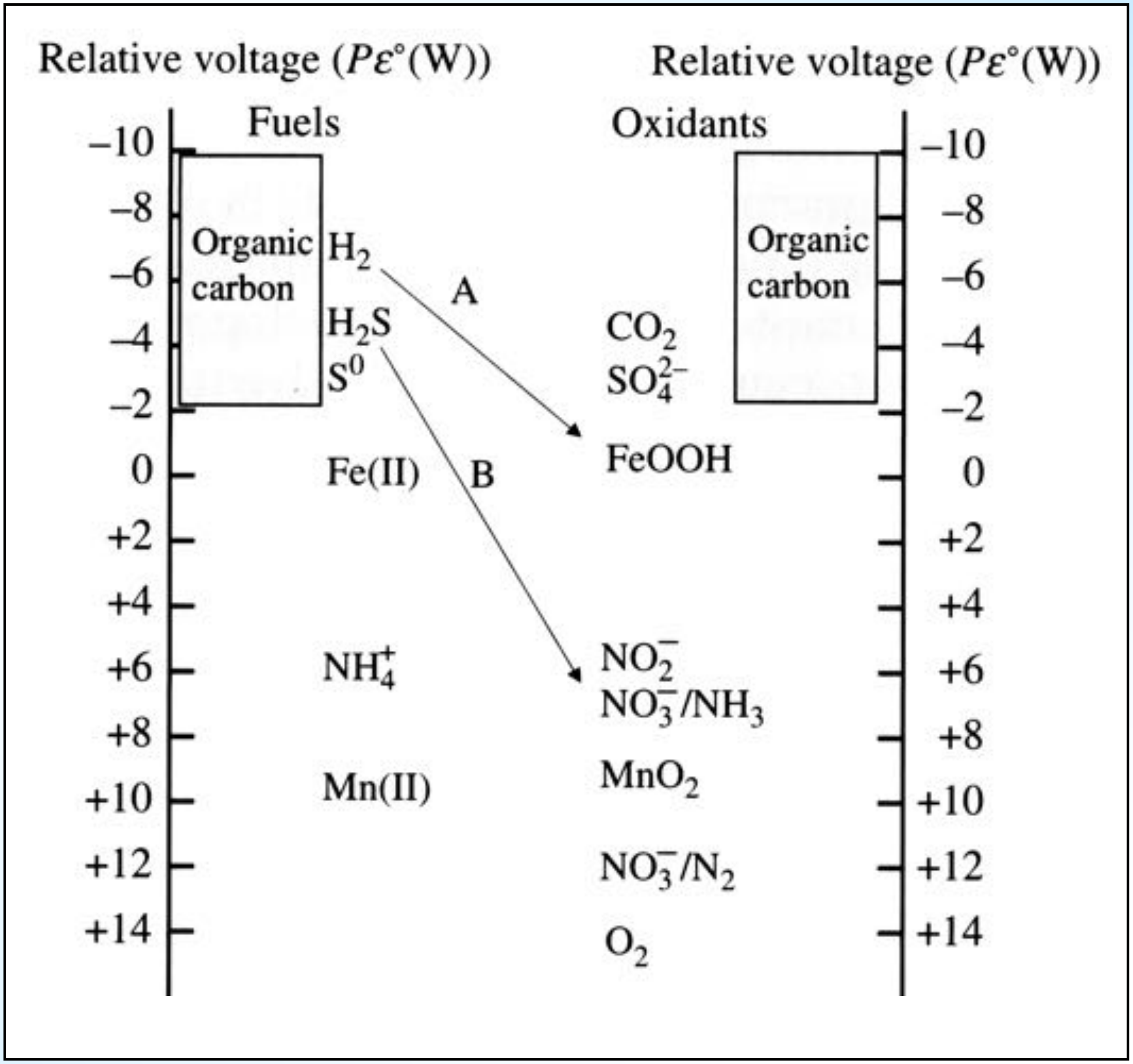
$$\Delta G^{o}_{R} = -350 \text{ kJ/mol } CH_2O$$

$$2\ CH_2O \rightarrow CH_4 + CO_2$$

- Occurs below the zone of sulfate reduction -- *i.e.*, after all the sulfate in the porewater has been depleted

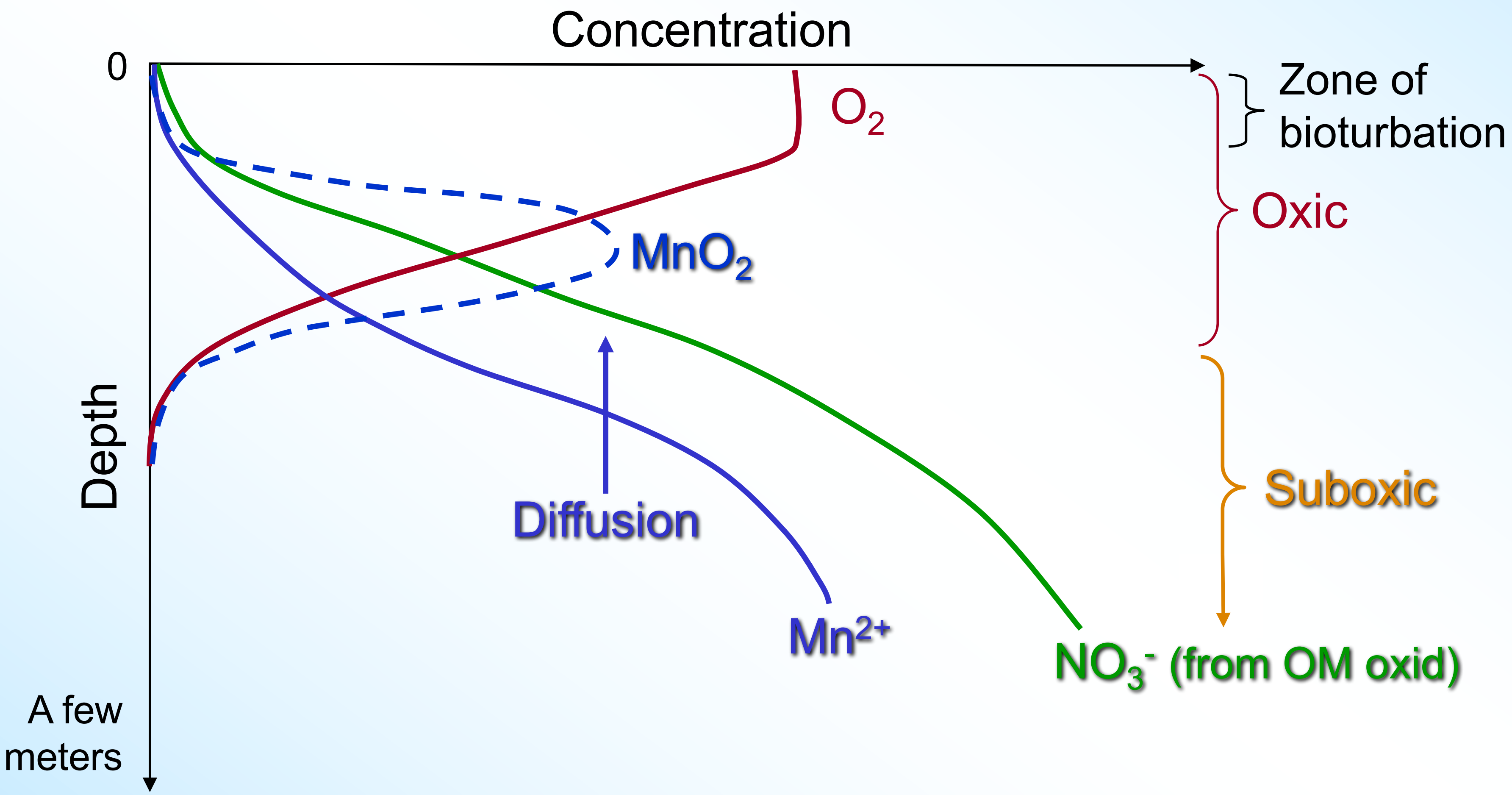
Types of metabolism

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

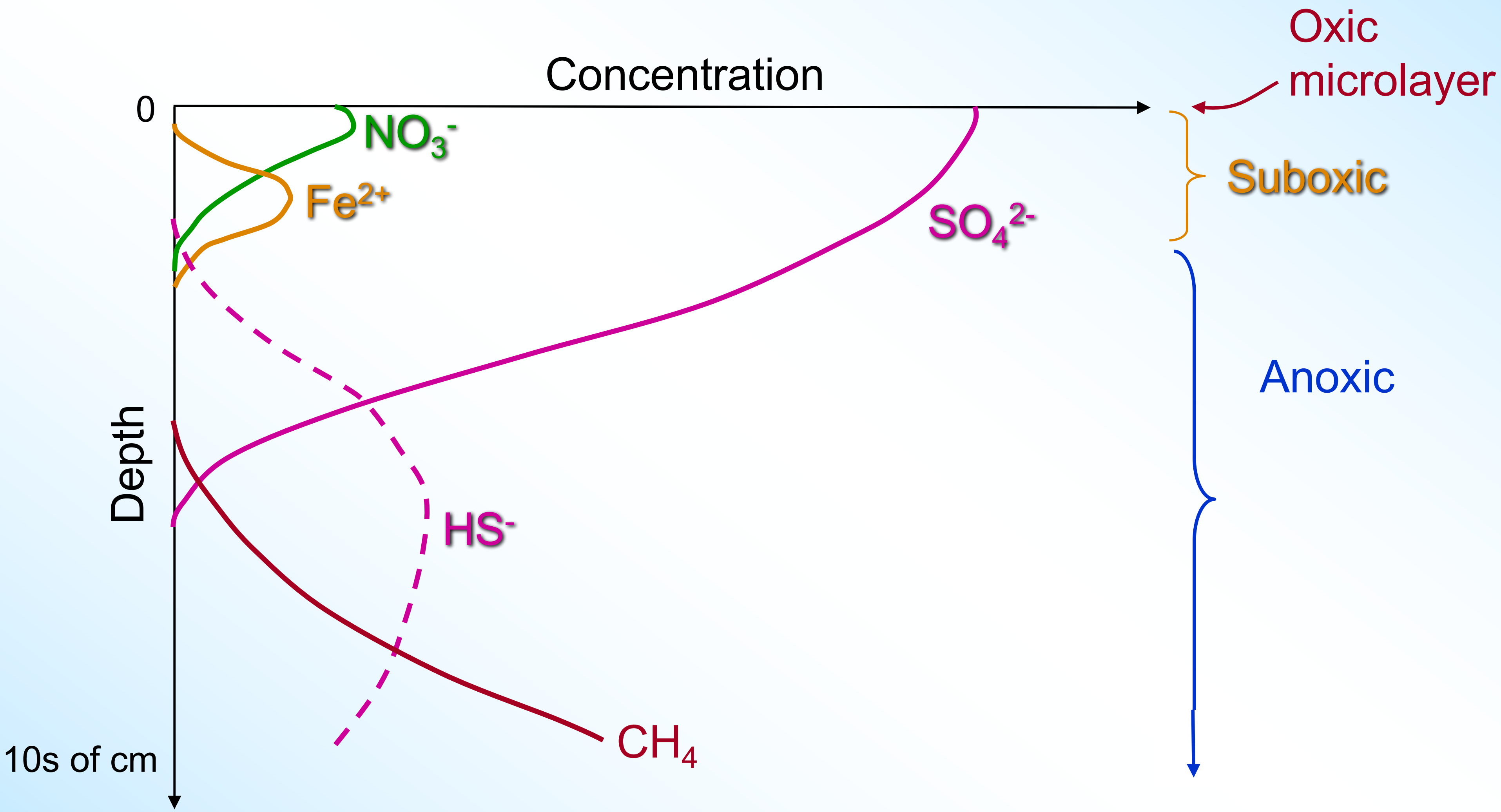


Nealson and Rye 2004

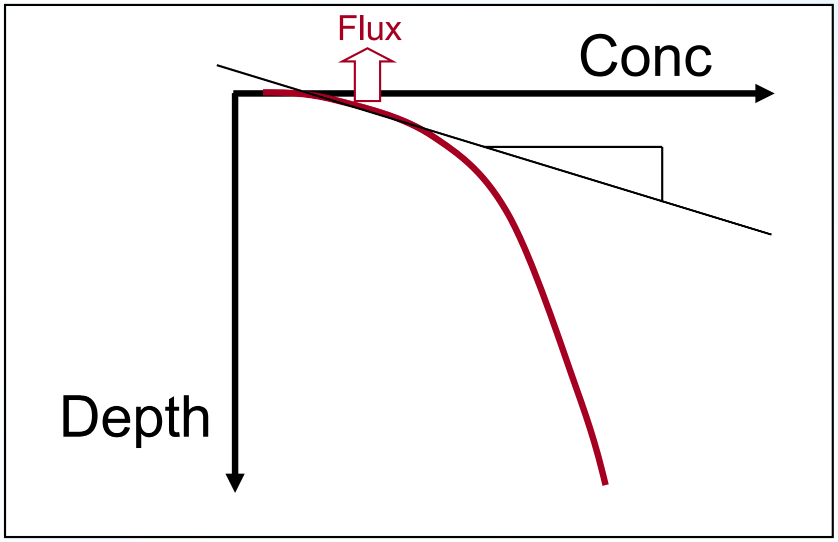
Deep Sea Sediment



Nearshore Sediment



Estimating Benthic Fluxes From Concentration Profiles



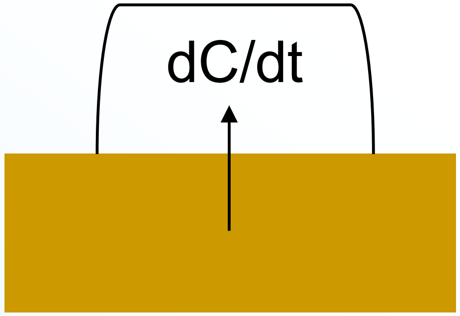
- Measure the slope of profile at given depth (dC/dZ, *moles/cm^3/cm*)
- Measure porosity of sediment (ϕ) (cm_{water}^3 /cm_{sed}^3)
- Estimate bulk sediment diffusivity (D_s, cm^2/sec)
- Assume no bioturbation or irrigation
- Apply modification of *Fick's 1st law of diffusion*:

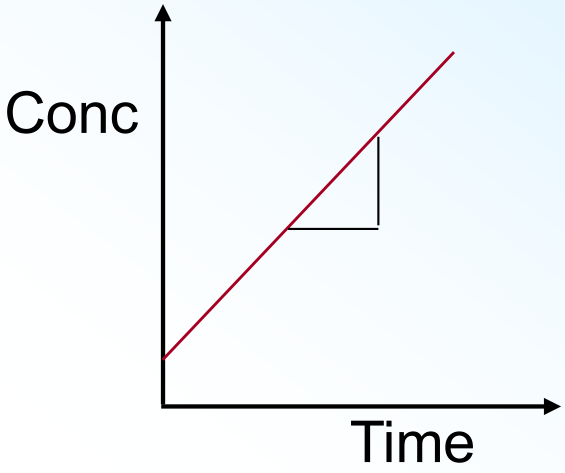
Vertical flux = $F_z = - D_s \phi (dC/dZ)$ *(moles/cm^2/sec)*

Potential Problems:

1. Macrofaunal irrigation
2. D_s is poorly known
    - 1×10^{-5} cm^2/sec for seawater
    - $2\text{-}5 \times 10^{-6}$ cm^2/sec for muddy sediments
3. Effects of adsorption reactions
4. Reactions at sediment/water interface

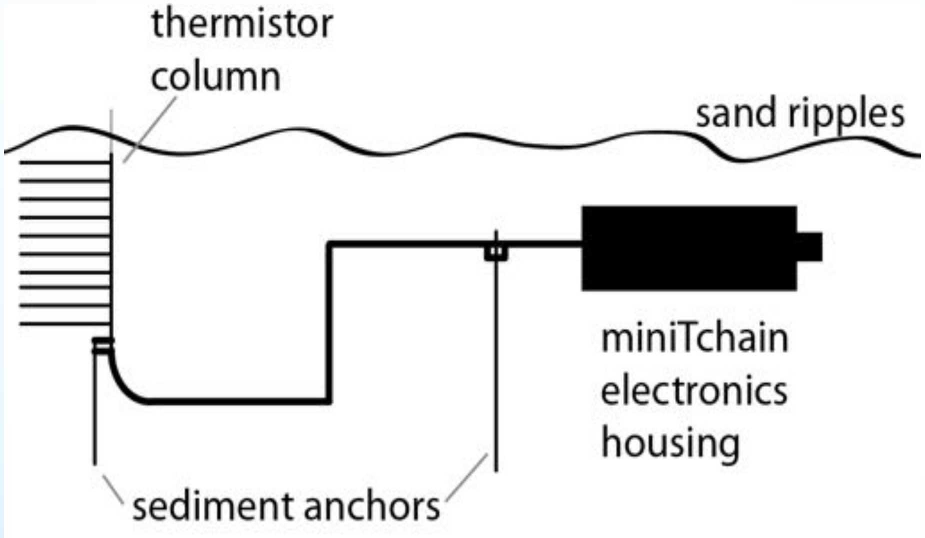
Direct Measurement of Benthic Fluxes to Seawater

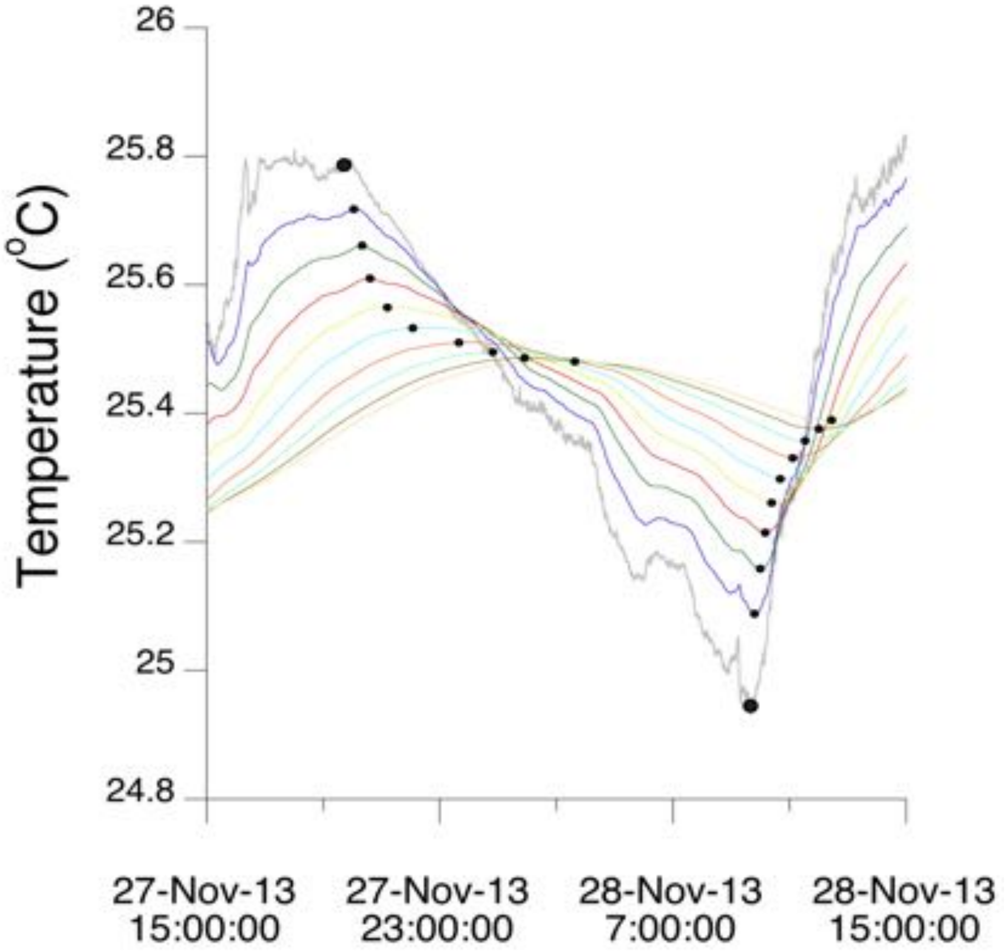




- Use of benthic “chambers” or “domes”
- Installed by divers or automated “benthic landers”
- Alternatively, can use cores in lab
- Measure concentration of parameter of interest over time in water
- Flux is proportional to slope of plot of conc. vs time (normalized to area under the dome)

A More Direct Measurement?





- Use of highly sensitive, high-resolution thermistors
- Based upon premise of diurnal temperature fluctuations in water column propagating (with a lag) into the upper sediment
- Couple *measured* porewater velocity and *measured* biogeochemical profiles for a *measured* flux

Fram et al. 2014

Often the calculated diffusion-supported surface flux is greater than the measured flux… WHY?

Uptake at surface microlayer occurs, especially if:

- Dealing with flux of nutrients across an illuminated surface sediment
- Dealing with flux of reduced compounds into aerobic seawater

Directions of common sediment fluxes:

NH_4^+	positive (*i.e.*, upwards)
CH_4	positive
HS^-	positive
DOC	positive
O_2	negative (*i.e.*, downwards)
$SO_4^=$	negative

Berner’s Sediment Classification

- Because of problems with Eh-pH measurements, and classification based on O_2 and $HS^- + H_2S$ concentrations, each environment is characterized by a suite of authigenic minerals

- The succession of sedimentary environments corresponds to the succession of reactions for the decomposition of OM:

$$\text{Oxic} \rightarrow \text{Sub-oxic} \rightarrow \underbrace{\text{Sulfidic} \rightarrow \text{Methanogenic}}_{\text{Anoxic}}$$

Oxic: $[O_2] > 100\ \mu M$

- Oxidation of OM by molecular oxygen
- Relatively low OM (especially continental fluvial sediments) because the OM is partially oxidized prior to sediment burial
- Fe-oxy-hydroxide phases are not reduced -- they are transformed to *hematite* (Fe_2O_3) during diagenesis (*e.g.*, Red beds)
- Presence of oxidized Mn phases
- Usually light brown sediment

Suboxic: $100\ \mu M > [O_2] > 1\ \mu M$

Non-sulfidic environment -- $[H_2S] < 1\ \mu M$

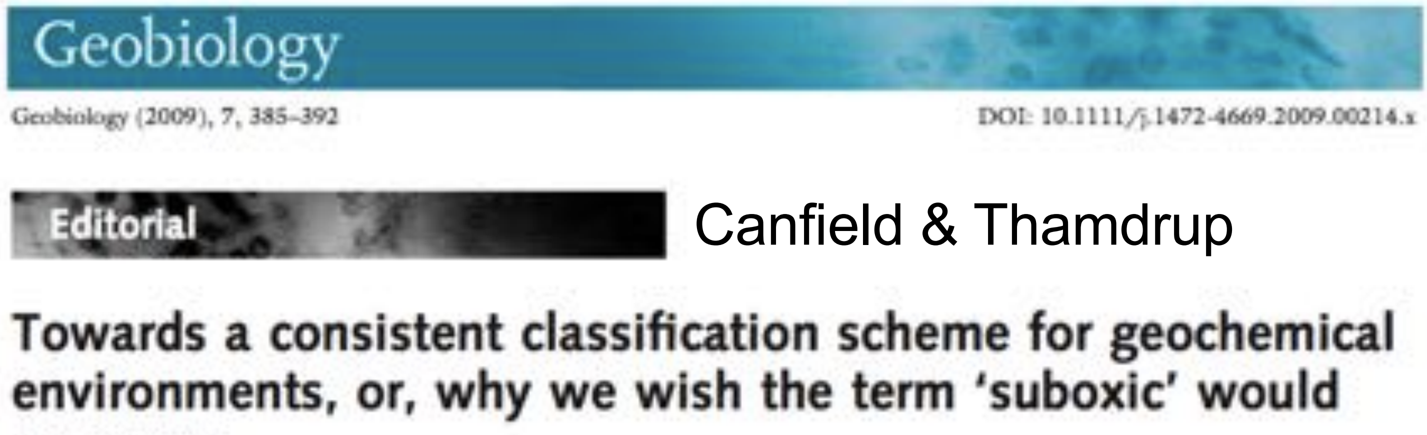
- Although the oxidation of OM consumes O_2, there is insufficient OM to generate much H_2S
- NO_3^-, MnO_2, and FeOX reduction
- Fe^{2+} and Mn^{2+} increase and become supersaturated with respect to *siderite* ($FeCO_3$), *rhodochrosite* ($MnCO_3$), *glauconite* ($(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$), and *vivianite* ($Fe_3(PO_4)_2 \cdot 8(H_2O)$)
- Usually grey sediment

Anoxic: $[O_2] < 1\ \mu M$

1) Sulfidic environments -- $[H_2S] > 1\ \mu M$

Oxidation of OM is by sulfate reduction

- *Greigite* (Fe_3S_4) and *mackinawite* ($Fe_{HX}S$) are first formed metastably, then react with H_2S to produce *iron monosulfide* (FeS) and *pyrite* (FeS_2).
- *Alabandite* (MnS) is only stable under very high concentrations of H_2S -- thus *rhodochrosite* ($MnCO_3$) is more common
- Requires large OM deposition rate
- Usually black sediment



Geobiology

Geobiology (2009), 7, 385–392

DOI: 10.1111/j.1472-4669.2009.00214.x

Editorial

Canfield & Thamdrup

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